Handbook of Adhesive Technology

Second Edition, Revised and Expanded

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Preface to the Second Edition

What can one say about the second edition of any book, especially one like this compendium that contains 50% more material and pages than the rather popular first edition, is heavily revised, expanded, and modernized, and contains 10 new chapters? As editors we can simply say we are elated. This is all true, of course, but it sounds so dull! Some readers (particularly younger ones) may expect some profound truth in a preface, a noteworthy dedication, or even an unusual phrase to remember such as the one that graced the preface of another book (*Advanced Wood Adhesives Technology*, Marcel Dekker, Inc., 1994). So here it is: On my (AP) first day as a university professor (at the University of the Witwatersrand in Johannesburg), I was profoundly impressed by the motto printed on the paper bookmark that was given to me by the administration clerk, ''Wherever a site of higher learning stands, there stands a light in the darkness of human folly.'' The university meant this to signify how good they were (and they *were* good, too). It goes much deeper than this, however. A site of learning does not need to be a university, or an industrial/research laboratory, but it can be more broadly defined as any source of learning, even, for instance, a book in such an arcane, specialized, but always fascinating, field as adhesives. It is for this reason that this volume has been revised and expanded, to function as a site of learning and a springboard for budding adhesive technologists. It is dedicated to next generations in the hope that they may build, and build rapidly, on the cumulative wisdom of many specialists distilled in this handbook.

This book, containing bountiful information, should serve for veterans as a commentary on the current state of knowledge regarding adhesives, and as a Baedeker for those who wish to make their maiden voyage into the wonderful and technologically important area of adhesives. In essence it should be valued by and of use to everyone interested, centrally or peripherally, in adhesives and should appeal to polymer chemists, surface chemists, adhesionists, and engineers, as well as users of adhesives.

We now have the pleasant task of thanking all those who helped in many and varied ways to bring this project to fruition. First, we are profoundly thankful to all the authors of the first edition for consenting to again be part of this much enlarged effort. Many contributors devoted time and effort to update their chapters. As any handbook can benefit from an injection of new blood, so our particular thanks must go to the contributors of new chapters. Our appreciation is extended to the staff of Marcel Dekker, Inc. for giving this book its form. In closing, we can happily say that it has been great fun working with all involved in this project.

A. Pizzi
K. L. Mittal

Preface to the First Edition

Bonding different materials together by means of an adhesive may appear to most people as a mundane occurrence. In reality a great deal of technology backs the apparently simple action of bonding. Thus, a complex and advanced technology, or series of technologies, has arisen to deal with adhesives and their applications in many fields. The diversity of substrates and the continuous introduction of new processes and materials has ensured that the field of adhesives technology is one of the more swiftly expanding manufacturing endeavors. Some excellent handbooks on adhesives already exist although there are very few indeed. However, the expansion and diversity of this field has by necessity limited the number of technologies and relevant aspects described in such volumes. This volume is no exception to such a trend.

The editors and authors do not pretend that overlaps with other similar works do not exist since basic background is often necessary to understand more advanced concepts. This volume however covers some aspects of technology that are not described in other volumes of this type. It also often looks at already reported technologies from a very different angle. It is hoped that such a volume will help to fill some of the technological gaps between the existing literature and industrial reality.

The volume is divided into four main sections, the first being an introductory overview. The remaining three sections are concerned with (1) fundamental aspects, (2) adhesive classes, and (3) some fields in which application of adhesives is very extensive. All the contributors are known specialists in their fields who practice their specialties on a daily basis. Their chapters are the results of considerable knowledge and experience in their particular niches.

It is a pleasant duty for the editors and authors, on completing a volume of this nature, to acknowledge the help willingly given by friends, colleagues, their companies, and their institutions. Without their help and encouragement most of the chapters presented would not have seen the light of day. Last, but definitely not least, our thanks go to Marcel Dekker, Inc. and its staff for originating this book, for their help and encouragement, and for prompting us to finish it.

A. Pizzi
K. L. Mittal

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1

Historical Development of Adhesives and Adhesive Bonding

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I. INTRODUCTION

The history of adhesives and sealants is closely related to the history of humankind. Some of what are thought of as relatively "new" uses of adhesives have their origins in ancient times, and although most of these materials have been subject to vast changes, others have been changed very little over time. As new materials are developed, a review of the history of uses can lead one to see where they might be applied to improve old applications, and sometimes to satisfy requirements of entirely new applications.

II. EARLY HISTORY OF ADHESIVES AND SEALANTS

"Insects, fish and birds know the art of producing mucous body fluids suitable for gluing. The load-carrying capacity of the hardened glue, as exemplified by egg-fastening and nest-building, is comparable to that of modern structural adhesives" [1, p. 1]. As humankind evolved, inquisitive persons observed and thought about insect and bird building and repair of nests with mud and clay. They encountered spider webs and naturally occurring "sticky" plant and asphaltic materials that entrapped insects, birds, and small mammals.

Unlike species that use an inherited instinct to perform a single task, human beings adopted the techniques of many species. They observed the natural phenomenon of sticky substances, then gathered and used these materials in locations away from their origins, exemplified today by the recently discovered Stone Age natives of South America's Amazon region and those in the interior of Borneo and New Guinea.

As rains fell, and then drying set in, many sticky materials regained their sticky properties, and some of the leaves used by ancient peoples to wipe sticky residues from their hands retained small quantities of water. Observing this, the first crude waterproof containers were manufactured using what we now call *pressure-sensitive adhesives*.

Our early ancestors used mud, clay, snow, and other natural materials to keep vermin, wind, and inclement weather out of their dens, warrens, caves, and other habitations. Today we use materials called *sealants* to perform similar functions in the construction and maintenance of modern buildings.

Straw and other vegetable material found its way into the muds and clays and reinforced them, forming the first crude *composites*. These materials later developed into bricks, which were in turn joined with the same or other materials used as mortars.

As human beings developed tools and weapons, sharp stones had to be fastened to handles to make axes and spears. Some of these were bound with vines, fibers, pieces of animal skin, or tendons or other body parts, and some had natural self-adhering properties to supplement the use of knots. To enhance the joining process, observing users soon smeared on sticky materials found locally.

When some natural materials fell on rocks heated by the sun, they softened and became sticky, and later hardened in the cool of the night. Observers made use of these natural *phase-change materials* as they chanced upon them. When lightning started fires, some materials melted and then cooled in interesting shapes. Observers, using the fires to harden their sharpened stick weapons, put out the fires by rubbing their sticks on the ground, and some contacted and melted resins, which when cooled, again hardened. Thus was born the technology we now call *hot-melt adhesives*.

Some of the other materials used by early human beings as adhesives are now called beeswax, rosin, rubber, shellac, sulfur, tar, and vegetable gums. Later, as people developed bows and arrows, it was found that feathers fastened to an arrow shaft helped to stabilize the arrow's flight. The same sticky or heat-softened materials soon supplemented the use of natural fibers to attach the feathers.

If Noah really did build an ark, the seams had to be sealed to keep out the water. And early human beings must have floated their possessions across bodies of water in bark or leaf containers with the seams sealed with sticky, waterproof materials.

Prehistoric peoples made pottery, and contrary to the Bible admonition in Jeremiah 19:11, "as one breaks a potter's vessel, so that it can never be mended," they often used rosin to reassemble broken vessels to retain food buried with the dead, as we know from remnants found in archaeological digs.

Bituminous cements were used to fasten ivory eyeballs in statues in 6000-year-old Babylonian temples, and combinations of egg whites and lime were used by the Goths 2000 years ago to fasten Roman coins to wood, bonds that remain intact today [2, p. ix]. "Bitumen was supposedly the mortar for the Tower of Babel; beeswax and pine tar were used in caulking Roman vessels that dominated the Mediterranean Sea" [3, p. 62]. "Plant gums and mucilage have been known and in use since very early times, reference being made to them in the Bible; they seem to have been of commercial value for several thousand years, especially in India, Asia, Africa, Australia, and China" [4, p. vii].

In historic times the Egyptians used crude animal and casein glues to laminate wood for bows and furniture, including wood veneers, many of which have endured to modern times in that dry climate. To make these products it is likely that they were familiar with the production of *bonded abrasives* in the form of sand bonded to papyrus or cloth with animal glue. They developed starch pastes for use in bonding papyrus to textiles and to bond leather, and a plaster of calcined gypsum identical to today's plaster of Paris. Later the Greeks used slaked lime as a mortar, and both the Greeks and Romans mixed the lime with volcanic ash and sand to create a material still known as *pozzolanic cement*. This was used in the construction of the Roman Pantheon and Colosseum. Thus was born the rude beginnings of the art and science we now call adhesive bonding technology.

III. MODERN ADHESIVES AND SEALANTS

From the earliest days, the materials that we later called cements, glues, gums, mucilage, mortars, resins, pastes, and finally, adhesives and sealants, were used interchangeably. Only in modern times have we attempted to differentiate between adhesives and sealants. For the most part it has been a vain attempt, as many so-called adhesives also serve as sealants, and all sealants have adhesive properties. Some polyurethane and silicone sealants have strength properties similar to those of structural adhesives. Only seals, which have no adhesive properties (gaskets, O-rings, stuffing boxes, etc.), have been excluded from the technical definitions, but even here, seals and sealants are often combined in the literature and in use, as they often perform in similar applications. Mixtures of glycerin and litharge, alone and with additives, were used for many years [5, p. 358] as both an adhesive and a sealant, and are still used in the repair and restoration of older aquariums.

In his book *The Technology of Adhesives* [6], John Delmonte tells us that the first commercial glue plant was founded in Holland in 1690, that casein glues appear to have been manufactured in Germany and Switzerland in the early nineteenth century, and that the first U.S. patent (number 183,024) on a casein glue was issued in 1876. He mentions that starch adhesives were used on postage stamps when they were first issued in 1840, and that the first U.S. patent (number 61,991) on a dextrin adhesive was issued in 1867.

Before the advent of synthetic resin adhesives, semisynthetic cellulosic materials were developed, but when they were first dissolved in solvents and used as an adhesive is not clear from the literature. "Historically, the first thermoplastic synthetic adhesive (only partly synthetic) was the cellulose ester cellulose nitrate, often called nitrocellulose, and it is still one of the most important. Later, other esters such as the acetate were developed, as well as certain mixed esters" [1, p. 295].

Inorganic sodium silicate adhesives had minor commercial use in 1867, but it was not until 1900 that their use as a glue became of commercial importance as a replacement for starch in the production of corrugated and solid fiber paperboard [5, p. 279]. Very fine silicate frit mixed with phosphoric acid was used as a dental cement [5, p. 376] before the twentieth century. Magnesium chloride inorganic cements were used at least as far back as 1876 in hospital kitchen floors, as they provide resistance to greases and oils [5, pp. 355–356].

There is little agreement in the literature about the dates when various adhesives and sealants were first developed or used in a specific application. This is due to simultaneous developments in many parts of the world and the fact that references in the literature are almost exclusively from the more developed countries. Table 1 show Delmonte's [6, p. 4] viewpoint on the times of adhesive developments, up to the year of publication of his work. In the accompanying text he notes that "The developments are tabulated according to their first public disclosure, whether by patent or citation in technical literature."

Some experts trace the roots of the first modern adhesives technology to 1839, when Charles Goodyear discovered that a mixture of rubber and sulfur changed from a plastic to an elastic state when heated. In 1843 this process was termed *vulcanization* by Thomas Hancock, who is believed to have used his hard rubber (Ebonite) for bonding to metals, possibly discovering its effectiveness when trying to remove the mixture from metal containers used in its preparation. As it also bonded to natural rubber during vulcanization, it was used for many years as the only practical means of joining metal to rubber—but it had serious limitations as a thermoplastic [7, pp. 1–3].

The rubber cement used in early rubber-to-metal bonding was a simple dispersion of rubber sheeting in benzene and later toluene or other solvent. It was brushed on the metal

Table 1 Chronological Developments of Adhesives in the United States

Year	Material
1814	Glue from animal bones (patent)
1872	Domestic manufacture of fish glues (isinglass)
1874	First U.S. fish glue patent
1875	Laminating of thin wood veneers attains commercial importance
1909	Vegetable adhesives from cassava flour (F. G. Perkins)
1912	Phenolic resin to plywood (Baekeland-Thurlow)
1915	Blood albumin in adhesives for wood (Haskelite Co.)
1917	Casein glues for aircraft construction
1920–1930	Developments in cellulose ester adhesives and alkyd resin adhesives
1927	Cyclized rubber in adhesives (Fischer-Goodrich Co.)
1928	Chloroprene adhesives (McDonald–B. B. Chemical Co.)
1928–1930	Soybean adhesives (I. F. Laucks Co.)
1930	Urea–formaldehyde resin adhesives
1930–1935	Specialty pressure-sensitive tapes: rubber base (Drew–Minnesota Mining & Mfg. Co.)
1935	Phenolic resin adhesive films (Resinous Products & Chemical Co.)
1939	Poly(vinyl acetate) adhesives (Carbide & Carbon Chemicals Co.)
1940	Chlorinated rubber adhesives
1941	Melamine–formaldehyde resin adhesives (American Cyanamid Corp.) and Redux by de Bruyne (Aero Research Ltd).
1942	Cycleweld metal adhesives (Saunders-Chrysler Co.)
1943	Resorcinol–formaldehyde adhesives (Penn. Coal Products Co.)
1944	Metal-bond adhesives (Havens, Consolidated Vultee-Aircraft Corp.)
1945	Furane resin adhesives (Delmonte, Plastics Inst.) and Pliobond (Goodyear Tire and Rubber Co.)

Source: Ref. 6.

and dried prior to contact with the bulk rubber to be bonded to the metal by vulcanization in a heated press. In 1862, Charles Sanderson, in a British patent (number 3288), specified that metal be brass plated by electrodeposition to obtain a strong bond to rubber [7, p. 3]. In 1911 the process was used in the production of rubber rolls, but was not used as a general commercial process until the 1920–1930 period.

Efforts to bond rubber to metal without the use of metal plating led to what is believed to be the first research efforts in *surface preparation* prior to adhesive bonding. Strong and durable bonds of rubber to metal were necessary for rubber shock mounts for automobiles in the late 1920s, but they were limited to proprietary formulations used on specific metals. In 1927 solvent-based thermoplastic rubber cements for metal-to-rubber bonding were prepared from rubber "cyclized" by treatment with sulfuric or other strong acids. With these rubber cements strong bonds could be made to either vulcanized or unvulcanized rubber.

Thermosetting solvent-based rubber cements for rubber-to-metal bonding, based on halogenated rubber compounds, first became available between World Wars I and II, but like much of the rubber-to-metal bonding technology, most of the work was proprietary and only glimpses of the technology involved can be found in the patent literature. The first use of natural rubber-based "tacky" adhesives on a backing is credited to Henry Day, who was issued a U.S. patent (number 3,965) in 1845. James Corbin of Minnesota Mining and Manufacturing Co. (now 3M Company), in a 1952 paper, "Practical Applications of

Pressure-Sensitive Adhesives" [8, p. 139], states that 1925 is generally considered to be the birth date of the pressure-sensitive tape industry. He mentions that prior to the time, both cloth-backed surgical tapes and cloth-backed friction tape for use by electricians were in limited use. Both were apparently tried as masking tapes for the new two-toned automobiles, but failed to resist paint penetration and to strip clean. A crepe-paper backing, impregnated with animal glue and glycerin and coated with a pressure-sensitive adhesive (PSA), was developed in 1925.

Synthetic rubber, a dimethylbutadiene, was developed as a substitute for natural rubber in Germany during World War I and saw limited use as an adhesive. In the early 1930s, neoprene rubber (then called Duprene) became available to adhesive manufacturers in the United States, and shortly thereafter in Great Britain. Today, neoprene rubber adhesives are available as both thermoplastic and cross-linking systems in both solvent and emulsion formulations. Neoprene rubber is the major base resin for *contact adhesives*. A limited amount of neoprene rubber is also used in sealants.

It was not until the commercialization of synthetic plastics resins in the 1930s that an almost unlimited variety of base materials became available for compounding into adhesives and sealants. Most of the thermoplastic resins were soluble in organic solvents and were used as solvent adhesives for molded plastic articles of the same base composition and sometimes for other materials. Poly(vinyl chloride) (PVC), a thermoplastic developed in 1927, is used today in solvent formulations to bond PVC articles such as coated fabrics, films, foams, and pipe. In the early 1930s, phenolics came into importance as adhesive resins. Before that time they were used as coating varnishes [9, p. 239]. "About 1931 development of the use of a new phenolic resin for plywoods and veneers began" [9, p. 239].

Poly(vinyl acetate) was used as a solvent-based adhesive in the 1930s, and later as a hot melt, but was not of commercial importance until its introduction in the 1940s, as an emulsion adhesive used mainly to bond paper and wood. Today, in emulsion form as a white glue, it is the most widely used thermoplastic adhesive worldwide. Vinyl acetate–ethylene (VAE) emulsion adhesives, with over 55% vinyl acetate content, were developed in the early 1950s but did not become of commercial importance in the United States until the mid-1960s.

Acrylic adhesives first appeared about 1937; "the acrylic resins may be considered as belonging to the vinyl family" [1, p. 305]. Today, acrylic adhesives appear in many forms: as both pressure-sensitive and non-pressure sensitive formulations in organic solvent and emulsion forms; as monomer and polymer cements; as anaerobics; as cyanoacrylates; as so-called reactive or "honeymoon" two-part systems; and as radiation curing formulations. "Commercial production of acrylic polymers began in the late 1920s, but it was not until 1958 that the first acrylic sealant was developed" [10, p. 226]. "The solvent-based acrylic sealants were first introduced to the construction industry in about 1960" [11, p. 121].

Urea–formaldehyde adhesives were patented in 1920 but were first commercialized around 1937. During World War II, starch was modified with urea resins to make both waterproof adhesives and impregnants for paper, which led in the 1940s to phenolic-impregnated paper for the first durable honeycomb core for lightweight rigid honeycomb panels.

Prior to World War II only in Germany was bonding to synthetic rubber being done. Polyisocyanate adhesives for rubber-to-metal bonding were developed under Otto Bayer in Germany during World War II. During the war there was widespread bonding of synthetic rubbers to metals in other countries, but documentation is almost nonexistent.

It was only with the development of high-strength *toughened* phenolic thermosetting adhesives during World War II for metal-to-metal bonding that high-strength bonding of vulcanized rubber to metal became practical. Today, both vulcanized and unvulcanized rubber may be bonded to most materials of commercial importance, with a variety of room- or elevated-temperature setting- or curing-type adhesives.

During World War II, synthetic rubber and resin-modified phenolics were used to bond aluminum sheets (available only in $\frac{1}{16}$-in. thickness at that time) into billets from which airplane propellers were carved, thus replacing laminated wood, which often shattered on impact with a bullet. Similar adhesives were used to bond rubber to metal in a variety of vibration-damping applications. "The most successful widely known product of the new technology was the automotive bonded brake lining first introduced in 1947, and now regarded as a symbol of quality and integrity" [12, p. 490].

In a book entitled *Adhesives* [2] published in 1943, only six of 150 pages are devoted to synthetic adhesives, and many of these are combined with animal glue and other natural adhesives. There are chapters entitled "Flour Pastes and Starch Adhesives," "Dextrin Adhesives," "Casein Adhesives," "Vegetable Glues," "Animal Glues," "Sodium Silicate Adhesives," "Rubber Dispersions and Solutions as Adhesives," "Rosin and Its Derivatives," "Wax Adhesives," "Putties," and other chapters on adhesives from natural raw materials. In one chapter, "Miscellaneous Adhesives," there is a single formulation where a synthetic, poly(vinyl alcohol), is combined with starch. There is one chapter, "Gums and Resins (Natural and Synthetic)," with no mention of any synthetic material, and a single small chapter, "Adhesives Derived from Synthetic Material," where phenol–-formaldehyde, urea–formaldehyde, and acrylic resins are mentioned, which suggests that they can be blended with animal glues to produce strong, waterproof adhesives. Also mentioned are poly(vinyl acetate), used alone or combined with ethyl cellulose. There is no mention of the rubber-modified phenolic adhesives developed during World War II, possibly because such formulations were classified as "secret."

One interesting omission in the book *Adhesives* is the use of poly(vinyl butyral) as the adhesive in safety glass. In 1936, Carbide and Carbon Chemicals Corporation first describes the use of poly(vinyl butyral) for laminating "high-test" safety glass [13, p. 165]. But in this book, poly(vinyl acetate), used as an adhesive for cellulose nitrate or cellulose acetate film, is mentioned as one laminating material for safety glass. This omission was particularly evident to the author of the present article, as poly(vinyl butyral) was a major product of my employer, E.I. DuPont, at their Plastics Division in North Arlington, New Jersey, in 1941. It had two major uses, as a safety glass laminating adhesive and as a box-toe softener for leather shoes.

To see just how far progress in adhesives and sealants extended during World War II, one has only to compare the book *Adhesives* with a book completed three years later, in December 1946. The *Technology of Adhesives* [6] had 516 pages, over 4000 index entries, and 1900 references. It covers in great detail the history, chemistry, theoretical background, testing, and technology of adhesives, It "seems" to have been written decades after the other volume. The term "pressure-sensitive adhesives," not found in the first volume, has 13 index entries, and similarly, "hot melts" has six index entries. Resorcinol–formaldehyde for wood bonding, introduced commercially in 1943, is covered in detail in the second volume, and an entire chapter, "Cementing of Organic Plastics," covers both thermoplastic and the thermosetting materials, whereas the other volume mentions neither.

Again, this was of particular interest to the author, as in 1941 I helped with the formulation of a number of the solvent cements for acrylics used in the fabrication and repair of transparent acrylic aircraft enclosures. These adhesives, by the way, are still being sold by a number of vendors and are widely used by sign, incubator, and other fabricators of acrylic plastics. ASTM Committee D-20 on Plastics was organized in the United States in 1937–1938, and adhesives were a regular topic of discussion. From this committee came the nucleus of members who organized ASTM Committee D-14 on Adhesives in 1944.

Silicone adhesives were introduced commercially in 1944 [5, p. 213]. "In 1960 the silicone sealants were introduced to the construction industry" [11, p. 86]. Silicones are useful at both high and low temperatures and are available today as solvent-based moisture-curing adhesives, one-part moisture-curing adhesives and sealants, two-part curing adhesives and sealants, and pressure-sensitive adhesives.

According to one author, epoxy–phenolic adhesives for high-temperature applications were developed during World War II at Forest Product Laboratories in Madison, Wisconsin, and nitrile phenolic adhesives shortly after World War II [9, pp. 153, 156]. A patent for epoxy resins was applied for in Germany in 1934, "and the inventor disclosed that it could be hardened with equivalent amounts of amines, diamines, or polyamines and that it showed strong adhesion" [14, p. 8]. Epoxy resins are believed to have been commercialized in the United States first by the former Jones Dabney Company sometime after 1942.

Polyurethanes had their commercial beginning with the work of Otto Bayer in Germany in 1937. "In addition, American patent literature revealed that in the early 1940s much study was directed toward the use of di-isocyanates as adhesive assistants, particularly in adhering elastomers to metals and fibers" [15, p. 4]. "...The following working definition of polyurethanes may be derived—they are polymers produced by addition reactions between polyisocyanates (difunctional or higher) and hydroxyl-rich compounds (at least two hydroxyl groups per molecule) such as glycols polyesters, polyethers, etc." [15, p. 3]. Today, polyurethane adhesives are available as solvent-based moisture-adhesives, thermoplastic hot melts, thermosetting systems, and emulsions.

During World War II, from 1939 to 1945, under the pressure of wartime shortages and the development of new and improved weapons of war, great progress was made in adhesives and adhesive bonding. However, due to wartime secrecy, much that went on has never been formally published. The homopolymer polyisobutylene was used in pressure-sensitive adhesives (PSAs) in 1939 as a replacement for natural rubber PSAs. Today, butyl rubber, the copolymer, has minor use in adhesives but is widely used in sealants. Polyvinyl acetals [poly(vinyl formal) and poly(vinyl butyral)] were used as flexibilizers for phenolic resins to make tough metal-bonding adhesives.

Styrene–butadiene rubber (SBR) adhesives, used to replace natural rubber adhesives, saw limited use during World War II, but commercialization took place during the 1950s. Today, in terms of monetary value, SBR adhesives are the most important adhesives in the United States. Their use in sealants is minor.

When glass-fiber reinforcements were used in organic resins in the 1940s, they lost much of their strength during prolonged exposure in water. In 1947 silanes were found to be effective primers or "coupling agents." "Silane monomers may be used in integral blends of fillers and liquid resins in the preparation of composites. The modified polymer I 'adhesive' in this case is termed a matrix resin" [16, p. 4]. In a chapter entitled "The Chemistry of Tackifying Terpene Resins," we learn that terpene resins were first produced for adhesive applications in the early 1950s, first for pressure-sensitive adhesives and were then combined with wax in early synthetic resin hot melts [17, pp. 396–397].

Anaerobic materials were discovered in the 1940s but were not commercialized until the early 1950s as a new form of acrylic adhesives, termed "anaerobics" by their inventor, Vernon Krieble, then a professor at Trinity College in Hartford, Connecticut. Their first use was as “threadlocking” sealants, to lock nuts on threaded fasteners as a replacement for metal lock washers, and to lock threaded fasteners in tapped holes in metal parts. They were the first products termed “sealants” to have a viscosity lower than that of water. Today, such anaerobic adhesives and sealants are used in almost all mechanical equipment that is subject to vibration.

Polysulfide rubber was first produced in 1929, and the liquid polymers were used in sealants and as flexibilizers for epoxy adhesives around 1950. “In 1952 the polysulfide sealant was introduced to the construction industry” [11, p. 74]. “In the 1950s the first butyl rubber caulks appeared in the construction market” [11. p. 108] and “latex caulks” [vinyl acrylic and poly(vinyl acetate)] appeared sometime after 1956.

Polyester resins (alkyds) were commercialized for coatings use in 1926, and unsaturated polyesters were used as thermoset fiberglass composite matrix resins in the 1940s, but the early resins made poor adhesives. When flexibilized resins appeared in the 1950s, they were used as adhesives. Today, unsaturated polyesters are widely used as adhesives for thermoset plastics bonding, and even for metal bonding in most countries, but are seldom used as adhesives in the United States, where the more expensive epoxy adhesives are used in similar applications. The saturated polyesters, used as thermoplastic hot-melt adhesives, seem to have appeared in the literature first in the 1954–1957 period.

Polyethylene seems to have been mentioned first for use in a hot-melt adhesive in a 1954 patent application. Patent 2,894,925 was issued in 1959 [18, p. 62]. Today, polyethylene is the most important of the hot-melt adhesives in terms of tonnage, and is second, after ethylene–vinyl acetate (EVA), in dollar value in the United States. EVA (containing less than 55% vinyl acetate) adhesives, developed in the late 1960s, “wet” more substrates, had better low-temperature properties, and were compatible with more formulating ingredients—but all at a higher price.

By the early 1960s, the raw materials used in adhesive formulations were so numerous that in the first handbook on the subject, the editor said: “It would be a virtual impossibility for any single volume to list all the ingredients which might conceivably be employed in an adhesive compound. Such a list would encompass practically every known chemical compound currently available in the United States” [19, p. 11].

It was only in the late 1950s and early 1960s that raw material suppliers established marketing programs that specifically targeted the adhesives industry. Before that time, a person formulating adhesives of more than a single chemical type had to have an extensive knowledge of the product lines of hundreds of supplier firms. For this reason, almost all formulators had backgrounds in the coatings or rubber industries. Many of today’s adhesive manufacturing firms reflect the earlier period by combining adhesives and sealants with the coatings or rubber areas of their businesses. Almost all synthetic resins used in adhesive formulations were used previously in coatings or rubber technology. The few people in the adhesives technical areas that were not from the coatings or rubber areas were mechanical engineers, who could evaluate the physical properties of the compounds developed by the chemists and the strength and durability of bonded assemblies.

From the chemists has come the *classification* of adhesives and sealants by chemical type, and from the mechanical engineers the classification as either “structural” or “nonstructural.” Neither is a “pure” system, since many adhesives and sealants have more than a single chemical base resin, and many “structural”-based resin systems are used in nonstructural applications. In a chapter entitled “Structural Adhesives” we are told that the term *structural adhesive* came into general use in the 1960–1970 period, but to this day all definitions are inadequate [9, Chap. 7]. “Adhesive manufacturers and their advertising departments now miss no opportunity to use, or abuse, the word. Companies which formerly sold urethane, acrylic, or anaerobic adhesives now call their products 'structural urethane,' 'structural acrylic,' or 'structural anaerobic' adhesives. Recently, this usage has further escalated, and these products are now called 'second generation' or 'third generation' structural adhesives" [9, pp. 133–134].

α-Cyanoacrylates were discovered in 1949, but "the adhesive properties of α-cyanoacrylates were first recognized during the investigation of a series of 1,1-disubstituted ethylenes, in the laboratories of Eastman Kodak" [20, p. I]. Cyanoacrylate adhesives were first offered commercially by Eastman Kodak, their developer, in 1958 [9, p. 305].

Nylon epoxy adhesives were developed in the early 1960s. These extremely "tough" adhesives were used to laminate helicopter rotor blades and in honeycomb core-to-skin bonding [9, p. 157].

Urethane sealants were first used in in-plant assembly applications. "In 1960 the two-component urethane sealants were introduced to the construction industry.... The properties of the urethanes, in general, are intermediate between the polysulfides and the silicones.... The two names, 'urethane' and 'polyurethane,' are both used when referring to this class of sealants" [11, p. 93].

Thermoplastic rubber block copolymers, with completely new adhesive performance, were developed in 1965 [21]. The first commercial product was Shell Chemical's Kraton 101, of styrene–polybutadiene–styrene composition. This development led to the carboxy-terminated nitrile (CTBN) rubber modifiers used to flexibilize epoxy and other brittle resin adhesives in the late 1960s. Today, the thermoplastic rubber block copolymer adhesives are used in hot melt-, solvent- and water-based adhesives, and as hot melt- and solvent-based sealants. Major applications are as pressure-sensitive adhesives, construction adhesives and sealants, and general assembly adhesives.

Polymercaptan sealants were commercialized in 1969. "The polymercaptans are a new group of sealants just entering the sealant market.... The polymercaptans, with respect to their properties, are intermediate between the polysu1fides and the urethanes" [11, p. 102].

Some adhesive-based resins are also used as additives, modifiers, or curing agents in other adhesive formulations. For example, starch is used in urea and phenol–formaldehyde adhesives as an extender. Poly(vinyl alcohol) is often combined with poly(vinyl acetate) to control solubility in warm or cold water in paper adhesives of the type used in schools. Polyamide higher-molecular-weight resins were first used commercially as solid hot-melt adhesives for leather shoe bonding in 1953, while the lower-molecular-weight liquid resins were first used in the mid-1950s as curing agents for epoxy resin adhesives. Today, many base resins are combined at the molecular level by the raw material suppliers. This is the case with acrylics, which have been combined with many other polymers to provide a large number of specialty resins for specific customers and applications.

In recent years a technique has been developed in which large quantities of adhesive resins called *compatibilizers* are used between layers of noncompatible extruded films, primarily in packaging applications. With this technology, up to seven layers of film (foil, paper, or plastic), up to three of which may be adhesive, may be combined to offer properties unlike that of any single-film material. The adhesive layer(s) may also contribute special properties to the multilayer composite film, in addition to acting as the compatibilizer. It is interesting to note that a particular plastic resin with adhesive properties may be used alone as an extruded plastic film, or in a multilayer composite film, where no compatibilizer is required, in which case it should not be counted in the adhesive statistics. This example is just one of hundreds where an intermediate or final user makes a decision to use a product sold as an adhesive, or a product sold as a nonadhesive as an adhesive, which make difficult the job of an analyst compiling industry statistics. Other common examples are the use of products labeled as coatings, encapsulants, dipping or potting compounds, modified concrete, paints, solvents, tar, thermoplastics or thermoset resins in many forms, varnishes, wheat and other flour, and so on, as adhesives. Conversely, products labeled as adhesives are often used as coatings or for other applications.

Today, even in the most developed countries, natural adhesives dominate the market because they are less expensive than synthetic-based materials, and they perform the intended function. Natural rubber is still the most widely used base material in pressure-sensitive adhesives. The first such modern uses were "flypaper" to trap flying insects, and medical bandages and tapes. Because of restrictions on the use of pesticides in many countries, both natural rubber and "sticky" synthetic materials have returned full circle to one of their original uses in trapping rodents and other small mammals. Natural rubber solvent solution adhesives are widely used throughout the world as general-purpose adhesives.

It is important to note that many adhesive technologists include brazing, soldering, and welding of metals as adhesive bonding [1, Chap. 10]. "Welding, brazing, soldering and gluing have flow processes as a common denominator.... Soldering is a true adhesive bonding method, as the flow process is restricted to the metallic adhesive" [2, p. 2]. This is not as unreasonable as might be thought, as a close study of the subjects show that there is much in common with other hot-melt joining of materials. It is just that the temperatures are often higher with the metals. However, indium and other low-temperature-melting metal alloys are often used interchangeably and at temperatures comparable to those of thermoplastic synthetic-resin hot-melt adhesives in joining metal to themselves and to other materials. FEP Teflon (copolymer of tetrafluoroethylene and hexafluoropropylene) and other high-temperature-melting thermoplastics are used today as hot-melt adhesives at temperatures equivalent to or exceeding those used for ordinary metal solders.

Inorganic adhesives and cements are also often classified differently by various experts. For example, sodium silicate is always classified as an adhesive when used in smaller quantities for bonding in electrical and electronic applications and for bonding paper and corrugated paperboard. But when used in larger quantities in furnace construction, they may be grouped with the portland and other hydraulic cements used in construction. Again, this makes it difficult to compile industry statistics. In the United States, the Department of Commerce has a Standard Industrial Classification (SIC) system for statistical purposes in which hydraulic cements are listed with stone, clay, and glass products as SIC 3241. Under chemicals and allied products are listed adhesives and sealants as SIC 2891 (including silicates) and dental adhesives under SIC 2844. One other class of materials, not usually considered as adhesives, that are used in large quantities worldwide for bonding thermoplastics are organic solvents. When they contain dissolved polymers, all adhesive technologists consider them as plastic cements. But when used alone, they are usually left out of the literature and the statistics. The best modern reference to their use as adhesives is Chapter 8 in the *Adhesives Technology Handbook* [22].

The history of the modern adhesives and sealants industry is closely tied to the development of the aircraft and aerospace industries. From the earliest flights to the most modem aerospace equipment, light weight has been one of the most vital considerations. Adhesive bonding was an ideal joining method for the early wood and textile aircraft, and today is the most important joining method for aluminium, titanium, and other metals in advanced military air- and spacecraft and some advanced commercial airplanes.

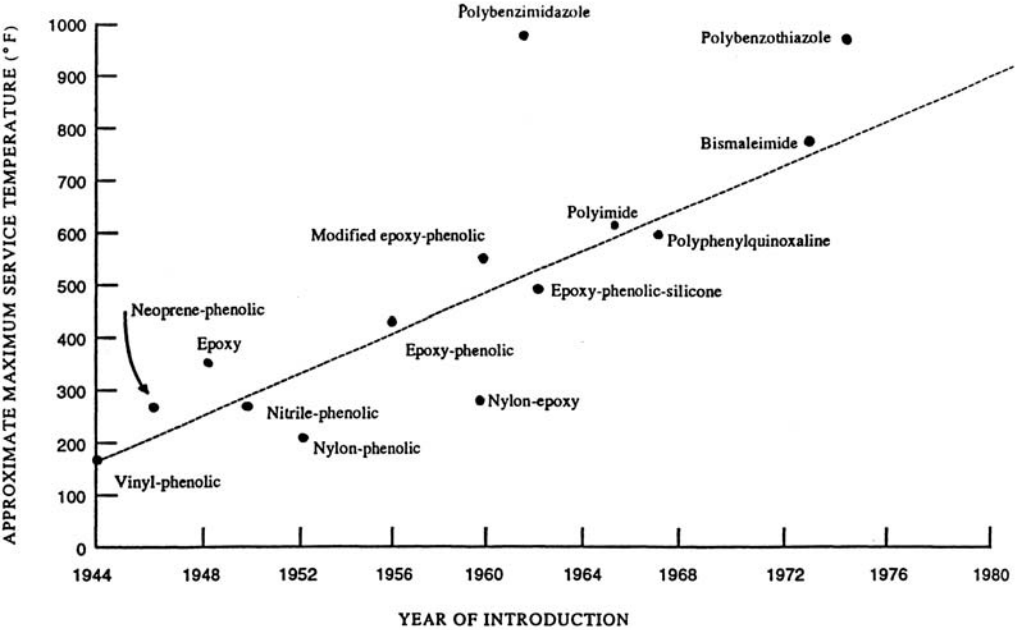

Figure 1 Sequence of development of heat-resistant adhesives. (Adapted from Ref. 23.)

Except for a very few very high-temperature brazed panels, all honeycomb panels are adhesive bonded.

Figure 1 shows the approximate maximum service temperatures for adhesives and the approximate year of introduction [23]. The maximum service temperatures of the highest-temperature adhesives are not indicative of usefulness for prolonged exposure at these temperatures but show that systems are available for certain applications. These adhesives tend to be brittle rather than tough and are usually much more difficult to apply than are the lower-temperature systems. Other newer adhesives are usually considered experimental rather than production systems.

One of the more interesting uses of modern adhesives and sealants is by museums in the repair and restoration of antiquities. Nitrocellulose-based adhesives are widely used in such applications, as are epoxies and polyurethanes. In the United States, the Guggenheim Museum has made exhaustive, expensive, and highly scientific evaluations of the effects on durability of such repairs on irreplaceable artifacts from the past. Thus adhesives and sealants have come full circle back to some of their original uses.

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2

Information Resources

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I. INTRODUCTION

We are now living in the Information Age, according to many of today's pundits and commentators. This followed naturally from the Computer Age, which obviously followed the Post Modern Industrial Age, which followed the Industrial Revolution Age, and so forth and so on, all the way back through the thousands of years to the Stone Age, where adhesives were first used. Quite frankly, we are not entirely convinced there has been a lot of progress.

Editorial comments aside, what those commentators are trying to point out is that we live in an age when information on virtually all of humankind's knowledge, and research, and data, and inventions, and news, and everything else, is usually readily available to whoever wants to find it. In fact, the average person can easily become swamped with too much information, to the point where it can become difficult to decipher the good from the bad, the old from the new, the important from the trivial, or the temporary from the permanent. Every business person, whether technical or administrative, is inundated with reports, forms, meetings' minutes, conference proceedings, workshop manuals, books, trade publications, association news, trade shows, annual reports, CD-ROMs, and more. As a consumer, we are besieged by the telephone, TV, cable TV, radio, newspapers, magazines, more CD-ROMs, community meetings, and the Internet. A major task for any person in this Information Age is simply to be able to sort, categorize, and utilize that information which is pertinent, and wash away the chaff, no matter how interesting or intriguing.

Information is the lifeblood of business, commerce and technology. It has been reported that engineers typically spend about 20% of their time looking for information, and it would be surprising if chemists spent less time than that. It is obvious why this is such a major component of the day's activities. Given the diversity of manufacturing, even with a somewhat unlimited bank of usable raw materials with which to fabricate goods, it is possible that someone else has already resolved a dilemma similar to the one presently confronting the engineer. And if not the exact problem, probably one pretty close to it, or at least a problem involving one or more materials germane to the problem. In fact, engineers go to school and get a degree based on their ability to learn how engineers have solved problems in the past, and to learn about basic materials and assembly methods.

Now, one would think that an industry as important to the assembly process and as chemically diverse as the Adhesives Industry would have all kinds of resources available to the engineer and researcher. And that assumption would essentially be correct, except for one small factor. And that small factor is, no matter how many products are made with adhesives, no matter how important those adhesives are to making the product a success, no matter how integral a part the adhesive is of the manufacturing process, the fact remains that the Adhesives Industry is a small industry. The Adhesives Industry simply does not have the kind of visibility enjoyed by the Transportation Industry, or the Packaging Industry, or the Construction Industry, or even the Electronics Industry, notwithstanding the fact that none of those industries can survive in today's economy without adhesives and sealants. Unfortunately, adhesives are a material component of those industries, and as such, information about adhesives becomes submerged in the detail of other processes and products. Which, to a certain degree, compounds the problem of searching for information about adhesives, sealants, tapes, encapsulants, cements, mastics, potting compounds, and grouts. And that very listing illustrates a second part of the problem, which is the diversity of products available in the marketplace.

Almost any organic material, and several inorganic materials, can be made into an adhesive or sealant. Each one of those organic materials can be compounded with myriads of different organic and inorganic materials to achieve a specific set of characteristics. And this has been done by thousands of chemists at hundreds of adhesive manufacturing companies in the United States alone. The result of this startling array of diversity is hundreds of thousands of formulations that leave little pockets of knowledge and data strewn across the manufacturing landscape. Many, many technologies interface with adhesives and their processing. And that diversity of applications and products makes it difficult, if not nearly impossible, to collect information about adhesives in a cogent and coherent format for dispensation to engineers and researchers.

But, it has been done. Originally it was published as a 1981 paper by Fred Keimel, called "Where Can I Find the Information I Need?" and presented at an Adhesive and Sealant Council meeting. Mr. Keimel was the founding editor of the *Adhesives and Sealants Newsletter* in 1977 and was able to compile the research sources he reported on in the Newsletter into the *Information Resource Guide*, an intermittently published compendium of resources on adhesives and associated technologies. That work continues on an irregular basis, with the sixth edition of the Guide published in 1997. While the total complement of resources reported in that Guide is far too great to be considered for publication here, what follows is an abridged version of that Guide, and a working model for finding the information needed.

An important caveat is needed at this point. Information is available on three different levels. The first is the *academic* level and includes pure research into the whys and hows of the world around us, even the worlds we cannot see. Pure research is more concerned with developing a rational understanding of the elements of surfaces, the physical nature of bonding materials, the nature of bonds themselves, the kinetics of reaction, modeling adhesive performance, developing appropriate test criteria, and so on. Quite often, this type of basic research is conducted at universities and government sponsored laboratories around the world, but sometimes forward thinking industrial firms sponsor pure research in their own laboratories. The second level of information is *developmental* and is produced by companies that make raw materials for adhesives and sealants and by companies that manufacture adhesives and sealants. By and large, these companies have determined a need for a particular kind of product in a specific industry to solve a particular set of parameters and set forth to develop and produce that product.

Sometimes the kind of work accomplished by industry is quite similar to that accomplished by academic research, but generally more focused on resolving a specific problem or application. Once that goal has been achieved, product(s) are introduced to the trade with varying amounts of information, based on the level of inquiry originally undertaken. Finally, the third level of information is *anecdotal*. It comes from people who actually use adhesives and sealants, or people who help companies use adhesives and sealants. This includes the engineers and applications people at user companies, but also sales, laboratory, and technical service people from adhesive manufacturing companies, and from manufacturers of applicating and curing equipment. The information at this level often is generally more specific as to end use applications and materials of construction for a particular purpose. Papers, journal and magazine articles, book chapters, and conference presentations are made based on the results of all three levels of research and information. All three levels have differing degrees of value to individual engineers and researchers.

II. FINDING THE INFORMATION NEEDED

Information sources fall rather naturally into several categories, which are listed alphabetically in Table 1. This, of course, says nothing about the validity of information available from any of these sources. Nor does it indicate the ease or difficulty in mining information from a particular source. Each of these categories will be reported on separately.

A great deal of information has a degree of interconnectedness. That is, papers presented at a conference may also get published in a book, or in a trade magazine. Data for a technical bulletin may become part of the background information that forms the foundation of knowledge used by a consultant. Many companies participate in standards' setting, and many companies participate in market surveys of different market segments. Members of some adhesive manufacturing companies conduct workshops for users. Company websites are designed to disseminate information to whosoever is interested.

That being stated, it is important that the engineer, or researcher, have a basic plan or stated objective when conducting an information search. Some information may be appropriate and germane to the project, other information may simply be interesting, or provocative. Given the diversity of information available, it is very easy to become distracted from the purpose at hand. While it appears obvious that different goals will require different search protocols, not everyone approaches the problem from a logical point of view. For instance, the most common goal is to find an adhesive which will bond Substrate A to Substrate B. The engineer should do his/her level best to define all known parameters of that

Table 1 Information Sources

Associations
Books
Consultants and Other Services
Courses and Conferences
Directories and Market Research
Government Agencies
Journals and Trade Publications
Libraries
Manufacturers
Online Sources

bonding situation so that it can be detailed properly to the representatives of adhesive manufacturers. The next logical step is to find out what kinds of adhesives or sealants typically are used to bond these substrates together, so referring to available books might be a good starting point. Second, a literature search through the "Reader's Guide to Periodicals" might prove fruitful. Third, a search of paper presentations at one or more conferences may be of value, which would require contact with the sponsoring organizations. Finding companies that manufacture products of a particular adhesive type would require using directories of one sort or another. The engineer may have to purchase the services of a consultant to better define product requirements and locate companies that supply appropriate materials. Conversely, contact with an association may lead to a member company with the right types of products. If the kind of adhesive required is known to a definitive degree, an online search may list a number of companies in that category.

Of course, other types of bonding problems may require a totally different kind of search, perhaps one more heavily weighted towards academic research results. Which just reinforces the need to conduct searches in a structured, well-defined manner. A search without focus will generate a great deal of information, some of which might actually be useful.

A. Associations

People form naturally groups of like interests. Sometimes these are social organizations, some are service organizations, some are religious in nature, some are special interest groups. Some groups are professional organizations formed around a particular occupation, and some groups are formed to promote the benefits of a particular industry or trade. According to the *Encyclopedia of Associations* published by Gale Research (see Directories), there are over 22,000 associations of one sort or another in the United States. Be assured that no matter what industry segment a researcher's company may be a part of, there is a trade association, and probably several, directly oriented to that particular industry segment. There are usually other associations oriented to the researcher's particular occupation that work to improve the professionalism of that occupation.

There is usually some overlap between associations that serve the same industry, or segments of an industry, but often the focus and charter of each association is different enough to warrant the existence of each. For the most part, trade associations serve to promote the interests of companies participating in that industry segment. A variety of functions are performed by most associations, and these are listed below. Not every association performs every function, and some do a better job on certain functions than others. Some charge fees for many of these services, some provide certain portions of the elements listed for members only, and some even provide information for free. Each and every association reflects its charter and the desires of the participating, and dues-paying, membership.

Promoting professionalism Most industry oriented trade associations work to promote the image of products produced by members of the association, and/or the members themselves, to the rest of the world. A number of associations oriented to specific occupations promote advancement and continued learning by their members. Often, associations sponsor and conduct workshops and tutorials to aid that learning experience.

Symposia and conferences Symposia are typically oriented to technical topics and are often thematically linked to a central topic. Conferences held by associations often cover technical topics, but also will cover other topics, such as government affairs, or management and marketing issues of interest to members.

Trade shows Often held in conjunction with an association meeting, although some of the bigger trade shows attract associations to co-sponsor, or hold conferences or workshops in conjunction with a show organized by others.

Publishing Associations publish a wide variety of materials, including: Conference proceedings, workshop manuals, membership directories, buyer's guides, journals, magazines, newsletters, books, and standards and specifications.

Research Some organizations sponsor research at academic institutions, a few even have their own facilities in which to conduct research.

Education Many associations have scholarship programs for high school and college age students. Some fund fellowships and grants at universities. Many have education foundations that serve as a collection point for member contributions. Some have even developed programs and products for educating students on topics important to the industry, others are funding degree programs.

Specifications and standards Each segment of industry has its own set of rules and regulations that guide and/or govern activities of companies in the field. Specifications are developed to elicit agreement among members of a segment on the most acceptable materials or processes. Standards represent an agreement among members of a segment as the most appropriate methods for testing and/or level of performance accepted. Some associations set their own rules, some work through encompassing associations such as ASTM International or the American National Standards Institute (ANSI) to accomplish specification and standards' development.

Compiling databases and libraries Some associations serve as a repository for any pertinent information associated with their industry or occupations, collecting books, proceedings, magazines, and other published data of relevance.

Government liaison An important activity for many associations is to keep track of the rules and regulations being developed by and imposed by government agencies, and to report this information to members on a regular basis.

Market research A few associations sponsor market research to determine the parameters of the market(s) for their members' products. The results of these studies, often conducted by independent companies, are usually disseminated on a low or no cost basis to members. Some charge for nonmembers to receive the reports, others do not disseminate the reports to nonmembers.

Appendix A lists a few of the numerous organizations that can provide information on adhesives and sealants, particularly of the type noted above. Only those that are more or less directly associated with these materials are listed, rather than any organization that has had reports or papers or books on the subject. The list runs several pages longer when user associations and organizations are added to it. Of necessity, the concentration of organizations listed is for the United States, although similar organizations will exist in Europe and Asia. There are, in fact, many national adhesive associations and similarly associated organizations around the world.

B. Books

Books are the mainstay of the researcher and educator. They contain the collected wisdom and knowledge of humankind. Somewhere, sometime, someplace there has been published a book on every topic known to man. Finding the book that has the vital piece of information needed is the key, of course. It is doubtful that any library will ever be complete enough, although there are some corporate libraries that do try.

Books range from the academic to the practical. Some are readily accessible to the average reader, some are not. Some are oriented to providing an overview of the entire technology, some concentrate on a minute portion thereof. And some books are simply the hardback version of conference proceedings, some are peer reviewed, some are not. There are no textbooks for adhesives and sealants technology (although some come close) simply because the technology is not taught at more than one or two institutions of higher learning (and then typically only a semester's worth) across the entire United States.

Most technical books have a limited shelf life, with a limited production run made by the publisher. Review copies are typically sent to a number of journals and trade press for write-up and promotion. A few publishers keep extra copies of published technical books for a period of time, typically until the inventory runs low, at which time the rest of the books are sold at discount to mass marketers. Finding copies of older technical books is like finding the lost treasure of the Incas, and the rule is: Buy it when you find it.

Many older companies in the industry still have a decent library with a good collection of older books, but some companies have eliminated libraries from their budgets (a very shortsighted practice), which puts more books into the used book stores. It is unlikely that the local or even big city library has any texts on adhesive or sealant technology—there just is not much demand for them and the money can be better spent elsewhere. A good source for determining if a desired book is still available is to go to the reference desk at the local library and request the location of *Books in Print*. It is a relatively comprehensive review that uses information provided by individual publishers. Some universities and colleges maintain a decent library for their technical schools, and may carry a selection of books on adhesive and sealant technology and related subjects, but since the topics are not usually taught, this is a questionable pursuit.

Appendix B provides a listing of a variety of books that are directly related to adhesives, sealants, their use and processing. By no means is this listing comprehensive, or considered a complete bibliography. It is very difficult to leave out any book that is related to adhesives and sealants, because each author has his/her point-of-view, his/her own organization of the subject matter, and differences in coverage of different topics. For the most part, books published by companies within the industry are excluded since many promote their products. So much has changed with the technology in the past 10–15 years that many books from the period prior to 1980 have been excluded, even though there may be some uniqueness about certain of these books. Many of those older books are referenced in more current publications. Each edition of books deemed important is listed, since many changes occur with an update, not always for the better.

One book in the listing should be available to every researcher for chemical information, even though its main subject is not directly about adhesives. In 1998, Wiley–Interscience published *How to Find Chemical Information—A Guide for Practicing Chemists, Educators, and Students, third edition*, by Robert E. Maizell. This book is a clear and lucid guide book for finding information of all types in the chemical industry, and contains numerous references. In addition, this book provides considerable detail on certain types of information tracking approaches and programs. Also covered well are sections on developing a search strategy and maintaining current awareness.

C. Consultants and Other Services

Consultants are individuals or companies, i.e., groups of individuals, that market their expertise in specific areas to those who do not possess that expertise, or perhaps have limited expertise and wish to obtain more. Sometimes, a degree of the expertise desired may be available from individuals within an organization, but there simply is not the time, or space, or capital, or whatever to capitalize on that limited base, so outside sources are hired. Some experts do not come as consultants, but are sales, technical service and marketing personnel from manufacturing and supply companies within the industry. These ‘‘consultants’’ are also selling expertise, but typically in the form of a recommended product and process that their company manufactures.

The adhesive and sealant business is so diverse, with so many suppliers and manufacturers, that it can be confidently stated that there is no consultant, or consultant company, who knows all about every facet of the industry. There is a high degree of specialization among most producing companies, and generally, many consultants are former employees of manufacturing firms. So it stands to reason that those consultants will be specialized, at least to a degree, with what their former employer specialized in producing. There are some individuals who do have a wide breadth of experience simply from working with a broad line of products under many different circumstances over a long period. Whether any consultant can help with a given situation depends on the particulars of that situation, the timeframe allowed for analysis, and the value placed on finding an answer.

Consultants come in many shapes and sizes, some of which have already been alluded to in the previous paragraph. For the sake of clarity, this section will only refer to consultants or service organizations who address the technical side of the ledger. There are extensive numbers of consulting firms that specialize in management issues, markets and marketing issues, and in quality control issues; none of which/whom are covered in this section. It should be noted that, very obviously, some associations and some market research companies will have varying degrees of technical expertise among the members of their organization. Many of these companies and organizations will also be found elsewhere in this publication. Included in Appendix C is a collection of, in no particular order:

consultants, individuals
consultants, organizations
testing organizations
other information collectors/dispensers

One of the problems with any ‘‘expert’’ is the exact area of expertise that is being offered. It is simply impossible to find any one person or organization that covers all areas simply because of the sheer magnitude of numbers and technologies involved in the product mix, raw materials processed, equipment used, and applications considered in all the areas where these products may be made or used. There are some individuals and organizations that do have a great depth of knowledge and understanding, and given sufficient resources and time, a good technologist can become proficient enough in specific technologies to provide substantial assistance.

D. Courses and Conferences

Every year, every month, every week there are meetings, workshops, trade shows, symposia, conferences, expositions, and short courses of interest to those who use or make adhesives and sealants. These are regional, national and international in scope. An interested student of the technology could easily spend a major portion of each month throughout the year attending such events. Some events are conducted several times a year, some are annual, and some are biennial. And some events are held once only.

These events separate generally into two categories, the line of demarcation being whether one intends to be educated (gain information), or one intends to participate in an event (share information). It is a bit of a fine line in many circumstances but specifically, there is a difference between the kinds of information that can be gained from workshops and short courses, and from conferences and symposia. Workshops and short courses tend to introduce a student to a new technology, or intensify the learning experience to gain a better understanding of the technology. Conferences and symposia, while introducing new research and developments, tend to expand the existing experience base of the attendee.

Many courses and conferences are held in conjunction with a trade show, and sometimes vice versa. Often, if the trade show is an important one to a particular industrial segment, one or more associations will sponsor workshops or conferences. Some trade shows transcend individual associations and are sponsored by a whole host of associations, each of which may sponsor an event to coincide with the show. Trade shows, by themselves, are usually an excellent source of information since dozens, and often hundreds, of companies exhibit their wares and services, provide brochures and data sheets, and have knowledgeable personnel in the booth ready to assist.

The compilation in Appendix D lists specific events and meetings that have taken place in the past. The list is fairly representative of what has been available but may not be complete in every case. The fact that an event has been held in the past is no guarantee that it will be conducted in the future. Since many of the events are sponsored by associations, there are obvious duplications in the listings between Appendices A and C.

E. Directories and Market Research

Directories come from a variety of sources, and although most typically consist of an alphabetical listing of names and addresses, they often cover a much broader range of topics. Most magazines oriented to the industrial market publish some sort of buyer's guide or directory issue each year for their readers. These are handy reference publications to have, since addresses and phone numbers are items often provided in addition to listing members of organizations, companies involved in niche markets, suppliers of raw materials, suppliers of equipment, and much more.

Market research is a relatively late business concept. It is a technology that began to emerge in the 1950s and matured in the 1970s. It is still growing, and refining, and developing new techniques. Given the information resources and technology available today, market research is a healthy, growing industry, no matter what segment of industrial society one happens to be part of or selling to. Serving the adhesive and sealant market are several companies that specialize in technology-based market research, some of which focus one or more studies/reports on selected segments of this industry. Most companies use a Delphi or modified Delphi research method, i.e., researchers question key members of an industrial segment to develop a working sense of the nature and size of that segment, or even small sections of that segment. That information, combined with data from the federal government, from annual reports and other company sources, from associations, and from trade publications, forms the foundation for a report. The value of the research depends on the skill of the researcher and the qualitative and quantitative assessments compiled compared to the needs of the purchaser.

One point worth noting and discussing about market research is comparative data between studies. While there are a number of organizations that survey segments of the adhesives and sealants market, and the total market, it is virtually impossible to match up data from one report to another. Each researcher develops their own set of protocols for each study, and establishes specific parameters for the scope of the study. For instance, some studies of the entire market include products used for the manufacture of plywood and other composite wood products, others do not. Some researchers are unfamiliar with certain end use markets, others are quite knowledgeable. Some researchers may have better access to a member of an adhesive company that is more knowledgeable about user markets, or may provide more detailed information than others. Some studies identify only the adhesives used to make tapes and labels, others include the converted product. Because of these and other differences, each marketing study must be evaluated strictly on its own merit.

Directories, of course, are a mild form of market research, and often necessary for conducting that research. In addition, most studies and reports include a directory as part of the study. Some directories and market studies are updated on a regular cycle, some are updated irregularly. Most directories published by associations and trade publications are up-dated annually.

In Appendix E, directories and/or market studies are listed for each publisher, but most individual titles are not listed because there are so many from some publishers. Many are updated on a regular schedule basis. One directory is unique to the adhesive industry and covers the contents of this chapter in comprehensive detail. That directory is the *Information Resource Guide* published by Adhesive Information Services, also publisher of the *Adhesives & Sealants Newsletter*. The *Information Resource Guide* also contains the most complete bibliography of books for the adhesive and associated industries.

F. Government Agencies

There are an astonishing number of departments, agencies, bureaus, services, boards, administrations, laboratories, and commissions in the U.S. federal government that interface in one way or another with the adhesive and sealant industry, or impact the conduct of business. Researching resources at the federal level gives a new perspective to the term "big government." One directory runs to over 800 pages.

Some agencies are the sole source of information in a particular area of expertise, in other areas, several agency contacts may be required to find the information being sought. Furthermore, it is not practical to list every agency that *may* impact activity in a given area. For instance, on environmental issues of one sort or another, a person could conceivably interface with virtually every single department and several different agencies of the federal government. In this subject area, there are offices and groups within the following agencies: Environmental Protection Agency (of course), Executive Office, Agriculture Department, Commerce Department, Defense Department, Energy Department, Health and Human Services Department, Housing and Urban Development Department, Interior Department, Justice Department, State Department, Transportation Department, plus various committees within the House and Senate.

Not only do some government agencies publish new rules and regulations that industry must abide by, but they also investigate and enforce those rules, and assess penalties for noncompliance. But there are other agencies that conduct their work in specific areas to benefit various segments of industry. Those agencies often have research laboratories, or compile data for dissemination, or purchase materials for production and maintenance, or document ownership of concepts, publications and inventions. Others provide census reports on industry and commerce, or trade reports; some provide assistance to small businesses, and others work with companies that wish to develop foreign trade.

A listing of all government agencies that may be of interest is not practical. However, the *U.S. Government Manual* is available from the Government Printing Office, and often at the reference desk of the local library. Appendix F is a limited listing of a few departments and agencies that are particularly interested in technology development and transfer with industry.

G. Journals and Trade Publications

Just as with associations, for every facet of industrial and commercial activity, there is at least one publication dedicated to reporting on the activities of that segment of the economy. In fact, there almost always are more than one publication, each covering the news in its own distinctive way, and with its own focus on that market segment.

Trade publications sell advertising to supplier firms for that market segment and are thus able to send the publications free, or at minimal cost, to interested parties in the target market. Others sell by subscription only with no advertising. And some do both. In addition to being a primary source of information about an industry, trade publications serve the function of being a vehicle for promoting the industry's products and/or services.

Journals could be considered technically sophisticated trade magazines. Like their more commercial brothers, journals cover a wide gamut of topics, but each journal tends to have a tightly focused subject area. By and large, journals are more often oriented to the scientific, academic, and research communities, and articles are typically written by members of those same communities. Most journals require peer review of submitted papers prior to publication, which normally will take topics out of the range of the more commercially oriented to the generally technical/scientific side.

The format of trade publications is variable, depending on the editorial focus of the publisher. Some trade publications are straight news summaries and reviews, some are only product review formats (tabloids), others contain mixtures of news releases and feature articles, case study presentations, and roundup articles. Most trade magazines will contain a coming events calendar, personnel notices, government activity summaries, association activities and announcements, business news, environmental news, and other specialty columns as appropriate. Many also publish an annual directory—some listing many companies within the industry, others serving as buyer's guides for readers of the publication. A variety of supplements are offered to subscribers to different trade magazines. Some have offered a step-by-step guide to processing technology, some have described materials technology used in a particular industry, others have produced handbooks for understanding different phases of specific technologies. Most trade publications are sent free to qualified members of targeted audiences.

While some journals cover "news" topics, many do not, concentrating instead on research topics and peer-reviewed presentations of on-going research projects. There may be development summaries, an events calendar, personnel news, sometimes a "classified" section, and sometimes news of government activities. Some, depending on the publisher, will add a buyer's guide, membership directory, or other supplemental publications. However, the primary focus of most journals remains the reporting of research and development. Very little advertising is found in these journals. Most distribute by subscription only with little or no advertising.

Publications oriented specifically to adhesives and sealants are listed in Appendix G. Although there are many publications which do provide feature articles and news items on adhesives and sealants, those trade publications and journals are not listed here for the sake of brevity. Some of the directories in Appendix E will list publications in more detail.

H. Libraries

Universities and colleges have them, cities and municipalities have them, many associations have them, even some corporations have them. Libraries serve as a collection point for books, magazines, journals, newspapers, films, directories, encyclopedias, reference books, art, and other expressions of communication. Obviously, not all libraries have the same focus, and the degree of specialization is typically a matter of funding and charter. Many corporate libraries purchase books that feature their own industry and those industry segments that the company serves, subscribe to magazines and newsletters that serve the same purpose, purchase helpful resources and reference publications, and serve as a central distribution point and collection agency for company papers. Even some departments within a company may have their own distinct library for the edification of members of that department.

The reference desk at most public libraries represents a valuable resource for researchers, at very low cost (other than taxes paid to support it). Most will contain one or more sets of encyclopedias, most contain a guide to government agencies, most have a copy of one or more corporate directories, and most have directories for books, trade publications, and associations. In addition, most public libraries subscribe to a variety of newspapers and magazines. Many university and college libraries have reference books and encyclopedias, books on specific subjects, magazines and other materials related to topics and curricula taught at the school. Many libraries belong to a network that may encompass local and state libraries, and state supported university libraries, and which permits interlibrary loan.

I. Manufacturers

Not only do hundreds of manufacturers (in the United States alone) produce a staggering array of hundreds of thousands of adhesives and sealants for every conceivable application in industry, but these same companies produce even more literature that describes these products. Brochures typically provide a summary of key products in the manufacturer’s line, but often will provide information on basic properties and applications for individual products. Many will provide a selector guide to aid the user in finding the most appropriate adhesive type for a specific application, which sometimes is included in the brochure, or sometimes is printed as a supplement.

Data sheets and technical bulletins are more detailed than a typical brochure and provide precise data points or property ranges on individual products. In addition, technical bulletins often provide processing suggestions and recommendations, safety and handling information, and charts and tables of comparative performance data. Some manufacturers have published user guides and other educational publications to aid their customers, such as basic adhesive technology, or surface preparation techniques, or information on adhesives for ultraviolet technology, or working with adhesives to assemble plastics and other materials. Some have even published books.

Beyond this wealth of information, each company typically has a staff of technically astute personnel that can assist in finding the right product or process. This would include chemists, technical service specialists, and sales professionals. The experience base in each of these groups is quite variable, but a great deal of information can be obtained just through open-ended discussions with potential supplier companies.

A caveat is in order here. The primary purpose of any manufacturing firm is to sell the goods and services they offer to the consuming audience. Naturally, when contact is made with a company about a particular application, their inclination is to try to present solutions from their own line of products, which may or may not be the best product for the application. This is not to say that a specific recommended product may not work—it probably will. It just may not be as good as the ideal product would be. Working with several companies, at least in the early stages of a project, is more likely to generate more information about what that ideal product might be. Plus the simple fact of being aware that competing firms may be on board usually provides for more acute attention from each manufacturer.

No attempt has been made to compile a listing for manufacturer firms, for several reasons. The first is that others already do this and the listings are noted in the directories in Appendix E. Secondly, no matter how hard a researcher tries, there is rarely a truly comprehensive listing compiled of all manufacturer companies. And lastly, because of mergers and acquisitions activity over the past several years, too many changes occur to give any kind of credence to a compiled listing.

There is also a segment of industrial society that serves as an extension of the manufacturer, and that is the Distributor. The primary role of a distributor is usually to provide place and time utility for a manufacturer's products. Some distributors perform only that function, serving as a stocking distributor. Others do much more, even to the point of serving as technical specialists in a particular industry or technology area. Many specialized distributors request, and obtain, technical training comparable to the training provided to new members of a manufacturing company. In some cases, distributors will carry several different, but complementary, lines of products to broaden their reach into end user markets. In some cases, technically trained members of distributor organizations are as knowledgeable about certain adhesive and sealant chemistries as are manufacturer's representatives. Most distributors serve a distinct geographical area, larger operations will establish regional offices.

J. Online Sources

Perhaps the most remarkable achievement of the last decade of the twentieth century was the growth of the Internet and access to it. Starting as a tool of the defense and academic establishments to facilitate scientific communication, the Internet has grown to encompass every segment of industry and society. There is an absolutely astonishing amount of information and data available on the Internet and the World Wide Web. That being noted, it must be pointed out that some of the information is not very good, some of it is expensive, and sometimes for some situations, all that is there is still not enough. In fact, more people still have access to a library than have access to the Internet, although most libraries themselves now have computers available for patrons to search the Internet.

The Internet is a remarkable tool for many users and can be extremely helpful, depending on the types of information desired. But it can also come up short in finding the specific information needed because, even with the exponential growth of recent years, not everyone, or every company, is on the Internet or World Wide Web yet. In many cases, even with a presence on the Web or Internet, not every company or association has posted, or even plans to post, all of the data and information at their disposal. However, most of the information sources mentioned above, and listed in the appendices, have some sort of presence on the Internet to permit easier accessing of information. In fact, part of the rapid Web growth is simply a result of companies placing pages and pages of data about their products online. Specific data, such as marketing studies, are harder to come by since most of that information is copyrighted and generally not readily available except through shielded and paying portals. Most magazines have not put full articles on the Internet simply because it devalues the magazine itself, thus losing a source of revenue from subscriptions and/or advertising sales.

Searching for information on any topic requires a great deal of refining and reviewing, and wading through the duplications, to find the few sites most appropriate for detailed reading. A keyword search using such entries as adhesive, sealant, encapsulant, cement, glue, or tape brings back anywhere from dozens to thousands, sometimes tens of thousands, of site addresses, depending on the search engine used. Which is good, because that means that there is lots of adhesive information on the Web. But it is also bad from the standpoint that most search engines are indiscriminate. Depending on who has updated most recently, or who has paid for priority listing, certain sites show up early. Many "hits" are simply additional pages of the same site. And truthfully, rare is the researcher who will manually sift through even a few hundred websites. Most search engines use Boolean logic as a structure for querying, which does help reduce the number of responses that are reported, if used properly. A few minutes reading through the Help instructions at each search engine site helps focus and speed searches. Be aware that a study reported in 1999 that no single online search engine tracks more than 17% of all websites, and all search engines combined barely exceed 50% of all websites. It is likely that results from certain search engines have improved since that study was conducted, and results may be even better by using available metasearch engines which cover all, or a series of, search engines.

There are a number of adhesive sites that are very well done and very user-friendly. There are others that are nothing more than a sophisticated form of business card, and many that are somewhere in-between these extremes. One other point worth noting is that some sites are updated regularly, some not at all, and some disappear after a period of time. Most corporate, association, trade publication, and even government websites provide for contacting the home office, usually by e-mail, but occasionally by phone, fax, or regular postal routing. Some websites, however, do not include all of this information, which can reduce the effectiveness of online searches.

There are only a few websites, at this point in time, which warrant a specific listing in Appendix H. Some sites are being established as gateways, portals, or shopping marts, but it remains to be seen if this practice will grow as the influence of the Internet continues to spread, and the number of companies with a presence online continues to grow.

III. SUMMARY

There is a wealth of information available to the researcher on adhesives and sealants. Finding the exact item of interest on those materials, however, can be a daunting and very time-consuming task. There is no central collection point for this information. There are, literally, hundreds of companies that manufacture adhesives and sealants, there are dozens of market research firms that report on the activities of those manufacturers, there are numerous government agencies that track the activity of those manufacturers, and there are several types of directories that list companies working in this industry.

There is a constant flow of information being generated from courses and conferences conducted throughout the year and around the world. Even more information is generated by the manufacturers themselves in the form of brochures and data sheets, while other publishers produce books and magazines to educate and inform the researcher.

Given the diversity of information available, and the many different sources for accessing information, it is important for the researcher to establish internal groundrules for any information search. The intensity of the search, coupled with a listing of potential sources, should be established before initiating the search.

NOTES TO THE APPENDICES

1. For the most part, only addresses and phone numbers are provided for the contents of each of the listings. Websites exist for virtually every single entry and can be found through most search engines.
2. Book publishers' addresses are not provided, since this information is also mostly available from libraries, or from the Internet. Some publishers are now defunct or have merged into other publishing firms.
3. Some duplication of entries between appendices will occur, since some associations and companies perform multiple functions. A limited reduction of the listings occurred due to controlling these duplications. In particular, since conferences are a normal function of associations, associations are not listed again under Courses and Conferences unless offering specialized short courses or workshops.
4. Addresses and phone numbers change constantly, companies and organizations merge, and some go bankrupt or otherwise become defunct. In addition, there is much more information available in several categories than is practical to list here. This listing is relatively accurate as of the time of compilation.
5. The listings are predominantly from the United States, however, comparable organizations exist in other countries. Books and publications of a similar type are also frequently available in other languages besides English.

APPENDIX A—ASSOCIATIONS

Academy of Dental Materials
Baylor College of Dentistry
3302 Gaston Avenue
Dallas TX 75246
Phone: (214) 828-8307

Adhesion Society
2 Davidson Hall
Virginia Tech
Blacksburg VA 24061-0201
Phone: (540) 231-7257

Adhesive and Sealant Council
7979 Old Georgetown Road
Bethesda MD 20814
Phone: (301) 986-9700

Adhesives Manufacturers Association
2300 North Barrington Road, Suite 400
Hoffman Estates IL 60195
Phone: (847) 490-5377

Association of Industrial Metallizers, Coaters & Laminators
2166 Gold Hill Road
Fort Mill SC 29708
Phone: (803) 802-7820

ASTM International
100 Barr Harbor Drive
West Conshohocken PA 19428-2959
Phone: (610) 832-9500

Composite Panel Association (Wood)
18928 Premiere Court
Gaithersburg MD 20879-1569
Phone: (301) 670-0604

Composites Manufacturing Association—SME
P.O. Box 930, 1 SME Drive
Dearborn MI 48121
Phone: (313) 271-1500

Concrete Anchor Manufacturers Association
1603 Boonslick Road
St. Charles MO 63301-2244
Phone: (314) 925-2212

Controlled Release Society
1020 Milwaukee Avenue, Suite 235
Deerfield IL 60015
Phone: (708) 808-7071

Converting Equipment Manufacturers Association
66 Arlington Avenue
Springfield NJ 07081
Phone: (201) 379-1100

Flexible Packaging Association
971 Corporate Blvd., Suite 403
Linthicum MD 21090
Phone: (410) 694-0800

Forest Products Society
2801 Marshall Court
Madison WI 53705
Phone: (608) 231-1361

Institute of Packaging Professionals
481 Carlisle Drive
Herndon VA 22070
Phone: (703) 318-8970

Insulated Glass Manufacturers Alliance
27 Goulburn Avenue
Ottawa ONT K1N 8C7, Canada
Phone: (613) 233-1510
(formerly the Sealed Insulated Glass Manufacturers Association)

International Society of Coating Science & Technology
15638 East Cerro Alto Drive
Fountain Hills AZ 85268-1720
Phone: (480) 836-9452

IPC Association Connecting Electronics Industries
2215 Sanders Road
Northbrook IL 60062-6135
Phone: (847) 509-9700

Label-Pack Converting Institute
P.O. Box 9
Gorham ME 04038
Phone: (207) 892-2216

Laminating Materials Association
116 Lawrence Street
Hillsdale NJ 07642-2730
Phone: (201) 264-2700

Pine Chemicals Association
P.O. Box 105113
Atlanta GA 30348-5113
Phone: (770) 446-1290

Pressure Sensitive Tape Council
2514 Stonebridge Lane
Northbrook IL 60065-0609
Phone: (847) 562-2530

Radtech International
3 Bethesda Metro Center, Suite 100
Bethesda MD 20814
Phone: (301) 664-8408

Sealant Waterproofing and Restoration Institute
2841 Main
Kansas City MO 64108
Phone: (816) 472-7974

SPI Thermoset Technology Division
1801 K Street NW, Suite 600
Washington DC 20006-1301
Phone: (202) 974-5200
(formerly Epoxy Resin Formulators)

Surface Mount Technology Association
5200 Wilson Road, Suite 100
Edina MN 55424
Phone: (612) 920-7682

Tag & Label Manufacturers Institute
40 Shuman Blvd., Suite 295
Naperville IL 60563
Phone: (630) 357-9222

TAPPI
Technology Park
P.O. Box 105113
Atlanta GA 30348
Phone: (770) 446-1400

APPENDIX B—BOOKS

Acid–Base Interactions: *Relevance to Adhesion Science and Technology*, edited by K.L. Mittal and H.R. Anderson Jr., 1991, VSP BV. Volume 2 published in 2000, also by VSP.

Adhesion and Adhesives: *Science and Technology*, by A.J. Kinloch, 1987, 572 pp., Chapman and Hall.

Adhesion and Adhesives Technology: *An Introduction*, by A.V. Pocius, 1997, 279 pp., Hanser Gardner Publications. Excellent book for introduction to adhesive technology and science. Second edition published 2002, 319 pp.

Adhesion and the Formulation of Adhesives, by W.C. Wake, 1976, 325 pp., Elsevier Applied Science. Second edition published 1982. Concentrates on the broader aspects of adhesion and principles underlying formulation rather than a list of recipes.

Adhesion Promotion Techniques: *Technological Applications*, edited by K.L. Mittal and A. Pizzi, 1999, 404 pp., Marcel Dekker. Summarizes state-of-the-art techniques for improving adhesion to various substrates. Theories of adhesion and advanced analytical techniques are reviewed.

Adhesive Bonding, edited by L.H. Lee, 1991, 476 pp., Plenum Press. Good coverage of theoretical background.

Adhesive Bonding of Aluminum Alloys, edited by E.W. Thall and R.W. Shannon, 1985, 520 pp., Marcel Dekker.

Adhesive Bonding of Wood and Other Structural Materials, edited by R.F. Blomquist, A.W. Christianen, R.H. Gillespie, and G.E. Myers, 1983, 436 pp., Materials Research Laboratory. Volume 3 of the Clark C. Heritage Memorial Series on Wood.

Adhesive Joints: *Formation*, *Characteristics and Testing*, edited by K.L. Mittal, 1984, 931 pp., Plenum Press. Volume 2, 2002, VSP, Utrecht.

Adhesively Bonded Joints: *Testing*, *Analysis*, *and Design*, STP 981, edited by W.S. Johnson, 1988, 320 pp., ASTM International.

Adhesives, *Sealants*, *and Coatings for Space and Harsh Environments*, edited by L.H. Lee, 1988, Plenum Press.

Adhesives and Adhesive Tapes, edited by G. Gierenz and W. Karmann, 2001, 138 pp., Wiley-VCH.

Adhesives in Manufacturing, edited by G.L. Schneberger, 1983, 696 pp., Marcel Dekker. Six chapters on fundamentals, ten on types of adhesives, five on bonding practices, and five on testing.

Adhesives in Packaging: *Principles*, *Properties*, *and Glossary*, edited by the Adhesion Committee, Institute of Packaging Professionals, 1995, 72 pp., softbound. Part 1 of a two-book series for packaging personnel.

Advanced Wood Adhesives Technology, A. Pizzi, 1994, 289 pp., Marcel Dekker.

Advances in Pressure Sensitive Adhesive Technology: Volumes 1, 2, and 3 edited by D. Satas. Volume 1 published in 1992, 219 pp., Volume 2 published in 1995, Volume 3 published in 1999; all three volumes from Satas & Associates and are supplemental to and technology updates of the 1989 *Handbook of Pressure Sensitive Adhesive Technology* (see entry)

Building Sealants: *Materials*, *Properties and Performance*, *STP 1069*, edited by T.F. O'Connor, 1991, 351 pp., ASTM International.

Converting for Flexible Packaging, by A. Miller, 1994, 182 pp. softcover, Technomic Publishing. First book published for this technology, excellent coverage of all factors.

Cyanoacrylate Resins, edited by H. Lee, 1981, 241 pp., T/C Press. Covers history, synthesis of various monomers, compounding, and applications.

Engineered Materials Handbook, *Volume 3—Adhesives and Sealants*, 1990, 893 pp., ASM International. Best coverage on types and use of "engineering" adhesives.

Fundamentals of Adhesion, edited by L.H. Lee, 1990, Plenum Press.

The Glue Book, by W.T. Young, 170 pp., softbound, Taunton Press. A very well illustrated and written book, oriented to the Do-It-Yourselfer, but usable for anybody in the woodworking trade.

Handbook of Adhesive Technology, edited by A. Pizzi and K.L. Mittal, 1994, 680 pp., Marcel Dekker. Forty chapters designed to be useful to both adhesive manufacturers and users, with strong emphasis on applications.

Handbook of Adhesives, edited by I. Skeist, 1962, 683 pp., Reinhold. Second editon published in 1977, 921 pp., by Van Nostrand Reinhold. Third edition published in 1989, 800 pp., also by Van Nostrand Reinhold. Necessary volumes for any library on adhesives. Second edition has an excellent chapter on adhesives for different substrates.

Handbook of Adhesives and Sealants, by Edward Petrie, 1999, 900 pp., McGraw-Hill.

Handbook of Aluminum Bonding Technology and Data, by J.D. Minford, 1993, 790 pp., Marcel Dekker.

Handbook of Pressure Sensitive Adhesive Technology, edited by D. Satas, 1982, 620 pp., Van Nostrand Reinhold. Second editon published in 1989, 960 pp., also by Van Nostrand Reinhold. Third edition published in 1999, 1017 pp., by Satas & Associates. Most important books in the industry for tape, label and other pressure sensitive adhesive (PSA) technologies.

Handbook of Rubber Bonding, edited by B. Crowther, 2001, 386 pp., Rapra Technology. Excellent coverage of most facets of this technology.

How to Find Chemical Information: *A Guide for Practicing Chemists*, *Educators and Students*, *third Edition*, by R.E. Maizell, 1998, 515 pp., Wiley–Interscience. An essential research tool for finding information about chemical materials. Very little on adhesives directly, but excellent coverage of chemical data sources, particularly online.

Industrial Packaging Adhesives, by K.S. Smith, 1990, 288 pp., CRC Press. An immeasurably practical book.

Machinery Adhesives for Locking, *Retaining and Sealing*, by G.S. Haviland, 1986, 360 pp., Marcel Dekker.

Plywood and Adhesive Technology, by T. Sellers, 1985, 661 pp., Marcel Dekker. Essential reference volume for this industry.

Polyurethane Sealants: *Technology and Applications*, by R.M. Evans, 1993, 186 pp., softcover, Technomic Publishing. Written for the compounding chemist, with four chapters on applications and five on materials.

Pressure Sensitive Adhesive Tapes: *A Guide to Their Function*, *Design*, *Manufacture and Use*, by J. Johnston, 2001, 192 pp., Pressure Sensitive Tape Council. Well written book by industry expert and a necessary reference book for anyone involved with PSA tapes.

Pressure Sensitive Adhesives Technology, by I. Benedek and L.J. Heymans, 1996, 600 pp., Marcel Dekker. Focuses on pressure sensitive label materials and production, but covers other PSAs.

Quality Assurance in Adhesive Technology, by A.W. Espie, J.H. Rogerson and K. Ebtehaj, 1998, 176 pp. softbound plus disk, Abington Publishing. This book develops a generic quality assurance model to accurately identify those areas of bonded products requiring attention.

Radiation Curing: *Science and Technology*, edited by S.P. Pappas, 1992, 448 pp., Plenum Press. Reviews both the science of radiation curing and application technology.

Science and Technology of Building Seals, *Sealants*, *Glazing and Waterproofing*, ASTM International (see also Building Sealants above). Books presenting papers from the annual conference sponsored by Committee C-24 on Building Seals, Sealants, Glazing and Waterproofing.

- *STP 1069*, edited by T.F. O'Connor, 1991, 351 pp.
- *STP 1168*, edited by C.J. Parise, 1992, 169 pp.
- *STP 1254*, edited by J.C. Myers, 1994, 106 pp., softcover.
- *STP 1243*, edited by D.H. Nicastro, 1995, 149 pp., softbound.
- *STP 1271*, edited by M.A. Lacasse, 1996, 300 pp., softbound.
- *STP 1286*, edited by J.C. Myers, 1996, 155 pp., softbound.
- *STP 1334*, edited by J.M. Klosowski, 1999, 313 pp., hardcover.

Sealants: *The Professional's Guide*, published by the Sealant, Waterproofing and Restoration Institute (see Appendix A), last updated in 1995, 74 pp. Excellent summary of design factors, chemical types, testing, and has a ten-page glossary.

Sealants in Construction, by J.M. Klosowski, 1989, 310 pp., Marcel Dekker. Excellent coverage of joint design and materials, particularly silicones.

Silane Coupling Agents, *second edition*, by E.P. Plueddemann, 1991, 253 pp., Plenum Press. This book is *the* basic text for this technology.

Silanes and Other Coupling Agents, edited by K.L. Mittal, 1992, VSP BV. Volume 2 published in 2000, also by VSP BV.

Surface Preparation Techniques for Adhesive Bonding, by R.F. Wegman, 1989, 150 pp. Noyes Data.

Surgical Adhesives and Sealants: *Current Technology and Applications*, edited by D. Sierra and R. Saltz, 1995, 247 pp., softbound, Technomic Publishing.

Treatise on Adhesion and Adhesives,

- Volumes 1–6, edited by R.L. Patrick, Marcel Dekker.
- Volume 1: Theory, 1967, 476 pp.
- Volume 2: Materials, 1969.
- Volume 3: Special Topics, 1973, 240 pp.
- Volume 4: Structural Adhesives, Aerospace, 244 pp.
- Volume 5: 1981, 416 pp.
- Volume 6: 1989, 290 pp. Recommended for sophisticated students of adhesion theory.
- Volume 7: edited by J.D. Minford, 1990, 528 pp. Excellent coverage of adhesives for bonding specific substrates of wood, elastomers, plastics and titanium.

Wood Adhesives: *Chemistry and Technology*, edited by A. Pizzi, Vol. 1, 1983, 364 pp., Vol. 2, 1989, 420 pp. Marcel Dekker.

APPENDIX C—CONSULTANTS AND OTHER SERVICES

ACIL: AMERICAN COUNCIL OF INDEPENDENT LABORATORIES 1629 K Street NW, Washington DC 20006, (202) 887-5872, regularly publishes the *Directory*: *A Guide to Leading Independent Testing*, *Research and Inspection Firms in America*. This membership directory provides key information on 447 companies, and is cross referenced into 300 product and service categories and 200 testing fields.

ADHESION ASSOCIATES Raymond F. Wegman, 34 Mt. Arlington Road, Ledgewood NJ 07852, (201) 584-5232. Consultant in areas of adhesion, adhesives, surface treatments for adhesive bonding and non-destructive testing.

ADHESIVE CONSULTANTS INC. 383 Stanton Avenue, Akron OH 44301, (216) 773-9161. Founded 1972. Experienced in analysis, formulating, in-plant technical service, start-ups, testing.

ARMBRUSTER ASSOCIATES David C. Armbruster, 43 Stockton Road, Summit NJ 07901, (908) 277-1614. Founded 1982. Business and technical consulting services to chemical and allied industries. Includes adhesives, coatings, radiation curing, epoxies, urethanes, water soluble polymers.

ASM INTERNATIONAL 9639 Kinsman Road, Materials Park OH 44073-0002, (216) 338-5151, and **The Institute of Materials**, Minerals and Miningh 1 Carlton House Terrace, London SW1Y 5DB UK, +44 (0)20 7451-730, provide a joint service called *Materials Information*. Search-in-print bibliographies cover adhesive bonding, other joining technologies, composites, and more. Up to 250 references per bibliography.

ASTM INTERNATIONAL 100 Barr Harbor Drive, West Conshohocken PA 19428-2959, (610) 832-9707. Publishes the *Directory of Scientific and Technical Consultants and Expert Witnesses*. Consultants are listed in 280 categories of specialized services, 165 pp., softbound. Also publishes the *International Directory of Testing Laboratories*. Over 1100 laboratories listed with capabilities, 384 pp.

BUSINESS FACTORS INC. William E. Klein, 6200 Plateau Drive, Springfield OH 45502, (937) 390-2528. Marketing research, consulting and strategic planning. Extensive experience in the PSA industry. Author of *They Built an Industry*, chronicle of the PSA labels market.

CENTER FOR ADHESIVE AND SEALANT SCIENCE Virginia Tech, Davidson Hall, Room 2, Blacksburg VA 24061-0201, (540) 231-6824. Funded by the Education Foundation of the Adhesive and Sealant Council, basic and applied research is conducted by graduate and undergraduate students under the direction of faculty. Some work is directly funded by companies interested in specific technologies or applications. Conducts workshops and seminars on-campus.

CHEMICAL ABSTRACTS SERVICE Division of the American Chemical Society, 2540 Olentangy River Road, Columbus OH 43210, (614) 447-3731. Established 1907. Over 13 million abstracts of chemical related literature and patents, and over 16 million material records. Publishes numerous abstracts, current awareness bulletins, and registry handbooks. Most literature now also available on CD-ROMs and online through STN International, which has 200 databases available. Connected to international databases.

CHEMIR/POLYTECH LABORATORIES INC. 2672 Metro Blvd., Maryland Heights MO 63043, (314) 291-6620. Analytical and testing organization.

CHEMQUEST GROUP INC. 8150 Corporate Park Drive, Suite 250, Cincinnati OH 45242, (513) 469-7555. Multi- and single-client studies of U.S. and European adhesives and sealants markets. Strategic analysis and assistance. Consulting on market research and market development. Numerous papers and articles by principals of the company.

CHEMSULTANTS INTERNATIONAL 9349 Hamilton Drive, P.O. Box 1118, Mentor OH 44061-1118, (216) 352-0218. In-depth background in research, purchasing, pilot plant and manufacturing. Also laboratory testing service, and manufacture of equipment for testing pressure sensitive materials.

DIVERSIFIED ENTERPRISES 101 Mulberry Street, Suite 2N, Claremont NH 03743, (603) 543-0038. Started the Polysurface book store and lists over 2000 titles including several on adhesives, pressure sensitive adhesives, coatings, polymers, plastics, packaging, surface properties, wetting, solubility parameters, and much more. Most books are discounted from their original list price, some as much as 30%.

D/L LABORATORIES 116 East 16th Street, New York NY 10003, (212) 777-4445. Market research and analysis, testing, certification and specification of sealants and caulks.

DPNA INTERNATIONAL 126 Allendale Circle, Troutman NC 28166, (704) 528-3985. Global analysis and market studies. Multi-client studies. Extensive consulting in market development.

EDISON WELDING INSTITUTE 1250 Arthur E. Adams Drive, Columbus OH 43210, (614) 688-5000. Extensive research and development of joining processes, including adhesive bonding. Applications laboratory and consulting. Testing and analysis.

EINHORN ASSOCIATES INC. 2323 North Mayfair Road, Suite 490, Milwaukee WI 53226, (414) 453-4488. Specialists in mergers and acquisitions, corporate analysis, divestitures, joint ventures, and other financial and strategic issues.

EPIC CONSORTIUM FOR ADHESIVES, SEALANTS AND COATINGS (ECASC) 4040 Embassy Parkway, Suite 150, Akron OH 44333, (330) 668-9411. Joint research sponsored by the University of Akron and Case Western Reserve University.

EPOXY CONSULTING INC. 696 Knollwood Road, Franklin Lakes NJ 07417, (201) 848-1444. Formulation and product development, patent investigation, and market and sales development.

FOREST PRODUCTS LABORATORY Mississippi State University, Department of Forest Products, Box 9820, Mississippi State MS 39762-9820, (601) 325-2116. Extensive research into all phases of wood bonding and technology, wood composites, and lignin resin technology.

GALE RESEARCH INC. P.O. Box 33477, Detroit MI 48232-5477, (313) 961-2242 or (800) 877-4253. Publishes *Consulting and Consulting Organizations Directory*, *Encyclopedia of Business Information Sources*, and many other directories. Business information catalog.

MALAYSIAN RUBBER PRODUCERS RESEARCH ASSOCIATION Tun Abdul Razak Laboratory, Brickendonbury Hertford SG13 8NL UK, +44 (0)1992 554657. Extensive research, testing and analysis of natural rubber and associated technologies.

MATERIALS ENGINEERING RESEARCH LABORATORY LTD. Tamworth Road, Hertford SG13 7DG UK, +44 (0)1992 500120. Conducting a joint industry project called "Rubber/Metal Bonding—Reliability for Future Needs" to develop understanding of the durability of these bonds in automotive, aerospace and civil engineering applications. Associated with RAPRA (see below).

PIRA INTERNATIONAL Randalls Road, Leatherhead, Surrey KT22 7RU UK, +44 (0)1372 376161. Conducting research to resolve problems caused by adhesives in paper and packaging recycling.

JOSEPH W. PRANE 213 Church Road, Elkins Park PA 19027, (215) 635-2008. A consultant in adhesives, coatings, plastics and sealants since 1969. Numerous seminars and lectures on adhesives and sealants in Germany, Israel, Japan, Sweden as well as the United States. Former writer of the "Consultants Corner" for *Adhesives Age*.

RAPRA TECHNOLOGY LTD. Shawbury, Shrewsbury, Shropshire, SY4 4NR UK, +44 (0)1939 250383. Publishes *Adhesives Abstracts*, a monthly alerting service covering nearly 500 journals, international conferences, standards, specifications and more. Has numerous Published Searches, which are bibliographies in selected technology areas from online literature searches, many of which are adhesive industry related. Also has several Review Reports covering adhesive industry related topics.

RUBBER WORLD 1867 West Market Street, Akron OH 44313, (216) 864-2122. Each January issue provides an "Independent Testing Laboratories Directory."

TELTECH RESOURCE NETWORK CORPORATION 2850 Metro Drive, Minneapolis MN 55425-1566, (612) 851-7500. Telephone and computer access to leading specialists through the consulting network. Can also conduct literature search, vendor search, and establish an intelligence update and strategic technology tracking system.

TWI Abington Hall, Abington, Cambridge UK, +44 (0)1223 891162. Combined with the **Center for Adhesives Technology**, also of Cambridge, provides a comprehensive service in adhesives contract research and development, consulting, training, and technology transfer.

UNDERWRITERS LABORATORIES 333 Pfingsten Road, Northbrook IL 60062, (708) 272-8800. National testing, analysis and certification agency for products made for industrial, commercial, construction and consumer use.

UNITED SOYBEAN BOARD 16305 Swingley Ridge Drive, Suite 110, Chesterfield MO 63017, (314) 530-1777, or Omni Tech International Ltd., 2715 Ashman Street, Midland MI 48640, (517) 631-3377. Published *Precursors for the Manufacture of Soy Protein-Based Engineered Wood Adhesives*, and funds research into soy-based adhesive products.

UTILITY RESEARCH COMPANY Harry S. Katz, 112 Naylon Avenue, Livingston NJ 07039, (201) 994-4334. Research and development on plastics, advanced composites, adhesives, elastomers.

APPENDIX D—COURSES AND CONFERENCES

Conferences and symposia

AMERICAN CHEMICAL SOCIETY 1155 16th Street NW, Washington DC 20036, (202) 872-4396. A wide variety of symposia related to adhesives, polymers, surfaces, emulsions, colloids. Also, numerous short courses in the same areas.

AMERICAN DEFENSE PREPAREDNESS ASSOCIATION 2101 Wilson Blvd., Suite 400, Arlington VA 22201-3061, (703) 522-1820. International Symposium on Structural Adhesive Bonding.

ARMBRUSTER ASSOCIATES 43 Stockton Road, Summit NJ 07901, (908) 277-1614. Advanced Radiation (UV/EB) Curing Marketing/Technology Seminar.

ASSEMBLY MAGAZINE 191 South Gary Avenue, Carol Stream IL 60188, (708) 462-2293. Assembly Technology Expo, with numerous workshops and conferences.

CANON COMMUNICATIONS 3340 Ocean Park Blvd, Suite 1000, Santa Monica CA 90405-3216, (310) 392-5509. Medical Design and Manufacturing.

CENTRE FOR ADHESIVE TECHNOLOGY TWI, Abington Hall, Abington, Cambridge CB1 6AL UK, +44 (0)1223 891162. Joining Technology for Medical Devices and Equipment, plus other topics.

CHINA NATIONAL ADHESIVES INDUSTRY ASSOCIATION 20-A Xin Yuan Street, Chaoyang District, Beijing 100027 China, 86-10-6466 4618. China International Adhesives and Sealants.

DECHEMA POB 97 01 46, Theodor-Heuss-Allee 25, D-6000 Frankfurt am Main 97, Germany, phone +49 (069) 7564 280/241, fax +49 (069) 7564 201. Euradh: European Adhesion Congress, held in conjunction with Institute of Materials, Adhesion Society, and others. World Congress on Adhesion and Related Phenomena.

DERMIL RESEARCH LTD. 24 Buckingham Square, Wickford Business Park, Wickford, Essex SS11 8YO UK, phone +44 (0)1268 732573, fax +44 (0)1268 732516. Intabond: Specialty Adhesives for Laminating and Coating.

FOREST PRODUCTS SOCIETY 2801 Marshall Court, Madison WI 53705-2295, (608) 231-1361. Wood Adhesives, Green Chemistry for Adhesives.

GORDON RESEARCH CONFERENCES University of Rhode Island, West Kingston RI 02892-0984. Several adhesion and bioadhesion oriented conferences.

GORHAM INTERNATIONAL P.O. Box 9, Gorham ME 04038, (207) 892-2216. Pressure Sensitive Label Products. Science of Adhesion. Release Papers.

INSTITUTE OF MATERIALS 1 Carlton House Terrace, London SW1Y 5DB UK, +44 (0)20 7451-7300. Also, **Adhesives Group**, Technology Centre, SATRA House, Rockingham Road, Kettering, Northants NN16 9JH UK, +44 (0)1536 410000, A wide variety of topics covering adhesives, bonding composites, durability, and more.

INSTITUTE OF PACKAGING PROFESSIONALS 481 Carlisle Drive, Herndon VA 22070, (703) 318-8970. A variety of topics covering adhesives, cure of adhesives, hot melt tackifying Resins, labels, packaging, and more.

INTERNATIONAL SOCIETY OF COATING SCIENCE AND TECHNOLOGY c/o Edward Cohen, 15638 East Cerro Alto Drive, Fountain Hills AZ 85268-1720. Annual International Coating Science and Technology Symposium.

INTERNATIONAL UNION OF TESTING AND RESEARCH LABORATORIES FOR MATERIALS AND STRUCTURES (RILEM) TC 139-DBS, Building Research Establishment, Garston Watford WD2 7JR UK, +44 (0)1923 894040. Durability of Building Sealants, in conjunction with Building Research Establishment.

LOUGHBOROUGH UNIVERSITY University School of Technology, Leicestershire LE11 3TU UK, +44 (0)1509 223340. The Science and Technology of Adhesive Bonding (Joining Technology Research Centre). Conference on Adhesion and Surface Analysis (Institute of Surface Science and Technology).

MESSE FRANKFURT GMBH Bondtec-Team, Postfach 15 02 10, D-60062 Frankfurt am Main Germany, phone +49 (069) 7575-6710, fax +49 (069) 7575-6541. Bondtec Trade Fair for Surface Preparation and Bonding Technology.

MILLER FREEMAN One Penn Plaza, New York NY 10119-1198, (212) 615-2200. Converting Machinery/Materials Conference and Expo (CMMI).

MST CONFERENCES 3 Hammer Drive, Hopewell Junction NY 12533-6124, (845) 227-7026. A variety of conferences concentrating on scientific aspects of adhesion, adhesives, adhesive joints, surface and interface, specialty polymers and other related topics.

NETWORK GMBH Wilhelm-Suhr-Str. 14, D-3055 Hagenburg Germany, phone +49 05033-7057, fax +49 05033-7944. Eurobond.

OXFORD BROOKS UNIVERSITY Joining Technology Research Centre, Oxford Brooks University, Gipsy Lane Campus, Headington, Oxford OX3 0BP UK, +44 (0)1865 741111. Annual Conference on Adhesion and Adhesives.

PAINT RESEARCH ASSOCIATION 8 Waldegrave Road, Teddington, Middlesex TW11 8LD UK, +44 (0)20 8614 4800. Conferences and expos covering Advances in Coatings, Adhesives and Sealants Technology.

PIRA TECHNOLOGY Randalls Road, Leatherhead, Surrey KT22 7RU UK, +44 (0)1372) 376161. Adhesives in Packaging. Converting Flexible Webs.

PLASTICS AND RUBBER INSTITUTE Adhesives Group, SATRA Footwear Technology Centre, SATRA House, Rockingham Road, Kettering, Northants, NN16 9JH, UK, +44 (0)1536 410000. Adhesion. Bonding Advanced Composites.

RAPRA TECHNOLOGY Shawbury, Shrewsbury, Shropshire SY4 4NR UK, phone +44 (0)1939 250383, fax +44 (0)1939 251118. Bonding and Repair of Composite Materials. Rubber to Metal Bonding Seminar.

RBS TECHNOLOGIES INC. 8912 East Pinnacle Peak Road, Suite 609, Scottsdale AZ 85255, (602) 473-0301. International In-Mold Labeling Conference.

REED EXHIBITIONS 383 Main Avenue, Norwalk CT 10106, (203) 840-5360, or (203) 840-5878. National Manufacturing Week—Design Engineering and Plant Equipment & Maintenance.

SOCIETY OF MANUFACTURING ENGINEERS P.O. Box 930, Dearborn MI 48121, (313) 271-1500. Annual Adhesives Conference.

SWIBOTECH ENGINEERING Ulmenstrasse 6. D-26689 Apen-August-fehn Germany, phone +49 (0)4489 940158, fax +49 (0)4489 410206.. Swiss Bonding.

TAPPI P.O. Box 105113, Atlanta GA 30348-5113, (770) 446-1400. Hot Melt Symposium, plus other division conferences covering polymers, laminations, recycling, and related topics.

TARSUS CONFERENCES 16985 West Bluemound Road, Suite 210, Brookfield WI 53005, (262) 782-1900. Labelexpo.

TECHNOMIC PUBLISHING COMPANY 851 New Holland Avenue, Lancaster PA 17604, (717) 291-5609. A variety of conferences covering adhesives, polyurethanes, pressure sensitive adhesives, medical adhesives, and other related topics.

VERFAHRENSTECHNIK PAPIER UND KUNSTSTOFFVERARBEITUNG Fachhochschule München, Fachbereich 05, Postfasch 20 01 13, D-80001 Munich Germany, phone +49 (189) 1265-1526, fax +49 (189) 1265-1502. Munich Adhesive and Finishing Seminar.

VINCENTZ VERLAG Schiffgraben 43, D-30175 Hannover Germany, phone +49 (511) 9910-272, fax +49 (511) 9910-279. Adhesion Congress: Tracking Adhesion—Selecting the Right Binders.

WOOD AND WOOD PRODUCTS MAGAZINE P.O. Box 1400, Lincolnshire IL 60069, (708) 323-7214. Laminating—A Technical Seminar on Decorative Materials, Trends and Technology.

SHORT COURSES AND WORKSHOPS ABARIS TRAINING 5401 Longley Lane, Suite 49, Reno NV 89511, (775) 827-6568. Several courses related to adhesives and composites bonding and repair for aircraft.

ADHESION SOCIETY 2 Davidson Hall, Virginia Tech, Blacksburg VA 24061-0201, (540) 231-7257. Short Course on Adhesion—Theory and Practice.

ADHESIVE AND SEALANT COUNCIL 7979 Old Georgetown Road, Suite 500, Bethesda MD 20814, (301) 986-9700. Numerous short courses on adhesives, applicating equipment, Caulks and sealants, end use applications, process development, additives, equipment, and more.

ADVANCED POLYMER COURSES 536 Main Street, Unit #1, Falmouth MA 02540, (508) 540-9587. Inherently Conductive Polymers.

AKRON RUBBER DEVELOPMENT LABORATORY 2887 Gilchrist Road, Akron OH 44305, (330) 794-6600. High Tech Adhesives, co-sponsored by American Engineering Group. Also several workshops on fundamentals of adhesion, testing, and more.

CENTER FOR PROFESSIONAL ADVANCEMENT P.O. Box 1052, East Brunswick NJ 08816-1052, (908) 613-4535. Numerous courses and workshops on nearly every facet of polymers, emulsions, dispersions, adhesives, catalysts, surface analysis, converting, rheology, mixing, and more.

CENTRE FOR ADHESIVE TECHNOLOGY TWI, Abington Hall, Abington, Cambridge CB1 6AL UK, +44 (0)1223 891162. Joining Technology for Medical Devices and Equipment.

CHEMSULTANTS INTERNATIONAL 9349 Hamilton Drive, P.O. Box 1118, Mentor OH 44061-1118, (216) 352-0218. Numerous courses on pressure sensitive adhesives, testing equipment, and more.

CONVERTING EQUIPMENT MANUFACTURERS ASSOCIATION 66 Morris Avenue, Suite 2A, Springfield NJ 07081, (201) 379-1100. Fundamentals of Coating Equipment Technology, and other converting courses.

ECASC–EPIC CONSORTIUM FOR ADHESIVES, SEALANTS AND COATINGS 4040 Embassy Parkway, Suite 150, Akron OH 44333, (330) 668-9411 and **Edison Polymer Innovation Corporation** (216) 838-5015. Intensive Short Course: Chemistry and Physics of Adhesion.

EDISON WELDING INSTITUTE 1250 Arthur E. Adams Drive, Columbus OH 43210, (614) 688-5252. Principles of Adhesive Bonding.

GUTOFF CONSULTING 194 Clark Road, Brookline MA 02445, (617) 734-7081. Coating and Drying Technology.

INSTITUTE OF MATERIALS SCIENCE State University of New York, P.O. Box 369, New Paltz NY 12561, (845) 255-0757. Several short courses covering polymer colloids/emulsion polymers, and adhesion.

INTERNATIONAL SOCIETY FOR OPTICAL ENGINEERING (SPIE) P.O. Box 10, Bellingham WA 98227-0010, (206) 676-3290. Adhesives in Optical Applications.

OHIO STATE UNIVERSITY NEMJET Office, 190 West 19th Avenue, Columbus OH 43210, (614) 292-1182. Structural Adhesive Joining.

PRESSURE SENSITIVE TAPE COUNCIL 2514 Stonebridge Lane Northbrook, IL 60065-0609, (847) 562-2530. Fundamentals of Pressure Sensitive Adhesive Tapes. Tape University Workshops 101 and 102.

RBS TECHNOLOGIES INC. 8912 E. Pinnacle Peak Road, St Scottsdale, AZ 85255, (480) 473-0301. ABCs of In-Mold Labeling. Regulatory Concerns for Adhesives and Coatings: A Practical Guide.

SAE INTERNATIONAL 400 Commonwealth Drive, Warrendale PA 15096-0001, (724) 772-7148. Adhesive Bonding Technology. Adhesives for Automotive Plastics.

SOCIETY OF MANUFACTURING ENGINEERS P.O. Box 930, Dearborn MI 48121, (313) 271-1500. Numerous courses and workshops on adhesives, and processing. Fundamentals of Adhesive Bonding.

TAPPI P.O. Box 105113, Atlanta GA 30348-5113, (800) 332-8686, (404) 446-1400. Hot Melt Tutorial.

TARSUS EXHIBITIONS 131 Southlands Road, Bromley, Kent BR2 9QT UK, +44 (0)20 313-3713 (formerly known as Cowise). Numerous courses on coating and laminating, films, pressure sensitive adhesives, release liner, and other related topics.

TECHTRAX P.O. Box 2070, Brighton MI 48116, (810) 229-6111. Joining, Sealing and Adhesives Technology for Packaging Lines.

UNIVERSITY OF MASSACHUSETTS LOWELL One University Avenue, Lowell MA 01854, (978) 934-2405. Adhesives and Adhesion.

UNIVERSITY OF MICHIGAN 400 Chrysler Center, North Campus, Ann Arbor MI 48109-2092, (313) 764-8490. Paints, Plastics and Adhesives for Automotive Usage.

UNIVERSITY OF MINNESOTA 204 Nolte Center, 315 Pillsbury Drive SE, Minneapolis MN 55455-0139, (612) 625-3530. Coating Process Fundamentals Short Course.

UNIVERSITY OF WISCONSIN–MADISON Department of Engineering Professional Development, 432 North Lake Street, Madison WI 53706, (608) 262-1299. Numerous courses and workshops on polymers, adhesives, processing, management, and more.

UNIVERSITY OF WISCONSIN–MILWAUKEE 929 North Sixth Street, Milwaukee WI 53203, (414) 227-3200. Numerous courses and workshops on polymers, adhesives, processing, management, and more.

APPENDIX E—DIRECTORIES AND MARKET RESEARCH

ADHESIVE INFORMATION SERVICES P.O. Box 1123, Mishawaka IN 46546, (219) 255-6749. *Information Resource Guide* is the most complete compilation of information sources available for the adhesive industry. The only comprehensive bibliography of books. These appendices are an abridged version of the 122-page book.

ADHESIVES AGE 110 William Street, 11th Floor, New York NY 10038, (212) 621-4900. Annual supplier directory issue, plus a limited adhesive and sealant manufacturer listing.

ADHESIVE AND SEALANTS INDUSTRY P.O. Box 400, Flossmoor IL 60422, (708) 922-0761. Annual buyer's Guide for raw materials and equipment.

ALEXANDER WATSON ASSOCIATES Barford View, Churt, Surrey GU10 2NX UK, +44 (0)1428 717661. Self-Adhesive Labelstock and Graphic Arts European Annual Review: Release Liners, European Annual Review.

AMERICAN COUNCIL OF INDEPENDENT LABORATORIES 1629 K Street NW, Suite 400, Washington DC 20006, (202) 887-5872. Directory of Laboratories.

ASTM INTERNATIONAL 100 Barr Harbor Drive, West Conshohocken PA 19428-2959, (610) 832-9707. Publishes the *Annual Book of Standards*, plus specific books of standards for each industry segment represented by a committee. Also publishes directories of consultants and testing laboratories.

BUSINESS COMMUNICATIONS COMPANY 25 Van Zant Street, Norwalk CT 06855, (203) 853-4266. Numerous market research studies on a wide variety of subjects, including adhesives, polymers, and more. Detailed brochure.

BUSINESS TRENDS ANALYSTS 2171 Jericho Turnpike, Commack NY 11725, (516) 462-5454; U.S. Adhesives and Sealants Industry. Market for Converted Flexible Packaging.

CHEMICAL WEEK 110 William St; 11th Floor, New York, NY 10038 (212) 621-4802. Several limited directories printed within, or supplied with, specific issues of the magazine, including Adhesive Manufacturers, Chemical Consulting Services Directory, and Website Directory.

CHEMQUEST GROUP INC. 8150 Corporate Park Drive, Suite 250, Cincinnati OH 45242, (513) 469-7555. *The U.S. Adhesive Industry*, six-volume study, updated regularly.

D.A.T.A. BUSINESS PUBLISHING 15 Inverness Way East, Englewood CO 80112, (303) 799-0381. A number of directories of industrial segments and products of producers, including adhesives, epoxies, films, sheets and laminates, plastics.

DATAMONITOR 1 Park Avenue, 14th Floor, New York NY 10016-5802, (212) 686-7400. United States–Adhesives and Sealants.

DELPHI MARKETING SERVICES INC. 400 East 89th Street, New York NY 10128, (212) 534-4868. Directory of Custom Chemical Manufacturers.

DPNA INTERNATIONAL 126 Allendale Circle, Troutman NC 28166, (704) 528-3985, in conjunction with **CHEM Research GmbH**, Hamburger Allee 26-28, D-60486 Frankfurt Germany, +49 (069) 970-8410. The Global Adhesives and Sealants Industry, An Executive Market Trend Analysis, updated regularly. Also particpates with other agencies to publish studies in specific markets.

E.I. DUPONT DE NEMOURS AND COMPANY P.O. Box 80010, Wilmington DE 19880-0010, (800) 441-7111. *Delphi Forecast of the Future of the Adhesives Industry*, edited by G.M. Estes, six-volume unpaged study by 382 individuals in 132 organizations, 1975.

ECONOMIST INTELLIGENCE UNIT 215 Park Avenue South, New York NY 10003, (212) 460-0600. Market studies on rigid and flexible packaging.

EUROTRENDS RESEARCH 16 Lyonsdown Avenue, New Barnet, Herts EN5 1DU UK, +44 (0)20 8440-4919. Adhesives in the West European Car Industry.

FMJ INTERNATIONAL PUBLICATIONS LTD. Queensway House, 2 Queensway, Redhill, Surrey RH1 1QS UK, +44 (0)1737 768611. European Adhesives and Sealants Yearbook.

FREEDONIA GROUP 3570 Warrensville Center Road, Suite 201, Cleveland OH 44122-5226, (216) 921-6800. A wide variety of market research studies, including adhesives, tapes, polymers, resins, epoxies, hot melts, labels, silicones, waxes, and a selection of natural and synthetic raw materials, plus several end user markets.

FROST AND SULLIVAN INTERNATIONAL 7550 West Interstate 10, Suite 910, San Antonio TX 78229-5616, (210) 348-1000, or Sullivan House, 4, Grosvenor Gardens, London SW1W 0DH UK. A wide variety of market research studies, including adhesives, tapes, polymers, resins, epoxies, hot melts, labels, waxes, and a selection of natural and synthetic raw materials, plus some end user markets.

GALE RESEARCH INC. P.O. Box 33477, Detroit MI 48232-5477, (800) 877-4253. Business Information Catalog describes the many different resource directories available, including detailed directories of associations, publications, databases, business information sources, consultants, and many more.

GLOBAL INDUSTRY ANALYSTS INC. 5645 Silver Creek Valley Road, Suite 200, San Jose CA 95138, (408) 528-9966. Adhesives and Sealants: A Global Strategic Business Report.

GOWER PUBLISHING COMPANY Old Post Road, Brookfield VT 05036, (802) 276-3162 (also known as **Synapse Information Systems**, see separate entry). A number of cross-referenced directories of chemical additives, surfactants, elastomers, trade names, and more.

HOCHBERG AND COMPANY P.O. Box 222, Chester NJ, (908) 879-7170. Several studies on naval stores, adhesives, dispersants, polymers, and more.

IAL CONSULTANTS 109 Uxbridge Road, Ealing, London W5 5TL UK, +44 (0)20 8810-0919. A wide range of studies, including the European Adhesives Industry, European Structural Adhesives, Radiation Curing Markets in North and South America, Europe, and Asia, and Polyurethane CASE Markets.

IMPACT MARKETING CONSULTANTS INC. P.O. Box 1226, Torbank Suite 3, Manchester Center VT 05255, (802) 362-2325. Rauch Guides to the U.S. Adhesives and Sealants Industry, and to the U.S. Paint Industry.

INTERNATIONAL DEVELOPMENT ASSOCIATES INC. P.O. Box 702, Mendenhall PA 19357, (610) 388-2135. Study of International Rosin Markets.

KLINE AND COMPANY Overlook @ Great Notch, 150 Clove Road, Little Falls NJ 07424, (973) 435-6262, or **KLINE EUROPE LTD.** 1, Avenue Gribaumont, B-1160 Brussels Belgium, +32(2) 770-4740. A wide variety of market research studies, including adhesives, tapes, polymers, plus some end user markets. Both US and global market coverage.

KUSUMGAR AND NERLFI INC. 6 Stonybrook Drive, North Caldwell NJ 07006, (201) 364-0438. Studies on radiation-cured products, hot melt adhesives, and more.

LABEL-PACK CONVERTING INSTITUTE P.O. Box 6185, Venice FL 34292, (941) 473-0807. Global Directory of Labeling and Packaging Converters. Over 2500 converters in the U.S. alone.

LABEL-PACK CONVERTING INSTITUTE in conjunction with **DPNA International** (see above) and **Business Factors**. Studies of PSA Label Markets and Folding Carton and Flexible Packaging Markets of the Asia Pacific Region.

LABELS AND LABELLING DATA 60 High Street, Potters Bas Herts ENG 5AB UK, +44 (0)1707-645322. Self-Adhesive Label Markets in Western Europe.

MARKET AND BUSINESS DEVELOPMENT LTD. Barnett House, 53 Fountain Street, Manchester M2 2AN UK, +44 (0)161 247-8600. UK Adhesives Market Development.

MARKET TRACKING INTERNATIONAL 6 Archway Business Center, Wedmore Street, London N19 4RU UK, +44 (0)20 7263-1365. World Adhesives.

MATERIALS INFORMATION Cambridge Scientific Abstracts, 7200 Wisconsin Avenue, Bethesda MD 20814-4823, (301) 961-6750, in cooperation with **ASM International and Institute of Materials (UK)**. Search in Print—300 bibliographies available on specific topics including adhesives.

MEDMARKET DILIGENCE LLC 51 Fairfield, Foothill Ranch CA 92610-1856, (949) 859-3401. Worldwide Wound Sealant Market.

OFF-THE-SHELF PUBLICATIONS INC. 2171 Jericho Turnpike, Commack NY 11725, (516) 462-2410. The European Market for Consumer Adhesives, 492 pp. (by **E.R.C. Statistics**).

PACKAGING GROUP INC. P.O. Box 345, Milltown NJ 08850, (908) 636-0885. The Guide to Latin American Packaging/Converting Industries. Thousands of companies are listed, 250 pp.

PACKAGING STRATEGIES INC. 122 South Church Street, West Chester PA 19382-3223, (610) 436-4220. Annual Packaging Outlook study, plus specialty reports for the packaging industry. Flexible Packaging in the US.

PAPERLOOP PUBLICATIONS Miller Freeman, 55 Hawthorne, Suite 600, San Francisco CA 94105, (415) 947-3600. Directory of North American Converters.

PIRA INTERNATIONAL Randalls Road, Leatherhead, Surrey KT22 7RU England, +44 (0)1372 802000. The Future of Labels and Labelling for the European Market.

PRESSURE SENSITIVE TAPE COUNCIL 401 North Michigan Avenue, 24th Floor, Chicago IL 60611, (312) 644-6610. Tape Products Directory, annual.

RAPRA TECHNOLOGY LTD. Shawbury, Shrewsbury, Shropshire, SY4 4NR UK, +44 (0)1939 250383. A wide variety of abstracting and research reports available covering elastomers of various types, adhesives, bonding, and plastics.

REED USA 1100 Summer Street, Stamford CT 06905-0824, (203) 328-2500. U.S. Industrial Directory, annual directory of U.S. manufacturers.

RUBBER AND PLASTICS NEWS 1725 Merriman Road, Suite 300, Akron OH 44313, (330) 836-9180. Rubber Directory and Buyer's Guide, annual.

SKEIST INC. 375 Route 10, Whippany NJ 07981, (973) 515-2020. A wide variety of market research studies, including adhesives, sealants, pressure sensitive products, polymers, hot melts, radiation curing, and more.

SPECIALISTS IN BUSINESS INFORMATION INC. 3375 Park Avenue, Suite 2000A, Wantagh NY 11793, (516) 781-7277. Market Profile on Pressure Sensitive Products. Adhesives and Sealants.

SPENCER RESEARCH RFD 3 Box 1123, Bridgton ME 04009, (207) 647-8144. Release Papers and Films–Worldwide Markets.

SPRINGBORN MATERIALS SCIENCE CORPORATION One Springborn Center, Enfield CT 06082, (203) 749-8371. Automotive Adhesives, Sealants and Sound Deadeners.

SRI CONSULTING 333 Ravenswood Avenue, Menlo Park CA 94025, (650) 859-3627. Directory of Chemical Producers.

STANDARD RATE AND DATA SERVICE (SRDS) 3004 Glenview Road, Wilmette IL 60091, (708) 256-6067. Business Publication Rates and Data, monthly profiles of 5300 U.S. business, technical and trade publications.

STUDIO TAMBURINI Via P. Fornari 46, 20146 Milano Italy, 39 (2) 48704572. The European Market for Specialty Adhesives and Sealants.

SYNAPSE INFORMATION SYSTEMS INC. 1247 Taft Avenue, Endicott NY 13760, (607) 748-4145. (see also **Gower Publishing**). Handbook of Adhesive Chemical and Compounding Ingredients.

TAG AND LABEL MANUFACTURERS INSTITUTE 40 Shuman Blvd., Suite 295, Naperville IL 60563, (630) 357-9222. North American Market for Pressure Sensitive Labels (with **Frost and Sullivan**, see above).

TECHNOLOGY ASSESSMENT ASSOCIATES P.O. Box 1362, Amherst NH 03031-9939, (603) 673-0312. A number of studies on Adhesives in Electronics, Bonding and Joining Composites, Markets for Adhesive Tapes and Films, Conductive Adhesives, Aerospace Sealants, and Growth Markets for Adhesives.

TECHNOLOGY CATALYSTS INTERNATIONAL 605 Park Ave., Falls Church VA 22046, (703) 237-9600. Advances in Functional Adhesives: Global Business Opportunities and Commercial Intelligence. Dirass Report E13-16: Functional Industrial Adhesives (by **DIA Research Institute of Japan**).

THOMAS PUBLISHING One Penn Plaza, New York NY 10119, (212) 695-0500 *Thomas' Register of American Manufacturers*, multivolume directory of U.S. manufacturers, annual.

TPC BUSINESS RESEARCH GROUP Pathfinder Operations, 851 New Holland Avenue, Box 3535, Lancaster PA 17604, (717) 291-5609, or Missionsstrasse 44, CH-4055 Basel Switzerland, +41 (061) 43-52-26. Radiation-CuredPolymers in the U.S. Structural Adhesives in Western Europe.

TURRET WHEATLAND LTD. Penn House, Rickmansworth, Herts WD3 1SN UK Adhesives Directory, published annually since 1966.

US GOVERNMENT PRINTING OFFICE 732 North Capitol Street NW, Washington DC 20401, (202) 512-1800. *Standards Activities of Organizations in the United States* (NIST Special Publication 806). This directory summarizes the standards activities of 80 federal agencies and more than 600 organizations.

VERLAG WINTER GMBH 5 Breslauer Strasse, D-6056 Heusenstamm Germany, +49 (06104) 61631. Winterbond Adhesive Technology.

VINCENTZ VERLAG Schiffgraben 43, D-30175 Hannover Germany, +49 (05 11) 99 10-000. RadCure Directory.

WORLD PUBLICATIONS SERVICE P.O. Box 7717, East Rutherford NJ 07073, (201) 365-1278. Directory of Custom Chemical Manufacturers.

APPENDIX F—GOVERNMENT AGENCIES

AGRICULTURE DEPARTMENT 14th Street & Independence Avenue SW, Washington DC 20250, (202) 720-2791. Variety of programs oriented to finding different uses for commodity crops. Also collects and disseminates wide array of statistics, publishes numerous documents. Has 122 domestic and eight overseas research facilities.

Agricultural Research Service Beltsville Agricultural Research Center, Building 003, West Beltsville MD 20705.

Forest Products Laboratory One Gifford Pinchot Drive, Madison WI 53705, (608) 231-9200.

National Agricultural Library 10301 Baltimore Blvd., Beltsville MD 20705-2351, (301) 504-5248.

BUREAU OF ENGRAVING AND PRINTING 14th & C Streets SW, Washington DC 20228, (202) 874-2778. Designs, engraves, and prints currency, bonds, notes, bills, certificates, Federal Reserve notes, and revenue, customs, postage, and savings stamps.

COMMERCE DEPARTMENT 14th Street & Constitution Avenue NW, Washington DC 20230, (202) 482-2000. Major source of information on business activity, both international and domestic. Domestic activity can be tracked through publications of the Census Bureau (see below for location), which surveys business every five years by Standard Industrial Classification (SIC), and forecasts activity for each segment each year (U.S. Industrial Outlook, available from NTIS). Adhesives, SIC 2891, report included in Miscellaneous Chemical Products, last surveyed in 1992. Manufacturers are required by law to respond to surveys, but not every producer of adhesive and sealant products is represented because of nuances in the conduct of the survey. However, lots of good information for comparative valuation of business, workforce output, etc.

Bureau of the Census Suitland and Silver Hill Roads, Suitland MD, (301) 763-4040; mailing address: Washington DC 20233.

International Trade Administration same address, (202) 482-3808.

Office of Business Liaison same address #4824, (202) 482-3942.

Office of Technology Administration same address, (202) 482-1575.

DEFENSE DEPARTMENT The Pentagon, Washington DC 20301-1000, (703) 695-5261, or (703) 545-6700. Not only does the Defense Department purchase a great deal of adhesives, sealants, coatings, tapes, composites, and other miscellaneous materials from the Adhesive and Specialty Chemicals industries, but they also fund a great deal of research and development on materials, both internally and externally, some of which is related to these same products. Listed below are a number of locations and groups with the Defense Department which have interfaced at some point with the Adhesive industry.

Advanced Research Projects Agency 3701 N. Fairfax Dr., Arlington VA 22203-1714, (703) 696-2400.

Defense Research and Engineering Pentagon #3E1045, 20301-3080, (703) 695-0598.

Defense Technical Information Center Cameron Station, Alexandria VA 22304-6145, (703) 274-7633. Central repository for Defense Department collection of current and completed R&D efforts in all fields. Alternate address is 8725 John Jay Kingman Road #0944, Fort Belvoir VA 22060-6218, (703) 767-9100.

Research and Engineering Pentagon #3E1014, 20301-3030, (703) 697-5776.

Department of the Air Force R&D, Acquisitions Office, 20330-1060, (703) 697-6361.

Aerospace Materials Laboratory Wright Patterson Air Force Base OH 45433.

Air Force Office of Scientific Research 110 Duncan Avenue, Bolling AFB, Washington DC 20332-0001, (202) 767-4960.

Department of the Army R&D, Acquisitions Office, 20310-0103, (703) 695-6153.

Army Armament R&D Center Picatinny Arsenal, Dover NJ 07806-5000, (201) 724-4104. Extensive library with contract search and R&D services available. Home of PLASTEC library.

Army Belvoir Research, Development & Engineering Center Ft. Belvoir VA 22060-5606, (703) 704-2234.

Army Chemical Research & Development Center Edgewood Site, Aberdeen Proving Ground MD 21010-5423, (301) 671-2309.

Army Materials Technology Laboratory Watertown MA 02172-0001, (617) 923-5005.

Army Natick Research, Development and Engineering Center 258 Kansas Street, Natick MA 01760-5008, (508) 651-4995.

Army Research Laboratory 2800 Powder Mill Road, Adelphi MD 20783-1145, (301) 394-3590.

Army Research Laboratory Watertown MA 02172-0001, (617) 923-5275.

Department of the Navy R&D, Acquisitions Office, 20350-1000, (703) 695-6315.

Department of the Navy Test Evaluation and Technology Requirements, 20350-2000, (703) 601-1870.

Navy Joining Center 1100 Kinnear Road, Columbus OH 43212, (614) 486-9243. Works partly in conjunction with Edison Welding Institute.

Naval Research Laboratory 4555 Overlook Ave. SW, Washington DC 20375-5320, (202) 767-3301.

Office of Naval Research Ballston Tower 1, 800 North Quincy Street, Arlington VA 22217-5660, (703) 696-5031.

ENVIRONMENTAL PROTECTION AGENCY 401 M Street SW, Washington DC 20460, (202) 260-4355. Administers federal environmental policies, establishes regulations, sponsors and conducts research, enforces regulations, and provides information on environmental subjects. Numerous branches based on type of environment, i.e., air, radiation, disposal, water, etc. Ten regional offices. On-line access points for database retrieval. Hazardous Waste and Cleanup Information Hotline same address, (800) 424-9346.

Science Advisory Board same address, (202) 260-4126.

Small Business Ombudsman Hotline same address, (800) 368-5888.

EUROPEAN COMMISSION Directorate General XII–Science, Research and Development, Rue de la Loi 200, B-1049 Brussels Belgium. Net site: www.CORDIS. Administers research funds, research projects having a continental European dimension on several aspects of adhesion and adhesives in a variety of industrial and academic fields.

GENERAL SERVICES ADMINISTRATION 18th and F Streets NW, Washington DC 20405, (202) 501-5082. Purchasing agent and storehouse for the federal government. Publishes the *Commerce Business Daily*, a reporting of all contract awards and future procurements.

Regulatory Information Service Center 750 Seventeenth Street NW, #500, Washington DC 20006, (202) 634-6222. Provides Executive branch, Congress, and the public with information on regulatory policies.

GOVERNMENT PRINTING OFFICE 732 North Capitol Street NW, Washington DC 20401, (202) 512-1991. Responsible for printing, binding, selling and distributing all text matter for the federal government. Numerous locations around the country. Many publications available for purchase through the Superintendent of Documents, including a monthly listing of new publications.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 300 E Street SW, Washington DC 20546, (202) 358-1547. Manager of all activities related to space flight, including evaluation of new technologies and materials. Provides information on technology derived from activities that may have practical applications in other fields. Conducts advanced R&D at eight field centers and sponsors research programs with small companies. Also has seven technology transfer offices around the country.

Small Business Innovation Research Program same address, (202) 358-4661.

Ames Research Center Moffett Field CA 94035, (415) 604-4044.

Goddard Space Flight Center Greenbelt MD 20771, (301) 286-6242.

Jet Propulsion Laboratory 4800 Oak Grove Drive, Pasadena CA 91109, (818) 354-5179.

Lyndon B. Johnson Space Center Houston TX 77058, (713) 483-3809.

Langley Research Center 10 West Taylor Road, Hampton VA 23665-5225, (757) 864-2484.

Glenn Research Center 21000 Brookpark Road, Cleveland OH 44135, (216) 433-2225.

George C. Marshall Space Flight Center Marshall Space Flight Center AL 35812, (205) 544-3151.

John C. Stennis Space Center Stennis Space Center MS 39529, (601) 688-2042.

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY Route I270 and Quince Orchard Road, Building 101, Gaithersburg MD 20899, (301) 975-2762. National repository for information on voluntary industry standards for domestic and foreign products, conducts basic research into numerous fields (including dental materials), and promotes the standardization of labeling, packaging and measuring devices. Retains standard materials.

Chemical Science and Technology Laboratory same address, (301) 975-3145.

Materials Science and Engineering Laboratory same address, (301) 975-5658.

NATIONAL SCIENCE FOUNDATION 4201 Wilson Blvd., Arlington VA 22230, (703) 306-1070. Sponsors scientific and engineering research, and educational science programs. Acts as liaison for small business in awards of NSF grants and contracts.

Chemistry same address, (703) 306-1845.

Materials Research same address, (703) 306-1811.

NATIONAL TECHNICAL INFORMATION SERVICE 5285 Port Royal Rd., Springfield VA 22161, (703) 487-4636. Distribution center that markets government funded R&D reports, other technical analyses, SIC economic forecasts, and other publications prepared by federal agencies, their contractors or other grantees. Publishes abstract journal, a newsletter, and a Directory of Federal Laboratory and Technology Resources—A Guide to Services, Facilities, and Expertise. Extensive search capabilities and online database.

Adhesives: A Bibliography with Abstracts.

Published Search Master Catalog, 28 bibliographies on adhesives and adhesion, two on sealants.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION 200 Constitution Avenue NW, Washington DC 20210, (202) 219-8151. Sets and enforces rules and regulations for workplace safety and health. Implements the OSHA Develops standards. Provides federal agencies and private industry with compliance guidance and assistance.

PATENT AND TRADEMARK OFFICE 2121 Crystal Park II, #906, Arlington VA, (703) 305-8341; mailing address: Washington DC 20231. Grants patents and registers trademarks, provides patent and trademark information, maintains scientific library and search files.

POSTAL SERVICE 475 L'Enfant Plaza SW, Washington DC 20260, (202) 268-2284. Designs, manufactures and distributes postage stamps throughout the country.

STATE DEPARTMENT Main State Building, 2201 C Street NW, Washington DC 20520, (202) 647-2492. Besides the activity and information available through the Commerce Department, the State Department has information and assistance for companies doing business, or planning to do business, internationally.

Bureau of Economic and Business Affairs same address, (202) 647-1942.

Bureau of Intelligence and Research same address, (202) 647-6575.

TRADE AND DEVELOPMENT AGENCY 1621 North Kent Street, #309, Arlington VA, (703) 875-4357; mail address: State Annex 16, Washington DC 20523. Assists companies exporting to developing and middle income countries. Provides technical assistance and identifies commercial opportunities.

TRANSPORTATION DEPARTMENT 400 Seventh Street NW, Washington DC 20590, (202) 366-4570. Governs all U.S. transportation activities, including packaging and labeling requirements for chemicals, hazardous materials, poisons, and radioactive products. Conducts R&D programs and investigates accidents.

National Transportation Safety Board 490 L'Enfant Plaza East SW, Washington DC 20594, (202) 382-6600.

Research and Special Programs Administration same address, (202) 366-4461.

Interstate Commerce Commission Twelfth Street and Constitution Avenue NW, Washington DC 20423, (202) 927-5350. (While not strictly part of DOT, it does cover some of the same ground.)

APPENDIX G—JOURNALS AND TRADE PUBLICATIONS

Journals

Holz als Roh- und Werkstoff Springer-Verlag, 3020-Zeitschriftenherstellung, Heidelberger Platz 3, D-14197 Berlin Germany. Monthly.

Holzforschung Walter de Gruyter GmbH & Company, Postfach 303421, D-10728 Berlin Germany. Founded 1946. Monthly.

Holzforschung und Holzverwertung Osterreichische Gesellschaft fur Holzforschung, Franz-Grill-Strasse 7, A-1030 Vienna Austria. Founded 1948. Trimonthly.

International Journal of Adhesion and Adhesives Elsevier Science/Butterworth-Heinemann Ltd., Linacre House, Jordan Hill, Oxford OX2 8DP UK, +44 (0)1865 310366. Monthly.

Journal of Adhesion Taylor & Francis Group, 325 Chestnut Street, Suite 800, Philadelphia PA 19106, (215) 625-8914. Monthly.

Journal of Adhesion Science and Technology VSP B.V., P.O. Box 346, 3700 AH Zeist, The Netherlands. Founded 1987. Monthly.

Journal of Adhesive Dentistry 551 Kimberly Drive, Carol Stream IL 60188-1881, (630) 682-3223. Quarterly. Quintessence Publishing, publisher.

Journal of Applied Polymer Science John Wiley & Sons, 605 3rd Avenue, New York NY 10016, (212) 850-6000. Weekly.

Journal of Coating Technology Federation of Societies for Coatings Technology, 492 Norristown Road, Blue Bell PA 19422, (610) 940-0777. Monthly.

Journal of Dental Research American Association for Dental Research, 1619 Duke Street, Alexandria VA 22314, (703) 548-0066. Monthly.

Journal of Dispersion Science and Technology Marcel Dekker, 270 Madison Avenue, New York NY 10016, (212) 696-9000. Founded 1980. Bimonthly.

Journal of Elastomers and Plastics Technomic Publishing Company, 851 New Holland Avenue, Box 3535, Lancaster PA 17604, (717) 291-5609. Founded 1969. Quarterly.

Journal of Packaging Technology Technical Publications, One Lethbridge Plaza, Mahwah NJ 07430, (201) 529-3380. Bimonthly.

Journal of Radiation Curing Technology Marketing Corporation, 1 Technology Plaza, Norwalk CT 06854, (203) 852-6800. Founded 1974. Quarterly.

Journal of Water Borne Coatings Technology Marketing Corporation, 1 Technology Plaza, Norwalk CT 06854, (203) 852-6800. Founded 1978. Semi- annual.

Trade Publications Adhesives and Sealants Newsletter P.O. Box 1123, Mishawaka IN 46546, (574) 255-6749. Founded 1977. Monthly. Adhesive Information Services Inc., publisher.

Adhesives Age 110 William Street, 11th Floor, New York NY 10038, (212) 621-4900. Monthly. Chemical Week Associates, publisher.

Adhesives and Sealants Industry P.O. Box 400, Flossmoor IL 60422, (708) 922-0761. Monthly. Business News, publisher.

Adhesive Technology Queensway House, 2 Queensway, Redhill, Surrey RH1 1QS UK, +44 (0)1737 768611. Quarterly. FMJ International, publisher.

Adhesive Trends 2300 North Barrington Road, Suite 400, Hoffman Estates IL 60195, (847) 490-5377. Bimonthly newsletter. Adhesive Manufacturers Association, publisher.

The Applicator 2841 Main, Kansas City MO 64108, (816) 472-7974. Three times yearly technical newsletter. Sealant, Waterproofing and Restoration Institute, publisher.

Catalyst 7979 Old Georgetown Road, Bethesda MD 20814, (301) 986-9700. Monthly newsletter. Adhesive and Sealant Council, publisher.

Chemical and Engineering News 1155 16th Street NW, Washington DC 20036, (202) 872-4600. Weekly. American Chemical Society, publisher.

Chemical Marketing Reporter 2 Rector Street, New York NY 10006-1819, (212) 791-4200. Weekly. Schnell Publishing, publisher.

Composites and Adhesives Newsletter P.O. Box 36006, Los Angeles CA 90036, (213) 938-6923. Founded 1983. Quarterly. T/C Press, publisher.

Chemical Week 110 William Street, 11th Floor, New York NY 10038, (212) 621-4900. Weekly. Chemical Week Associates, publisher.

Converting Magazine 2000 Clearwater Drive, Oak Brook IL 60523, (630) 320-7000. Monthly. Reed Business Information, publisher.

Labels and Labeling 16985 West Blue Mound Road, Suite 210, Brookfield WI 53005, (262) 782-1900. Monthly. Tarsus Group, publisher.

Paper, Film and Foil Converter 29 North Wacker Drive, Chicago IL 60606, (312) 726-2802. Monthly. Primedia Business, publisher.

Radtech Report 3 Bethesda Metro Center, Suite 100, Bethesda MD 20814, (301) 664-8408. Bimonthly. Radtech International, publisher.

Surface Mount Technology 98 Spit Brook Road, Nashua NH 03062-5737, (603) 891-9395. Monthly. Pennwell, publisher.

APPENDIX H—ONLINE

Accelrys formerly the Oxford Molecular Group. Has a Cheminformatics database that specializes in multiple supplier databases, plus a variety of software tools for chemists. *http://www.accelrys.com/chem*

Adhesive and Sealant Council Offers licenses for an 11 course online training program in adhesive science and technology. Developed by the ASC Education Foundation and the Center for Adhesive and Sealant Science at Virginia Tech, these training modules are designed to provide an introductory level course for employees new to the technology. *www.ascouncil.org*

Adhesives Headquarters A user-friendly site tied directly to Thomas Register online that has a variety of adhesive and sealant categories pre-listed for quick access. Over 35 categories are listed on the home page, each of which will open even more categories at the Thomas Register website. Also have News and Headlines, and Events and Tradeshows. *www.adhesiveshq.com*

AdhesivesMart Provides a question and answer in Adhesive Selector format to generate best suggestion for product. Can also use keyword search. Database includes thousands of adhesives from manufacturers. *http://www.adhesivesmart.com*

American National Standards Institute Established the Global Standards Network, a comprehensive source of information on U.S. and international standards from government, associations, and private sector companies. Over 100,000 worldwide standards in database. *http://nssn.org*

Assembly Magazine In cooperation with EWI, Columbus OH, have developed an interactive tool called Adhesive Selector Guide, now in Version 2. Question and answer format. *http://www.assemblymag.com*

ASTM International Full index to all tests, specifications and standards, searchable by keyword and test number, and provides a summary for each with order information for fax delivery. Also has laboratory and consultants directories, new publications, and training program information. *http://www.astm.org/*

Chemcyclopedia Chemical buyer's guide published by the American Chemical Society (ACS) and fully searchable. Now operated independent of ACS, but still accessible through their website or directly. *http://mediabrains.com/client/chemcylop*

Chemical Abstracts Service/STN International The most comprehensive collection of national and international scientific and technical databases for the chemist. Maintained by the American Chemical Society. Covers literature, patents, CAS registries, and databases. Hundreds of scientific databases, nearly 20 million abstracts, search engines, including SciFinder. *http://info.cas.orghttp://stneasy.cas.org*

CleanTech Central An extensive range of information covering news, suppliers, directories, and contains a glossary and technical profiles on major cleaning technologies. *http://www.cleantechcentral.com*

ConvertingLoop An information and e-business network for the converting and package printing trades. News, product information, publications data, calendar events, and more. *http://www.convertingloop.com*

Delphion Formerly the IBM Patent Web. Has access to the world's patent databases. *http://delphion.com*

Duck Products Home page of Henkel Consumer Products, formerly Manco, that offers ideas on what to do with duct tape, including some really interesting idea, for the fashion industry. Also has history and Duck Tape Club. *http://www.duckproducts.com*

Duct Tape Web Page Home page of two writers who wrote five popular humor books on duct tape, which can be ordered through the site. Also has information on interesting uses of duct tape that are not likely to be found anywhere else, and connections to other duct tape pages. Lots of duct tape products available. *http://www.ducttapeguys.com*

Federal Research and Development Program in Materials Science and Engineering Part of NIST, and lists researchers in government, industry and universities involved in nine federal government and agency programs. *http://www.msel.nist.gov*

Green Seal Established an environmental standard for adhesives. Concentrating on flooring adhesives, building and construction adhesives, and material bonding adhesives. Previously had posted a standard on Building Sealing and Ventilation that named specific sealants and caulks. *http://www.greenseal.org*

Infocus Marketing A virtual mall for the converting industry. Contains links to coating, coverting, and laminating suppliers and sources. *http://www.webcoating.com*

Micropatent Free access to the current issue of the Official Gazette of the US Patent and Trademark Office. Offers patent and trademark searching. Services include full text printing and database searches. *http://www.micropatent.com*

Mindbranch Reseller of over thousands of directories, newsletters, and market studies from over 300 firms. Several are from companies listed in Appendix E. *http://www.mindbranch.com*

National Institute of Standards and Technology A vast resource of chemical property information, including several databases of chemical data. *http://nist.gov*

National Technical Information Service (Department of Commerce) Best source for finding and ordering nonclassified government reports from most agencies. Nearly 1000 records related to keyword "Adhesive." *http://www.ntis.gov*

National Technology Transfer Center Offers access to a wide range of technology commercialization and economic development. Covers EPA, NASA, Missile Defense Agency and more. *http://nttc.edu*

Pacific Northwest Pollution Prevention Resource Center Recommends three alternative technologies to solvent based adhesives and advantages of each. Covered are: water based, hot melts, and radiation cured. *http://www.pprc.org*

Patent and Trademark Office (Department of Commerce) Fully searchable index for all patents of this and the last century, full text. Also, images of 800,000 trademarks. *http://www.uspto.gov*

75 years of Band-Aid Web page started by person who found several very old Band-Aid boxes. Has received pictures from others and has a link to Johnson & Johnson home page, which has history. *http://www.savetz.com/bandaid/ http://www.jnj.com*

Techstreet Formerly the Custom Standards Services. Company offers access to the collections of technical information of 1000 publishers, industry associations, and technical societies that issue standards, specifications and test methods. Online information includes document number, title, publication date, price, and order information. *http://www.cssinfo.com*

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3
Theories and Mechanisms of Adhesion

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> There are agents in nature able to make the particles of joints stick together by very strong attraction and it is the business of experimental philosophy to find them out.
>
> —*Sir Isaac Newton*

I. INTRODUCTION

The adhesion phenomenon is relevant to many scientific and technological areas and has become in recent years a very important field of study. The main application of adhesion is bonding by adhesives, this technique replacing, at least partially, more classical mechanical attachment techniques such as bolting or riveting. It is considered to be competitive primarily because it allows us to save weight, to ensure a better stress distribution, and offers better aesthetics since the glue line is practically invisible. Applications of bonding by adhesives can be found in many industries, particularly in such advanced technical domains as the aeronautical and space industry, automobile manufacture, and electronics. Adhesives have also been introduced in such areas as dentistry and surgery.

Adhesive joints are not, however, the only applications of adhesion. Adhesion is involved whenever solids are brought into contact, as in coatings, paints, and varnishes; multilayered sandwiches; polymer blends; filled polymers; and composite materials. Since the final performance of these multicomponent materials depends significantly on the quality of the interface that is formed between the solids, it is understandable that a better knowledge of the adhesion phenomenon is required for practical applications.

Adhesion began to create real interest in scientific circles only about 60 years ago. At that time adhesion became a scientific subject in its own right but is still a subject in which empiricism and technology are slightly in advance of science, although the gap between theory and practice has been shortened considerably. In fact, the term *adhesion* covers a wide variety of concepts and ideas, depending on whether the subject is broached from a molecular, microscopic, or macroscopic point of view or whether one talks about formation of the interface or failure of the formed system. The term *adhesion* is therefore ambiguous, meaning both the establishment of interfacial bonds and the mechanical load required to break an assembly. As a matter of fact, one of the main difficulties in the study of adhesion mechanisms lies in the fact that the subject is at the boundary of several scientific fields, including macromolecular science, physical chemistry of surfaces and interfaces, materials science, mechanics and micromechanics of fracture, and rheology. Consequently, the study of adhesion uses various concepts, depending very much on one's field of expertise, and therefore treatment of the phenomena observed can be considerably different. This variety of approaches is emphasized by the fact that many theoretical models of adhesion have been proposed, which together are both complementary and contradictory:

1. Mechanical interlocking
2. Electronic theory
3. Theory of boundary layers and interphases
4. Adsorption (thermodynamic) theory
5. Diffusion theory
6. Chemical bonding theory.

Among these models, one usually distinguishes rather arbitrarily between mechanical and specific adhesion, the latter being based on the various types of bonds (electrostatic, secondary, chemical) that can develop between two solids. Actually, each of these theories is valid to some extent, depending on the nature of the solids in contact and the conditions of formation of the bonded system. Therefore, they do not negate each other and their respective importance depends largely on the system chosen.

II. MECHANISMS OF ADHESION

A. Mechanical Interlocking

The mechanical interlocking model, proposed by MacBain and Hopkins in 1925 [1], conceives of mechanical keying, or interlocking, of the adhesive into the cavities, pores, and asperities of the solid surface to be the major factor in determining adhesive strength. One of the most consistent examples illustrating the contribution of mechanical anchoring was given many years ago by Borroff and Wake [2], who have measured the adhesion between rubber and textile fabrics. These authors have clearly proved that penetration of the protruding fiber ends into the rubber was the most important parameter in such adhesive joints. However, the possibility of establishing good adhesion between smooth surfaces leads to the conclusion that the theory of mechanical keying cannot be considered to be universal. To overcome this difficulty, following the approach suggested primarily by Gent and Schultz [3,4], Wake [5] has proposed that the effects of both mechanical interlocking and thermodynamic interfacial interactions could be taken into account as multiplying factors for estimating the joint strength G:

$$\begin{aligned} G = {} & (\text{constant}) \times (\text{mechanical keying component}) \\ & \times (\text{interfacial interactions component}) \end{aligned}$$

Therefore, according to the foregoing equation, a high level of adhesion should be achieved by improving both the surface morphology and physicochemical surface properties of substrate and adhesive. However, in most cases, the enhancement of adhesion by mechanical keying can be attributed simply to the increase in interfacial area due to surface roughness, insofar as the wetting conditions are fulfilled to permit penetration of the adhesive into pores and cavities.

Work by Packham and co-workers [6–9] has further stressed the notable role played by the surface texture of substrates in determining the magnitude of the adhesive strength. In particular, they have found [6] that high values of peel strength of polyethylene on metallic substrates were measured when a rough and fibrous type of oxide surface was formed on the substrate. More recently, Ward et al. [10–12] have emphasized the improvement in adhesion, measured by means of a pull-out test, between plasma-treated polyethylene fibers and epoxy resin. In that case, long-time plasma treatments create a pronounced pitted structure on the polyethylene surface, which can easily be filled by the epoxy resin by means of good wetting.

One of the most important criticisms of the mechanical interlocking theory, as suggested in different studies [9,13,14], is that improved adhesion does not necessarily result from a mechanical keying mechanism but that the surface roughness can increase the energy dissipated viscoelastically or plastically around the crack tip and in the bulk of the materials during joint failure. Effectively, it is now well known that this energy loss is often the major component of adhesive strength.

B. Electronic Theory

The electronic theory of adhesion was proposed primarily by Deryaguin and co-workers [15–19] in 1948. These authors have suggested that an electron transfer mechanism between the substrate and the adhesive, having different electronic band structures, can occur to equalize the Fermi levels. This phenomenon could induce the formation of a double electrical layer at the interface, and Deryaguin et al. have proposed that the resulting electrostatic forces can contribute significantly to the adhesive strength. Therefore, the adhesive–substrate junction can be analyzed as a capacitor. During interfacial failure of this system, separation of the two plates of the capacitor leads to an increasing potential difference until a discharge occurs. Consequently, it is considered that adhesive strength results from the attractive electrostatic forces across the electrical double layer. The energy of separation of the interface G_e is therefore related to the discharge potential V_e as follows:

$$G_e = \frac{h\varepsilon_d}{8\pi}\left(\frac{\partial V_e}{\partial h}\right)^2 \tag{1}$$

where h is the discharge distance and ε_d the dielectric constant. Moreover, according to such an approach, adhesion could vary with the pressure of the gas in which the measurement is performed. Hence Deryaguin et al. have measured, by means of a peel test, the work of adhesion at various polymer–substrate interfaces, such as poly(vinyl chloride)–glass and natural rubber–glass or steel systems, in argon and air environments at various gas pressures. A significant variation in peel energy versus gas pressure was indeed evidenced and very good agreement between the theoretical values, calculated from Eq. (1), and the measured values of G_e was obtained whatever the nature of the gas used. However, several other analyses [5,20] have not confirmed these results and seem to indicate that the good agreement obtained previously was rather causal. According to Deryaguin's approach, the adhesion depends on the magnitude of the potential barrier at the substrate–adhesive interface. Although this potential barrier does exist in many cases (see, e.g., [21,22]), no clear correlation between electronic interfacial parameters and work of adhesion is usually found. Moreover, for systems constituted of glass substrate coated with a vacuum-deposited layer of gold, silver, or copper, von Harrach and Chapman [23] have shown that the electrostatic contribution to peel strength, estimated from the measurement of charge densities, can always be considered as negligible. Furthermore, as already mentioned, the energy dissipated viscoelastically or plastically during fracture experiments plays a major role on the measured adhesive strength, but it is not included conceptually in the electronic theory of adhesion. Finally, it could be concluded that the electrical phenomena often observed during failure processes are the consequence rather than the cause of high bond strength.

C. Theory of Weak Boundary Layers: Concept of Interphase

It is now well known that alterations and modifications of the adhesive and/or adherend can be found in the vicinity of the interface leading to the formation of an interfacial zone exhibiting properties (or properties gradient) that differ from those of the bulk materials. The first approach to this problem is due to Bikerman [24], who stated that the cohesive strength of a weak boundary layer (WBL) can always be considered as the main factor in determining the level of adhesion, even when the failure appears to be interfacial. According to this assumption, the adhesion energy G is always equal to the cohesive energy G_c(WBL) of the weaker interfacial layer. This theory is based primarily on probability considerations showing that the fracture should never propagate only along the adhesive–substrate interface for pure statistical reasons and that cohesive failure within the weaker material near the interface is a more favorable event. Therefore, Bikerman has proposed several types of WBLs, such as those resulting from the presence at the interface of impurities or short polymer chains.

Two main criticisms against the WBL argument can be invoked. First there is much experimental evidence which shows clearly that purely interfacial failure does occur for many different systems. Second, although the failure is cohesive in the vicinity of the interface in at least one of the materials in contact, this cannot necessarily be attributed to the existence of a WBL. According to several authors [25,26], the stress distribution in the materials and the stress concentration near the crack tip certainly imply that the failure must propagate very close to the interface, but not at the interface.

However, the creation of interfacial layers has received much attention in recent years and has led to the concept of "thick interface" or "interphase," widely used in adhesion science [27]. Such interphases are formed whatever the nature of both adhesive and substrate, their thickness being between the molecular level (a few angstroms or nanometers) and the microscopic scale (a few micrometers or more). Many physical, physicochemical, and chemical phenomena are responsible for the formation of such interphases, as shown from examples taken from our own recent work [28]:

1. The orientation of chemical groups or the overconcentration of chain ends to minimize the free energy of the interface [29]
2. Migration toward the interface of additives or low-molecular-weight fraction [30]
3. The growth of a transcrystalline structure, for example, when the substrate acts as a nucleating agent [31]
4. Formation of a pseudoglassy zone resulting from a reduction in chain mobility through strong interactions with the substrate [32]
5. Modification of the thermodynamics and/or kinetics of the polymerization or cross-linking reaction at the interface through preferential adsorption of reaction species or catalytic effects [33,34].

It is clear that the presence of such interphases can strongly alter the strength of multicomponent materials and that the properties of these layers must not be ignored in the analysis of adhesion measurement data. A complete understanding of adhesion, allowing performance prediction, must take into account potential formation of these boundary layers.

D. Adsorption (or Thermodynamic) Theory

The thermodynamic model of adhesion, generally attributed to Sharpe and Schonhorn [35], is certainly the most widely used approach in adhesion science at present. This theory is based on the belief that the adhesive will adhere to the substrate because of interatomic and intermolecular forces established at the interface, provided that an intimate contact is achieved. The most common interfacial forces result from van der Waals and Lewis acid–base interactions, as described below. The magnitude of these forces can generally be related to fundamental thermodynamic quantities, such as surface free energies of both adhesive and adherend. Generally, the formation of an assembly goes through a liquid–solid contact step, and therefore criteria of good adhesion become essentially criteria of good wetting, although this is a necessary but not sufficient condition.

In the first part of this section, wetting criteria as well as surface and interface free energies are defined quantitatively. The estimation of a reversible work of adhesion W from the surface properties of materials in contact is therefore considered. Next, various models relating the measured adhesion strength G to the free energy of adhesion W are examined.

1. *Wetting Criteria, Surface and Interface Free Energies, and Work of Adhesion*

In a solid–liquid system, wetting equilibrium may be defined from the profile of a sessile drop on a planar solid surface. Young's equation [36], relating the surface tension γ of materials at the three-phase contact point to the equilibrium contact angle θ, is written as

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} \cos\theta \tag{2}$$

The subscripts S, L, and V refer, respectively, to solid, liquid and vapor phases, and a combination of two of these subscripts corresponds to the given interface (e.g., SV corresponds to a solid–vapor interface). The term γ_{SV} represents the surface free energy of the substrate after equilibrium adsorption of vapor from the liquid and is sometimes lower than the surface free energy γ_{S} of the solid in vacuum. This decrease is defined as the spreading pressure $\pi\,(\pi = \gamma_{\mathrm{S}} - \gamma_{\mathrm{SV}})$ of the vapor onto the solid surface. In most cases, in particular when dealing with polymer materials, π could be neglected and, to a first approximation, γ_{S} is used in place of γ_{SV} in wetting analyses. When the contact angle has a finite value ($\theta > 0°$), the liquid does not spread onto the solid surface. On the contrary, when $\theta = 0°$, the liquid totally wets the solid and spreads over the surface spontaneously. Hence a condition for spontaneous wetting to occur is

$$\gamma_{\mathrm{S}} \geq \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} \tag{3}$$

or

$$S = \gamma_{\mathrm{S}} - \gamma_{\mathrm{SL}} - \gamma_{\mathrm{LV}} \geq 0 \tag{4}$$

the quantity S being called the spreading coefficient. Consequently, Eq. (4) constitutes a wetting criterion. It is worth noting that geometrical aspects or processing conditions, such as surface roughness of the solid and applied external pressure, are able to restrict the applicability of this criterion.

However, a more fundamental approach leading to the definition of other wetting criteria is based on analysis of the nature of forces involved at the interface and allows calculation of the free energy of interactions between two materials to be made. For low-surface-energy solids such as polymers, many authors have estimated the thermodynamic surface free energy from contact-angle measurements. The first approach was an empirical one developed by Zisman and co-workers [37–39]. They established that a linear relationship often exists between the cosine of the contact angle, $\cos\theta$, of several liquids and their surface tension, γ_{LV}. Zisman introduced the concept of critical surface tension, γ_c, which corresponds to the value of the surface energy of an actual or hypothetical liquid that will just spread on the solid surface, giving a zero contact angle. However, there is no general agreement about the meaning of γ_c and Zisman himself has always emphasized that γ_c is not the surface free energy of the solid but only a closely related empirical parameter.

For solid–liquid systems, taking into account Dupré's relationship [40], the adhesion energy W_{SL} is defined as

$$W_{\mathrm{SL}} = \gamma_{\mathrm{S}} + \gamma_{\mathrm{LV}} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{LV}}(1 + \cos\theta) \tag{5}$$

in agreement with Eq. (2) and neglecting the spreading pressure. Fowkes [41] has proposed that the surface free energy γ of a given entity can be represented by the sum of the contributions of different types of interactions. Schultz et al. [42] have suggested that γ may be expressed by only two terms: a dispersive component (London's interactions) and a polar component (superscripts D and P, respectively), as follows:

$$\gamma = \gamma^{\mathrm{D}} + \gamma^{\mathrm{P}} \tag{6}$$

The last term on the right-hand side of this equation corresponds to all the nondispersion forces, including Debye and Keesom interactions, as well as hydrogen bonding. Fowkes [43] has also considered that the dispersive part of these interactions between solids 1 and 2 can be well quantified as twice the geometric mean of the dispersive component of the surface energy of both entities. Therefore, in the case of interactions involving only dispersion forces, the adhesion energy W_{12} is given by

$$W_{12} = 2(\gamma_1^{\mathrm{D}}\gamma_2^{\mathrm{D}})^{1/2} \tag{7}$$

By analogy with the work of Fowkes, Owens and Wendt [44] and then Kaelble and Uy [45] have suggested that the nondispersive part of interactions between materials can be expressed as the geometric mean of the nondispersive components of their surface energy, although there is no theoretical reason to represent all the nondispersive interactions by this type of expression. Hence the work of adhesion W_{12} becomes

$$W_{12} = 2(\gamma_1^{\mathrm{D}}\gamma_2^{\mathrm{D}})^{1/2} + 2(\gamma_1^{\mathrm{P}}\gamma_2^{\mathrm{P}})^{1/2} \tag{8}$$

For solid–liquid equilibrium, a direct relationship between the contact angle θ of the drop of a liquid on a solid surface and the surface properties of both products is obtained from Eqs. (5) and (8). By contact-angle measurements of droplets of different liquids of known surface properties, the components $\gamma_{\mathrm{S}}^{\mathrm{D}}$ and $\gamma_{\mathrm{S}}^{\mathrm{P}}$ of the surface energy of the substrate can then be determined.

More recently, it has been shown, in particular by Fowkes and co-workers [46–49], that electron acceptor and donor interactions, according to the generalized Lewis acid–base concept, could be a major type of interfacial force between the adhesive and the substrate. This approach is able to take into account hydrogen bonds, which are often involved in adhesive joints. Moreover, Fowkes and Mostafa [47] have suggested that the contribution of the polar (dipole–dipole) interactions to the thermodynamic work of adhesion could generally be neglected compared to both dispersive and acid–base contributions. They have also consindered that the acid–base component W^{ab} of the adhesion energy can be related to the variation of enthalpy, $-\Delta H^{ab}$, corresponding to the establishment of acid–base interactions at the interface, as follows:

$$W^{ab} = f(-\Delta H^{ab})n^{ab} \tag{9}$$

where f is a factor that converts enthalpy into free energy and is taken equal to unity, and n^{ab} is the number of acid–base bonds per unit interfacial area, close to about 6 μmol/m^2. Therefore, from Eqs. (7) and (9), the total work of adhesion W_{12} becomes

$$W_{12} = 2(\gamma_1^D \gamma_2^D)^{1/2} + f(-\Delta H^{ab})n^{ab} \tag{10}$$

The experimental values of the variation of enthalpy $(-\Delta H^{ab})$ can be estimated from the work of Drago and co-workers [50,51], who proposed the following relationship:

$$-\Delta H^{ab} = C^A C^B + E^A E^B \tag{11}$$

where C^A and E^A are two quantities that characterize the acidic material at the interface, and similarly, C^B and E^B characterize the basic material. The validity of Eq. (11) was clearly evidenced for polymer adsorption on various substrates [49]. Another estimation of $(-\Delta H^{ab})$ can be carried out from the semiempirical approach defined by Gutmann [52], who has proposed that each material may be characterized by two constants: an electron acceptor number AN and an electron donor number DN. For solid surfaces, similar numbers, K_A and K_D, respectively, have been defined and measured by inverse gas chromatography [53–55]. In this approach, the enthalpy $(-\Delta H^{ab})$ of formation of acid–base interactions at the interface between two solids 1 and 2 is now given by [52,53]

$$-\Delta H^{ab} = K_{A1}K_{D2} + K_{A2}K_{D1} \tag{12}$$

This expression was applied successfully by Schultz et al. [55] to describe fiber–matrix adhesion in the field of composite materials.

Finally, it must be mentioned that acid–base interactions can also be analyzed in terms of Pearson's hard–soft acid–base (HSAB) principle [56,57]. At present, the application of this concept to solid–solid interactions and thus to adhesion is under investigation.

2. *Models Relating the Adhesion Strength G to the Adhesion Energy W*

Although described also in Section II.F, these models also apply to other types of interfacial interactions. One of the most important models in adhesion science, usually called the *rheological model or model of multiplying factors*, was proposed primarily by Gent and Schultz [3,4] and then reexamined using a fracture mechanics approach by Andrews and Kinloch [58] and Maugis [59]. In this model, the peel adhesion strength is simply equal to the product of W by a loss function Φ, which corresponds to the energy irreversibly dissipated in viscoelastic or plastic deformations in the bulk materials and at the crack tip and depends on both peel rate v and temperature T:

$$G = W\Phi(v, T) \tag{13}$$

As already mentioned, the value of Φ is usually far higher than that of W, and the energy dissipated can then be considered as the major contribution to the adhesion strength G. In the case of assemblies involving elastomers, it has been clearly shown in various studies [3,4,58,60–62] that the viscoelastic losses during peel experiments, and consequently, the function Φ, follow a time–temperature equivalent law such as that of Williams et al. [63].

It is more convenient to use the intrinsic fracture energy G_0 of the interface in place of W in Eq. (13), as follows:

$$G = G_0\Phi(v, T) \tag{14}$$

Effectively, when viscoelastic losses are negligible (i.e., when performing experiments at very low peel rate or high temperature), $\Phi \rightarrow 1$ and G must tend toward W. However, the resulting threshold value G_0 is generally 100 to 1000 times higher than the thermodynamic work of adhesion, W.

From a famous fracture analysis of weakly cross-linked rubbers called the *trumpet model*, de Gennes has derived [64] an expression similar to equation (14) when the crack propagation rate v is sufficiently high. He distinguished three different regions along the trumpet starting from the crack tip: a hard, a viscous, and finally, a soft zone. The length of the hard region is equal to $v\tau$, where τ is the relaxation time, and then the viscous region extends to a distance $\lambda v\tau$. Factor λ is the ratio of the high-frequency elastic modulus to the zero-frequency elastic modulus of the material, and obviously represents the viscoelastic behavior of the rubber. Hence according to this approach, it is shown that the total adhesive work is given by the following expression, similar to Eq. (14):

$$G \sim G_0\lambda \tag{15}$$

where G_0 is the intrinsic fracture energy for low velocities (i.e., when the polymer near the crack behaves as a soft material).

Carré and Schultz [65] have reexamined the significance of G_0 on cross-linked elastomer–aluminum assemblies and proposed that it can be expressed as

$$G_0 = Wg(M_c) \tag{16}$$

where g is a function of molecular weight M_c between cross-link nodes and corresponds to a molecular dissipation. Such an approach is based on Lake and Thomas's argument [66], which states that to break a chemical bond somewhere in a chain, all bonds in the chain must be stressed close to their ultimate strength. More recently, de Gennes [67] has proposed further analysis of this problem. He postulates that the main energy dissipation near the interface could be due to the extraction of short segments of chains in the junction zone during crack opening, this phenomenon being called the *suction process*. From a volume balance and a stress analysis, the following expression of the intrinsic fracture energy G_0 is obtained for low fracture velocity:

$$G_0 = \sigma_c a^2 \nu L \tag{17}$$

where σ_c is a threshold stress that can be considered as a material constant to a first approximation, and a^2, ν, and L are, respectively, the cross-sectional area, the number per unit interfacial area, and the extended length of chain segments sucked out during the crack propagation. At present, no experimental verification of this approach has yet been published. Obviously, this analysis holds only for values of L less than L_e (i.e., the critical length at which physical entanglements between macromolecular chains just occur). The case where $L > L_e$ implies at least a disentanglement process, but above all, a process of chain scission, which is analyzed below.

Concerning the adhesion phenomena occurring at the fiber–matrix interface in composite materials, Nardin and Schultz [68] have recently proposed that the shear strength τ_i of the interface, measured by means of a fragmentation test on single fiber composites, is related directly to the free energy of adhesion W, calculated from Eq. (10), according to

$$G \sim \kappa\tau_i = \left(\frac{E_m}{E_f}\right)^{1/2} W \tag{18}$$

In this expression, κ is a constant equal to about 0.5 nm, corresponding to a mean intermolecular distance when only physical interactions (dispersive and acid–base interactions) are involved; E_m and E_f are the elastic moduli of the matrix and the fiber, respectively. This model is equivalent to that of Gent and Schultz [3,4] for a cylindrical geometry and in the case of pure elastic stress transfer between both materials. It is very well verified experimentally for various fiber–matrix systems. The influence of the formation of interfacial layers exhibiting mechanical behavior completely different from that of the bulk matrix has also been examined [31].

Finally, it is worth examining the analyses concerning tack, in other words, the instantaneous adhesion when a substrate and an adhesive are put in contact for a short time t (of the order of 1 s) under a given pressure. This tack phenomenon is of great importance for processing involving hot-melt or pressure-sensitive adhesives. First, it has clearly been shown [69] that the viscoelastic characteristics of the adhesive, in particular its viscous modulus, play a major role on the separation energy. Recently, de Gennes [70] has suggested that the measured tack could be related to both the free adhesion energy W and the rheological properties of the bulk adhesive, as follows:

$$G_{\text{tack}} \sim \begin{cases} W\dfrac{\mu_\infty}{\mu_0} & \text{for weakly cross-linked elastomers} \qquad (19) \\[2ex] W\dfrac{\mathrm{t}}{\tau} & \text{for uncross-linked elastomers} \qquad (19') \end{cases}$$

where μ_∞ and μ_0 are the high-frequency and zero-frequency moduli of the adhesive, respectively, and τ is the reptation time of the macromolecular chains (see the next section). The latter equation holds for time t much larger than this reptation time. The experimental verification of this approach is under investigation.

E. Diffusion Theory

The diffusion theory of adhesion is based on the assumption that the adhesion strength of polymers to themselves (autohesion) or to each other is due to mutual diffusion (interdiffusion) of macromolecules across the interface, thus creating an interphase. Such a mechanism, mainly supported by Voyutskii [71], implies that the macromolecular chains or chain segments are sufficiently mobile and mutually soluble. This is of great importance for many adhesion problems, such as healing and welding processes. Therefore, if interdiffusion phenomena are involved, the joint strength should depend on different factors, such as contact time, temperature, nature and molecular weight of polymers, and so on. Actually, such dependences are experimentally observed for many polymer–polymer junctions. Vasenin [72] has developed, from Fick's first law, a quantitative model for the diffusion theory that correlates the amount of material w diffusing in a given x direction across a plane of unit area to the concentration gradient $\partial c/\partial x$ and the time t:

$$\partial w = -D_f \, \partial t \frac{\partial c}{\partial x} \tag{20}$$

where D_f is the diffusion coefficient. To estimate the depth of penetration of the molecules that interdiffused into the junction region during the time of contact t_c, Vasenin assumed that the variation of the diffusion coefficient with time is of the form $D_d t_c^{-\beta}$, where D_d is a constant characterizing the mobility of the polymer chains and β is on the order of 0.5. Therefore, it is possible to deduce the depth of penetration l_p as well as the number N_c of chains crossing the interface, which are given by

$$l_p \sim k\,(\pi D_d t_c^{1/2})^{1/2} \tag{21}$$

$$\mathrm{N}_c = \left(\frac{2\mathrm{N}\rho}{M}\right)^{2/3} \tag{22}$$

where k is a constant, N is Avogadro's number, and ρ and M are, respectively, the density and the molecular weight of the polymer. Finally, Vasenin assumed that the measured peel energy G was proportional to both the depth of penetration and the number of chains crossing the interface between the adhesive and the substrate. From Eqs. (21) and (22), G becomes

$$G \sim K\left(\frac{2\mathrm{N}\rho}{M}\right)^{2/3} D_d^{1/2} t_c^{1/4} \tag{23}$$

where K is a constant that depends on molecular characteristics of the polymers in contact, Experimental results and theoretical predictions from Eq. (23) were found [72] in very good agreement in the case of junctions between polyisobutylenes of different molecular weights. In particular, the dependence of G on $t_c^{1/4}$ and $M^{-2/3}$ was clearly evidenced.

One important criticism of the model proposed by Vasenin is that the energy dissipated viscoelastically or plastically during peel measurements does not appear in Eq. (23). Nevertheless, in his work, the values of coefficients K and D_d are not theoretically quantified but determined only by fitting. Therefore, it can be assumed that the contribution of hysteretic losses to the peel energy is implicitly included in these constants.

In fact, the major scientific aspect of interdiffusion phenomena is concerned with the dynamics of polymer chains in the interfacial region. Recently, the fundamental understanding of the molecular dynamics of entangled polymers has advanced significantly due to the theoretical approach proposed by de Gennes [73], extended later by Doi and Edwards [74] and Graessley [75]. This new approach stems from the idea that the chains cannot pass through each other in a concentrated polymer solution, a melt, or a solid polymer. Therefore, a chain with a random coil conformation is trapped in an environment of fixed obstacles. This constraint confines each chain inside a tube. De Gennes has analyzed the motion, limited mainly to effective one-dimensional diffusion along a given path, of a polymer chain subjected to such a confinement. He described this type of motion as wormlike and gave it the name *reptation*. The reptation relaxation time τ associated with the movement of the center of gravity of the entire chain through the polymer was found to vary with the molecular weight M as M^3. Moreover, the diffusion coefficient D, which defines the diffusion of the center of mass of the chain, takes the form $D \sim M^{-2}$.

One of the most important and useful applications of the reptation concept concerns crack healing, which is primarily the result of the diffusion of macromolecules across the interface. This healing process was studied particularly by Kausch and co-workers [76]. The problem of healing is to correlate the macroscopic strength measurements to the microscopic description of motion. The difference between self-diffusion phenomena in the bulk polymer and healing is that the polymer chains in the former case move over distances many times larger than their gyration radii, whereas in the latter case, healing is essentially complete in terms of joint strength in the time that a macromolecule initially close to the interface needs to move about halfway across this interface. This problem was analyzed by several authors, who have considered that the healing process is controlled by different factors, such as (1) the number of bridges across the interface for de Gennes [77], (2) the crossing density of molecular contacts or bridges for Prager and Tirrell [78], (3) the center-of-mass Fickian interdiffusion distance for Jud et al. [76], and (4) the monomer segment interpenetration distance for Kim and Wool [79]. The resulting scaling laws for the fracture energy versus time t during healing are the following:

$$G \sim \begin{cases} t^{1/2}M^{-3/2} & \text{for (1) and (2)} \qquad (24) \\ t^{1/2}M^{-1} & \text{for (3)} \qquad (24') \\ t^{1/2}M^{-1/2} & \text{for (4)} \qquad (24'') \end{cases}$$

If there are some differences in the exponent of the molecular weight in these expressions, all the approaches agree with the dependence of G on the square root of healing time, such a dependence having been clearly evidenced experimentally for poly(methyl methacrylate) polymer, for example [76], in contradiction with Vasenin's model.

Finally, it can be concluded that diffusion phenomena do actually contribute greatly to the adhesive strength in many cases involving polymer–polymer junctions. Nevertheless, the interdiffusion of macromolecular chains requires both polymers to be sufficiently soluble and the chains to possess a sufficient mobility. These conditions are obviously fulfilled for autohesion, healing, or welding of identical polymers processes. However, diffusion can become a most unlikely mechanism if the polymers are not or only slightly soluble, if they are highly cross-linked or crystalline, or put in contact at temperatures far below their glass transition temperature. Nevertheless, in the case of junctions between two immiscible polymers, the interface could be strengthened by the presence of a diblock copolymer, in which each molecule consists of a block of the first polymer bonded to a block of the second polymer, or each of the two blocks is miscible with one of the polymers. The copolymer molecules concentrate generally at the interface and each block diffuses or "dissolves" into the corresponding polymer. Therefore, the improvement in joint strength can also be related to an interdiffusion process. When the molecular weight M of each block of the copolymer is inferior to the critical entanglement weight M_e for which entanglements of chains just occur in the polymer, the adhesion strength could be interpreted in terms of the suction mechanism described in Section II.D. On the contrary, when $M > M_e$, the failure of the joint generally requires the rupture of the copolymer chains. The latter phenomenon (i.e., chain scission or more precisely rupture of chemical bonds) is analyzed in the next section.

F. Chemical Bonding Theory

It is easily understandable that chemical bonds formed across the adhesive–substrate interface can greatly participate to the level of adhesion between both materials. These bonds are generally considered as primary bonds in comparison with physical interactions, such as van der Waals, which are called *secondary force interactions*. The terms *primary* and *secondary* stem from the relative strength or bond energy of each type of interaction. The typical strength of a covalent bond, for example, is on the order of 100 to 1000 kJ/mol, whereas those of van der Waals interactions and hydrogen bonds do not exceed 50 kJ/mol. It is clear that the formation of chemical bonds depends on the reactivity of both adhesive and substrate. Different types of primary bonds, such as ionic and covalent bonds, at various interfaces have been evidenced and reported in the literature. The most famous example concerns the bonding to brass of rubber cured with sulfur, adhesion resulting from the creation of polysulfide bonds [80]. One of the most important adhesion fields involving interfacial chemical bonds is the use of adhesion promoter molecules, generally called *coupling agents*, to improve the joint strength between adhesive and substrate. These species are able to react chemically on both ends, with the substrate on the one side and the polymer on the other, thus creating a chemical bridge at the interface. The coupling agents based on silane molecules are the most common type of adhesion promoters [81]. They are widely employed in systems involving glass or silica substrates, and more particularly in the case of polymer-based composites reinforced by glass fibers. In addition to the improvement in joint strength, an important enhancement of the environmental resistance of the interface, in particular to moisture, can be achieved in the presence of such coupling agents.

The influence of chemical bonds on the joint strength G, and more precisely on the intrinsic adhesion fracture energy G_0, defined earlier, has been analyzed in several studies. The most relevant and elegant work in this area was performed by Gent and Ahagon [82], who have examined the effect on the adhesion of polybutadiene to glass of chemical bonds established at the interface by using silane coupling agents. In these experiments the surface density of interfacial covalent bonds between the glass substrate and the cross-linked elastomer was varied by treating the glass plates with different mixtures of vinyl- and ethyl-terminated silanes. Obviously, both species form siloxane bonds on the glass surface. Moreover, it was assumed that the vinylsilane can react chemically with the polybutadiene during the cross-linking treatment of this rubber, where a radical reaction is involved. On the contrary, a chemical reaction between the ethyl group of the latter silane and the elastomer is unlikely. Therefore, Gent and Ahagon [82] have shown that the intrinsic peel energy G_0 increases linearly with the surface concentration of vinylsilane, in good agreement with their assumptions, and thus proved the important effect of primary bonds on adhesive strength.

Another experimental evidence of the chemical bond effect on the interfacial strength is relative to the adhesion between two sheets of cross-linked polyethylene [83]. To control the number of chemical bonds at the interface, the assemblies were prepared as follows. First, polyethylene containing 2% by weight of dicumylperoxide (DCP) was molded into sheets at rather low temperature (120°C) to prevent the decomposition of DCP. Second, partial pre-cross-linking of the two separate polymer sheets was performed at 140°C for a given time. Since the decomposition kinetics of DCP is known at this temperature, the degree of cross-linking can be varied as a function of time. Finally, assemblies of the two resulting sheets are obtained under pressure by heating at 180°C to ensure the total decomposition of DCP. Hence this technique leads to complete cross-linking in the bulk of the assembly, the mechanical properties of which therefore remain constant, whereas the surface density of interfacial bonding can be varied. In agreement with previous results obtained by Gent and Ahagon [82], a linear relationship has been established between the peel energy G and the number of bonds v per unit interfacial area, insofar as v does not exceed 1×10^{13} bonds/cm^2.

More recently, in a series of papers [84–86], Brown has analyzed the improvement in adhesion between two immiscible polymers [i.e., poly(methyl methacrylate) (PMMA) and polyphenylene oxide (PPO)] by the presence of polystyrene–PMMA diblock copolymers. Since one of the blocks is PMMA and the other is polystyrene (PS), which is totally miscible with PPO, it was reasonably expected that the copolymer organizes at the interface, due to the fact that each block dissolves in the respective homopolymer. The molecular weight of these blocks is always superior to the critical molecular weight M_e, for which entanglements of chains occur in the homopolymers. Experimentally, Brown employed partially or fully deuterated copolymers in order to be able to determine the deuterium on the fracture surface after separation by secondary-ion mass spectrometry (SIMS) and forward-recoil spectroscopy (FRES) [85]. A scission of the copolymer chains near the junction point of both blocks is observed, indicating that the diblock copolymers are well organized at the interface, whatever their molecular weights, with their junction accurately located at the PMMA–PPO interface. Moreover, Brown has proposed [86] a molecular interpretation of the toughness of glassy polymers, which can also be applied to the failure of interfaces between immiscible polymers. This approach stems from the idea that the cross-tie fibrils, which exist between primary fibrils in all crazes, can transfer mechanical stress between the broken and unbroken fibrils and thus strongly affect the failure mechanics of a craze. It is based on a simple model of crack tip stress concentration. Finally, assuming that all the effectively entangled chains in the material are drawn into the fibril, the fracture energy G of a polymer is found to be directly related to the square of both the areal density v of entangled chains and the force f required to break a polymer chain:

$$G \sim v^2 f^2 \frac{D}{S} \tag{25}$$

where D is the fibril diameter and S is the stress at the craze–bulk interface, which is assumed to be constant. Brown has considered [86] that diblock copolymer-coupled interfaces between PMMA and PPO are ideal experimental systems for testing the validity of his model. Indeed, a linear dependence of the interfacial fracture energy G on the diblock copolymer surface density v, in logarithmic scales, is observed for copolymers of different molecular weights. A slope of 1.9 ± 0.2 was found for the master straight line in good agreement with Eq. (25). Nevertheless, it is worth noting that Brown's results involving chain scission at the interface and leading to a dependence of G on v^2 are in contradiction with both previous examples, where linear relationships between G and v are established.

III. CONCLUDING REMARKS

Adhesion is a very complex field beyond the reach of any single model or theory. Given the number of phenomena involved in adhesion, the variety of materials to be bonded, and the diversity of bonding conditions, the search for a unique, universal theory capable of explaining all the experimental facts is useless. In practice, several adhesion mechanisms can be involved simultaneously. However, it is generally assumed that the adsorption or thermodynamic theory defines the main mechanism exhibiting the widest applicability. It describes the achievement of intimate contact and the development of physical forces at the interface. This is a necessary step for interlocking, interdiffusion, and chemical bonding mechanisms to occur subsequently, further increasing the adhesive strength.

Finally, one can consider that the measured adhesive strength of an assembly could be expressed as a function of three terms relating, respectively, to (1) the interfacial molecular interactions, (2) the mechanical and rheological properties of bulk materials, and (3) the characteristics of the interphase. The first two terms have received a great deal of attention during recent decades, as a result of studies in the physical chemistry of surfaces and fracture mechanics. The third term constitutes the real challenge for a proper and complete understanding of adhesion.

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4

The Mechanical Theory of Adhesion

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I. INTRODUCTION: PRACTICAL AND THEORETICAL KNOWLEDGE

The sensation of stickiness is among the commonplace experiences of humanity. Resin oozing from a pine branch and the sap from a dandelion stem are among a multitude of natural examples from which it can be asserted with confidence that humans have "always" been aware of the phenomenon of adhesion. Indeed for millennia, as a species, we have made use of viscous liquids capable of setting to solids. In the Upper Palaeolithic era (between 40,000 and 10,000 years ago) stone and bone points were glued with resin to wooden shafts to produce spears. Some 31,000 years ago colored pigments were being glued to the walls of the Chauvet cave in Vallon-Pont-d'Arc in the Ardèche to create the earliest known cave paintings [1]. By the first dynasty of ancient Egypt (ca. 3000 B.C.) natural adhesives were used to attach inlays to furniture [2].

The technological use of adhesives implies a tacit [3] knowledge of the practical principles necessary for their success. In time, these principles were made explicit. In the thirteenth century Bartholomaeus Angelicus [4] recognized the need to exclude "dust, air and moisture" ("pulvere, vento et humore") for success in the ancient craft of laminating silver to gold.

Galileo was aware of the significance of surface roughness. In his *Due Nuove Scienze*, he discusses adhesion between sheets of glass or marble, placed one upon the other. If the surfaces are finely (*esquisitamente*) polished, they are difficult to separate, but if contamination prevents perfect (*esquisito*) contact, the only resistance to separation is the force of gravity [5]. Rough surfaces require "introdur qualche glutine, visco o colla"—"the introduction of some sticky, viscous or gluey substance"—for adhesion to occur. In addition to showing an appreciation of practical considerations which are significant to the successful use of adhesives, Galileo placed the phenomenon of adhesion within the then traditional scientific paradigm, arguing that the Aristotelian principle of nature's abhorrence of a void provided the resistance to separation of the materials joined [6].

The seventeenth century was, of course, a time of paradigm change, indeed Galileo himself made a major contribution to this process. So we see that by the 1730s Newton, having abandoned the Aristotelian paradigm, was arguing that adhesion was a result of "very strong attractions" between the particles of bodies. After mention of gravitational, magnetic, and electrical attractions, he postulated "some force [between particles], which in immediate contact is exceeding string,. . . and reaches not far from the particles with any sensible effect." What these attractions were, Newton did not speculate, but left the change: "it is the business of experimental philosophy to find them out"! [7].

Schultz and Nardin, in the previous chapter, reminded us of this challenge of Newton's, and presented a broad review of the extent to which contemporary science had succeeded in answering it. This chapter focuses on one part of that answer—the *mechanical theory of adhesion*, which is concerned with the effect of surface roughness on adhesion. Starting from the early formulation of the theory in 1925, its changing fortunes up to the 1970s are outlined; since this time, it has not been seriously questioned. Next, the concepts that underlie the terms *surface* and *roughness* are examined, and it is emphasized that these terms are essentially arbitrary in nature. This leads to a discussion of how concepts, such as work of adhesion, spreading coefficient, and fracture energy, may be adapted for adhesive bonds where the interface is rough. This theoretical basis is then employed in the next section of the review in which selective published work is discussed that illustrates different ways in which interfacial roughness may affect the strength of an adhesive joint. The discussion moves from examples of roughness on a macroscale, through microroughness to roughness on the nanoscale. Mechanisms are described whereby roughness may enhance fracture energy by increasing plastic, or even elastic losses. Chain pull-out and scission may also make contributions. The conclusions point out how the concepts of various "theories" of adhesion, such as mechanical, adsorption and diffusion, merge and overlap, and caution lest an excessive reductionism be counterproductive.

II. DEVELOPMENT OF THE MECHANICAL THEORY [8]

Most historical surveys treat the work of McBain and Hopkins in 1925 as the earliest application of modern scientific investigation to the study of adhesion [9]. McBain and Hopkins considered that there were two kinds of adhesion, specific and mechanical. Specific adhesion involved interaction between the surface and the adhesive: this might be "chemical or adsorption or mere wetting." Specific adhesion has developed into the model we today describe in terms of the adsorption theory.

In contrast, mechanical adhesion was only considered possible with porous materials. It occurred "whenever any liquid material solidifies in situ to form a solid film in the pores." They cite as examples adhesion to wood, unglazed porcelain, pumice, and charcoal. For McBain and Hopkins mechanical adhesion was very much a common sense concept, "It is obvious that a good joint must result when a strong continuous film of partially embedded adhesive is formed in situ."

Despite its "obvious" nature, the mechanical theory of adhesion fell out of favor, and was largely rejected by the 1950s and 1960s. This rejection was prompted by observations that the roughening of surfaces in some instances lowered adhesion and by the tendency to rationalize examples of increased adhesion to rough surfaces in terms of the increased surface area available for "specific adhesion" to take place. In 1965 Wake summarized the position by stating that "theories that mechanical interlocking ... added to the strength of a joint have been largely discredited" [10].

However, by the 1970s the mechanical theory was again being taken seriously. The extent of the change can be judged by again quoting a review by Wake, writing this time in 1976: "adhesive joints frequently possess an important mechanical component essential to the performance of the joint" [11].

This radical change resulted from new work from the 1960s cited by Wake, most of which falls into one of two categories. The first is associated with the electroless deposition of metals onto plastics such as acrylonitrile–butadiene–styrene (ABS) copolymer and polypropylene. In the process the plastics must be etched in a way which produces pits on a micrometer scale. Such a topography had been shown to be a necessary, but not sufficient condition for adequate adhesion.

The second category was concerned with adhesion to microfibrous or porous surfaces on metals, examples of which are shown Fig. 1. A range of polymers had been shown

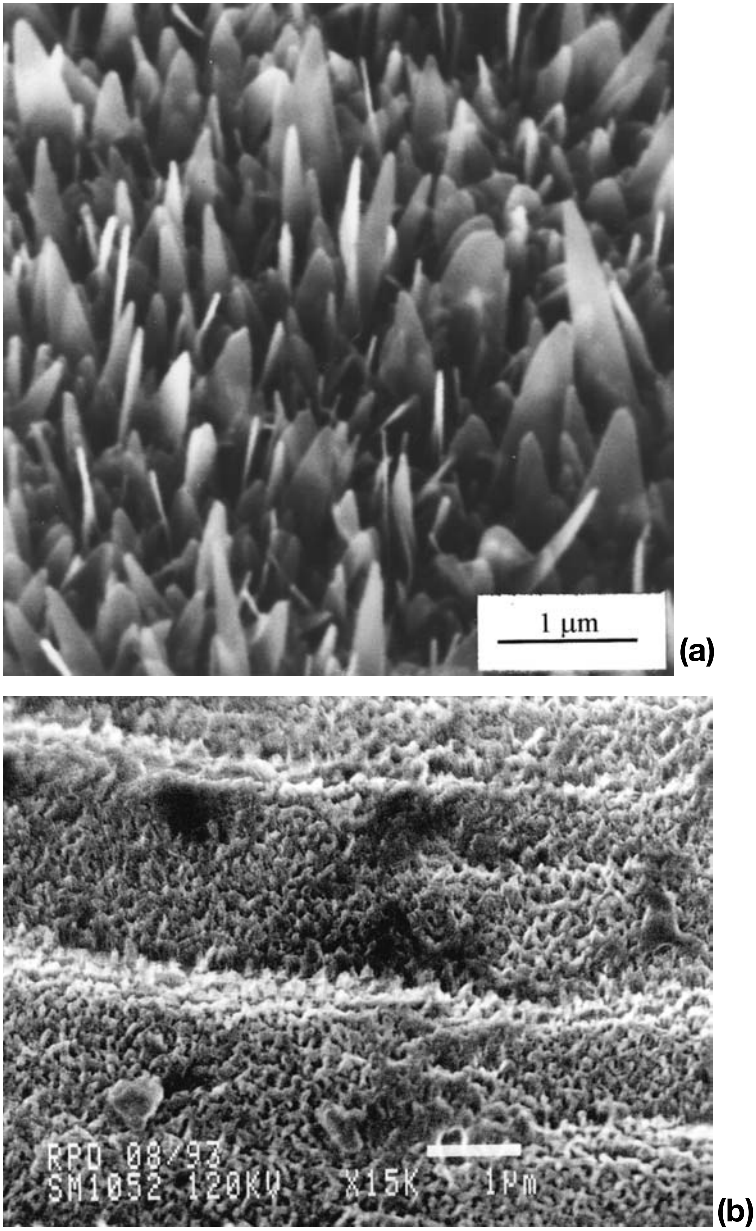

Figure 1 (a) Microfibrous oxide on steel (after Ref. 16); (b) porous anodic oxide on aluminum formed by phosphoric acid anodizing followed by further treatment with the acid (after Ref. 17).

to penetrate pores on anodized aluminum [12], dendritic electrodeposits on copper and nickel [13], and needlelike oxides on copper [14] and titanium [15].

Following these theoretical developments in the late 1960s and early 1970s, there was a burgeoning of interest in the relation between surface topography and adhesion [18]. This was facilitated by developments in electron microscopy (scanning electron microscopy and scanning transmission electron microscopy) and in electron spectroscopy (Auger and x-ray photoelectron spectroscopies) that enabled the physical structure and chemical composition of surface layers to be established in detail previously impossible. Considerable work on pore-forming surface treatments for aluminum and titanium was stimulated by the increasing need of the aerospace industry for strong, consistent, and durable adhesive bonds [19–30]. Such work led to Boeing's adopting a standard phosphoric acid anodizing pretreatment producing a porous surface for structural bonding of aluminum [31].

The broad consensus that comes from most of this work is that strong bonds, and more particularly bonds of high durability, tend to be associated with a highly porous surface oxide, providing, of course, that the values of viscosity and surface tenstion of the adhesive are such as to allow it to penetrate the pores [18]. The importance of porosity was brought out strongly in a 1984 review by Venables [32]. He concluded that for aluminum and titanium "certain etching or anodization pretreatment processes produce oxide films on the metal surfaces, which because of their porosity and microscopic roughness, mechanically interlock with the polymer forming much stronger bonds than if the surface were smooth." This is as unequivocal a statement of the mechanical theory of adhesion as can be found in the original work of McBain and Hopkins.

Since this time, the acceptance of a "mechanical theory" has not been seriously challenged, and it now has a generally accepted place within the canon of adhesion theories [33–37]. The main features of the mechanical theory have been confirmed in a wide range of experimental situations. Plasma treatment of polymers [38] and of carbon [39] and polymer fibers [40] usually results in a roughening which has been seen as making a mechanical contribution to subsequent adhesion. In developing pretreatments for metals, interest has broadened to include techniques, such as plasma-sprayed coatings [41,42] and metal sintering [43], which produce roughness on a coarser scale. Here again mechanical effects have been postulated as adding significantly to the adhesion.

Thus the theory has proved a "useful" one in the sense that it has stimulated the development of new surface treatments for metals, polymers and fibers and has assisted in giving an understanding of their efficacy. There has perhaps been a tendency, now that the theory is again "respectable," to invoke "mechanical effects" somewhat uncritically wherever an increase in surface roughness has been observed. A more detailed review of these developments may be found in references [18] and [44].

Given that the roughening of surfaces often has a beneficial effects on adhesion, how can it be explained? It might have been sufficient in 1925 for McBain and Hopkins [9] merely to assert that the mechanism of adhesion to a porous surface was "obvious," but the wide range of experimental examples known today demands a more detailed discussion of the mechanisms involved. This, in turn, requires a critical examination of the common sense terms "surface" and "roughness."

III. SURFACES

It may be adequate in everyday life to think of a flat surface as the two-dimensional plane of Euclidean geometry. This, like the perfectly straight line with length but no breadth, is a

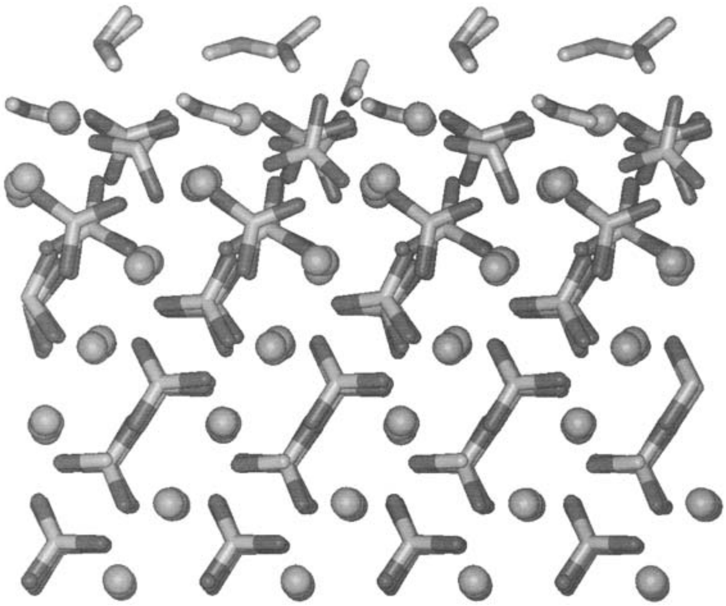

Figure 2 Fully hydrated calcite $\{\overline{1}01\overline{1}\}$ surface showing (top) rotation of surface carbonate groups with (bottom) bulk ordering below the surface (after Ref. 45).

model constructed in our minds. In the present discussion it is necessary to recognize that the surfaces of science and technology depart from this idealization.

An atom or molecule within the bulk of a phase, surrounded by other atoms, is attracted in all directions. The asymmetry of the intermolecular force field as an interface is approached means that the surface molecules are more strongly attracted in one direction, usually towards the bulk. As a consequence, the density of molecules in the surface regions differs from that in the bulk. This perturbation may extend over many atomic spacings. Figure 2 gives the structure predicted by atomistic simulation techniques for a calcite ($CaCO_3$) surface, and shows rotation of surface groups and adsorbed water [45].

Even for an interface between two highly insoluble phases some interpenetration of molecules will occur, lowering the entropy. Liquids, and even solids, exert a vapor pressure. Thus the concentration profile across an interface is never sharp, there is always a finite and varying gradient (Fig. 3(b) cf. Fig. 3(a)). Further, where a multi-component phase is concerned, there is in general no reason to suppose that the concentration profile of each component will be the same (Fig. 3(c)). Although it is sometimes convenient to speak of a surface as if it were defined by a plane, it is necessary to recognize that the positioning of the plane, for real materials, is arbitrary: it is a matter for convention.

Considerations of surface thermodynamic functions, especially of surface energy, are usually regarded as fundamental to an understanding of both the formation and the failure of adhesive bonds. A brief outline will be given of how these concepts are applied to smooth surfaces as a preliminary to describing their application to rough surfaces.

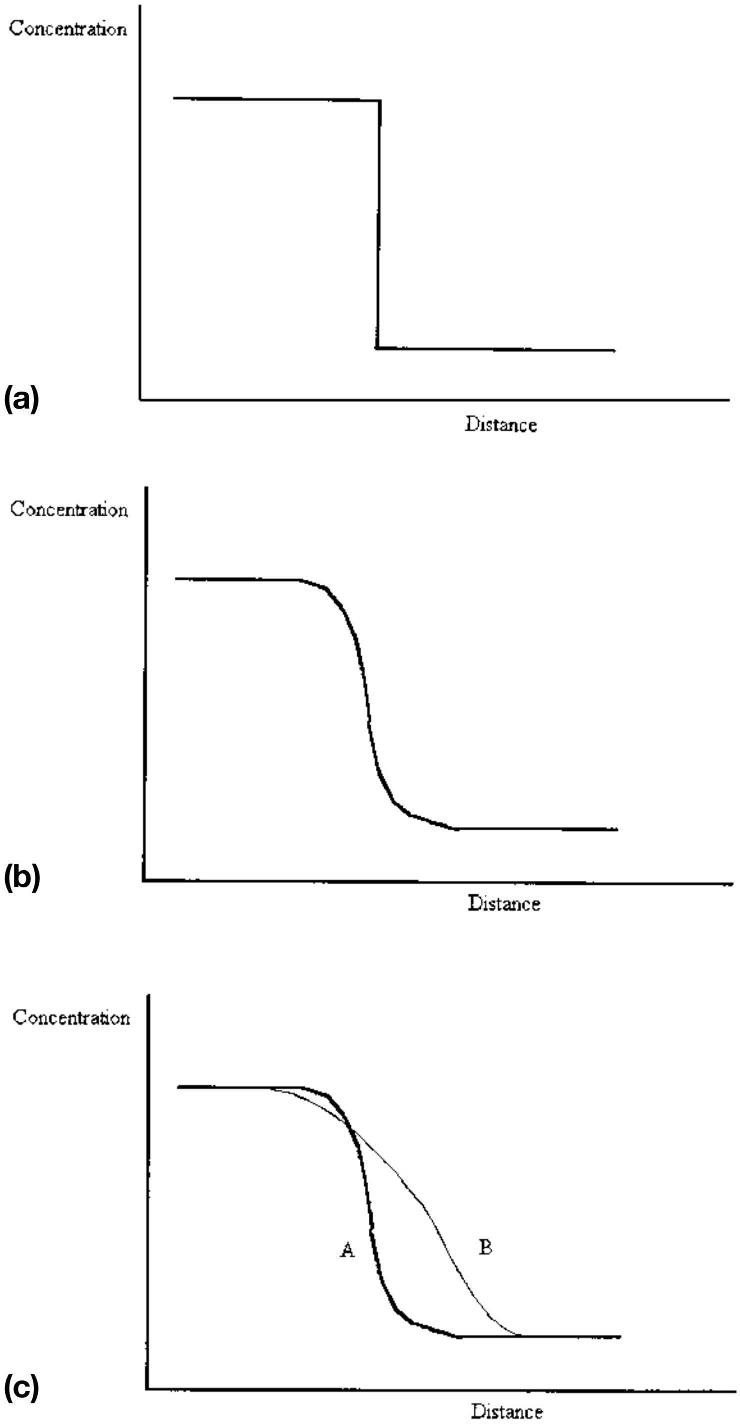

Figure 3 Concentration profiles at an interface: (a) sharp (not realistic), (b) typical profile, (c) with two components A and B.

In defining surface thermodynamic functions, the difficulty over the absence of a unique surface plane is circumvented by defining these functions in terms of surface excess— "total" minus "bulk" value of the property concerned [46,47]. Thus the Gibbs surface free energy is defined as

$$G^{\mathrm{S}} = \left[\frac{G - G^{\mathrm{b}}}{A}\right] \tag{1}$$

where A is the area of the surface, G is the total value of the Gibbs free energy in the system, and G^{b} is the value the total Gibbs free energy would have if all the constituent particles (atoms, molecules, etc.) were in the same state as they are in the bulk of the phase. It is because the local environment of molecules in or near the surface is different from that of those in the bulk (cf. Fig. 2), that there is an excess energy, the surface energy. In oversimplified terms, a surface can be thought of as being generated by breaking bonds along what becomes the surface. The energy to break these bonds is reflected in the surface energy.

Surface energies are associated with *formation* of the adhesive bond because they determine the extent to which, at equilibrium, a liquid adhesive will come into contact with a solid surface. This is reflected in the value of the contact angle, θ, which is related to the surface energies (written, following common usage, as γ) by Young's equation [48]

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} \cos\theta \tag{2}$$

where V refers to the vapor present in equilibrium with the solid (S) and liquid (L).

The energy change (per unit area) when liquid L spreads over the surface of solid S is called the spreading coefficient or spreading energy, S [48], and is necessarily related to the surface energies:

$$S = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} - \gamma_{\mathrm{LV}} \tag{3}$$

Equations (2) and (3) enable the extent of contact between a liquid adhesive and a solid substrate to be gauged. Some consequences are shown in Table 1 where the concept of the "reduced spreading coefficient" S/γ_{LV}, employed by Padday [49], has been used to clarify the situation. As is readily seen, if S is positive, the liquid at equilibrium will be spread completely over the solid, but if S/γ_{LV} is less than -2, spontaneous dewetting will occur.

Surface energies are also associated with *failure* of an adhesive bond, because failure involves forming new surfaces and the appropriate surface energies have to be provided.

Table 1 Contact Angle, θ, and Spreading Coefficient for a Liquid on a Solid Surface. Comparison of Spreading Coefficient S for a Smooth Surface with S' for a Surface of Roughness Factor r

		Smooth Surfaces	Rough Surfaces
"$\theta < 0$"[a]	Spontaneous spreading	$S > 0$	$S' > S$
$90^\circ > \theta > 0$	Finite contact angle	$0 > S/\gamma_{\mathrm{LV}} > -1$	$S' > S$
$180^\circ > \theta > 90^\circ$	Finite contact angle	$-1 > S/\gamma_{\mathrm{LV}} > -2$	$S' < S$
"$\theta > 180^\circ$"[a]	Spontaneous dewetting	$S/\gamma_{\mathrm{LV}} < -2$	$S' < S$

[a] These are in quotation marks because strictly $0^\circ < \theta < 180^\circ$.

The surface energy term may be the work of adhesion, W_A, or the work of cohesion, W_C, depending on whether the failure is adhesive or cohesive. For phases 1 and 2, these are defined as follows [49]:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \tag{4}$$

$$W_C = 2\gamma_1 \tag{5}$$

The practical adhesion, for example fracture energy G, will comprise a surface energy term $G_0(W_A$ or $W_C)$ to which must be added a term ψ representing other energy absorbing processes—for example plastic deformation—which occur during fracture:

$$G = G_0 + \psi \tag{6}$$

Usually ψ is very much larger than G_0. This is why practical fracture energies for adhesive joints are almost always orders of magnitude greater than work of adhesion or work of cohesion. However, a modest increase in G_0 may result in a large increase in practical (measured) adhesion as ψ and G_0 are usually coupled. For some mechanically simple systems where ψ is largely associated with viscoelastic loss, a multiplicative relation has been found:

$$G = G_0\{1 + \phi(c, T)\} \approx G_0\phi(c, T) \tag{7}$$

where $\phi(c, T)$ is a temperature and rate dependent viscoelastic term [50,51]. In simple terms, stronger bonds (increased G_0) may lead to much larger increases in fracture energy because they allow much more bulk energy dissipation (increased ψ) during fracture.

IV. ROUGHNESS OF SURFACES

We have seen how the concept of surface energy in principle relates to adhesion. The surface energy terms discussed (e.g., Eqs. (1) to (7)) are all energies per unit area. We now need to consider carefully what we mean by the interfacial area.

If the interface between phases 1 and 2 is "perfectly" flat, there is no problem in defining the interfacial area, A. However, this chapter is particularly concerned with rough surfaces: indeed almost all practical surfaces are, to a degree, rough. We first consider modest degrees of roughness, where a simple geometric factor may be applied. It is argued, however, that the complexity of many rough surfaces makes them different in kind, that is qualitatively different, from a flat surface. Ultimately the ascription of a numerical value to quantify roughness itself may be arbitrary, depending on the size of the probe chosen to measure it. It is concluded that the only practicable interpretation of "unit area" is the nominal geometric area. The consequence is that the production of a rough surface per se increases surface energy (Eq. (1)), and from this, work of adhesion and fracture energy of the joint (Eqs. (4) and (7)).

A. Roughness Factor

Where the surface roughness is not very great it might be adequately expressed by a simple Wenzel roughness factor [52],

$$r = \frac{A}{A_o} \tag{8}$$

where A is the "true" surface area and A_o the nominal area. For simple ideal surfaces, r can be calculated from elementary geometric formulæ. Thus a surface consisting of a hemisphere would have a roughness factor of 2, one consisting of square pyramids with all sides of equal length, a roughness factor of $\sqrt{3}$. For simple real surfaces the roughness factor can be calculated from straightforward measurements, such as profilometry. In such cases we could substitute a corrected area into the definition of surface energy (Eq. (1)) and thence via Eqs. (3) and (4) evaluate the spreading coefficient and work of adhesion. Thus the spreading coefficient S' for a rough surface becomes

$$S' = r(\gamma_{SV} - \gamma_{SL}) - \gamma_{LV} \tag{9}$$

Some of the effects of roughness on the spreading of a liquid can be predicted from Eqs. (2), (3), and (9), providing the liquid does not trap air as it moves over the surface. These are summarized in Table 1.

It is important to appreciate the assumption implicit in the concept of the roughness factor: chemical nature and local environment of surface molecules on the rough surface and on the smooth surface are the same.

B. Further Conceptual Development

Can the simple roughness factor approach (Eq. (8) be applied if the surface is very much rougher? Many of the surfaces encountered in adhesion technology are very rough indeed. Figure 1 shows a microfibrous oxide on steel and a porous oxide layer on aluminum. Figure 4(a) shows a phosphated steel surface prepared for rubber bonding [53], Fig. (4b) surface treated polytetrafluoroethan (PTFE) [54]. As the scale of roughness becomes finer, the application of a simple roughness factor becomes increasingly unrealistic and unconvincing. It becomes unconvincing not just because of increasing practical difficulty in measuring the "true" area of such surfaces, it becomes conceptually unconvincing. The roughness itself is an essential characteristic of the surfaces. As we approach molecular scale roughness, indeed long before we get there, the energy of the surface molecules is modified as a consequence of the topological configurations they take up. For example, consider a solid–vapor interface. Half of the volume of a sphere centered on a molecule of the solid on a plane surface would comprise solid, half vapor. If, however, the molecule was on the surface of an asperity of a rough surface, less than half of the volume of the sphere would be made up of solid, more than half of vapor, so the energy of this latter molecule would be higher. In terms of the simple "bond breaking" concept, more bonds between molecules of the solid would have been broken to create the environment of the molecule on the rough surface than for that on the smooth. The intrinsic energy of a molecule on a rough surface is higher than that on a smooth surface. It is unjustifiable to regard these surfaces (Figs. 1 and 4) as essentially the same as smooth surfaces which happen to be rough!

Moreover, roughness at an interface may actually develop as a result of bringing the two phases together. They will take up these configurations as a consequence of the molecular interactions at the interface: they are an essential feature of bringing together the two phases 1 and 2. An ideally smooth surface being highly ordered would have low entropy: the development of surface roughness can be seen as an increasing of surface entropy in accordance with the Second Law of Thermodynamics [55–58].

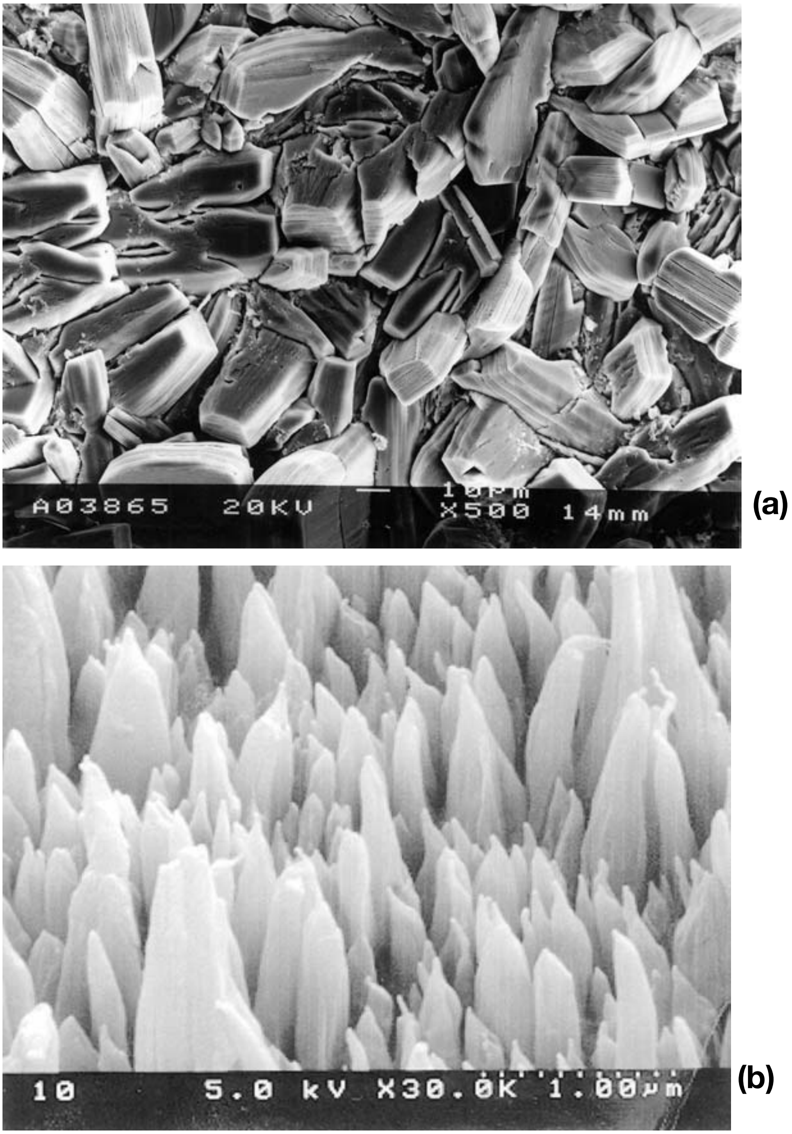

Figure 4 Examples of rough pretreated substrate surfaces. (a) Phosphated steel prepared for rubber bonding (cf. Ref. 53); (b) PTFE irradiated by argon ions (after Ref. 54).

C. Fractal Surfaces

It may not be possible, even in principle, to ascribe a unique "surface area" to a surface. It has long been recognized from work on gas adsorption on porous solids that the surface area measured depends on the size of the probe molecule. A small probe can enter finer surface features and therefore may give a larger value. The surface area is, as Rideal [59] recognized in 1930, in a sense arbitrary, not absolute. More recently evidence has been produced suggesting that many engineering surfaces and many fracture surfaces are fractal in nature [60,61]. For a fractal surface, the area depends on the size of the "tile" used to measure it, the actual relationship depending on the fractal dimension of the surface. The area of such a surface tends to infinity as the tile size tends to zero.

The roughness factor may be calculated for a fractal surface. As demonstrated below, its value varies according to the probe size and the fractal dimension [62].

Consider the adsorption of probe molecules of various sizes (cross-sectional area σ)* on a fractal surface [63,64]. Let n be the number of molecules required to form a monolayer. If log $n(\sigma)$ is plotted against log σ, a straight line with negative slope is obtained which can be represented as

$$\log n(\sigma) = \left(\frac{-D}{2}\right)\log \sigma + C \tag{10}$$

where D is the fractal dimension of the surface and C is a constant. Therefore

$$n(\sigma) = \beta\sigma^{-D/2} \tag{11}$$

where β is another constant. (For an ideal plane surface ($D=2$), this equation reduces to the trivial relationship that the number of probes required to cover a given surface is inversely proportional to the probe area.)

The area (in dimensionless form) can be expressed as

$$A = n(\sigma)\sigma \tag{12}$$

therefore

$$A(\sigma) = \beta\sigma^{1-D/2} \tag{13}$$

Consider the roughness factor, r, for such a fractal surface

$$r = \frac{A}{A_o} \tag{8}$$

where A is the "true" surface area, A_o the nominal area, i.e., the area of a plane surface. For a plane surface $D=2$, so

$$r = \frac{A}{A_o} = \frac{\beta\sigma^{1-D/2}}{\beta} = \sigma^{1-D/2} \tag{14}$$

For a fractal surface $D > 2$, and usually $D < 3$. In simple terms the larger D, the rougher the surface. The intuitive concept of surface area has no meaning when applied to a fractal surface. An "area" can be computed, but its value depends on both the fractal dimension and the size of the probe used to measure it. The area of such a surface tends to infinity, as the probe size tends to zero.

Obviously the roughness factor is similarly arbitrary, but it is of interest to use Eq. (14) to compute its value for some trial values of D and σ. This is done in Table 2. In order to map the surface features even crudely, the probe needs to be small. It can be seen that high apparent roughness factors are readily obtained once the fractal dimension exceeds two, its value for an ideal plane.

The roughness factor concept may be useful for surfaces which exhibit modest departures from flatness. Beyond this, it is misleading as changes in the local molecular environment make the rough surface qualitatively different from a flat one. In many cases it is not meaningful to talk of *the* area of a rough surface as if it had, in principle, a unique

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*The treatment (Eqs. 10–14) requires that σ be in dimensionless form. σ then is a "normalized area," i.e., a ratio of the cross-sectional area to some large, fixed area, such as the sample area.

Table 2 "Roughness Factor" Calculated for a Fractal Surface, According to the Fractal Dimension D and Probe Area σ

	Roughness Factor for Values of σ as Indicated			
D	$\sigma = 10^{-4}$	10^{-8}	10^{-12}	10^{-18}
2	1	1	1	1
2.1	1.6	2.5	4	7.9
2.5	10	100	1,000	32,000
2.8	40	1,600	63,000	16,000,000

value. What area, then, should be used for a rough surface in the context of surface energy and work of adhesion, Eqs. (1) to (7)? It seems inescapable when we refer to the surface area A that we must use the ideal, formal area, i.e., macroscopic area of the interface. This has important implications for the effect of surface roughness on adhesive joint strength. Surface energy is defined in Eq. (1) as the excess energy per unit area, and it is now clear that this area is the "nominal" area, i.e., the macroscopic area of the interface. The production of a rough surface raises the energy of the molecules in the surface, as discussed above. This raised energy is still normalized by reference to the same nominal, macroscopic area as before. Consequently, the production of a rough surface per se increases surface energy (per unit nominal area, Eq. (1), and consequently increases the work of adhesion and fracture energy of the joint (Eqs. (4) and (7)).

V. ADHESION AND ROUGHNESS OF INTERFACES

Having discussed the nature of surfaces and of surface roughness we now move on to examine some recently published work, selected to illustrate different ways in which interfacial roughness may affect the strength of an adhesive joint. Interfacial roughness of potential significance in adhesion may be on a scale ranging from the macroscopic to the molecular. At all of these scales there are connections between roughness and adhesion appropriate for consideration in terms of the mechanical theory. Of course, for surfaces that are fractal in nature, the question of the "scale" of the roughness becomes arbitrary. In the following sections, the discussion moves from examples of roughness on a macroscale, through microroughness to roughness on the nanoscale.

A. Some Effects Observable on a Large Scale

For moderately rough surfaces, an increase in surface area may well lead to a proportionate increase in adhesion, so long as the roughness does not reduce contact between the surfaces. Gent and Lai have convincingly demonstrated the effect in careful experiments with rubber adhesion [65]. In comparing adhesion to smooth and to grit blasted steel, they observed increases in peel energy by factors of two to three times which they ascribed to the increase in surface area. This is consistent with the concept of the Wenzel roughness factor, and many authors would discount this as coming within the scope of the mechanical theory of adhesion.

A classic instance of the mechanical theory of adhesion is where one phase is "keyed" into the other. Here the adhesion is enhanced above the increase proportional to the surface area by exploiting the mechanical properties of the "keyed" material (strength or toughness) in enhancing the measured adhesion. There are many descriptions of this in the literature. A simple example is provided by the adhesion of silica to copper discussed by van der Putten [66], who was concerned to bond copper directly to silicon in the context of integrated circuit technology.

Copper sticks poorly to silica but titanium tungstide sticks well. Using conventional lithographic techniques islands of TiW 0.1 μm thick, a few micrometers in width, were sputtered onto the silica and the photoresist was removed (Fig. 5(a)).

Palladium acts as a nucleating agent for the electroless deposition of copper. By treating the surface with palladium [II] chloride in hydrochloric acid a monolayer or so of palladium is deposited on the TiW surface. The palladium chloride solution also contains 1% of hydrofluoric acid which attacks the silica, undercutting the TiW islands (Fig. 5(b)). Electroless copper is now deposited, nucleating on the palladium-covered TiW and growing from it. Finally copper is electrodeposited and is thus mechanically anchored to the silicon surface (Figs. 5(c) and (d)).

Here the stress is directed away from the low W_a interface (silica/copper) towards the stronger silica/palladium interface by the topography produced. The surface topography protects weak regions from a high stress field.

Another example may be cited from the field of polymer–polymer adhesion. When sheets of semicrystalline polymers, such as polypropylene and polyethylene, are laminated by cooling from the melt, a key may form. There are examples where the lower-melting polymer has been shown to flow into the structure of the higher-melting material as its volume contracts on crystallization [67–70]. These influxes, which may be hundreds of

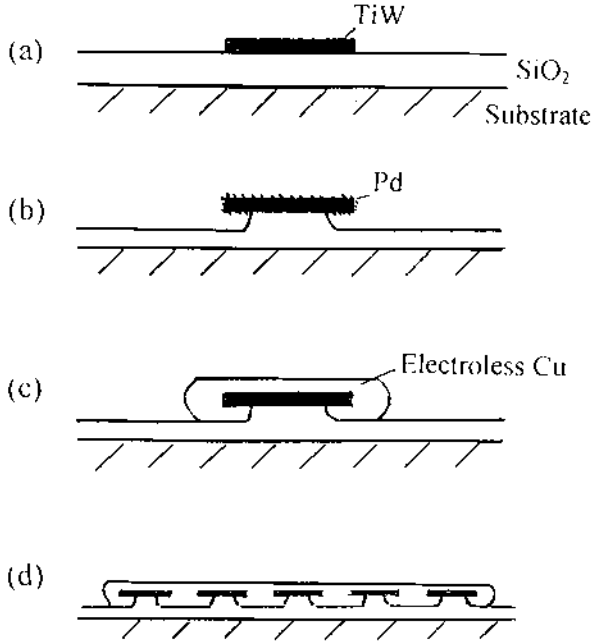

Figure 5 Adhesion of copper to silica using a mechanical key: (a)–(d) successive stages (see text) (after Ref. 66).

micrometers in size, lead to a mechanically reinforced interface associated with enhanced adhesion (cf. Eq. (6)).

1. *Elastic and Plastic Losses*

The increased energy dissipated for adhesion to a rough surface is usually a result of plastic dissipation processes, evidence of which can often be obtained by examining the fracture surfaces. However Gent and Lin have shown that large amounts of energy can also be involved in peeling an *elastic* material from a rough surface [71]. The energy is essentially used for the elastic deformation of embedded filaments: this energy is lost because when the filaments become free, they immediately relax.

Gent and Lin experimented with rubber bonded to a model aluminum surface, consisting of plates with regular arrays of cylindrical holes. The peel energy was low for the plates in the absence of holes. An energy balance analysis given the ratio of fracture energy for peeling from the material with cylindrical pores G'_a to that from a smooth substrate G_a as

$$\frac{G'_a}{G_a} = 1 + 4\frac{\phi l}{a} \tag{15}$$

where l is the pore length, a its radius, and ϕ the ratio of pore area to total area of the plate [71]. Their experimental results demonstrated the essential validity of this relationship. Where pull-out alone occurred the work of detachment for their system increased by up to 20 times.

They further considered the additional energy lost where fracture of strands occurred. An extra term, $lU_b\phi$, is added to the value of G'_a given by Eq. (15). U_b is the energy to break per unit volume, which for the rubber they used is an elastic stored energy. Because this additional term is proportional to the depth of the pores, it dominates for deep pores. For Gent and Lin's system, it could be several hundred times the work of detachment from a smooth surface.

B. Microporous Surfaces

There are obvious similarities between the polymer which has solidified within the pores of a microfibrous surface and fibers embedded in the matrix of a composite material (cf. Fig. 1). Standard treatments of fiber composites (e.g., [72]) draw attention to the significance of the critical length of fiber. When short fibers are stressed axially, shear failure at, or close to the fiber/matrix interface is considered to occur, and the fibers may be pulled out of the matrix. Fibers greater than the critical length, with a consequently larger fiber matrix interfacial area, fail in tension, and only the broken ends are pulled out. This, of course, is one of the points that Gent and Lin were demonstrating. The fracture toughness of the composite may be enhanced by energy terms associated with fiber fracture, with fiber matrix adhesion, and with fiber pull-out. By assuming that the fiber is linearly elastic and equating the interfacial shear force to the tensile force for a fiber of critical length l, it immediately follows that

$$\frac{2l}{a} = \frac{\sigma}{\tau} \tag{16}$$

where a is the fiber radius, σ its tensile strength, and τ the interfacial shear strength. As in Eq. (15), the l/a ration is significant.

Arslanov and Ogarev [73] use Eq. (16) to argue that the critical length of a filament of adhesive in a microporous anodic film is very small, so the filaments will fail in tension and most of the pore length is irrelevant to adhesion. Application of the simple model of Eq. (15) to this situation shows that even with a short length of elastic adhesive filament a useful increase in peel strength might be expected. For polyethylene embedded in a film formed by anodising in phosphoric acid, a ratio G'_a/G_a of three to four times is obtained.

In a realistic situation the adhesive filament will not act as a perfect elastic body uniformly stressed up to fracture. Uneven stress distributions and plastic yielding would be expected to increase the energy dissipation observed beyond that calculated for the ideal elastic model. It will be very interesting to see whether in the future auxetic materials can be developed to an extent that they can be used as coatings for such porous substrates. Even greater increases in fracture energy can then be anticipated.

While calculations like those discussed involve serious simplifications and idealizations, they do serve to show mechanisms by which surface roughness per se is capable of significantly increasing the fracture energy of an adhesive joint.

C. Cognate Chemical Change

It has been emphasized above that a surface molecule on a rough surface will often have a different environment—for example, fewer nearest neighbors, more “broken bonds”—than a similar molecule on a smoother surface. In addition to this, it must be remembered that most, if not all, of the chemical or physical treatments used to produce a rough surface will also alter the chemical nature of the surface molecules. There are many reports in the literature of treatments which produce both mechanical and chemical effects. Sometimes these are seen as supplementing, sometimes as opposing each other.

Zhuang and Wightman’s work on carbon fiber–epoxy adhesion provides a recent example [74]. They studied both the surface topography and the surface chemistry of carbon fibers modified by treatment with an oxygen plasma prior to incorporation into a epoxy matrix. Two types of fibers, differing in surface roughness, were studied. An increase in surface oxygen content was observed on treatment, mirrored by increases in the polar component of surface energy and in interfacial shear strength (IFSS). Here the rougher fibers had somewhat lower IFSS. The lower adhesion was associated with incomplete filling by the resin of valleys on the fiber surface striations. However, there is evidence that the rougher surface imparts better durability in a humid environment.

PTFE is a notoriously difficult substrate to bond, but severe treatment producing both roughening and surface chemical changes have been found to ease the difficulty. Recently, Koh et al. have used argon ion irradiation as a pretreatment both in the presence and absence of oxygen [54]. The treatment produced increasing roughness, eventually giving a fibrous forestlike texture (Fig. 4(b)). These treated surfaces were bonded with a thermoplastic adhesive cement, and generally considerably enhanced adhesion was found. The level of adhesion appeared to rise to a peak, which occurred at a treatment level of 10^{16} ions/cm^2.

High-resolution X-ray photoelectron spectra showed chemical changes also occurring. In the absence of oxygen, a 285 eV (C–C and C–H) peak developed with maximum intensity at a dose of 10^{16} ions/cm^2. In the presence of oxygen a strong O 1s signal developed which was attributed to the reaction of oxygen atoms with the free radicals created by argon ion bombardment. Here again, the enhanced adhesion is attributed to a combination of improved wettability and chemical reactivity of the surface, combined with mechanical keying to the increasingly rough surfaces. There is no convincing explanation of the fall in adhesion at the highest treatment time. It would be interesting to know at what level the difference between adhesion at 10^{16} land 10^{17} ions/cm^2 was statistically significant.

D. Fractal Surfaces

Wool [57] has considered the fractal nature of polymer–metal and polymer–polymer interfaces. He argues that diffusion processes often lead to fractal interfaces. Although the concentration profile varies smoothly with the dimension of depth, the interface, considered in two or three dimensions is extremely rough [75]. Theoretical predictions, supported by practical measurements, suggest that the two-dimensional profile through such an interface is a self-similar fractal—that is one which appears similar at all scales of magnification. Interfaces of this kind can occur in polymer–polymer and polymer–metal systems.

Polymer–polymer fractal interfaces may result from the interdiffusion of monomers or of polymers themselves. Hashimoto et al. [56,57] annealed the interface between polystyrene and a styrene–isoprene diblock polymer at 150°C and showed extensive roughening of the interface by mutual interdiffusion on a micrometer scale (Fig. 6).

Metal–polymer fractal interfaces may result from processes such as vacuum deposition and chemical vapor deposition where metal atoms can diffuse considerable distances into the polymer. Mazur et al. [76,77] electrodeposited silver within a polyimide film. The Silver [I] solution was able to diffuse into the polymer film where it

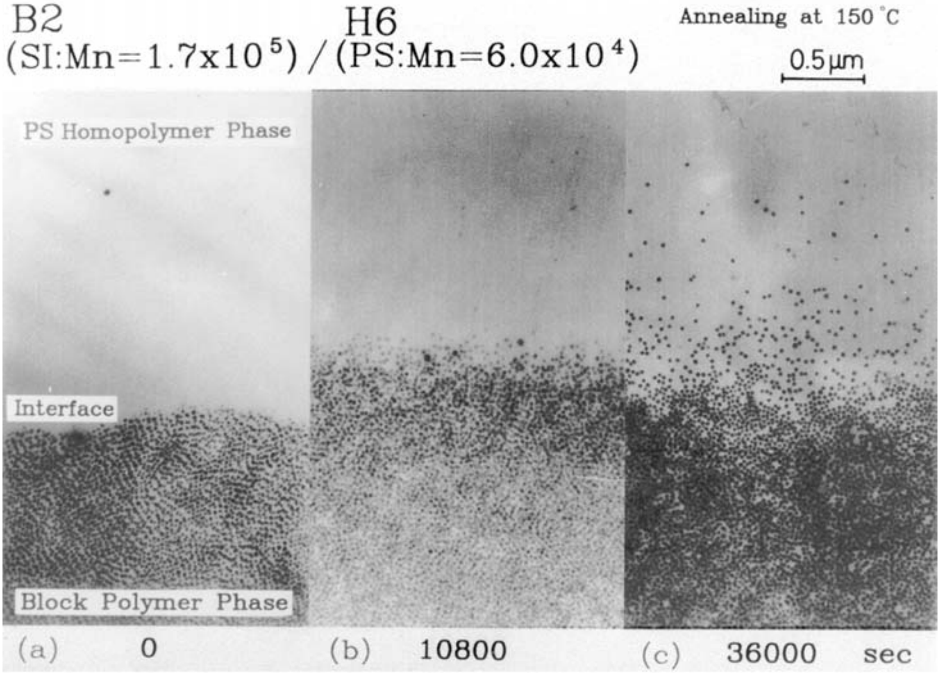

Figure 6 Electron micrographs showing the interface between (top) polystyrene and (bottom) a styrene–isoprene diblock polymer annealed at 150° C for the times shown. (Isoprene units are stained and appear black.) (Reproduced from Ref. 56, copyright 1990 American Chemical Society.)

was subsequently reduced to the metal. The adhesion was excellent: the only way that Mazur could remove the silver was by abrasion. Examination of a section through the interface by transmission electron microscopy showed an extremely rough interfacial region on the submicrometer scale. Wool [57] analysed the profile and showed the interface to be fractal with a dimension of around 1.6.

Wool [57,78] suggests that these principles could be used to develop pretreatments which give a highly ramified, fractal surface to which high adhesion by mechanical interlocking would be expected. Consider a blend of polyethylene with a second phase, perhaps starch, amenable to removal by selective attack or dissolution. Above a critical concentration some of the second phase particles will be connected, forming a fractal structure. Treatment of the polyethylene surface, then, will leave fractal voids, receptive to an adhesive, such as a liquid epoxy resin.

E. Development of Roughness on a Nanoscale

Adhesion of thermodynamically incompatible polymers is of current interest because of its implications for developing new multiphase polymer materials and for recycling of mixed plastic wastes. Many elegant experiments have been reported in which various types of copolymer are introduced at the interface as putative compatibilizers. The interface may be strengthened as a result of interdiffusion and roughening on a nanoscale.

A number of these experiments use the surface forces apparatus [79,80] in which extremely sensitive measurements of the force–distance characteristics can be made as surfaces of defined geometry, such as crossed cylinders or a sphere and a plane, are brought into contact and then separated. From these measurements a value of the interfacial energy of the two materials can be derived.

Creton et al. [58] studied the adhesion of a system somewhat similar to Hashimoto's discussed above, using a surface forces-type apparatus. Contact was made between a cross-linked polyisoprene hemisphere and a thin polystyrene sheet. Under these circumstances, the fracture energy was low, comparable in magnitude (although not numerically close) to the work of adhesion $0.065\,\mathrm{J/m^2}$. However, when the polylstyrene surface was covered with a layer of a styrene–isoprene diblock polymer considerably higher adhesion was observed which increased with crack speed. The limiting value at zero crack speed, G_0 increased with both surface density, Σ, and degree of polymerization, N_{PI}, of the polyisoprene chains (Fig. 7). While the blurring of the interface is on a much more limited scale than that shown by Hashimoto, Creton et al. argue that the isoprene end of the diblock copolymer molecules diffuses into the cross-linked polyisoprene, and that the additional fracture energy is associated with the frictional drag as these chains are pulled out under the influence of the applied load.

With suitable copolymers, roughening of the interface between two incompatible polymers by interdiffusion can lead to a range of values for fracture toughness G. For diblock copolymers both surface density (Σ) and degree of polymerization (N) of the blocks are important. If the blocks are shorter than the entanglement length N_e of the corresponding homopolymer, failure occurs, as with the isoprene above, by chain pull-out and G is low. If $N > N_e$ chain scission will occur at low surface density (Σ), but as Σ is increased the fracture energy G rises steeply and plastic deformation, for example crazing, occurs in the polymer followed by chain scission or pull-out.

These effects have been found by Creton et al. [81] who laminated sheets of incompatible polymers, poly(methyl methacrylate) (PMMA) and poly(phenylene oxide) (PPO), and studied the adhesion using a double cantilever beam test to evaluate fracture

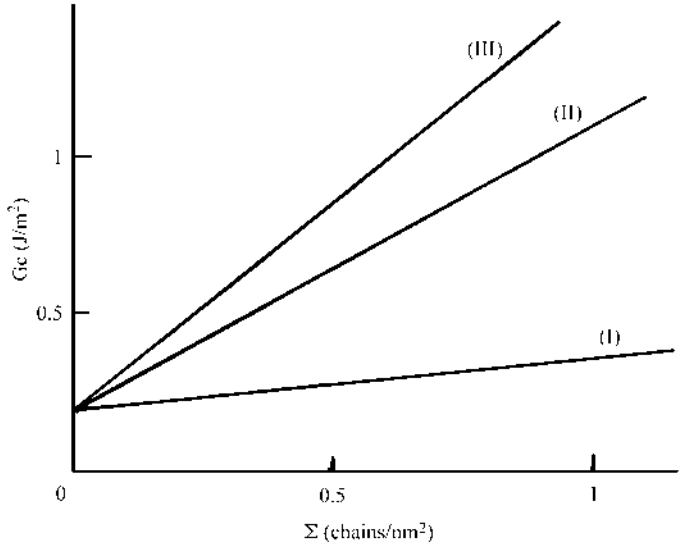

Figure 7 Increase in threshold fracture energy, G_0, with length, N_{PI}, and surface density, Σ of isoprene chains (after Ref. 58). Degree of polymerization: (I) 558, (II) 882, (III) 2205.

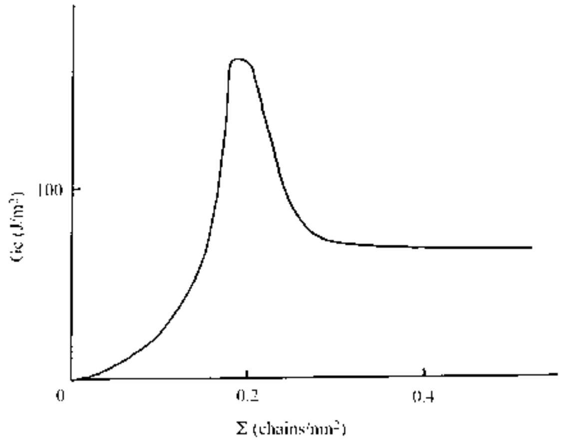

Figure 8 Adhesion of PMMA to PPO. Effect on fracture toughness, G_c, of interfacial density, Σ, of a reinforcing diblock copolymer (after Ref. 81).

toughness G_c. For the original laminate G_c was only 2 J/m^2, but when the interface was reinforced with increasing amounts of a symmetrical PMMA–polystyrene diblock copolymer of high degree of polymerization ($N > N_e$), the fracture toughness increased to around 170 J/m^2, and then fell to a steady value of 70 J/m^2 (Fig. 8).

At low surface coverage fracture occurs close to the junction point of the diblock, with each fragment remaining on the "correct" side of the interface. At higher values of Σ the surface saturates, crazing occurs during fracture, and G_c reaches a maximum. With further increase in surface density of the copolymer a weak layer forms at the interface and the fracture toughness falls to a limiting value.

Toughening of a polymer–polymer interface with random copolymers may be more effective than with diblocks, when polymers are not too incompatible [82]. This is of industrial, as well as of scientific, interest as random copolymers are usually cheaper to produce.

Diblock copolymers will form a single, strong chemical linkage across the interface, but a random copolymer—if incompatability not too large—will form Gaussian coils wandering many times across the interface. If the incompatibility is too large the copolymer will simply form collapsed globules at the interface, forming a weak boundary layer giving no enhancement of adhesion.

F. Results from the Surface Forces Apparatus

Some interesting light has been thrown on the nature and roughness of surface layers in contact by experiments of Israelachvili and co-workers with the surface force apparatus [55,79,83,84]. This apparatus enables the surface energy to be evaluated both when the surfaces are advancing into closer contact, γ_A, and when they are receding further apart, γ_R. These two values would be expected to be the same, as indeed they sometimes are. In many cases, however, there is hysteresis, with $\gamma_R > \gamma_A$. Israelachvili and colleagues have studied this phenomenon in some detail.

In a typical experiment, Israelachvili deposited monolayers of surfactants onto cleaved mica sheets, and evaluated the surface energies. For example, mica coated with monolayers of L-α-dipalmitoylphosphatidylethanolamine (DMPE) showed no hysteresis ($\gamma_A = \gamma_R = 27\,\mathrm{mJ/m^2}$, but when coated with hexadecyltrimethylammonium bromide (CTAB) it was found that $\gamma_A = 20\,\mathrm{mJ/m^2}$ and $\gamma_R = 50\,\mathrm{mJ/m^2}$.

Israelachvilli argues that the hysteresis is a result of reorganization of the surfaces after they are brought into contact. This may occur at a macroscopic, microscopic, or molecular level. Here he argues that interdigitation or interpenetration occurs, roughening the interface at the molecular level. He has classified his surface layers as crystalline (solid-like), amorphous solid, and liquidlike (Fig. 9). The first tend not to reorganize, so hysteresis is low. The liquidlike surfaces reorganize very quickly on both loading and unloading, so again hysteresis tends to be low. It is on the solid amorphous surfaces, where reorganization may take place over a significant time scale, that hysteresis is generally greatest. On a simplistic level, the analogy with viscoelastic loss is obvious, and it is not surprising to find that adhesional hysteresis is considered to have a temperature/rate dependence (Fig. 10). Under the experimental conditions employed, DMPE forms a crystalline ordered layer, but the CTAB layer is amorphous.

Thus this adhesion hysteresis is a result of a time-dependent roughening of the interface resulting from the intrinsic properties of the surface molecules. Israelachvili even interprets it in terms of a roughness factor effect (cf. Eq. (8), arguing that if $\gamma_R \approx 2\gamma_A$ then the true contact area has become about twice the nominal area of contact. It would seem more realistic to argue that the energy loss associated with the hysteresis is related to the frictional forces involved in disentangling the rough, interdigitated surfaces.

VI. DISCUSSION

Why does surface roughness affect adhesion? More particularly, why does increasing interfacial roughness often increase adhesion? In a simple way, we can rationalize this in terms of Eq. (6), at the same time summarizing the points made in the previous sections.

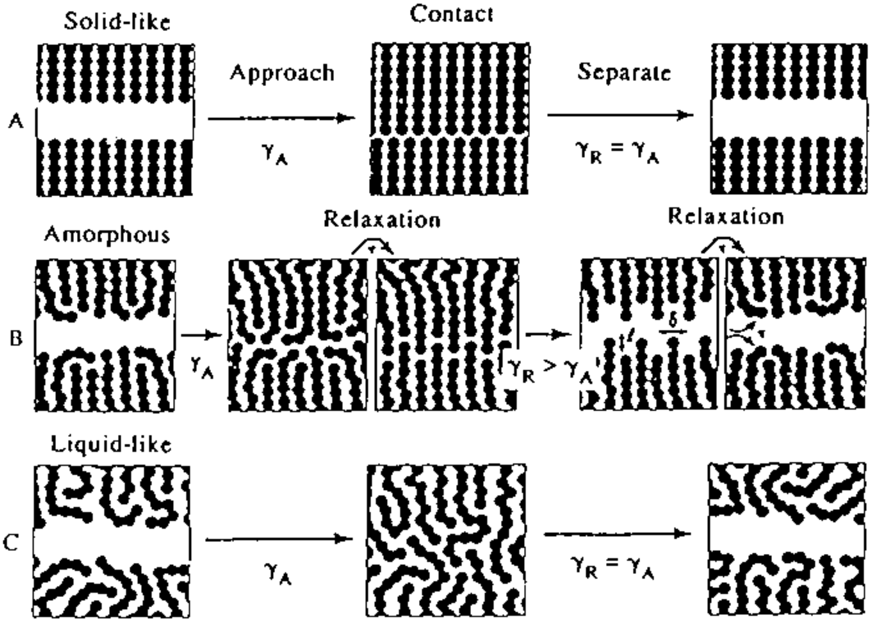

Figure 9 Schematic representation of solidlike (crystalline), amorphous solid, and liquidlike surface layers. (Reproduced from Ref. 83, copyright 1993 American Chemical Society.)

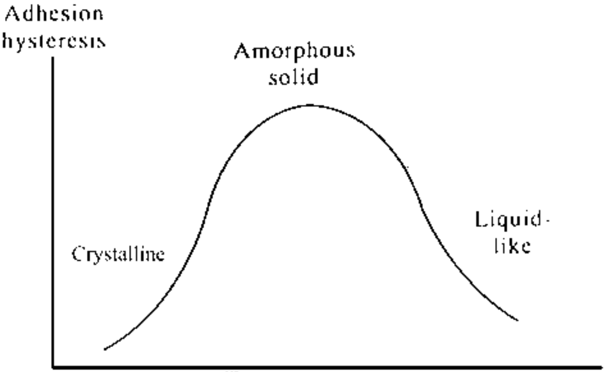

Figure 10 Effect of temperature on adhesion hysteresis (after Ref. 79).

Let us examine each term in turn, considering how it might contribute to the hypothetical fracture energy G of the adhesive joint:

$$G = G_0 + \psi \tag{6}$$

The *surface energy term* G_0 is of the form "surface excess energy" per unit area of surface (cf. Eq. (1)), so may be expressed as

$$G_0 = \frac{\Delta G}{A} \tag{17}$$

It is readily appreciated that surface treatments may increase ΔG by introducing more chemically active groups into the substrate surface. This is a central idea in the adsorption theory of adhesion. Surface treatments that are regarded as primarily roughening a surface will usually bring about cognate chemical change. Over and above this, ΔG will also be increased as a result of roughening the surface per se. An atom near an asperity peak or fine fractal feature will clearly have a much greater "atomic" surface energy than a chemically similar atom in a plane crystal surface.

Turning to *the area A* in Eq. (17), it is important to remember that A refers to the formal area, the macroscopic area of the interface. For the rough surface the "true" area will be greater. As we move from macroroughness towards roughness on a nanoscale and molecular scale, we move seamlessly from the historic realm of the mechanical theory into the realm of the diffusion theory, and at the same time the effective increase in A can become enormous. Consequently G_0 may be raised to a very high value. Indeed, as many engineering surfaces are fractal in nature [61], we can only retain the concept of "area" at all, if we accept that it can be considered as indefinitely large. The practical adhesion does not become infinite because the joint with a strong interfacial region will fail (cohesively) in some other region where G_0 is smaller.

It must further be remembered that G_0 will often be coupled to the "other" loss terms ψ (cf. Eq. (7)). This means that even a modest absolute increase in G_0 may lead to a much larger increase in fracture energy G.

Returning to Eq. (6), let us now consider explicitly the *other energy absorbing processes* ψ which occur during fracture. These often make the dominant contribution to G. As we have seen, where interdigitation of polymer chains is involved, these losses may include energy involved in chain pull-out or scission. It is notable that the highest fracture energy occurs where the interdigitation is sufficiently extensive to initiate crazing or other plastic dissipation processes.

For many adhesive bonds, there is a very large difference in elastic modulus between the two phases joined. This has the effect of concentrating applied stresses at the interface, leading to smooth crack propagation close to the interface, often giving a low fracture energy. A rough surface, especially a microfibrous or microporous one, can be seen as causing local stress concentrations which interfere with this smooth crack propagation. This discontinuity can lead to the deformation of larger volumes of material leading to increased energy loss [85]. Although this deformation is often plastic, the work of Gent and Lin [71] has clearly shown that loss of elastic strain energy can also be important.

A high modulus gradient at the interface is also avoided in materials that are joined as a result of the interdiffusion of materials to form a fractal surface [57]. The effect is to produce an interfacial composite region. This strengthens the interface and leads to a more gradual change in modulus and avoids the sharp concentrations of stress which would occur at a smooth interface.

The weakness of an interface may also be protected by features of macroscopic roughness deflecting applied stresses into a tougher bulk phase. Examples of this mechanism are provided by the influxes between incompatible crystalline polymers [67–70] and the copper–silica bond [66], both described above.

Let us finally return to Eq. (6) and consider the implications of *rough fracture surfaces*. It is significant that the fracture surfaces produced when strong adhesive bonds are broken are often extremely rough. (This, of course, holds for strong bonds irrespective of the roughness of the substrate surface.) Equation (6) gives the fracture energy in terms of the different energies which contribute to it. To be specific, suppose the failure mode is cohesive. Should the surface energy term be W_C, given by Eq. (5)? This would not take into account the very rough surfaces produced in the fracture. The surface energy term needs to be increased by two factors, the first, r, taking into account the larger surface area, the second, s, allowing for the increased "atomic" surface energy on the rough surface:

$$W_C^* = 2rs\gamma = W_C + (2rs - 2)\gamma \tag{18}$$

If the roughness of the fracture surface is large this may be written as

$$W_C^* = 2rs\gamma = W_C + 2rs\gamma \tag{19}$$

and Eq. (6) is now

$$G = G_0 + 2rs\gamma + \psi \tag{20}$$

The term r might be the roughness factor, but as argued above, it should often be a factor involving the fractal dimension of the fracture surfaces, which, as Table 1 shows, may extremely large. Substituting from Eq. (14) then gives

$$G = G_0 + 2s\gamma\sigma^{1-D/2} + \psi \tag{21}$$

Mecholsky [86] has proposed an equation of this sort to represent the brittle fracture of ceramics: it would be of interest to investigate its applicability to the fracture of adhesive bonds.

VII. CODA

Despite the advances since the days of Chauvet, it is still true today that the tacit knowledge of adhesion is in advance of our theoretical understanding. Nevertheless, we have, of course, made impressive advances since the time when Newton threw down his challenge. The development of theories of adhesion from the work of McBain and Hopkins to the present day has greatly contributed to this understanding. Much has been achieved by rationalizing adhesion phenomena in terms of these distinct theories. Of these, the mechanical theory of adhesion is associated with adhesion to rough and porous surfaces. It has proved valuable historically, as it has concentrated attention on surface roughness and the influence this may have on adhesion. It remains of value as the roughening of interfaces, on a scale which may range from hundreds of microns to nanometers, is important in the more effective use of bonding techniques, and in the development of new materials.

In surveying the effect of roughness on adhesion, we can see how the concepts of adsorption, diffusion, and mechanical theories overlap and merge seamlessly in providing a model of the empirical observations. This is not surprising. We should remember that scientific theories are intellectual models—mental constructs—which are used to rationalize observations "and [are] not more real than the phenomena from which they are drawn" [87]. While accepting that reductionism has been an extremely fruitful methodology in science, especially physical science, we should not forget that it *is* a methodological device and beware of attributing an immutable objective reality to the concepts it constructs. We should avoid the tendency to reduce the interpretation of adhesion phenomena to narrowly conceived theories of adhesion, and should not hesitate to take a broader view, using whichever blend of concepts best suits the purpose.

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5

Acid–Base Interactions: Relevance to Adhesion and Adhesive Bonding

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I. INTRODUCTION

The thermodynamic work of adhesion (W) is by definition the free energy change per unit area required to separate to infinity two surfaces initially in contact with a result of creating two new surfaces (see Fig. 1). It is related to the intermolecular forces that operate at the interface between two materials, for example, an adhesive and an adherend. However, in practice, W may be obscured by other factors (e.g., mechanical interlocking, interdiffusion) since it is always a few orders of magnitude lower than the measured adhesive joint strength [1,2]. One important contribution to practical joint strength is the energy loss due to irreversible deformation processes within the adhesive. Nevertheless, Gent and Schultz [3] showed using peel strength measurements that viscoelastic losses were proportional to the reversible work of adhesion. For this reason, it is important to determine the nature of interfacial chemical and physical forces and to understand how they control the reversible work of adhesion.

In 1964, Fowkes [4] proposed that both the reversible work of adhesion (W) and the surface tension (γ) had additive components:

$$W = W^{\mathrm{d}} + W^{\mathrm{p}} + W^{\mathrm{h}} + W^{\mathrm{m}} + \cdots$$

and

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}} + \gamma^{\mathrm{h}} + \gamma^{\mathrm{m}} + \cdots$$

since the intermolecular attractions at interfaces result from independent phenomena such as dispersion forces (d); dipole interactions (p); and hydrogen bonding (h); a subset of Lewis acid–base interactions, metallic bonds (m), etc. For convenience these intermolecular interactions were split into additive dispersive and nondispersive forces, the latter being unfortunately attributed to polar interactions including the hydrogen bond or acid–base interactions. However, as early as 1960, Pimentel and McClellan demonstrated that the

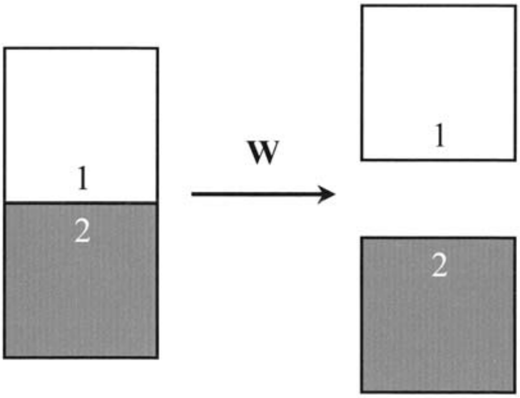

Figure 1 Definition of the work of adhesion, W.

heat of hydrogen bonding between two distinct molecules was related to the acid strength of the proton donor (or electron acceptor) and to the base strength of the proton acceptor (or electron donor) and was completely unrelated to their dipolar moments [5]. This led Fowkes to propose that the so-called "polar" term in the reversible work of adhesion was due to Lewis acid–base interactions (including hydrogen bonding) [6], whereas the true contribution of permanent dipole–dipole interactions and dipole–induced dipole interactions could rather be lumped together with the dispersive interactions term, since it is negligible in the condensed phase (ca. 1%) [7]. Distinguishing between acid–base interactions and "polar" interactions is thus fundamentally important and has also a practical implication since Fowkes demonstrated for complex systems that the former but not the latter led to a substantial improvement in adhesion. It is also important to point out that acid–acid and base–base interactions do not improve adhesion for they are of the van der Waals type only [8–10]. This is illustrated by the determination of the acid–base contribution to the work of adhesion ($W_{\mathrm{SL}}^{\mathrm{AB}}$) of liquids to poly(ethylene-co-acrylic acid) (P(E-AA)) of varying percentage of acrylic acid [8]. Figure 2 shows for dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 0.1 N NaOH solution (all three test liquids are basic) the $W_{\mathrm{SL}}^{\mathrm{AB}}$ increases with the percentage of acrylic acid. By contrast, $W_{\mathrm{SL}}^{\mathrm{AB}}$ for the phenol solution (Lewis acid) in tricresyl phosphate is zero and independent of the acrylic acid content in the copolymer.

Another important example of the role of acid–base interactions concerns polymer adsorption: Fowkes and Mostafa [11] demonstrated that the amount of poly(methyl methacrylate) (PMMA) (electron donor or Lewis base) adsorbed onto silica (electron acceptor or Lewis acid) was much higher than that of adsorbed chlorinated poly(vinyl chloride) (CPVC) (Lewis acid). When $CaCO_3$ (Lewis base) was used as the substrate, CPVC adsorbed with a greater amount than PMMA. In the case of the PMMA–silica system, it was demonstrated that the acid–base properties of the solvent were of significant importance since the solvent can interact via specific acid–base forces with the polymer (chloroform–PMMA interaction), or can preferentially adsorb onto the substrate (tetrahydrofuran–silica interaction). Both phenomena result in hindering polymer adsorption. By contrast, in a noncompeting solvent such as CCl_4, a much higher adsorbed amount of PMMA was obtained onto silica because in this case the polymer–substrate acid–base interactions were maximized.

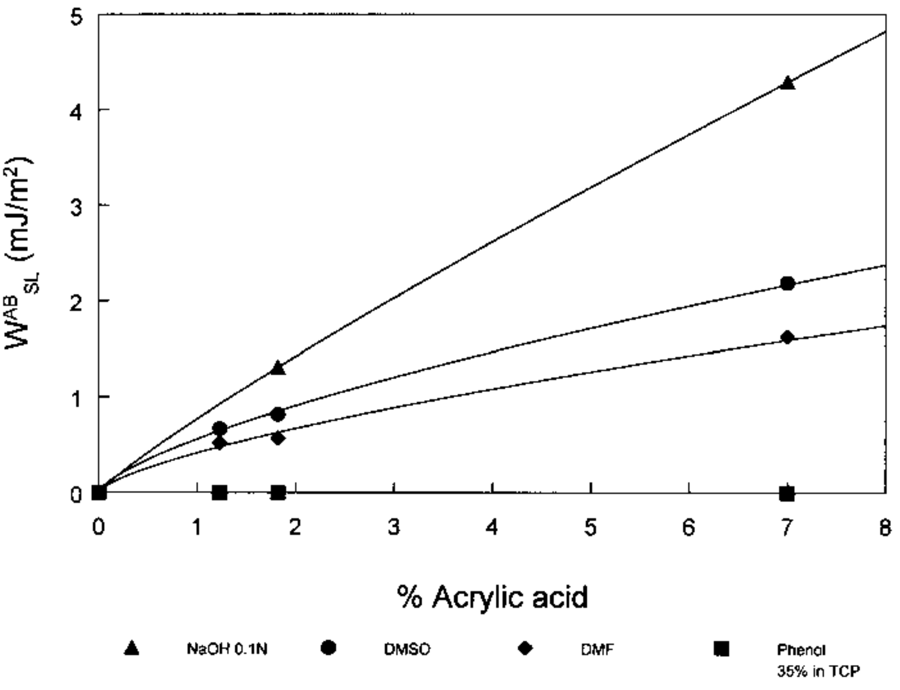

Figure 2 Acid–base contribution to the work of adhesion (W_{SL}^{AB}) determined by contact angle measurements for various liquid–acrylic acid copolymer pairs versus the acrylic acid content.

The pioneering developments of Professor Frederick M. Fowkes regarding the acid–base theory in adhesion have attracted the attention of several laboratories. A Festschrift in his honor on the occasion of his 75th birthday was published in 1991 [12]. This monograph constitutes an important step in the history of acid–base chemistry in general and adhesion science in particular. In the 1990s, progress in science and technology accomplished by academic and industrial researchers confirmed that acid–base interactions were a key parameter in improving adhesion, adsorption, dispersibility, solubility, and mixing of polymers and other materials [12–19]. These specific interactions even became measurable using scanning probe microscopy [19–21] (see Section IV.D). However, discordance of opinion or discrepancy also appeared on both the repulsive aspects of acid–base interactions, and the reliability of the van Oss–Chaudhury–Good (vOCG) theory [22] to calculate acceptable values of the acid–base components of the surface free energy. There was thus a need for a second "testament" on acid–base interactions in adhesion science and technology, which has recently been edited by K. L. Mittal [19].

The aim of the present contribution is to review the role of acid–base interactions in adsorption, wetting, and adhesion, and the methodologies and techniques to characterize the acid–base properties of materials. Examples have been selected from the authors' research work and from a survey of the literature. This chapter is organized into the following three sections: definition, properties, and strength of acid–base interactions; theory of acid–base interactions in adhesion; and experimental assessment of acid–base properties of polymers and other materials.

II. DEFINITION, PROPERTIES, AND STRENGTH OF ACID–BASE INTERACTIONS

A. Definition

Acid–base interactions including hydrogen bonds are specific and not ubiquitous like the London dispersive interactions. They occur when a base (electron donor or a proton acceptor) and an acid (electron acceptor or proton donor) are brought close together. This can be described by the general equation

$$\underset{\text{acid}}{A} + \underset{\text{base}}{:B} \rightarrow \underset{\text{acid–base complex}}{A:B} \tag{1}$$

Table 1 shows the three possible types of acids and bases and examples of corresponding molecules. These types of acids and bases lead to nine possible acid–base adducts. Five of these combinations, namely n–n, n–σ^*, n–π^*, π–σ^*, and π–π^*, yield the addition type complexes whereas the other four combinations lead to adducts with displacement [23]. For example, the interaction of PMMA in chloroform results in the formation of an n–σ^* acid–base adduct. PMMA is a Lewis base due to the nonbonding electron doublets from the oxygen in the C=O group whereas the acceptor site in chloroform is its C–H antibonding σ^* orbital.

Amphoters are those species which bear both acidic and basic sites and can thus interact specifically with either pure acids or bases. In the terminology of van Oss et al. [22] pure acids and bases are called "monopolar" whereas amphoters are called "bipolar." This is a rather unfortunate terminology since acid–base interactions are distinguished from "polar" interactions. For this reason, Berg [16] preferred the terms "monofunctional" for pure acids and pure bases, and "bifunctional" for amphoters.

B. Role of Acid–Base Interactions in Physical Chemistry and Materials Science

The water–water hydrogen bond is, for example, responsible for the anomalously high boiling point of water and contributes to 70% of the surface tension of this liquid at ambient temperature. It is also well known that the hydrogen bonds between complementary base pairs thymine–adenine (two bonds) and cytosine–guanine (three bonds) are the key to the double helical stucture of DNA. Finally, it has long been recognized that acid–base interactions have a dramatic effect on polymer macroscopic properties such as glass transition temperature [24], polymer miscibility [25,26], solubility in common solvents [14,27], swelling [27], adsorption [11], and adhesion [12,19].

Table 1 Types of Lewis Acids and Bases

Electron Donors (bases)		Electron Acceptors (acids)	
Type	Molecule	Type	Molecule
n	pyridine, EtAc	n	BF_3, $AlCl_3$
σ	alkanes	σ^*	I_2, $HCCl_3$
π	benzene	π^*	C_6H_5–NO_2

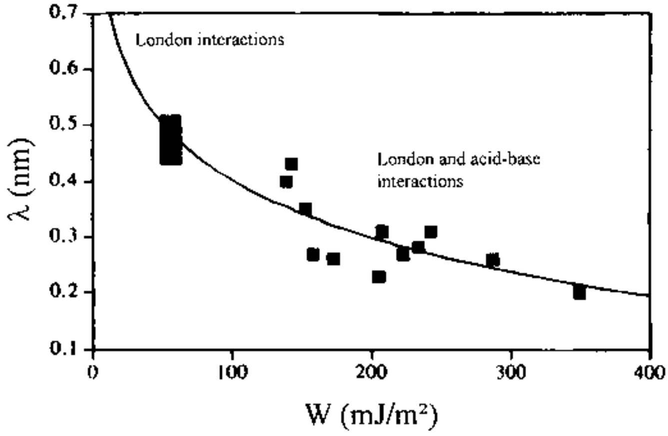

Figure 3 Variation of the intermolecular distance λ at the interface versus the reversible work of adhesion *W*.

Hydrogen or acid–base bonds are exothermic and their energy ranges from 8–50 kJ/mol [28,29]. This is comparable with London forces but exceeds dipole–dipole (Keesom) and dipole–induced dipole (Debye) interactions. With a large and negative value, the heat of an acid–base interaction can overcome the positive or the negligibly small negative entropic term $-T\Delta S$, so that adhesion and mixing can be substantially improved. The high energy associated with acid–base interactions is due to Coulombic forces acting at intermolecular distances of ca. 0.2–0.3 nm. Acid–base interactions are thus of the short range type by comparison to the long range London dispersive interactions which can operate at distances exceeding 10 nm. For example Nardin and Schultz [29] have demonstrated for a series of single-fiber composites that the maximal work of adhesion (W) was obtained for fiber–matrix systems interacting via both dispersive and acid–base interactions on the one hand and for the smallest intermolecular distance λ of ca. 0.2 nm on the other hand (see Fig. 3). For such a short distance, the highest heat of acid–base interaction (ca. 50 J/mol) between the fiber and the matrix was obtained.

The importance of acid–base interactions in various fields of chemistry led to extensive research in the 1960s to obtain acid–base scales. This resulted in the Hard and Soft Acids and Bases (HSAB) scales of Pearson [30], Drago's *E* and *C* constants [31], and Gutmann's donor and acceptor numbers [32]. Bolger and Michaels [33] have used Brönsted acid–base chemistry to predict the adhesion of organic and inorganic species.

C. Hard and Soft Acids and Bases

Pearson [30] proposed qualitative scales of acidity and basicity based on the numerical values of equilibrium constants for nucleophilic substitution reactions. Pearson noted that the stability of the acid–base adducts depended on the size and the charge of the adjacent acids and bases. Pearson identified hard and soft types of acids, and hard and soft types of bases.

Hard acids (or electrophiles) have a positive charge, are hard to reduce due to their high-energy lowest unoccupied molecular orbital (LUMO) and have a small size (e.g., H^+).

Soft acids have a low-energy LUMO and are thus easy to reduce, do not necessarily have a positive charge and have a large size (e.g., I_2, metals).

Hard bases (or nucleophiles) are difficult to oxidize for they have a low-energy highest occupied molecular orbital (HOMO), are usually negatively charged, and have a small size and a high pK_a (e.g., O^{2-}, ketones).

Soft bases are easy to oxidize due to their high-energy HOMO, do not necessarily have a negative charge, and have a large size and a small pK_a (e.g., amines).

Pearson proposed the following expression to rationalize his HSAB concept:

$$\log K = S_A S_B + \sigma_A \sigma_B \tag{2}$$

where S is a hardness factor, σ is a softness parameter, and A and B stand for acid and base, respectively. Implicitly, Eq. (2) indicates that like species form stable adducts. In other words "hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases." Unfortunately, the HSAB theory remained of very limited utility since it failed to predict quantitatively the stability of the adducts. Drago [34] pointed out that in the HSAB literature, results are explained after the answer is known. Nevertheless, Lee [35] has related chemical hardness to the average energy gap of a solid and has proposed the following classification of solids:

Metals: soft and mostly acidic
Semimetals: soft
Semiconductors: rather soft and mostly basic
Most insulators including polymers: hard.

Lee reported that a metal–metal interaction could be viewed as an acid–base interaction. This is, for example, the case for the chemical interaction at the Cr/Cu interface which has been modeled as an acid–base interaction where Cr is a Lewis acid and Cu a Lewis base because it has more filled than empty orbitals [35]. The work of Lee has contributed considerably to the extension of the HSAB principles, established for liquid solutions, to solid–solid interactions.

D. Drago's *E* and *C* Parameters

Drago proposed a four-parameter equation to predict the heat of acid–base adduct formation [31]:

$$-\Delta H^{AB} = (E_A E_B + C_A C_B) \tag{3}$$

where E and C are the susceptibilities of the acid (A) and the base (B) to undergo an electrostatic interaction (E) and a covalent bond (C), respectively. Drago showed that his equation estimated ΔH^{AB} for almost 1600 adducts with an accuracy of 0.1–0.2 kcal/mol (0.4–0.8 kJ/mol). Stable adducts are obtained when the acid and the base have both large E and C constants. Fowkes [6] suggested determining E and C parameters for polymers and other materials by using a set of reference acids and bases of known Drago parameters. However, this is best achieved by choosing a set of reference species of widely differing C/E ratios (where C/E can be considered to be a measure of relative softness). Table 2 displays Drago's parameters for some frequently used acidic and basic probes.

Fowkes and co-workers have used test acids (e.g., phenol and chloroform) and bases (e.g., pyridine and ethyl acetate) to determine Drago's parameters for polymers and metal oxides using essentially calorimetric heats and infrared (IR) measurements [13,27,37,38].

Table 2 Drago's Parameters for Some Commonly Used Acids and Bases

Acids	C_{A}	E_{A}	$C_{\mathrm{A}}/E_{\mathrm{A}}$
Iodine	1.00	1.00	1.0
$SbCl_5$	5.13	7.38	0.695
t-BuOH	0.30	2.04	0.147
Pyrrole	0.30	2.54	0.116
$CF_3CH(OH)CF_3$	0.62	5.93	0.105
Phenol	0.44	4.33	0.102
Chloroform	0.16	3.02	0.053
H_2O	0.26	2.61	0.010
Bases	C_{B}	E_{B}	$C_{\mathrm{B}}/E_{\mathrm{B}}$
TCHP=S[a,b]	9.67	0.61	15.8
Triethylamine	11.1	0.99	11.19
Pyridine	6.40	1.17	5.47
THF	4.27	0.98	4.37
Diethyl ether	3.25	0.96	3.38
1,4-Dioxane	2.38	1.09	2.18
Acetone	2.33	0.98	2.36
Ethyl acetate	1.74	0.98	1.79
$Et_3P{=}O$[a,c]	2.70	1.64	1.65

E and C in $(\mathrm{kcal/mol})^{1/2}$ from [31], except: [a][36]; [b]tricyclohexyl phosphine oxide; [c]triethyl phosphine oxide.

The approach of Fowkes was applied in combination with inverse gas chromatography (IGC) to determine E and C for conventional polymers [39], conducting polymers [40,41], and untreated and silane-treated glass beads [42]. It is also worth noting the potential use of nuclear magnetic resonance (NMR) [13] and x-ray photoelectron spectroscopy (XPS) [15,43] for the assessment of E and C.

Table 3 reports the E and C parameters for various polymers and metal oxides using a variety of techniques. Clearly, several methods can be used to determine E and C. Alternatively, it would perhaps be possible to assess these constants by using contact angles of diiodomethane solutions of specific probes such as phenol. Indeed, the determination of ΔH^{AB} for probe-surface systems was suggested by Fowkes et al. [49] on the basis of temperature-dependent contact angles and a substitution of the Young equation into the Gibbs equation for solute adsorption from diiodomethane onto the surface under investigation. Such applications include the surfaces of PMMA [49] and chemically modified Teflon [50].

E. Gutmann's Donor and Acceptor Numbers

Gutmann [32] proposed a two-parameter equation for the estimation of ΔH^{AB}:

$$-\Delta H^{\mathrm{AB}}(\mathrm{kcal/mol}) = \frac{(\mathrm{AN} \times \mathrm{DN})}{100} \tag{4}$$

where AN is the acceptor number of the acidic species and DN the donor number of the basic species. DN was defined as the negative of the enthalpy of formation of the

Table 3 Drago's E and C Parameters ($\mathrm{kcal}^{1/2}\ \mathrm{mol}^{-1/2}$) for Some Polymers and Fillers

Polymers	C_A	E_A	C_B	E_B	Method	Ref.
CPVC	—	3			IR	27
	0.36	2.70			IR	38
PVB	—	4			IR	27
Phenoxy resin	0.24	1.53			IR	44
Epoxy resin	0.29	1.72			NMR	13
PVdF	0.7	1.8			IR	45
PMMA			1.18	0.59	IR	44
			0.96	0.68	IR	27
PEO			5.64	0.77	IR	44
PPyCl	0.27	4.17	0.45	1.09	IGC	40
PPyTS	0.27	4.35	24.5	−0.36	IGC	41
PPO			9.5	≈ 0	XPS/IR	43
PP-N_2			0.32	1.46	XPS	46
PP-NH_3			0.91	1.65	XPS	46
Fillers						
SiO_2	1.14	4.39			MC/IR	37
TiO_2	1.02	5.67			MC	37
α-Fe_2O_3	0.8	4.50			MC	47
	1.1	0.50–1.0			MC	48
γ-Fe_2O_3	0.79	5.4			MC/IR	38
E glass	0.02	0.15	0.39	0.2	MC	37
Glass beads	0.70	6.0			IGC	42
APS-treated glass	1.60	0.62			IGC	42

CPVC, chlorinated poly(vinyl chloride); PVB, poly(vinyl butyral); PVdF, poly(vinyl difluoride); PMMA, poly(methyl methacrylate); PEO, poly(ethylene oxide); PPyCl, chloride-doped polypyrrole; PPyTS, tosylate-doped polypyrrole; PPO, poly(phenylene oxide); PP-N_2, nitrogen plasma-treated polypropylene; PP-NH_3, ammonia plasma-treated polypropylene; MC, microcalorimetry; APS, aminopropyltriethoxysilane.

acid–base adduct between the base under investigation and a reference Lewis acid, antimony pentachloride ($SbCl_5$) in 1,2-dichloroethane (inert solvent):

$$\mathrm{DN} = -\Delta H(\mathrm{SbCl_5{:}base}) \tag{5}$$

AN, the acceptor number of Lewis acids, was defined as the relative ^{31}P NMR shift obtained when triethylphosphine oxide (Et_3PO) was dissolved in the candidate acid. The scale was normalized by assigning an AN value of 0 to the NMR shift obtained with hexane, and 100 to that obtained from the $SbCl_5{:}Et_3PO$ interaction in dilute 1,2-dichloroethane solution. However, the total shift of ^{31}P NMR in two-component systems has an appreciable contribution of van der Waals interactions that must be accounted for in correlating spectral shifts with heats of acid–base interactions. Riddle and Fowkes [7] corrected the ^{31}P NMR shifts for van der Waals interactions and proposed a new scale of acceptor numbers. The new AN values ($\mathrm{AN}-\mathrm{AN}^d$) in ppm are converted into AN* in kcal/mol units by

$$\mathrm{AN}^* = 0.228(\mathrm{AN} - \mathrm{AN}^d) \text{ in kcal/mol} \tag{6}$$

where AN^d is the dispersive component of the original AN values published by Gutmann.

Table 4 reports values of DN and AN* for a selection of solutes. It should be noted that since $SbCl_5$ is a soft acid, the DN scale is thus a classification of softness for bases.

Table 4 DN and AN* Values (in kJ/mol) for Selected Purely Acidic, Purely Basic and Amphoteric Liquids

Liquid	DN	AN*
Chloroform	0	22.6
CH_3NO_2	11.3	18.0
Acetonitrile	59	19.7
Water	75.3	63.2
Acetone	71.1	10.5
Ethyl acetate	71.1	6.3
Diethylether	80.3	5.9
THF	83.7	2.1
Pyridine	138.5	0.6
Dioxane	61.9	0

Conversely, the AN* scale can be viewed as a scale of hardness for acids since Et_3PO is a hard reference base. Nevertheless, the merit of Gutmann's approach lies in the fact that his scales provide both acidic and basic parameters for amphoteric species, which is not the case with Drago's *E* and *C* classifications.

F. Bolger's Δ_A and Δ_B Interaction Parameters

In the case of organic–inorganic materials interaction (e.g., polymer–metal oxide), Bolger and Michaels [33] suggested a model based on Brönsted acid–base chemistry to account for the strength of the interaction. They defined a parameter Δ for organic acids and bases:

$$\Delta_A = \mathrm{IEPS(B)} - \mathrm{p}K_a(\mathrm{A}) \tag{7a}$$

and

$$\Delta_B = \mathrm{p}K_a(\mathrm{B}) - \mathrm{IEPS(A)} \tag{7b}$$

where the K_a is the dissociation constant of the organic species and IEPS* the isoelectric point of a solid, namely the metal oxide (see XPS, Section IV.C.1.a).

Bolger and Michaels identified three regimes of acid–base interactions:

(i) $\Delta \ll 0$: negligibly weak acid–base interactions
(ii) $\Delta \approx 0$: acid–base interactions of comparable forces to those due to dispersive interactions
(iii) $\Delta > 0$: strong acid–base interactions perhaps resulting in chemical attack or (metal) corrosion.

Table 5 reports Δ parameters for acetic acid ($\mathrm{p}K_a(\mathrm{A}) = 4.7$) and methylamine ($\mathrm{p}K_a(\mathrm{B}) = 10.6$) interacting with SiO_2, Al_2O_3, and MgO, whose IEPS values are 2, 8, and 12, respectively. The maximum positive values of Δ are obtained for the amine–SiO_2 and carboxylic acid–MgO interactions, thus for acid–base adducts. In

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*The IEP corresponds to the pH at which the zeta potential of the metal oxide is zero. If there is no specific adsorption of ions other than H^+ or OH^-, the IEP is simply the point of zero charge (PZC). The PZC is defined as the pH of the solution required to achieve zero net surface charge.

Table 5 Bolger's Δ Parameters for Selected Organic-Metal Oxide Pairs

	SiO_2 (2)	Al_2O_3 (8)	MgO (12)
CH_3COOH	−2.7	3.3	7.3
CH_3NH_2	8.6	2.6	−1.4

The numbers in parentheses correspond to the IEPS values.

contrast, Δ is negative for the carboxylic acid–silica and amine–MgO interactions as they are of the acid–acid and base–base types, respectively.

Bolger's concept has successfully been used to interpret the failure mechanisms of polyimide/MgO joints [51]. Similarly, a Δ_A value of 6.5 was estimated for the interaction of PMDA–ODA PAA [pyromellitic dianhydride–oxydianiline poly(amic acid), $pK_a(A) = 3$] with copper (IEPS of copper oxide = 9.5); this is a too strong predicted interaction, suggesting the migration of copper in the polymer film [52].

III. THEORY OF ACID–BASE INTERACTIONS IN ADHESION

A. The Thermodynamic or Reversible Work of Adhesion

In the absence of chemisorption and interdiffusion, the work of adhesion is the sum of the various intermolecular forces involved and can be related to the surface free energies (Dupré's equation):

$$W = \gamma_1 + \gamma_2 - \gamma_{12} \tag{8}$$

where γ_1 and γ_2 are the surface free energies of components 1 and 2, and γ_{12} is the interfacial free energy. For two materials interacting via London dispersive forces only across their interface, Fowkes [4] suggested that W be described by

$$W = W^{\mathrm{d}} = 2(\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}})^{1/2} \tag{9}$$

where W^{d} is the dispersive contribution to the work of adhesion and γ_i^{d} the dispersive contribution to the surface energy γ_i. In the case where both materials have "polar" interacting sites, W can be described by

$$W = W^{\mathrm{d}} + W^{\mathrm{p}} \tag{10}$$

where W^{p} is the polar contribution to the reversible work of adhesion. W^{p} was described by [53]

$$W^{\mathrm{p}} = 2(\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}})^{1/2} \tag{11}$$

where γ_i^{p} is the polar contribution to the surface energy of the ith species. This is known as "the extended Fowkes equation." However, Fowkes [13,54] has demonstrated that Eq. (11) is incorrect and cannot predict the magnitude of the nondispersive interactions. The main problem of the "extended Fowkes equation" is the wrong assumption that the nondispersive contribution to W of two polar materials can be represented by the geometric mean value of their polar properties. Indeed, when Eqs. (8)–(11) are applied to a liquid–liquid system, such as water–ethanol, it cannot predict their miscibility or immiscibility. Although the γ^{p} value for ethanol is only 1.1 mJ/m^2, this liquid is very hydrophilic and miscible in water in all proportions. Fowkes has shown that the use of the geometric mean expression for estimating the work of adhesion and interfacial tension between water and ethanol predicts these two liquids to be completely immiscible with an interfacial tension of 37.7 mJ/m^2, which, of course, is contrary to the physical reality. For this reason, γ^p is usually a very inadequate measure of polarity or hydrophilicity [13]. It was instead suggested that the nondispersive contribution to the work of adhesion attributed to Lewis acid–base interactions (W^{AB}) could be evaluated by

$$W^{AB} = W - 2(\gamma_1^d \gamma_2^d)^{1/2} \tag{12}$$

Two methods were developed to determine W^{AB}: the first was suggested by Fowkes and Mostafa in 1978 [11] and the second approach was introduced by van Oss and co-workers in 1988 [22].

B. The 1978 Method of Fowkes and Mostafa

This method makes use of ΔH^{AB} to assess W^{AB}:

$$W^{AB} = -f n_{AB} \Delta H^{AB} \tag{13}$$

where f is a free energy to enthalpy conversion factor and n_{AB} the number of acid–base adducts per unit area. ΔH^{AB} can be evaluated experimentally, e.g., by microcalorimetry [13], infrared spectroscopy [13,15,55], and contact angle measurements [49,50], or evaluated by Drago's four-parameter equation [31]. Equation (10) can thus be rewritten as

$$W = 2(\gamma_A^d \gamma_B^d)^{1/2} - f n_{AB}(E_A E_B + C_A C_B) \tag{14}$$

Equations (3) and (12) were applied to the benzene/water interface, using Drago's E_A and C_A constants for water and E_B and C_B for benzene. Drago's equation predicts a ΔH^{AB} value of -5.0 kJ/mol. The cross-sectional area of benzene (0.50 nm^2) leads to $n_{AB} = 3.3\ \mu\text{mol/m}^2$. Applying Eq. (13) yields $W^{AB}/f = 16.5$ mJ/m^2, which compares well with the value determined at 20°C using Eqs. (8) and (12):

$$\begin{aligned} W^{AB} &= \gamma_1 + \gamma_2 - \gamma_{12} - 2(\gamma_1^d \gamma_2^d)^{1/2} \\ &= 72.8 + 28.9 - 35 - 2(22 \times 28.9)^{1/2} = 16.3\ \text{mJ/m}^2 \end{aligned} \tag{15}$$

This implies that $f = 1$. However, f cannot be set equal to unity as found by Vrbanac and Berg [56] in their study of various neutral, acidic, and basic polymer surfaces. They checked Eq. (13) using a combination of wettability to determine W, conductimetric titrations for the assessment of n_{AB}, flow calorimetry to determine ΔH^{AB}, and temperature-dependent determination of surface tension and contact angle to estimate f. It was concluded that f (temperature dependent) was significantly below unity in most cases and that even including this effect, Eq. (15) was still not verified quantitatively when the terms were measured independently. Indeed for the DMSO–poly(ethylene-co-acrylic acid 5%) system, $W^{AB} = 1.3$ and 3 mJ/m^2 from wetting measurements and independent measurements of the various parameters in Eq. (13), respectively. As this procedure was applied to a single system one cannot claim or conclusively deny the quantitative (dis)agreement between the two ways of estimating W^{AB}.

Table 6 Total Surface Tension and Its Components (in mJ/m^2) for Commonly Used Test Liquids

Liquid	γ	γ^d	γ^{AB}	γ^+	γ^-	Ref.
Water	72.8	21.8	51	25.5	25.5	10
Glycerol	64	34	30	3.92	57.4	10
Formamide	58	39	19	2.28	39.6	10
Ethylene glycol	48	29	19	3	30.1	57
DMSO	44	36	8	0.5	32	10
α-Bromonaphthalene	44.4	43.5	0	0	0	10
CH_2I_2	50.8	50.8	0	0	0	10
Silicone oil	18.8	18.8	0	0	0	58
Tricresyl phosphate	40.9	40.9	0	0	0	4

DMSO: dimethylsulfoxide.

C. The 1988 Method of van Oss, Chaudhury, and Good (vOCG)

van Oss and co-workers [22] introduced the notion of acidic and basic components to the surface energy ($\gamma^+$and γ^-, respectively) to characterize the acid–base properties of materials and predict W^{AB}:

$$W^{AB} = 2(\gamma_1^+\gamma_2^-)^{1/2} + 2(\gamma_1^-\gamma_2^+)^{1/2} \tag{16}$$

γ^+ and γ^- for a solid can be determined by contact angle measurements using three reference liquids of known γ_L^d, γ_L^+, and γ_L^-. The acidic and basic surface tension components for test liquids were established with model surfaces and liquids on the assumption that for water $\gamma_L^- = \gamma_L^+ = 25.5\,\mathrm{mJ/m^2}$ and

$$\gamma_L^{AB} = 2(\gamma_L^+\gamma_L^-)^{1/2} \tag{17}$$

Application of Eq. (17) to water (w) yields

$$\gamma_w^{AB} = 2(25.5 \times 25.5)^{1/2} = 51\ \mathrm{mJ/m^2}$$

Table 6 reports the total surface tension and its components for some reference liquids. α-Bromonaphthalene, CH_2I_2, silicone oil, and tricresyl phosphate probe dispersive interactions only whilst the other liquids permit characterization of both dispersive and acid–base interactions of surfaces. Note that the surface tension of silicone oil is very low, so this liquid is expected to spread on surfaces.

IV. EXPERIMENTAL ASSESSMENT OF ACID–BASE PROPERTIES OF POLYMERS AND OTHER MATERIALS

There is a plethora of analytical techniques available to assess the acid–base properties of materials. They range from wettability and chromatographic measurements to spectroscopic approaches and more sophisticated scanning probe microscopic methods [12,13,15–19,59–61]. For the purpose of this contribution, the focus will be on contact angle measurements, inverse gas chromatography, x-ray photoelectron spectroscopy, and atomic force microscopy.

A. Contact Angle Measurements

1. *Determination of the Surface Tension Components*

The wetting of a solid surface by a liquid drop is expressed by Young's equation

$$\gamma_{\mathrm{S}} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{L}} \cos\theta \tag{18}$$

Combining this equation with Eq. (8) one obtains the Young–Dupré equation for the work of adhesion

$$W_{\mathrm{a}} = \gamma_{\mathrm{L}}(1 + \cos\theta) \tag{19}$$

Combining and rearranging Eqs. (19), (9), and (16) one obtains

$$\gamma_{\mathrm{L}}(1 + \cos\theta) = 2(\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-})^{1/2} + 2(\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+})^{1/2} \tag{20}$$

Using at least three of the test liquids indicated in Table 6 one can determine the surface tension components $\gamma_{\mathrm{S}}^{\mathrm{d}}$, γ_{S}^{+}, and γ_{S}^{-} for the surface under test and hence the total surface free energy

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{S}}^{\mathrm{d}} + 2(\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{S}}^{-})^{1/2} = \gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{S}}^{\mathrm{AB}} \tag{21}$$

where $\gamma_{\mathrm{S}}^{\mathrm{AB}}$ is the overall acid–base contribution to γ_{S}.The problem can be solved in two steps. First, $\gamma_{\mathrm{S}}^{\mathrm{d}}$ can be determined using an apolar liquid (e.g., diiodomethane or α-bromonaphthalene) for which $\gamma_{\mathrm{L}} = \gamma_{\mathrm{L}}^{\mathrm{d}}$. In this case, Eq. (20) reduces to

$$\gamma_{\mathrm{L}}(1 + \cos\theta) = 2(\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}})^{1/2} \tag{22}$$

where θ is the measurable value and $\gamma_{\mathrm{S}}^{\mathrm{d}}$ is the only unknown. Two unknowns are yet to be determined for the solid material following rearrangement of Eq. (20):

$$\gamma_{\mathrm{L}}(1 + \cos\theta) - 2(\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}})^{1/2} = 2(\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-})^{1/2} + 2(\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+})^{1/2} \tag{23}$$

To do so, one can use water and another test liquid of which γ_{L}^{+} and/or γ_{L}^{-} are greater than $0\,\mathrm{mJ/m^2}$. However, it must be borne in mind that the unknowns are $(\gamma_{\mathrm{S}}^{+})^{1/2}$ and $(\gamma_{\mathrm{S}}^{-})^{1/2}$ and must thus have values greater than or equal to $0\,\mathrm{mJ/m^2}$.

Table 7 reports the surface free energy values and their dispersive, acidic, and basic components for polymers and other materials. There are some interesting features about the γ^{+} (acidity) and the γ^{-} (basicity) scales reported in this table:

Receding contact angles show that the "real" PE surface is bifunctional with a significant basic character. This is most probably due to the low level of surface oxidation of the polymer [74].

PEO is a fairly basic polymer and this character is stronger than in the case of methacrylate polymers.

PS has a low degree of basicity as expected from its chemical structure.

Plasma-treated PP and OPP have comparable basicities, but the acidic character is stronger for the latter as a result of air plasma treatment.

All metal oxides and glass have strong basic character, but the least strong is silica. In contrast, silica behaves as a strong acidic oxide, which parallels the IEPS scale.

Acid-treated glass is much more acidic than APS-treated glass. The latter exhibits a very strong basic character due to the amino groups at the outermost layers. Glass-C18, has a low γ value, almost reducing to its $\gamma_{\mathrm{S}}^{\mathrm{d}}$, the acid–base character being very weak. This is most probably due to a quasi-total screening of the substrate by the hydrophobic octadecylsilane coupling agent.

Table 7 Surface Free Energy Components (in mJ/m^2) for Polymers, Fibres, Metal Oxides, Glass, Microorganisms and Proteins

	γ	γ^{d}	γ^{AB}	γ^{+}	γ^{-}	Ref.
Homopolymers						
PEO 6000	43	43	0	0	64	14
Dextran 10000	61.2	47.4	13.8	1.0	47.4	14
PMMA	39–43	39–43	0	0	9.5–22.4	10
	48.9	46.5	2.4	0.08	18.1	62
PVAc	44.5	42.6	1.9	0.041	22.3	62
PVC	43.7	43	0.7	0.04	3.5	10
	43.1	40.2	2.9	0.42	5.1	62
PS	42.0	42	0	0	1.1	10
	44.9	44.9[a]	0	≈ 0[a]	1.33[a]	63
	49.9	49.9[b]	0	≈ 0[b]	5.14[b]	63
PE[a]	33	33	0	0	0.1	10
PE[b]	57.9–62.5	42	15.9–20.5	2.1	30–50	10
PAI	52.6	42.8	9.8	1.04	23.15	64
PHEMA	50.6	40.2	10.4	2.07	13.1	65
Copolymers						
P(HEMA80/EMA20)	48.2	40.7	7.5	0.63	22.7	65
P(HEMA40/EMA60)	39.8	39.4	0.4	0.02	16.4	65
Conducting polymers						
PPyTS	47.0	41.0	6.0	0.81	10.9	66
PPyCl	43.5	36.6	6.9	0.43	28.3	66
PPyDS	41.7	34.8	6.9	1.35	8.85	66
Undoped POT		22.5		—	0.5	67
POT–AuCl$_4^-$		23.4–25[c]		—	0.7–4.7[c]	67
PS latices						
Anionic	41.4	41.4[a]	0	≈ 0[a]	≈ 13.13[a]	63
	57.6	50.8[b]	6.8	≈ 1.19[b]	9.73[b]	63
Cationic		39.4–41.9		0–0.4[d]	0.3–7[d]	63
		39.4–41.9		0–0.1[e]	1.8–8.2[e]	63
Plasma-treated PP						
Untreated PP	32.2	30.1	2.1	0.3	3.8	46
PP–O$_2$	43.1	36.7	6.4	0.5	22.0	46
PP–N$_2$	53.3	41.9	11.4	1.0	30.9	46
PP–NH$_3$	42.6	34.9	7.7	0.7	21.4	46
Corona-treated OPP						
Untreated[a]	32.6	32.6	0	0	0	68
Untreated[b]	39.2	37.0	2.2	1.3	0.9	68
OPP–air[a]	55.8	42.0	13.9	1.9	25.2	68
OPP–air[b]	64.7	46.2	18.5	2.0	25.2	68
Zoltek® carbon fibers						
Unsized	41.3	41.3	0	0	32.4	69
Ultem®, sized	40.2	38.6	1.6	0.03	20.5	69
PU, sized	35.8	33.2	2.6	0.11	15.3	69
Metal oxides and glass						
Chromium	59.6	45.8	13.8	0.86	55.5	62
Aluminum	57.4	46.7	10.7	0.50	57.5	62

(*continued*)

Table 7 Continued

	γ	γ^{d}	γ^{AB}	γ^{+}	γ^{-}	Ref.
Silicon wafer	61.9	38.6	23.3	4.00	33.98	70
Glass	59.3	42.03	17.80	1.97	40.22	70
Glass, H_2SO_4/HNO_3	64.5	42.03	22.47	2.82	44.76	70
Glass, C18	26.8	25.70	1.12	0.24	1.32	70
Glass, APS-treated	45.0	39.2	5.76	0.084	98.62	This work
Microorganisms and biological materials						
HSA, dry, pH 4.8	45	44.0	0.10	0.03	7.6	71
HSA, dry, pH 7	41.4	41.0	0.4	0.002	20	71
HSA, hydrated, pH 7	62.5	26.8	35.7	6.3	50.6	71
HIg-G, hydrated, pH 7	51.3	34	17.3	1.5	49.6	71
HIg-A, hydrated, pH 7	26.8	26.8	0	0	93.0	71
Bovine fibrinogen, dry	40.3	40.3	0	0	53.2	71
Human fibrinogen, dry	40.6	40.6	0	0	54.9	71
HLDLP, dry	41.1	35.5	5.66	0.26	30.8	71
Candida albicans (yeast)[f]	42.5	38.1	4.4	2.9	1.7	72
Candida albicans (yeast)[g]	47.7	37.3	10.4	0.6	43.7	72
Streptococcus gordonii (bacteria)[g]	38.9	35.8	3.1	4.2	0.6	72
Streptococcus oralis 34	57.0	35.0	22.0	2.7	45.0	73
Streptococcus oralis J22	48.7	38.0	10.68	0.5	57.0	73
Actinomyces naeslundii 5951	44.0	38.0	6	0.5	18.0	73
Actinomyces naeslundii 5519	40.0	37.0	2.97	0.1	22.0	73
Miscellaneous						
PSA	16.7	12.6	4.1	0.42	9.9	62
Cellulose acetate	40.2	35	5.2	0.3	22.7	10
Cellulose nitrate	45	45	0	0	16	10
Agarose	44.1	41	3.1	0.1	24	10
Gelatin	38	38	0	0	19	10

[a] Based on advancing contact angles; [b] based on receding contact angles; [c] surface energy components increasing with $AuCl_4^-$ doping; [d] using water/ethylene glycol; [e] using water/formamide; [f] cultured at 30°C; [g] cultured at 37°C. PVAc, poly(vinyl acetate); PVC, poly(vinyl chloride); PS, polystyrene; PE, polyethylene; PAI, iodinated polyacetylene; PHEMA, poly(2-hydroxyethyl methacrylate); P(HEMA/EMA), radiation-grafted poly(2-hydroxyethyl methacrylate-co-ethyl methacrylate)—the numbers refer to each monomer content; PPyDS, dodecyl sulfate-doped polypyrrole; POT, poly(octyl thiophene); PP, polypropylene; OPP, oriented polypropylene; Ultem®, polyetherimide; PU, polyurethane; HSA, human serum albumin; HIg-A and -G, human immunoglobulin A and G; HLDLP, human low density lipoprotein; PSA, pressure sensitive adhesive; —Scotch 610 Magic Tape®.

Despite these interesting trends, the vOCG method has been criticized for the following reasons:

(i) the results depend on the choice of the wetting liquids
(ii) almost all surfaces have γ^- values much higher than those of γ^+
(iii) all surface free energy components were determined on the assumption that $\gamma^+ = \gamma^- = 25.5\ \mathrm{mJ/m^2}$ for water whereas water is a stronger Lewis acid than a Lewis base [75,76].

Criticism (i) is totally unfair, because statistically one cannot determine γ_S^+ and γ_S^- with a set of only three test liquids of known surface tension components because a great extent of scatter in the results is to be expected. In the literature, sets of γ_S^+ and γ_S^- are

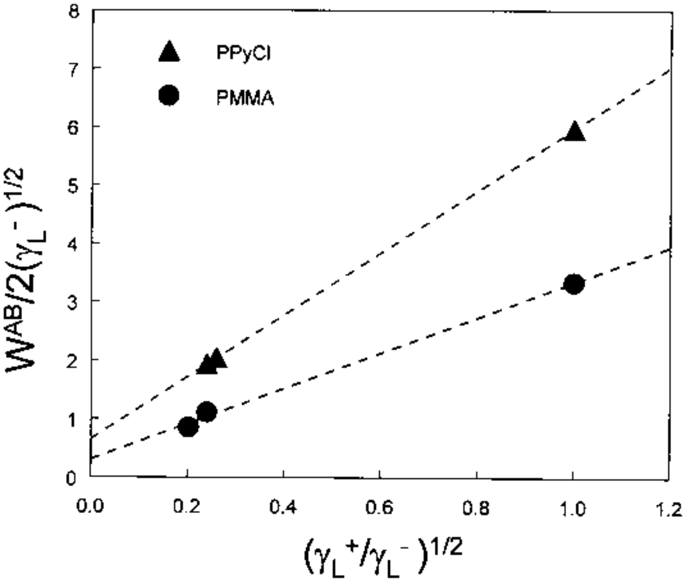

Figure 4 Plot of $W^{AB}/2(\gamma_L^-)^{1/2}$ versus $(\gamma_L^+/\gamma_L^-)^{1/2}$ for reference liquids interacting with PMMA and PPyCl. The correlation permits estimation of γ_S^+ and γ_S^- for the surfaces under test by contact angles. The contact angle data were taken from [77] for PMMA and [66] for PPyCl.

reported for each set of two liquids wetting the solid under investigation. Average values of γ_S^+ and γ_S^- are then derived. This can be avoided by rewriting Eq. (23):

$$\frac{\left[\gamma_L(1+\cos\theta)-2(\gamma_S^d\gamma_L^d)^{1/2}\right]}{2(\gamma_L^-)^{1/2}}=(\gamma_S^+)^{1/2}+(\gamma_S^-)^{1/2}\left(\frac{\gamma_L^+}{\gamma_L^-}\right)^{1/2} \tag{24}$$

The left-hand side of Eq. (24) equals $W^{AB}/2(\gamma_L^-)^{1/2}$ (see Eq. (16)). For a series of monofunctional and/or bifunctional test liquids used, one can plot $W^{AB}/2(\gamma_L^-)^{1/2}$ versus $(\gamma_L^+/\gamma_L^-)^{1/2}$. This leads to a linear correlation with $(\gamma_S^+)^{1/2}$ and $(\gamma_S^-)^{1/2}$ as the intercept and slope, respectively. Application of this simple approach is shown in Fig. 4 (frequently used in the IGC literature, see below) to the contact angle data of Good and Hawa [77] obtained for PMMA, and those obtained for PPyCl by Azioune et al. [66]. It is very important to obtain positive values for $(\gamma_S^+)^{1/2}$ and $(\gamma_S^-)^{1/2}$ prior to the determination of γ_S^+ and γ_S^-.

For PMMA, $\gamma_S^+=0.1$ and $\gamma_S^-=9.2\,\mathrm{mJ/m^2}$, comparable to the average values determined using the sets (water/ethylene glycol) and (water/formamide). The set (ethylene glycol/formamide) cannot be used here because these liquids have very comparable $(\gamma_L^+/\gamma_L^-)^{1/2}$ values as shown in Fig. 4. To plot such graphs one obviously needs to have test liquids with greatly differing values of $(\gamma_L^+/\gamma_L^-)^{1/2}$. This is comparable to the situation occurring when the *E* and *C* parameters for materials are to be determined using test probes with appreciably different *C*/*E* ratios [13]. Therefore, the use of water as a probe liquid is strongly recommended in this regard. However, one also needs other liquids with an appreciable acidity, liquids with $(\gamma_L^+/\gamma_L^-)^{1/2}$ ratios lying between 0.3 and 1 in order to improve the correlations similar to those plotted in Fig. 4.

Criticism (ii) is also unfair because it is well known that acid–base scales strongly depend on the choice of the test probes. For example, Gutmann's DN scale is based on the acid–base complexes of $SbCl_5$, a soft acid. It can thus be considered as a scale of softness. In contrast, Gutmann's AN scale is based on the complexes of $(C_2H_5)_3P{=}O$, a hard test base, thus yielding a scale of hardness. Taken separately, the γ_S^+ and γ_S^- values reported in Table 7 show that they are very useful in establishing novel acidity and basicity scales as discussed above.

Criticism (iii) is fair but McCafferty and Wightman [62] have, for example, shown that using surface tension components for liquids based on the values $\gamma_L^+ = 65.0\,\mathrm{mJ/m^2}$ and $\gamma_L^- = 10\,\mathrm{mJ/m^2}$ for water as suggested by Della Volpe and Siboni [76] yields the same trends of γ_S^+ and γ_S^- values as determined for PVC and PMMA. Similar trends of γ_S^+ and γ_S^- were obtained for PS lattices when the γ_L^+/γ_L^- ratio of 1.8 for water was used [63]. In trying different scales of γ_L^+ and γ_L^-, caution must be exercised as some sets of values may lead to unacceptable results. This is the case for the water–formamide pair for which an interfacial tension was calculated to be $6.8\,\mathrm{mJ/m^2}$ although these liquids are miscible [77].

Despite the criticisms above, the vOCG approach has been frequently and successfully used over recent years to interpret polymer solubility in water [14] (this is not possible using the "γ^p approach"), protein adsorption on clays [57] and conducting polymers (see Section IV.A.2 below), cell adhesion to copolymer surfaces [65], yeast–yeast and yeast–bacteria adhesion [72], fiber–matrix adhesion [69], and the hydrodynamic detachment of colloidal particles from glass plates [70].

2. *Application of the vOCG Theory to the Hydrophilic/Hydrophobic Interactions of Proteins with Polymer Surfaces*

Recent work from our laboratory has dealt with human serum albumin (HSA) adsorption onto the conducting polymers PPyCl, PPyDS, and PPyTS [66] in an aqueous medium at pH 7.4. The PPy–HSA (1–2) interaction in water (w) can be expressed by

$$\Delta G_{1w2} = \gamma_{12} - \gamma_{1w} - \gamma_{2w} \tag{25}$$

where γ_{12} is the interfacial tension between the two materials. Using the vOCG theory, Eq. (25) can be rewritten as a function of the surface tension components [57]:

$$\begin{aligned}\Delta G_{1w2} = {} & \left(\sqrt{\gamma_1^d} - \sqrt{\gamma_2^d}\right)^2 - \left(\sqrt{\gamma_1^d} - \sqrt{\gamma_w^d}\right)^2 - \left(\sqrt{\gamma_2^d} - \sqrt{\gamma_w^d}\right)^2 \\ & + 2\Big[\sqrt{\gamma_w^+}\left(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_w^-}\right) + \sqrt{\gamma_w^-}\left(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_w^+}\right) \\ & - \sqrt{\gamma_1^-\gamma_2^+} - \sqrt{\gamma_1^+\gamma_2^-}\Big]\end{aligned} \tag{26}$$

Numerical application of Eq. (26) to the PPy–water–HSA system yielded ΔG_{1w2} values of −7, −29.6, and $-46\,\mathrm{mJ/m^2}$ for PPyCl, PPyDS, and PPyTS, respectively. The negative values of ΔG_{1w2} indicate that the hydrophobic PPy–HSA interaction is favorable, and the values parallel the trends of HSA adsorption on the one hand, and the water receding contact angle ($\theta_{w,r}$) on PPy surfaces on the other hand ($\theta_{w,r} = 27^\circ$, 43°, and 49° for PPyCl, PPyDS, and PPyTS, respectively). More importantly, the dispersive and acid–base contributions to ΔG_{1w2} (ΔG_{1w2}^d and ΔG_{1w2}^{AB}, respectively) can be estimated from Eq. (26) and compared. Figure 5 depicts the extents of the dispersive and acid–base interactions for the PPy–water–HSA system for PPyCl, PPyDS, and PPyTS: there is a very strong

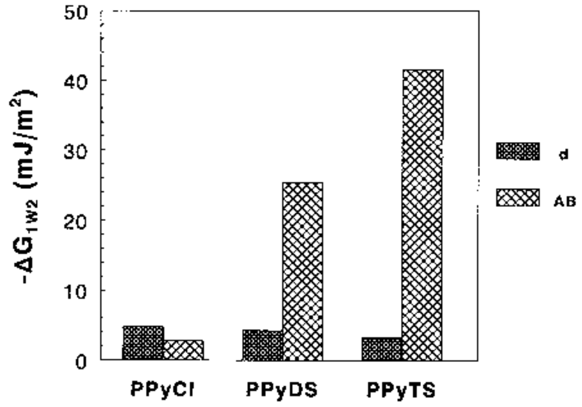

Figure 5 Contributions of dispersive and acid–base components to the interfacial interaction energies of the HSA–polypyrrole film systems immersed in water (ΔG_{1w2}).

contribution of acid–base forces to the hydrophobic conducting polymer–protein interaction, especially in the case of PPyTS.

3. *Contact Angle Titration*

Contact angle titration (CAT) relies on the contact angle measurements of aqueous solutions of HCl or NaOH (preferably buffered solutions), with a pH ranging from 0 to 14. For monofunctional surfaces, the highest work of adhesion is obtained for low (high) pH solutions in contact with basic (acidic) surfaces. It should be noted that in this approach, the total γ_L value of the acidic and basic solutions is pH independent and equals that of distilled water. The value of W_{SL}^{d} with NaOH or HCl solutions can be calculated after evaluation of γ_S^{d} using apolar CH_2I_2, α-bromonaphthalene, or tricresylphosphate. From Eq. (12), the acid–base contribution $W_{SL}^{AB} = W_{SL} - W_{SL}^{d}$.

An example of the assessment of the the acid–base properties by CAT is shown in Fig. 6 for poly(bisphenol A carbonate) (PBAC) and polyethersulfone (PES) surfaces. The titration curves show that both PES and PBAC are predominantly basic polymers since the highest W_{SL} is obtained at low pH. It is very interesting to note in Fig. 6 that W_{SL}^{AB} is slightly higher for PES, thus indicating a higher basicity, in agreement with an IGC study by Bolvari and Ward [78]. In a similar manner, low contact angles were obtained for Brönsted basic solution drops (high pH) at the surface of polyethylene carboxylic acid (PE-COOH), a Brönsted acidic polymer, indicating that acid–base interactions were maximized [79].

The CAT method has been applied to monitor the acid–base interactions of silica and carbon fibers [80], sintered silicon carbide [81], ammonia plasma-treated PP [82], and oxygen- plasma-treated PP [83] in relation to polymer metallization by evaporated aluminum [84]. In regards to the polymer–metal adhesion, it is also important to determine the IEPS of the metal oxide in question and this can be done by CAT. Experimentally, at the IEPS, the surface charge and concentration of dissociated hydroxyl groups are zero, and θ ($\cos\theta$) goes through a maximum (minimum) [62]. Since clean oxides are high surface energy materials, water or pH-controlled solution drops may spread on the surface. In this case the CAT method can still be applied in a two-liquid/solid system, the aqueous solution drop being deposited at the surface of the solid immersed in a hydrocarbon, for example, hexadecane [62].

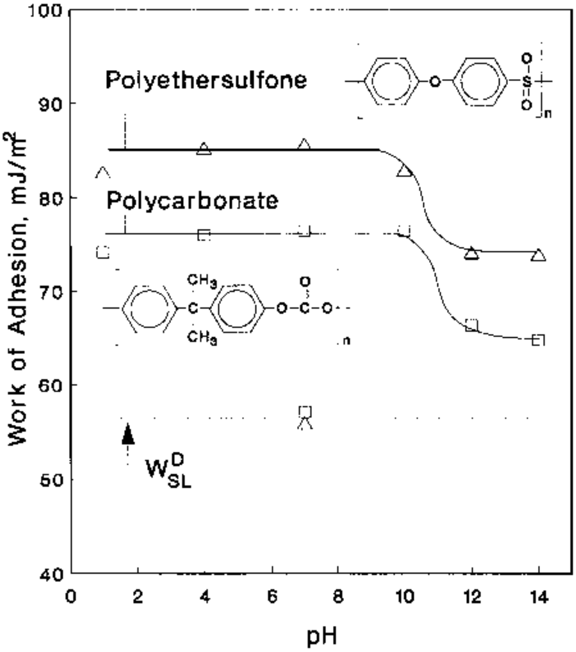

Figure 6 Variation of the work of adhesion W_{SL} versus pH for aqueous solution drops wetting polyethersulfone and polycarbonate.

B. Inverse Gas Chromatography

Inverse gas chromatography (IGC) is a method very well used by the adhesion community for obtaining thermodynamic and morphological information on a variety of materials such as fillers, pigments, colloids, fibers, powder, wood, and polymers [17,60,61,85–94]. The term "inverse" means that the stationary phase is of interest by contrast to conventional gas chromatography in which the mobile phase is of interest. Its success lies in the fact that it is simple, versatile, usable over a very wide range of temperature, and very low cost. IGC has a well established background for the assessment of $\gamma_{\mathrm{S}}^{\mathrm{d}}$ and acid–base parameters for polymers and fillers. Such thermodynamic parameters can be further used to estimate the reversible work of adhesion at polymer–fiber and polymer–filler interfaces [95,96].

IGC is based on the interfacial interactions between molecular probes and the stationary phase. Probes are injected at infinite dilution so that lateral probe–probe interactions are negligible and the retention is governed by solid–probe interactions only. The net retention volume, V_{N}, is defined as the volume of inert carrier gas (corrected for the dead volume) required to sweep out a probe injected in the chromatographic column. At infinite dilution (zero coverage), ΔG_{a}, the free energy of adsorption of 1 mole of solute from a reference state, is related to V_{N} by

$$-\Delta G_{\mathrm{a}} = RT \ln \left(\frac{V_{\mathrm{N}} P_0}{S m \pi_0} \right) \tag{27}$$

where R is the gas constant, T the column temperature, P_0 the partial pressure of the solute, π_0 the two-dimensional spreading pressure of the adsorbed film, and S and m the specific surface area and mass of the stationary phase, respectively [97]. Dispersive and acid–base properties of materials (e.g., polymers, fibers, and fillers) are deduced from ΔG_a or simply $RT \ln(V_N)$ data.

1. *Dispersive Properties*

There are three accepted methods of determining γ_S^d values at infinite dilution and which were published by Dorris and Gray [98], Schultz et al. [95] and Donnet et al. [99].

a. The Method of Dorris and Gray. This method [98] is based on the determination of ΔG^{CH_2}, the free energy of adsorption per methylene group, from the retention data of the n-alkane series (probes capable of dispersive interactions only). Figure 7 depicts plots ΔG_a or $RT \ln(V_N)$ values versus the number of carbon atoms in the n-alkanes (n_C) for PPyCl, PMMA, and a PMMA-coated PPy (the PMMA/PPy sample was prepared by adsorption of PMMA onto PPy from chloroform). Each plot generates an excellent linear correlation, the slope of which equals $\Delta G_a^{CH_2}$. For a solid–CH_2 interaction, Eq. (9) can be rewritten as

$$W = W^d = 2(\gamma_S^d \gamma_{CH_2})^{1/2} \tag{28}$$

where γ_{CH_2} is the surface free energy of the methylene group, taken as the γ values for polyethylene since this polymer contains only methylene groups. Given that W is a free

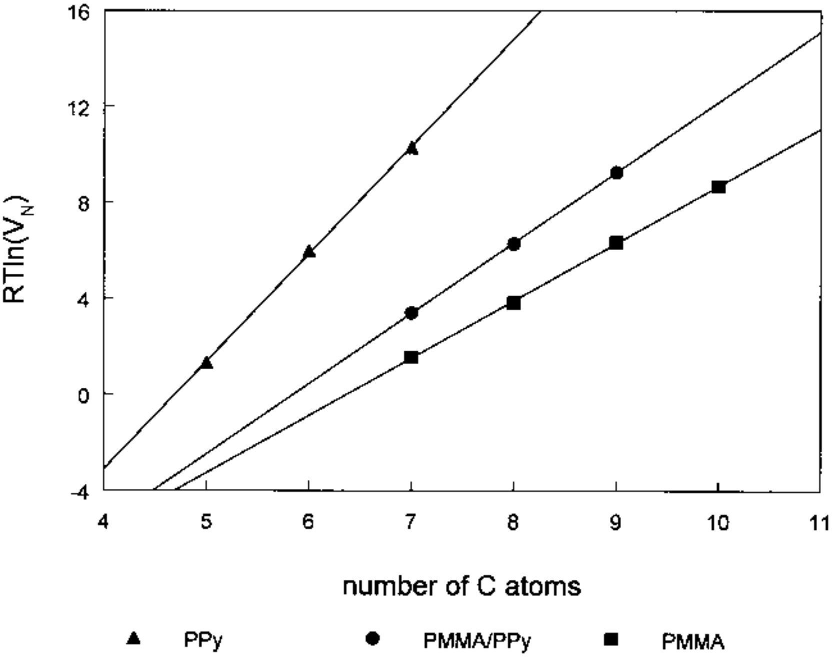

Figure 7 $RT \ln(V_N)$ versus the number of carbon atoms for n-alkanes adsorbed (at 48°C) onto PPyCl, PMMA, and PMMA-coated PPyCl prepared in chloroform (PMMA/PPy). The slopes yield γ_S^d values of 145, 36.6, and 55 mJ/m^2 for PPyCl, PMMA, and PMMA-coated PPyCl, respectively. The intermediate value obtained for PMMA/PPy is an indication of a patchy adsorbed layer of PMMA on the PPy surface.

energy change per unit area, it follows that

$$W = \frac{-\Delta G_a^{CH_2}}{Na_{CH_2}} \tag{29}$$

where N is the Avogadro number and, a_{CH_2} is the cross-sectional area of an adsorbed methylene (CH_2) group (6 Å^2). Combining Eqs. (28) and (29) one can determine γ_S^d using

$$\gamma_S^d = \left(\frac{1}{4\gamma_{CH_2}}\right)\left(\frac{\Delta G_a^{CH_2}}{Na_{CH_2}}\right)^2 \tag{30}$$

where γ_{CH_2} is temperature dependent and $\gamma_{CH_2}(\mathrm{mJ/m^2}) = 36.8 - 0.058\,T(^\circ\mathrm{C})$ [98]. The validity of this approach has been established on the basis that IGC and wettability measurements led to approximately the same γ_S^d value (ca. 40 mJ/m^2) for poly(ethylene terephthalate) [100].

b. The Method of Schultz et al. This approach [95] relates the retention data to the cross-sectional area and the dispersive contribution to the surface tension (γ_L^d) of the molecular probes. For probes interacting with the solid of interest via dispersive forces only (e.g., linear, branched, or cyclic alkanes), a combination of Eqs. (9), (27), and (29) leads to

$$RT\ \ln(V_N) = 2Na(\gamma_S^d\gamma_L^d)^{1/2} + C \tag{31}$$

where a is the area of an adsorbed probe molecule and C is a constant (all other variables were defined above). The method leads to values comparable to those obtained by Gray's approach at low temperature (error less than 4%), but significantly deviates at higher temperature (100°C) [17]. Hamieh and Schultz [101] proposed a temperature dependence of the cross-sectional area of the probe molecules to improve this approach. However, the refinements suggested in [101] to calculate γ_S^d values for a series of metal oxides were overshadowed by the poor reproducibility of the measurements [102].

c. The Method of Donnet et al. Donnet et al. [99] proposed to rewrite Eq. (27) in the form

$$RT\ \ln V_N + C = K(h\nu_S)^{1/2}\alpha_{0S}(h\nu_L)^{1/2}\alpha_{0L} \tag{32}$$

where $h\nu_S$ and $h\nu_L$ are the ionization potentials of the interacting materials, α_0 is the deformation polarizability, and K is a constant which takes into account the vacuum permittivity, the distance between interacting molecules, and the Avogadro constant. S and L refer to solid and liquid, respectively. $K(h\nu_S)^{1/2}\alpha_{0S}$ is a characteristic of the solid under investigation and is related to γ_S^d.

Table 8 provides γ_S^d values for some polymers, fillers, and fibers over a wide range of temperature, which constitutes an advantage over contact angle measurements. There are four important points which must be borne in mind concerning the IGC determination of γ_S^d values.

(i) For heterogeneous high energy surfaces characterized by IGC at infinite dilution, solutes will preferentially probe the high energy sites and the technique will thus lead to γ_S^d values higher than those obtained by contact angle measurements [17,112,117]. For example, γ_S^d values determined for conducting polymers by IGC were found to be always higher than those estimated by

Table 8 Values of γ_S^d for Some Polymers, Colloids, Fillers, Fibres and Pigments

Materials	γ_S^d (mJ/m^2)	Temperature (°C)	Ref.
Conventional and conducting polymers			
LLDPE	28.8	30	103
PMMA beads	38.8	25	104
PMMA-coated Chromosorb (5% w/w)	40	48	105
PTEDM	25.1	50	106
PNDM	39.8	50	106
PPDM	30.1	50	106
PVC	31	48	105
PET	37.9	26.5	100
PEEK	40	50	96
Solsperse (dispersant)	29.6	45	107
Albuperl (resin)	32.3	45	107
Luxtrak^{TM}	42.0	25	118
PPyCl	145	48	104
PPyCl, aged	37	48	109
PPyCl/PMMA/$CHCl_3$	55	48	104
PPyCl/PMMA/dioxane	39.2	48	104
PPyTS	88.5	25	41
$PPyNO_3$	113	48	105
$PPyNO_3$/PVC/PMMA	48–63	48	105
PANI	87.3	68	110
Colloids, fillers, fibers and pigments			
SiO_2 sol	60	60	111
PPyCl–SiO_2	225	60	111
Carbon black	42.8	30	103
Graphite	129	44.5	99
C(PAN)	104	50	112
Oxidized C(PAN)	78–89.2	50	112
E-glass fiber	49	25	113
E-glass/GPS fiber	48	25	113
E-glass/APS fiber	40	25	113
$CaCO_3$	44.6	30	103
PCC heated at 100°C, 24 h	55	100	114
PCC heated at 300°C, 24 h	250	100	114
MgO	95.6	25	92
Al_2O_3	42–100	110	115
Al_2O_3 powder, as received	50.8	60	116
Al_2O_3 hydrated	51.1	60	116
Al_2O_3-w-GPS93	53.6	60	116
Untreated TiO_2	53	30	103
TiO_2/CH_4 plasma	37.9	30	103
TiO_2/C_2F_4 plasma	26.1	30	103
TiO_2/NH_3 plasma	50.2	30	103
Shieldex AC3	43.9	45	107
K-White	47.1	45	107
Magenta	40.3	50	94

(*continued*)

Table 8 Continued

Materials	γ_S^d (mJ/m^2)	Temperature (°C)	Ref.
Yellow	34.4	50	94
Rutile	23.2–25.6	60	94
Monastral green	43.0	60	94

LLDPE, low density polyethylene; PTEDM, poly(2,2′-thiobisethanol dimethacrylate); PNDM, poly(*N*-methyldiethanolamine dimethacrylate); PPDM, poly(pentane-1,5-diol dimethacrylate); PET, polyethylene terephthalate; PEEK, poly(ether ether ketone); Luxtrak^{TM}, ultraviolet-methacrylate resin (470 nm); PPyCl, chloride-doped polypyrrole; PPyTS, tosylate-doped polypyrrole; $PPyNO_3$, nitrate-doped polypyrrole; $PPyNO_3$/PVC/PMMA, $PPyNO_3$ powder coated with blends of PVC and PMMA cast from THF or dioxane; PANI, polyaniline; C(PAN); poly(acrylonitrile)-based C fiber characterized before and following electrochemical oxidation; E-glass/GPS, E-glass fiber treated with γ-glycidoxypropyltrimethoxysilane; E-glass/APS, E-glass fiber treated with aminopropyltriethoxysilane (APS); Al_2O_3-w-GPS93, hydrated alumina powder treated with GPS and cured at 93°C. TiO_2/gas plasma is rutile treated with either CH_4, C_2F_4, or NH_3 plasma; PPyCl/PMMA/$CHCl_3$, PMMA-coated PPyCl in $CHCl_3$; PPyCl/PMMA/dioxane, PMMA-coated PPyCl in dioxane; Shieldex AC3 (pigment) is a calcium ion-exchanged amorphous silica; K-White is an aluminum triphosphate pigment; Monastral green is a phthalocyanine type of organic pigment.

wettability [66,118] (compare the values reported in Tables 7 and 8 for PPyCl and PPyTS).

(ii) The γ_S^d values reported for example for Al_2O_3 strongly depend on the nature and the concentration of metal oxide impurities such as silica which are likely to segregate to the surface and thus affect the surface energy [115]. Papirer et al. [89] have shown that the impurities significantly modify the acid–base properties of fillers such as alumina and thus considerably affect their adsorptive capacities towards polymers (see Acid–Base section, IV.B.2).

(iii) IGC yields very high values of γ_S^d for microporous and lamellar materials by comparison to the reference amorphous values [90]. Table 8 reports an extremely high γ_S^d value of 225 mJ/m^2 for the polypyrrole–silica nanocomposite at 60°C which is much higher than those of the reference silica sol and bulk polypyrrole powder (60 and 145 mJ/m^2, respectively). The apparent high surface energy of the nanocomposite [111] was interpreted in terms of the microporosity of these "raspberry-structured" colloidal materials [119].

(iv) The γ_S^d (and also acid–base descriptors) strongly depend on the conditioning temperature especially in the case of hydrated materials such as silica [120] and calcium carbonate [114].

2. *Acid–Base Interactions*

a. Determination of ΔG^{AB} and ΔH^{AB}. If "polar" probes interact via acid–base forces with the stationary phase, then ΔG_a has a contribution from such specific interactions. Assuming that dispersive and acid–base interactions are additive, then ΔG_a^{AB}, the acid–base contribution to the free energy of adsorption, is deduced from ΔG_a by

$$-\Delta G_a^{AB} = -(\Delta G_a - \Delta G_a^d) = RT \ln\left(\frac{V_N}{V_{N,\mathrm{ref}}}\right) \tag{33}$$

where V_N and $V_{N,\mathrm{ref}}$ are the net retention volumes of the polar probe and a hypothetical reference n-alkane having the same physicochemical property, respectively. There are

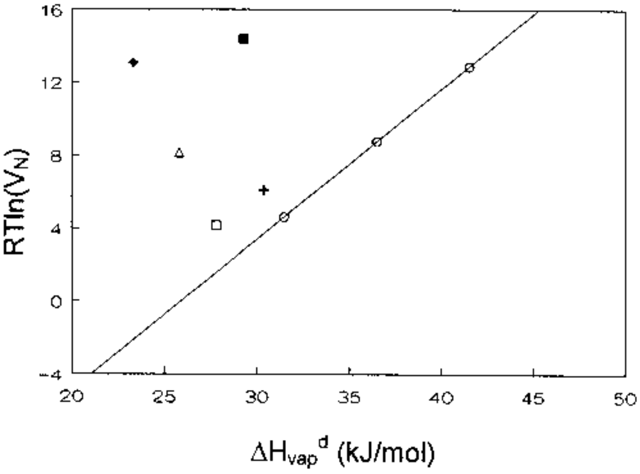

Figure 8 $RT\ln(V_N)$ versus ΔH_{vap}^{d} for alkanes and polar probes adsorbed onto PPyTS at 35°C. (○) C6–C8; (□) CH_2Cl_2; (+) $CHCl_3$; (△) diethylether; (■) EtAc; (◆) THF.

various approaches to the assessment of ΔG_a^{AB} in which the probes can be characterized by: the boiling point [121]; the logarithm of the vapor pressure [122]; $a(\gamma_L^d)^{1/2}$ [95] (where a and γ_L^d are the cross-sectional area of the probe and the dispersive contribution to the surface tension, respectively); the deformation polarizability [99]; and ΔH_{vap}^{d}, the dispersive contribution to the heat of vaporization [123]. All these methods have advantages and shortcomings which have been discussed elsewhere [123,124].

Practically, ΔG_a^{AB} is determined as shown in Fig. 8 where the variation of $RT\ln(V_N)$ versus ΔH_{vap}^{d} is plotted for tosylate-doped polypyrrole (PPyTS), a conducting polymer, at 35°C. The data for the n-alkanes lead to a linear correlation which defines the dispersive interactions for the PPyTS–probe pairs. For "polar" probes interacting via acid–base interactions, the corresponding markers will lie above the reference line with a vertical distance that accounts for ΔG_a^{AB}. In Fig. 8, the markers corresponding to the "polar" probes lie significantly above the reference line defined by the n-alkanes, thus indicating that PPyTS behaves amphoterically. However, the ΔG_a^{AB} values are significantly much higher for the Lewis bases (EtAc, THF, and diethylether) than for the acidic species $CHCl_3$ and CH_2Cl_2, an indication that PPyTS has a predominantly acidic character.

ΔH_a^{AB} is usually determined from the temperature dependence of ΔG_a^{AB}:

$$\frac{\Delta G_a^{AB}}{T} = \Delta H_a^{AB}\left(\frac{1}{T}\right) - \Delta S \tag{34}$$

In practice, for a given acidic or basic probe, plotting $R\ln(V_N/V_{N,ref})$ versus $1/T$ results in a linear correlation whose slope equals $-\Delta H_a^{AB}$. An example is given in Fig. 9 for the adsorption of CH_2Cl_2 onto a carbon fiber surface.

An alternative approach to Eq. (34) has been proposed [40,42,125]:

$$\Delta H_a^{AB} = (\Delta H_a - \Delta H_a^{d})_{probe} - (\Delta H_a - \Delta H_a^{d})_{model} \tag{35}$$

where ΔH_a is the absolute value of the total heat of adsorption and ΔH_a^{d} its dispersive contribution. The *model* probe must be neutral and of comparable size to that of the "polar" probe or have a comparable boiling point. If the probes have a negligible

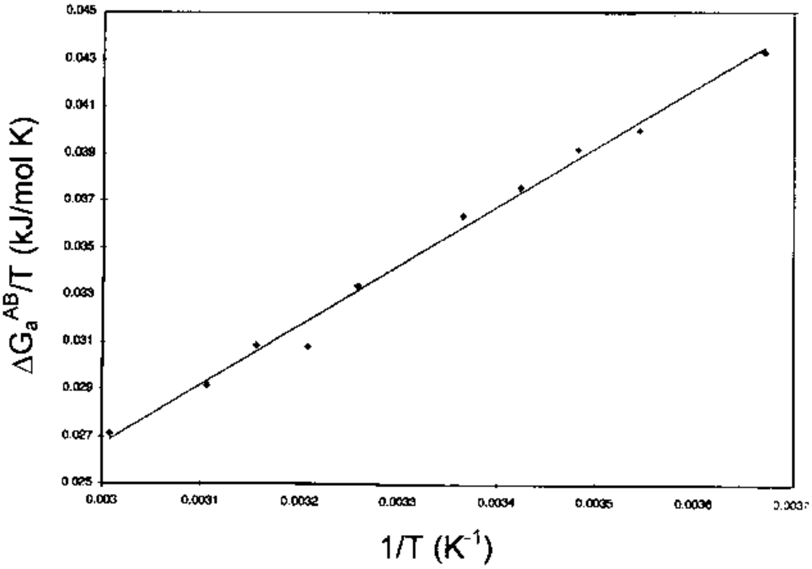

Figure 9 Plot of $\Delta G_a^{AB}/T$ versus $1/T$ for CH_2Cl_2 adsorption onto a carbon fiber (using the "polarizability" method [107]). Trend line: $\Delta G_a^{AB}/T$ (kJ/mol) $= 25.28(1/T) - 0.049$. (Reprinted from Ref. [86]).

degree of self-association, then ΔH_a^d can be replaced by ΔH_{vap}, the heat of vaporization. Alternatively, ΔH_a^d could be estimated from the adsorption (for either probe or model) onto an apolar material such as polyethylene. Equation (35) has been used to derive the E and C parameters for conducting polymers [40,41] and glass beads [42] (see Table 3).

b. Determination of Donor and Acceptor Constants. Saint Flour and Papirer [122] suggested to combining ΔH_a^{AB} values with Gutmann's DN and AN values in order to determine the acid–base parameters of materials:

$$-\Delta H_a^{AB} = \mathrm{DN} \times K_A + \mathrm{AN}^* \times K_D \tag{36}$$

where K_A and K_D are the acidity and basicity descriptors, respectively. Equation (36) can be rewritten as

$$\frac{-\Delta H_a^{AB}}{\mathrm{AN}^*} = \left(\frac{\mathrm{DN}}{\mathrm{AN}^*}\right) K_A + K_D \tag{37}$$

where AN* is the acceptor number corrected for van der Waals interactions. In practice, and for each probe, $-\Delta H_a^{AB}/\mathrm{AN}^*$ is plotted versus DN/AN* and the resulting linear correlation has a slope and intercept corresponding to K_A and K_D, respectively (see Fig. 10). Belgacem and Gandini [85] compiled a large set of K_A and K_D constants for various types of materials. These acid–base descriptors are reported in Table 9 for a selection of materials.

Kuczynski and Papirer [92] as well as Chehimi et al. [104] found that it was also simple to derive K_A and K_D values from the following equation:

$$-\Delta G^{AB} = \mathrm{DN} \times K_A + \mathrm{AN}^* \times K_D \tag{38}$$

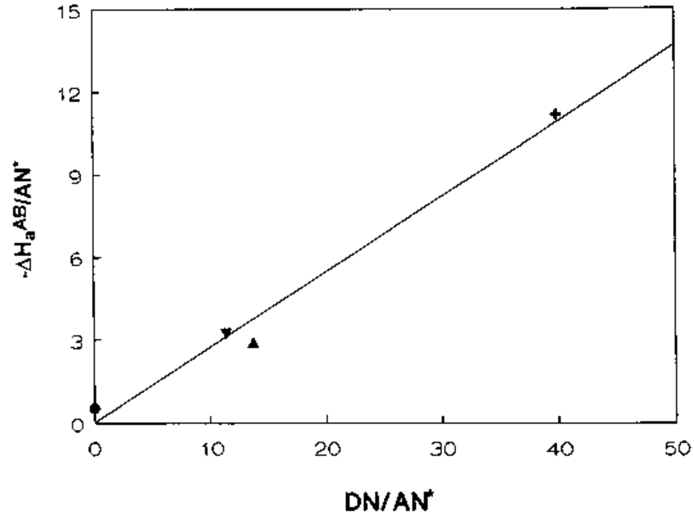

Figure 10 Plot of $-\Delta H_a^{AB}$/AN* versus DN/AN* for PPyTS. The slope and the intercept permit determination of K_A and K_D for PPyTS. (●) chloroform; (▼) EtAc; (▲) diethyl ether; (+) THF.

Although fundamentally this approach is not correct because it relates ΔG^{AB} values to Gutmann's numbers which are derived from ΔH^{AB} terms, it has proved to be a fast and effective semiquantitative approach to monitoring-changes in the surface properties of fillers and polymers [92,104,108,122,130]. It does not necessarily mean that the entropic term is ignored so that $\Delta G^{AB} = \Delta H^{AB}$. It simply produces different scales of K_A and K_D constants, but at one given temperature. In our laboratory, we found it very suitable for materials, such as conducting polypyrrole, which may degrade quite rapidly during their IGC characterization [110]. van Asten et al. [86] also agree that a single IGC characterization of a material (carbon fiber) batch could be performed in a couple of hours, hence the interest in this approach.

As far as conducting polymers are concerned, the change in the surface composition of conducting polymer powders has been monitored following coating with PMMA [104] and PVC/PMMA blends [131] (see Table 10). $CHCl_3$ and THF were chosen as reference acidic and amphoteric probes, respectively. The advantage in using this set of probes lies in the large difference between their DN/AN* ratios (0 for $CHCl_3$ and 39.9 for THF), which permits accurate determination of K_A and K_D for the sorbent under test.

The acid–base descriptors derived from ΔG^{AB} values clearly permit monitoring of the change in the surface thermodynamics of $PPyNO_3$ powder as a result of coating by PVC and PMMA blends. The K_A/K_D ratios so derived suggest that PMMA is depleted towards the surface of the blend-coated $PPyNO_3$ powder. This is explained by the intermediate K_A/K_D ratios found for the blend-coated conducting polymer by comparison to those determined for the reference PMMA, PVC, and $PPyNO_3$.

An alternative method for the determination of acid–base characteristics of solids was proposed by Lara and Schreiber [94] who defined

$$K_A = -\Delta G^{AB}(\text{THF}) \tag{39a}$$

Table 9 K_{A} (acidity) and K_{D} (basicity) Descriptors Determined for Selected Materials

Material	Treatment	K_{A}	K_{D}	$K_{\mathrm{A}}/K_{\mathrm{D}}$	Ref.
PAN-based C fiber	None	6.5	1.5	4.3	95
	Oxidation	10	3.2	3.1	95
	Sizing	8.6	13.0	0.7	95
Epoxy I		7.6	6.2	1.2	95
T300	None	0.143	15	0.009 5	96
	Oxidized	0.222	32	0.006 9	96
	sized	0.206	130	0.001 6	96
PEEK	powder	9.6	48	0.002	96
PEEK	fiber	0.06	108	0.000 55	96
PE fibers	None	0	0		126
	Ozonation 2 h	3.5	0.8	4.4	126
	Ozonation 3 h	3.3	1.0	3.3	126
	First degree of oxyfluorination	7.3	2.5	2.9	126
	Second degree of oxyfluorination	10.3	9.2	1.1	126
Natural Graphite	None	1.24	0.83	1.49	127
	n-BuOH plasma	1.37	0.89	1.54	127
	n-BuNH$_2$ plasma	0.38	0.87	0.44	127
PPyTS		0.273	0.026	10.5	41
PPyCl		0.261	0.436	0.6	41
POT		0.138	0.298	0.46	128
PTEDM	None	0.133	0.668	0.20	129
	Annealed, He 160°C	0.092	0.48	0.19	129
	Annealed, air 160°C	0.106	0.745	0.14	129
PNDM	None	0.122	0.551	0.22	129
	Annealed, He 160°C	0.136	0.754	0.18	129
	Annealed, air 160°C	0.119	0.962	0.12	129
Alumina	Pure	12.2	6.3	1.9	90
	1000 ppm silica	20.5	8.1	2.5	90

PAN, Epoxy I, DGEBA (diglycyl ether of bisphenol A) epoxy resin with 35% w/w of diamino diphenyl sulfone hardener, T300, polyacrylonitrile (PAN)-based C fiber; PTEDM, poly(2,2′-thiobisethanol dimethacrylate); PNDM, poly(*N*-methyldiethanolamine dimethacrylate). Oxyfluorination is a proprietary treatment of Air Products and Chemicals that results in surface oxidation and fluorination of fibers.

Table 10 K_{A} and K_{D} Constants Derived from ΔG^{AB} values, and $K_{\mathrm{A}}/K_{\mathrm{D}}$ Ratios for PPyNO$_3$ Before and After Coating with PVC and PMMA Blends (48°C)

Materials	K_{A}	K_{D}	$K_{\mathrm{A}}/K_{\mathrm{D}}$
PPyNO$_3$	11.5	19.2	0.6
PVC	14.9	21.8	0.68
PMMA	7.6	35.4	0.21
(PVC+PMMA)-coated PPyNO$_3$	10.1–11.5	24.4–29.2	0.38–0.43

Data taken from [131]. PMMA and PVC were coated onto PPyNO$_3$ from THF or dioxane. Initial concentrations of PMMA/PVC in g/l were 0.88/0.88, 1.56/0.88, and 2.64/0.88.

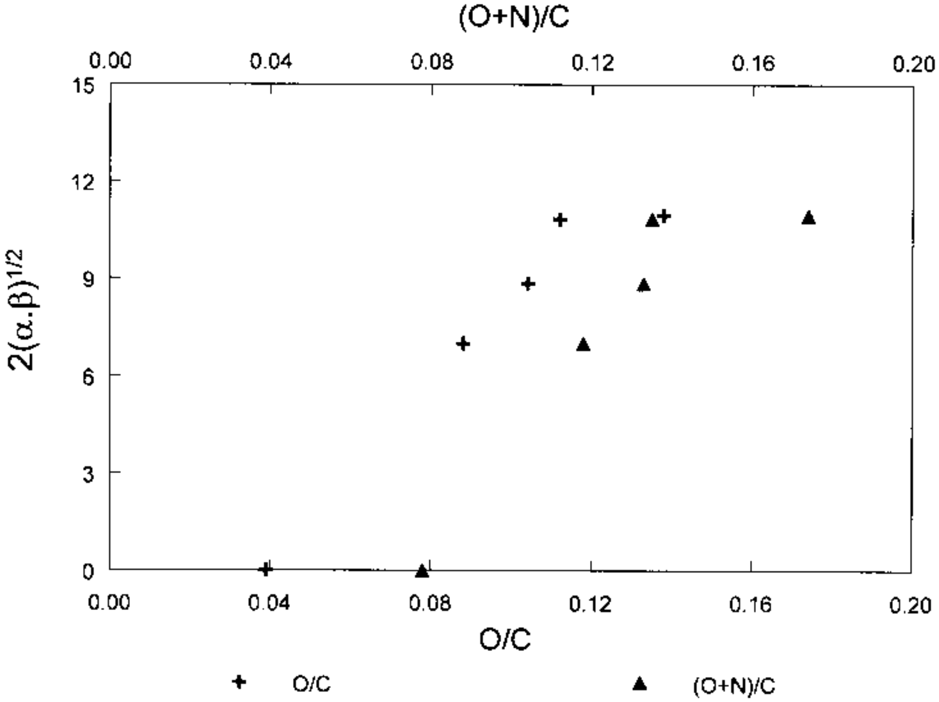

Figure 11 Plot of overall acid–base index versus O/C and (O+N)/C atomic ratios. The acid–base index $2(\alpha\beta)^{1/2}$ was determined by IGC and the atomic ratios by XPS. (Reprinted from Ref. [112].)

and

$$K_D = -\Delta G^{AB}(\mathrm{CHCl_3}) \tag{39b}$$

This is another simple empirical approach to assess acid–base properties of polymers and fillers. Of course, one can use other reference acids and bases if they are more suitable for the solid under test.

Recently, Vickers et al. [112] defined the constants in (39a) and (39b) as α and β, respectively, and suggested describing the overall acid–base character of the materials under test (PAN-based carbon fibers) by $2(\alpha, \beta)^{1/2}$ (in kJ/mol). Figure 11 depicts a plot of the acid–base descriptor $2(\alpha, \beta)^{1/2}$ versus the heteroatom content of the PAN-based C fiber surface for different degrees of fiber treatment. This illustrates the change in the acid–base characteristics of the various fibers.

3. *Fiber–Matrix and Filler–Matrix Specific Interaction Parameters*

Using K_A and K_D constants for polymer matrices (m) and fillers or fibers (f), one may define the pair specific interaction parameter (I_{sp}):

$$I_{sp} = K_A^f K_D^m + K_A^m K_D^f \tag{40}$$

Equation (40) was proposed by Schultz et al. [95] in their study of carbon fiber–epoxy composites, the K_D and K_A parameters being derived from ΔH^{AB} values (Eq. (36)). These authors found a linear relationship between the interfacial shear resistance τ and I_{sp}

(Fig. 12) and concluded that interfacial adhesion resulted from mainly acid–base interactions between the fiber and the matrix.

Following a similar approach, Lara and Schreiber [94] defined an interaction parameter to rationalize the acid–base forces at pigment–resin interfaces:

$$I_{\mathrm{sp}} = (K_{\mathrm{A}}^{\mathrm{p}} K_{\mathrm{D}}^{\mathrm{r}})^{1/2} + (K_{\mathrm{A}}^{\mathrm{r}} K_{\mathrm{D}}^{\mathrm{p}})^{1/2} \text{ in kJ/mol} \tag{41}$$

where the constants K_{A} and K_{D} were determined using Eqs. (39a) and (39b) for pigments (p) and resins (r). I_{sp} was then related to the adsorbed amount of polyester dispersion and binder resins onto rutile and organic pigments. Figure 13 depicts the relationship between adsorption and I_{sp} for an amine-modified polyester dispersion resin adsorbed onto mineral and organic pigments. It gives strong evidence that acid–base interactions are dominant in determining the adsorption behavior of polymer/pigment combinations.

4. *Linear Solvation Energy Relationship*

The above IGC approaches permit determination of $\gamma_{\mathrm{S}}^{\mathrm{d}}$ and acid–base parameters for solid surfaces, however, without the possibility of deducing them from one single equation. The linear solvation energy relationship (LSER) [75] permits connection of a measured value (e.g., partition coefficient) to the physicochemical parameters of the solute and the solvent (e.g., polymers in the liquid or viscous state) by a five-parameter equation:

$$\Delta G \cong \log K_{\mathrm{L}} = c + rR_2 + s\pi_2^* + b\alpha_2^{\mathrm{H}} + a\beta_2^{\mathrm{H}} + l \log L^{16} \tag{42}$$

where ΔG is the free energy of sorption of the solute and K_{L} the liquid support/mobile phase partition coefficient. The parameters R_2, π_2^*, α_2^{H}, β_2^{H}, and $\log L^{16}$ characterize the solute and the constants c, s, a, b, and l characterize the solvent (gas chromatographic support) and are obtained by multiple linear regression analysis. The explanatory variables are solute parameters, R_2 an excess molar refraction (polarizability), π_2^* the solute dipolarity–polarizability (polarity), α_2^{H} and β_2^{H} the solute hydrogen bond acidity and basicity,* and $\log L^{16}$ a dispersion interaction term where L^{16} is the gas/liquid partition coefficient of the solute on hexadecane at 25°C. Provided that the variety of solutes studied covers suitable ranges of the descriptors, the coefficients in the above equation then characterize the particular condensed phase (support) in terms of specific interactions. Thus r is the tendency of the phase to interact through π- and n-electron pairs, s is the phase dipolarity–polarizability, b is the phase (hydrogen-bond) basicity, a is the phase (hydrogen-bond) acidity†, and l is a constant that reflects a combination of cavity effects and general dispersion interactions and is related to the ability of the phase to distinguish between or to separate homologues in any homologous series. The constant c is a fitting parameter. Table 11 reports van der Waals (dispersion, polarity,

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*For multifunctional solutes one should really refer to $\sum \alpha_2^{\mathrm{H}}$ and $\sum \beta_2^{\mathrm{H}}$, the "effective" hydrogen-bond acidity or basicity. Indeed, α_2^{H} and β_2^{H} refer to 1:1 complexation whilst it is by no means obvious that such values are relevant to the solvation situation in which a solute is surrounded by solvent molecules and hence undergoes multiple hydrogen-bonding [75].

†In the literature, the acidity and basicity of the stationary phases (solvents) are defined by b and a, respectively which, in our opinion, can be misleading.

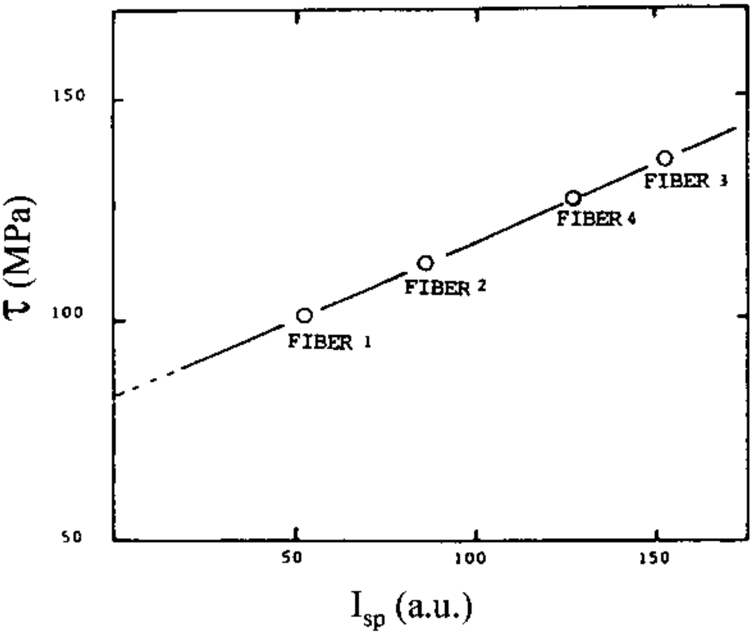

Figure 12 Interfacial shear resistance τ versus specific interaction parameter I_{sp} for C fibers and an epoxy matrix (DGEBA-DDS). The C fibers were (1) untreated, (2) oxidized, (3) sized, and (4) commercial sized PAN-based fibers. The epoxy matrix was a diglycidyl ether of bisphenol A with 35 parts by weight of diamino diphenyl sulfone (DGEBA-DDS). (Reprinted from Ref. [95].)

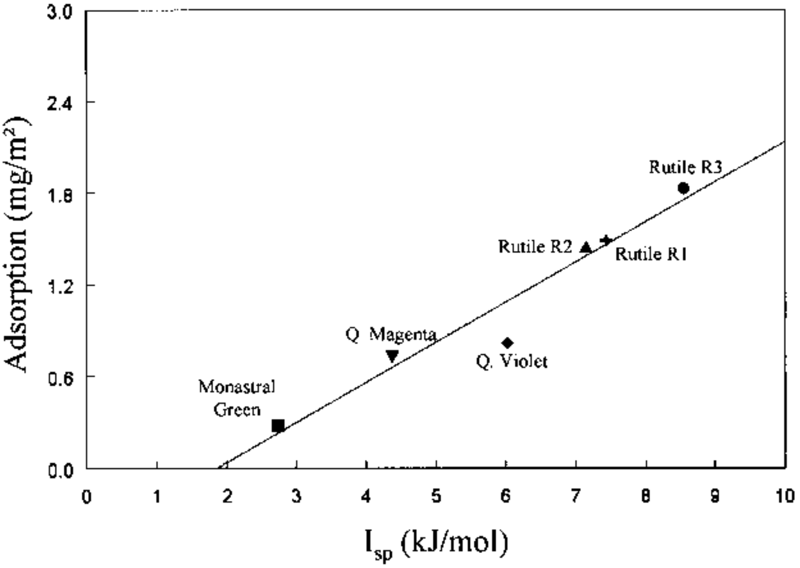

Figure 13 Adsorbed amount of a polyester resin (used as a dispersing agent for pigments and fillers) onto organic and mineral pigments versus the pair specific interaction parameter I_{sp} defined in Eq. (41). (Reprinted from Ref. [94].)

Table 11 Dispersion (*l*), Polarity (*s*), Polarizability (*r*), Basicity (*b*), and Acidity (*a*) Solvation Parameters for Polymers, Molten Salts, and Conventional Liquid Stationary Phases

Materials	*c*	*r*	*s*	*b*	*a*	*l*	Temp. (°C)	Ref.
PMHS	−0.077	0.139	0.203	1.025	−0.469	0.846	35	132
PLF	−0.296	−1.161	1.325	0.971	4.785	0.674	35	132
PBF	−0.331	−0.979	0.744	1.324	4.269	0.810	35	132
PMTFPS	−0.328	−0.757	1.443	0.112	1.221	0.721	35	132
	−0.391	−0.48	1.298	0.441	0.705	0.807	25	133
PCPMS	−0.258	0.167	1.48	1.997	0.694	0.674	35	132
SXCN	−1.63	0.00	2.28	3.03	0.52	0.773	25	133
	—	0.28	1.52	2.11	0.46	0.555	70	133
Carbowax	−2.01	0.25	1.26	2.07	0	0.429	120	75
Apiezon J	−0.48	0.24	0.15	0.13	0	0.596	120	75
PPE	−2.51	0.14	0.89	0.67	0	0.547	120	75
TBTS	−0.62	0.01	1.66	3.36	0	0.440	121	75
TBP	−0.54	0.10	1.56	1.42	0	0.445	121	75
FPOL	−1.21	−0.67	1.45	1.49	4.09	0.81	25	133
	—	−0.63	1.37	0.61	0.88	0.386	120	133
P4V	−1.329	−1.538	2.493	1.507	5.877	0.904	25	133
PEI	−1.602	0.495	1.516	7.018	—	0.770	25	133
PPyCl	−4.20	−4.64	7.69	5.31	−2.56	1.79	40	134
	−4.40	−4.40	5.35	4.00	−1.64	1.53	60	134

c is a fitting parameter derived from the five-parameter Eq. (42).

PMHS, poly(methyl hydrosiloxane); PLF, linear hexafluoro dimethyl carbinol-functionalized polysiloxane; PBF, branched hexafluoro dimethyl carbinol-functionalized polysiloxane; PMTFPS, poly(methyl-3,3,3,-trifluoropropylsiloxane); PCPMS, poly(methyl cyanopropylsiloxane); SXCN, poly{oxy[bis(3-cyanopropyl-1-yl)silylene]}; PPE, poly(phenylether); TBTS (molten salt), tetrabutylammonium 4-toluene sulfonate; TBP (molten salt), tetrabutylammonium picrate; FPOL, fluoropolyol; P4V, poly{1-[4-(2-hydroxy-1,1,1,3,3,3-hexafluoropropyl-2-yl)phenyl]ethylene}; PEI, poly(ethyleneimine).

and polarizability) and acid–base constants assessed by the LSER method for polymers, conventional gas–liquid chromatographic stationary phases, and molten salts.

As far as polysiloxanes are concerned, Demathieu et al. [132] showed that hexafluoro dimethyl carbinol-functionalized polysiloxanes exhibited a very strong acidity in comparison to PMHS, whereas the cyano-functionalized polysiloxanes had significantly high basicity values. The SXCN is much more basic than PCPMS since SXCN has two cyano pendent groups whilst PCPMS has only one.

It is important to note that the partition coefficients are strongly temperature dependent with a subsequent decrease in sorption with increasing temperature. Therefore, the solvation parameters determined for polymers used in sensor technology must be determined close to room temperature, that is at normal operating conditions of sensors, otherwise the sensitivity and selectivity of sensors will be underestimated. Table 11 actually indicates a sharp decrease in the acidity (*a*), basicity (*b*), and dispersion (*l*) parameters as a result of increasing temperature in for example FPOL, a fluoropolyol.

Clearly, the adhesion community should consider the LSER approach when IGC characterization of material surfaces is concerned. The price to pay, however, is to use a large number of solutes, at least 20–30 probes (parameters are available for 2000 organic molecules [133]), to derive accurately five solvation constants for the sorbents under test.

This is not usually done in the actual IGC studies relevant to adhesion science where γ_S^d is determined using three or four n-alkanes, and the K_A and K_D constants estimated with only a few acids and bases.

C. X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) has been used extensively in adhesion research for determining surface functional groups, studying the locus of failure of adhesive joints, determining molecular orientation following failure [135,136], monitoring the uptake of specific ions [137,138] at the interface, and identifying molecular species segregating at polymer–metal oxide interfaces [139–141]. It has also been found to be effective in determining adsorption isotherms of silane coupling agents onto metal oxides [142–145], and flexible polymers onto metal oxides [146] and stiff conducting polymer particles [147,148]. In the last case, the XPS results were interpreted in terms of acid–base interactions of the adsorbate, the conducting polymer and the casting solvent [147–149].

The success of XPS lies in its surface specificity (analysis depth of ca. 5 nm), low degree of degradation of tested materials, quantitative aspect, and detection of all elements (except hydrogen) and their chemical shifts. The so-called chemical shift is the cornerstone of XPS since it enables the surface scientist to study chemical bonding and to derive materials properties such as refractive indices of thin optical layers [150], the nondispersive component of the surface energy of polymers [151] and the acid–base properties of alcohols and amines [152].

In this section, we shall examine three approaches for the assessement of acid–base properties of molecules, polymers, and metal oxides by XPS:

(i) ion-exchange experiments to characterize hydroxylated metal oxide surfaces;
(ii) the use of the intrinsic chemical shifts experienced by the materials under investigation;
(iii) chemical shifts of molecular probes induced by specific adsorption onto polymers.

1. *Assessment of the Isoelectric Point of Solids of Metal Oxides*

The IEPS (or PZC) has been defined above in the Section II.F. This acid–base property of metal oxides can be one of the key parameters controlling the adhesion properties of polymer/metal assemblies. However, because of surface rearrangement phenomena (e.g., hydration) involving the overlayers of the oxides, it is expected that siginificant differences between the surface and the bulk features of the oxides may occur. This is the reason why XPS is a very interesting technique for the assessment of the IEPS or PZC. There are three different approaches to estimate the IEPS by XPS:

(i) monitoring the uptake of ionic species by the metal oxide surface, the so-called "method of Simmons and Beard";
(ii) chemical shifts of the core-shell electrons from the metal oxides;
(iii) Fermi level shift monitoring.

a. The Method of Simmons and Beard. The hydroxyl groups of a hydrated oxide surface in the presence of an aqueous solution may act as an acid or a base by release or uptake of protons [153]. This can be expressed by the following equilibria and corresponding constants:

$$\mathrm{MOH} + \mathrm{H}^+ \Leftrightarrow \mathrm{MOH}_2^+ \qquad K_1 = \frac{n\mathrm{MOH}[\mathrm{H}^+]}{n\mathrm{MOH}_2^+} \tag{43}$$

$$\mathrm{MOH} \Leftrightarrow \mathrm{MO}^- + \mathrm{H}^+ \qquad K_2 = \frac{n\mathrm{MO}^-[\mathrm{H}^+]}{n\mathrm{MOH}} \tag{44}$$

where M is the metal, K_1 and K_2 the acidity constants, and $n\mathrm{MOH}_2^+$, $n\mathrm{MOH}$, and $n\mathrm{MO}^-$ the surface concentrations of the different forms of the hydrated metal oxide. The PZC or the IEPS (in the absence of specific adsorption) is the pH for which $n\mathrm{MOH}_2^+ = n\mathrm{MO}^-$, that is:

$$\mathrm{PZC} \quad \text{or} \quad \mathrm{IEPS} = \frac{\mathrm{p}K_1 + \mathrm{p}K_2}{2} \tag{45}$$

Simmons and Beard [153] suggested treating solid metal oxide surfaces with solutions at a given pH containing X^+ cations that can be taken up by MO^- groups. Monitoring the uptake of X^+ by XPS leads to the determination of K_2. Similarly, one can monitor the uptake of A^- anions by the surface MOH_2^+ groups in order to determine K_1. Figure 14 illustrates the determination of K_1 and K_2 for a hydroxylated iron surface. The pK_1 and

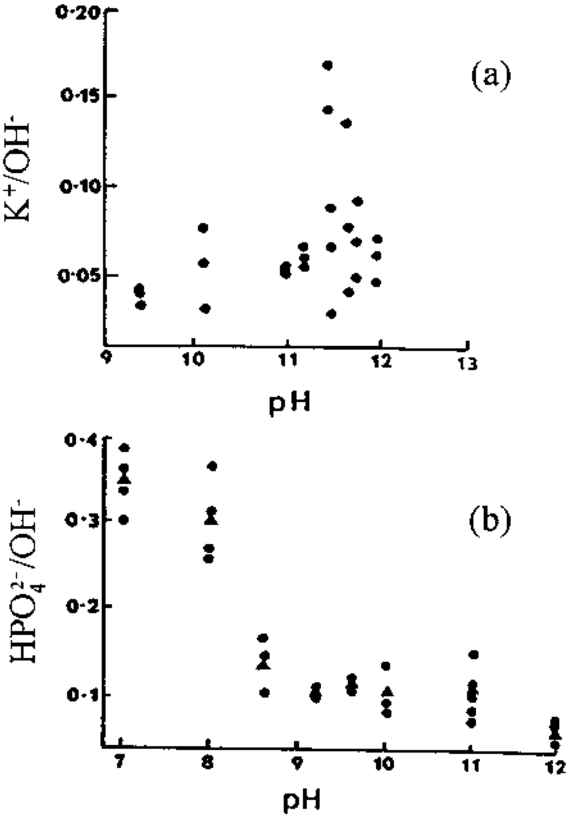

Figure 14 Determination by XPS of (a) potassium and (b) phosphate uptake per surface hydroxyl group on the oxidized iron surface as a function of pH. (Reprinted from Ref. [154].)

pK_2 values were found to be 8.4 and 11.5, respectively, and the IEPS equals ca. 10, in good agreement with results obtained by electrophoretic mobility [154].

However, as demonstrated by Delamar [155], the method of Simmons and Beard has some drawbacks. The most important is that it neglects the equilibrium of complexation of X^+ by MO^-:

$$MO^- + X^+ \Leftrightarrow MOX \qquad K_C = \frac{nMOX}{nMO^-[X^+]} \tag{46}$$

where K_C is the complexation constant. Because of this complexation, the equilibria shown in (43) and (44) are displaced so that all the hydroxyl formed originally at the surface could be transformed into MOX species. Combining (43), (44), and (46) one can express nMOX by:

$$nMOX = \frac{N}{1 + \dfrac{1}{K_C[X^+]} + \dfrac{[H^+]}{K_C[X^+]K_2} + \dfrac{[H^+]^2}{K_C[X^+]K_1K_2}} \tag{47}$$

where

$$N = nMOX + nMOH_2^+ + nMOH + nMO^- \tag{48}$$

Delamar proposed a protocol to determine IEPS values by XPS. However, his approach is yet to be checked experimentally.

b. Chemical Shifts of the Core Level Electrons from Metal Oxides. Delamar [156] used an XPS data bank and a compilation of IEPS values to establish a linear relationship between chemical shifts of the oxygen (ΔO) and those of the metal cations (ΔM) and the IEPS of the corresponding metal oxides. The chemical shifts were defined as follows:

$$\Delta O = BE(O1s) - 530\,eV \tag{49}$$

and

$$\Delta M = BE(M2p) - BE(M^0 2p) \tag{50}$$

where M is the metal in the oxidized state, M^0 is the metal in the reference metallic state, and 2p is the core level shell. The value 530 eV was chosen as an arbitrary reference binding energy (BE) value for O1s. Figure 15 shows a plot of IEPS versus ($\Delta O + \Delta M$) for various metal oxides. Therefore, a simple determination of the BE shifts for a given anhydrous oxide permits estimation of its IEPS. The IEPS versus ($\Delta O + \Delta M$) correlation was confirmed by Cattania et al. [157] in their electrophoretic and XPS characterizations of a series of metal oxides having the same history.

c. Fermi Level Monitoring. An alternative approach for the assessment of the IEPS or PZC is to monitor the Fermi level (E_F) shifts as proposed by Mullins and Averbach [158]. They established a correlation between E_F and PZC for silica, alumina, magnesia, and phosphate powders: $PZC = -2.9E_F + 16.8$. Clearly, the lower (higher) the Fermi level, the more basic (acidic) is the material under test. The results conform to a model of the water/oxide surface reaction that follows the generalized Lewis theory of acid–base adduct formation. They extended their approach to anodized and etched aluminum alloy surfaces [159].

Lopez et al. [160] applied the technique of Fermi level shift monitoring to characterize the acid–base properties of passive films on aluminum. The decreasing trend of relative basicity was found to be: boehmite > thermal oxide > NaOH-degreased surface > silicate containing detergent-degreased surface > phosphoric acid anodic film. The

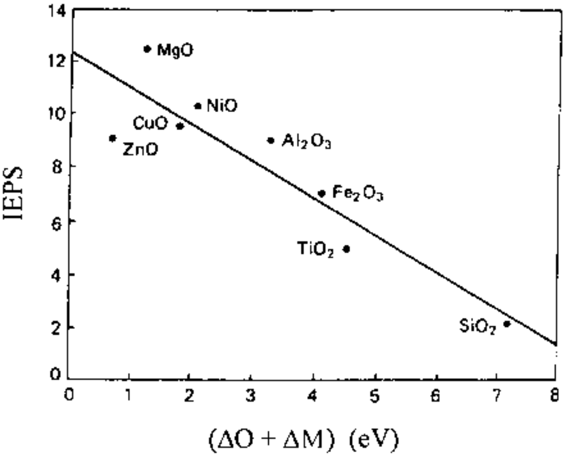

Figure 15 Plot of IEPS versus (ΔO+ΔM) for a series of metal oxides. ΔO was defined as BE(O1s)−530 eV, where BE is the binding energy and 530 eV an arbitrary reference BE value. ΔM was defined as BE(M2p)−BE($M^0$2p) where M is the metal in the oxidized state, M^0 is the metal in the reference metallic state, and 2p is the core shell. (Reprinted from Ref. [156].)

reader is referred to [161] for further information on the background to the Fermi level monitoring.

2. *Organic Molecules and Polymers*

The molecular probe technique in combination with XPS has seldom been used since the early 1970s and has mainly been applied to zeolites [162–164]. These studies were aimed at identifying and quantifying Lewis acidic and basic sites at catalyst surfaces by monitoring the BE shifts of N1s from adsorbed pyridine [162,163] and pyrrole [164], respectively. We shall discuss the application of this approach to molecular and polymeric species.

a. Molecules: Relationship with Gutmann's and Drago's Acid–Base Constants. Burger and Fluck [165] established, for quickly frozen solutions of $SbCl_5$–Lewis base complexes in 1,2-dichloroethane, a linear relationship between Sb3$d^{5/2}$ BE and DN, the donor number of the complexing Lewis bases. On this basis, Chehimi [166] showed that the Sb3$d^{5/2}$ BE was linearly correlated with the ΔH^{AB} of (base–$SbCl_5$) adduct formation calculated using Drago's equation. Figure 16 depicts a linear correlation of Sb3$d^{5/2}$ BE versus ΔH^{AB} (base–$SbCl_5$). Therefore, XPS is a potential tool for estimating Drago's parameters for polymer surfaces [166], which have actually been confirmed for PPO [167] and plasma-treated polypropylene [46] (see Table 3).

b. Polymers: Sorption of Specific Probes. Chehimi and co-workers [154,166,168–171] established protocols to quantitatively estimate the acid–base properties of polymer surfaces using (ad)sorbed molecular probes. In practice, a polymer is exposed to liquid vapors (solutes) of known acid–base properties for a few minutes. The polymer is then allowed to outgas the excess of solute and is transferred into the XPS equipment for surface characterization. If the polymer–solute interaction is strong enough (e.g., via acid–base forces) then a residual amount of solute is detected and quantified.

(i) *Choice of Molecular Probes.* Several molecular probes can be used to characterize the acid–base properties of solid surfaces by XPS. For example, chlorinated and

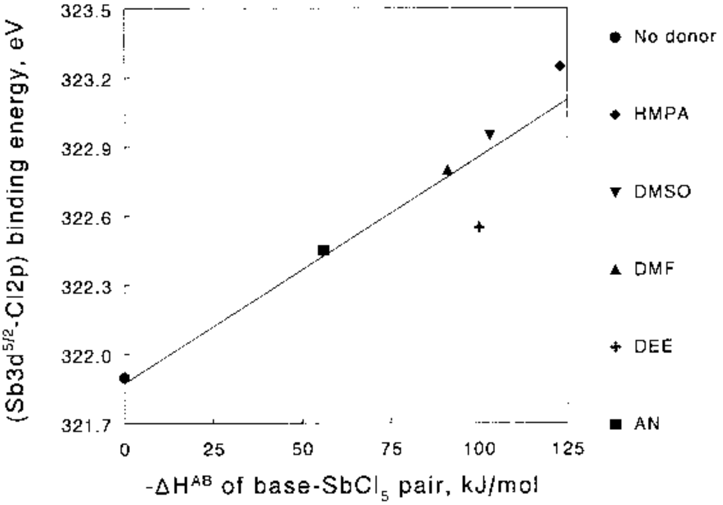

Figure 16 Plot of (Sb3d$^{5/2}$–Cl2p) BE energy difference versus ΔH^{AB} for Lewis base: SbCl$_5$ adducts in quickly frozen solutions of 1,2-dichloroethane. AN, acetonitrile; DEE, diethylether; DMF, dimethylformamide; DMSO, dimethylsulfoxide; HPMA, hexamethylphosphoramide. The data point corresponding to a zero value of ΔH^{AB} (corresponding to "No donor") is obtained for a quickly frozen solution of SbCl$_5$ in the absence of any basic solute. (Reproduced from Ref. [166] by kind permission of Kluwer Academic Publishers.)

Table 12 Molecular Probes Used for XPS Determination of Acid–Base Properties of Materials

Probe	Core Line	Material Property Investigated
$CHCl_3$	Cl2p	basicity
CH_2Cl_2	Cl2p	basicity
HFIP	F1s	basicity
CF_3COOH	F1s	basicity
I_2	I3d$^{5/2}$	basicity
Pyrrole	N1s	basicity
Pyridine	N1s	acidity
DMSO	S2p	acidity

fluorinated acidic species probe Lewis basicity, whereas pyridine [168,154,163] or DMSO [83] are suitable to characterize surface acidity (Table 12).

Figure 17 depicts a survey scan of a basic aromatic moisture-cured urethane resin (ArMCU) before and after exposure to the vapors of hexafluoroisopropanol (HFIP) ($CF_3CH(OH)CF_3$), a reference Lewis acid. The F1s from HFIP is easily detected indicating that it was retained by the ArMCU. This retention, despite the high vacuum, is believed to be governed by acid–base interactions between the OH group from HFIP and the carbamate (HN–C=O) group from the resin. The molar ratio of solute per polymer repeat unit (%S, where S stands for solute) was evaluated and used as a measure of the uptake (or retention) of solute by the host polymer. Figure 18 shows plots of

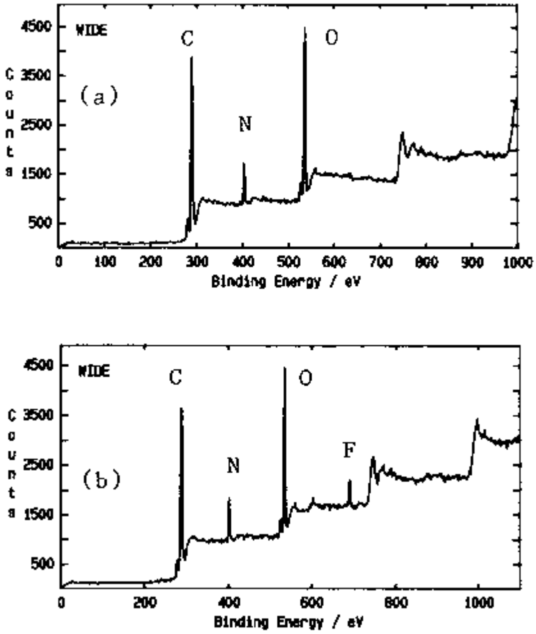

Figure 17 X-ray photoelectron survey spectra of ArMCU (a) before and (b) after exposure to HFIP. Uptake of the Lewis acid HFIP is indicated by the presence of the F1s feature.

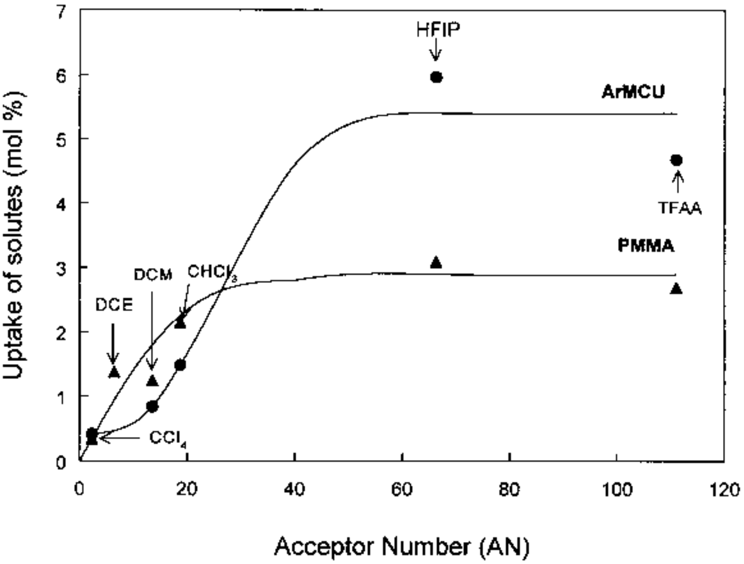

Figure 18 Uptake (%S) of Lewis acids by PMMA and ArMCU versus the acidic character of the solutes. The %S is the solute per repeat unit molar ratio in the case of PMMA and the solute per nitrogen atom in the case of ArMCU. The solutes were characterized by AN, the Gutmann acceptor number: CCl_4, 2.3; 1-2,dichloroethane (DCE), 6.4; dichloromethane (DCM) (CH_2Cl_2), 13.5; trichloromethane (TCM), (chloroform) 18.7; hexafluoroisopropanol (HFIP), 66.3; and trifluoroacetic acid (TFAA), 111.

%S versus AN (Gutmann's acceptor number) of the solute, for the host polymers PMMA and ArMCU. The plots are S shaped, showing an increasing uptake of solute with AN, which denotes the basic character of both polymers. This is in agreement with Fourier Transform Infrared (FTIR) studies of the Lewis basicity of PMMA [13] and ArMCU [170]. In contrast, XPS did not detect any retained chloroform at the polyethylene surface following exposure to the vapors because the polymer–solute interactions reduce to London dispersive forces only.

(ii) *Chemical Shifts of the Molecular Probes.* The binding energies (BEs) of core electrons from the solutes' elemental markers were also investigated for various polymers and resins (Table 13). Chloroform has been the most extensively used Lewis acid to characterize polymer basicity. Table 13 shows that acidic ($CHCl_3$ and $CF_3C\alpha$) and basic (pyridine) probes undergo negative and positive chemical shifts (lower and higher BEs), respectively, when they interact with host surfaces via acid–base forces. Indeed, a Lewis acid is an electron acceptor and upon interaction with a base via acid–base forces, electron density is transfered to the Lewis acid thus yielding a lower binding energy of its electrophilic site [43,168,169]. The opposite reasoning holds for basic probes [154,168].

Table 13 Binding Energy (eV) for Molecular Probes Adsorbed onto Polymers and Resins

	$CHCl_3$	CH_2Cl_2	CCl_4	HFIP	CF_3COOH	I_2	Pyridine	DMSO
Homopolymers								
PMMA	198.4[a]	198.8[b]	199.2[b]	688[b]/ 688.9[c]	688.7[b]/ 688.4[c]		399[b]	
PEMA				689.1[c]				
PnBMA	199.35[a]							
PCHMA	198.9[a]			688.8[c]	688.4[c]			
PVAc	199.35[a]			688.7[c]	687.7[c]			
PEO	197.6[a]				685.0[c]			
PVME				689.2[c]	687.1[c]			
PPO	199.5[d]				689[c]			
PBAC	198.4[c]			688.5[c]	687.9[c]			
PVB							399.7[e]	
PS						619–621[f]		
Plasma treated polymers								
$PP\text{-}NH_3$ 0.7s	197.1[g]							
$PP\text{-}NH_3$ 25s	198[g]							
$PP\text{-}He\text{-}NH_3$	197.6[f]							168.8[f]
$PP\text{-}N_2$	198.3[h]					619[h]		
$PP\text{-}NH_3$	197.8[h]					618.7[h]		
$PP\text{-}O_2$								166.5–168[i]
Resins								
ArMCU	197.9[a]	198.3[b]	198.4[b]	689.2[b]	686.5[b]			
Epoxy UVR-6110	195.5[f]							
Photo-initiator UVR-6110	200.6[f]							

[a]Ref. [162]; [b]Ref [168]; [c]this work; [d]Ref. [167]; [e]Ref. [59]; [f]Ref. [173]; [g]Ref. [172] (note that $I3d^{5/2}$ BE from I_2 decreased with the amount of sorbed probe); [h]Ref. [46]; [i]Ref. [83].

PEMA: polyethylenemethacrylate; PCHMA: polycyclohexyl methacrylate); PBAC: (polybisphenol A carbon).

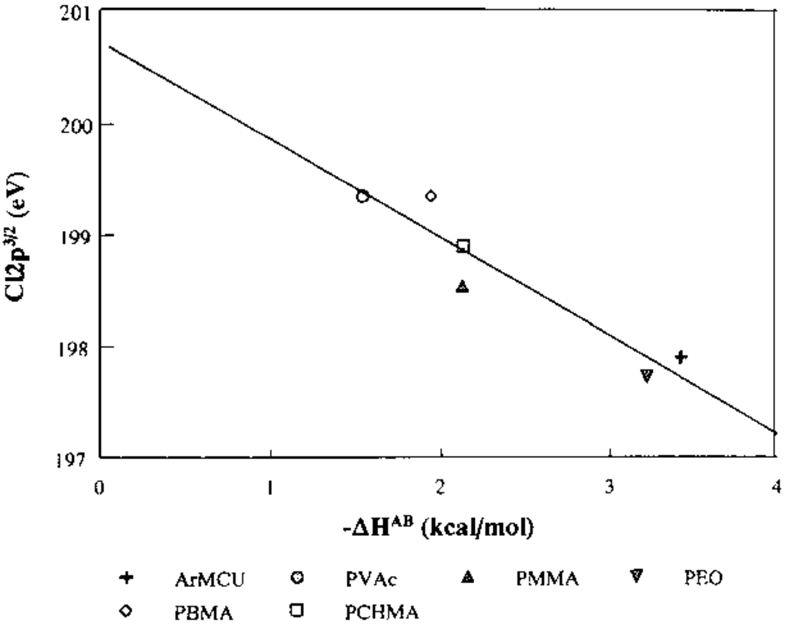

Figure 19 Cl2p$^{3/2}$ BE versus ΔH^{AB} for CHCl$_3$ sorbed in ArMCU, poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), poly(butyl methacrylate) (PBMA), and poly(cyclohexyl methacrylate) (PCHMA).

(iii) *Chloroform.* Chehimi et al. [169] established a linear Cl2p$^{3/2}$ BE–ΔH^{AB} correlation where ΔH^{AB} is the heat of acid–base adduct formation for the polymer–chloroform pairs in the liquid state (Fig. 19). The relationship is of the form:

$$-\Delta H^{AB}(\text{kcal/mol}) = 228.8 - 1.14\text{BE(eV)} \tag{51}$$

and was used to determine ΔH^{AB} for PPO:CHCl$_3$ adduct formation, ca. 1 kcal/mol [43]. This result, derived from XPS chemical shifts, was combined with the IR data reported by Kwei et al. [55] to deduce $E_B \approx 0$ and $C_B = 9.5\,(\text{kcal/mol})^{1/2}$ for PPO [15,43]. Equation (51) has been further used to characterize the acid–base and adhesion properties of plasma-treated polypropylene [46,172,174].

(iv) *Trifluoroacetic Acid.* Another Lewis acid used to probe surface acid–base properties of polymers was CF$_3$COOH (TFAA) for which a relationship between the F1s BE and DN (donor number) values of the host polymers was obtained [175,176]:

$$\text{DN(kcal/mol)} = 3593 - 5.21\text{BE(eV)} \tag{52}$$

DN values were computed using Gutmann's equation and the thermochemical data for binary polymer blends of a poly(styrene-co-vinylphenyl hexafluoro dimethyl carbinol) [55]. The copolymer contained 95% of styrene repeat units and its OH stretching frequency shifts were similar to those of HFIP [55]. For this reason the copolymer was assigned the Gutmann AN of HFIP [175].

(v) *Iodine.* Iodine (a Lewis acid) has tentatively been used to probe the basicity of polystyrene (PS). The polymer film turned purple on exposure to iodine vapor. However, in the high vacuum, there was a continuous desorption of the probe (the purple color was vanishing) leading to a very weak $I3d^{5/2}$ peak intensity. Nevertheless, the $I3d^{5/2}$ peak recorded during desorption shifted from 621 to 619 eV, thus towards a lower binding energy. This indicates that the strongly adsorbed iodine molecules were subject to electron density transfer from PS thus leading to low BE. Perhaps PS was not a strong enough Lewis base to retain adsorbed iodine in the high vacuum. Nevertheless, the ESCA group led by J. J. Pireaux in Namur was more successful in characterizing the basicity of plasma-treated polypropylene by iodine vapor [46,172].

(vi) *Pyridine*. Pyridine is a molecular probe for the acidic sites of catalysts [173]. When adsorbed on polymer surfaces, the N1s core electron undergoes a +1 eV chemical shift (in comparison to the N1s BE for pure pyridine) in the case of the host PMMA owing to the donation of electron density from pyridine to the carbonyl carbon of the methacrylate repeat unit (acidic site) [168]. The N1s chemical shift is even larger (+1.7 eV) when pyridine is sorbed in PVB since it is predominantly acidic due to its OH pendent groups. The N1s BE positions for pyridine–polymer complexes are higher than those of the pure pyridine because the pyridine–pyridine interaction occurs via dispersive forces only, for pyridine is a monofunctional species [7,54].

D. Atomic Force Microscopy

In adhesion science and technology, the manifestations of acid–base interactions have been observed at both macroscopic and microscopic scales (wetting, adhesion, metallization, etc.). The development of scanning probe microscopic methods (scanning tunneling microscopy (STM) and atomic force microscopy (AFM)) over the past decade has led to the possibility of measuring adhesion forces on the molecular scale in addition to imaging surfaces in atomic resolution.

In STM, atomically resolved images of the surface region are generated by bringing a metallic tip under piezoelectric control to within angstroms of a surface. At these small distances electrons can tunnel from the tip on application of a bias voltage. By using an electronic feedback system, one can keep the current (and hence the gap between tip and sample) constant as the tip is moved sideways across the surface. Because the current detection is so sensitive, the tip actually has to ride up over the atoms of the surface resulting in a “topographic” image of the surface.

The images generated from the variations in tunneling current are representative of differences in the local density of states across the surface. However, because STM relies on the conduction of electrons through the sample, it is generally not suitable for characterizing insulating samples such as organic polymers.

The atomic force microscope, an adaptation of the STM approach, can be used to measure interfacial forces with nanonewton sensitivity between the tip and a conducting or insulating surface in addition to topographic measurements. AFM monitoring of the long range attractive or repulsive forces between the tip and the sample surface permits elucidation of local chemical and mechanical properties such as adhesion and elasticity, and even thickness of adsorbed molecular layers. The forces that can lead to attractions of the tip to the surface include van der Waals interactions, hydrogen bonds, capillary action, or electrostatic fields. When the tip is brought near to the surface it may jump into contact in the case of sufficient attractive force. Once in contact, repulsive forces lead to a deflection of the cantilever in the opposite direction. Signals optically detected from either type of deflection (attractive or repulsive) can be used as the feedback signal. On withdrawal, adhesion during contact may cause the cantilever to adhere to the sample some distance past the initial contact. The tip becomes free from the surface at a point where adhesion is broken. The measured rupture force required to break adhesion is a key parameter of the AFM force curve.

In early studies, classical (tungsten or Si_3N_4) tips were found to be sensitive to the nature of the material surface. For example, adhesion forces between the tungsten tip and untreated and stearic acid-treated Al_2O_3/Al was much larger than between the tip and polytetrafluoroethylene (PTFE) most probably because the PTFE undergoes only dispersive interactions [177].

AFM has been used to measure the double layer interaction between the Si_3N_4 tip and a silica substrate [178]. The transition from the attractive to the repulsive double layer was found to be pH dependent. The double layer force measured at a distance of 17 nm is repulsive at $pH > 6.2$ because the tip and the surface are both negatively charged. In contrast, the double layer interaction becomes attractive at $pH < 6.2$, meaning that the tip and the silica have opposite signs. At $pH = 6.2$, the Si_3N_4 tip is not charged and hence the IEPS for the tip can be estimated by AFM.

Similar studies were aimed at measuring double layer forces between colloidal particles (silica, glass) glued to the tip and self-assembled monolayer-modified substrates. The rationale for using silica- or glass-modified tips is that silicon oxide has a low IEPS and bears a negative charge over a wide pH range. In contrast, the confined carboxylic acid is a weak Brönsted acid and can thus be either neutral at low pH or ionized at pH 5–6. This makes the study of electrostatic attractions and repulsions possible via AFM. In the case of interactions between carboxylic acid-terminated thiol and a glass-modified tip, it was found that below pH 6–6.3 the interaction was purely attractive (Fig. 20) because the terminal COOH groups were not ionized [179]. At higher pH, repulsive forces operate at the tip–COO^- interface. The force-to-distance curves showed a decrease in the repulsive component of the interaction as the electrolyte concentration was increased.

Hu and Bard [180] used a silica colloidal particle-modified tip to scan the surface of carboxylic acid-terminated thiols grafted onto gold substrate. They correlated the surface potential of the surface-confined COOH groups to the solution pH in which the substrate was immersed (Fig. 21). The sigmoidal shape of the plot suggests that surface potential is pH dependent. Since the surface potential is directly related to the fractional degree of surface carboxylic acid dissociation one can thus view the plot in Fig. 21 as a direct surface acid titration curve. It is noteworthy that the apparent pK_a of the adsorbed COOH is near pH 8.0, much higher (about 3.5 units) than the pK_a measured for similar acids in bulk aqueous solution. Similar studies using contact angle titration indicated such an increase in the apparent pK_a of confined COOH groups as compared to the situation in the bulk solution [79]. This has been attributed to strong lateral hydrogen bonding between the confined COOH groups [180].

In order to systematically study the surface acid–base phenomena in a controlled manner, both tip and surfaces were functionalized by alkyl-, COOH-, PO_3H_2-, and NH2-terminated thiols (Fig. 22). In this regard, thiol-functionalized tips and surfaces were used to obtain adhesion force titration curves for carboxylic acid, phosphonic acid, and amino groups [182]. Figure 23 shows the study of the acid–base properties of a diprotic acid by the pH-dependent adhesion force measurement between a PO_3H_2-functionalized tip and PO_3H_2-functionalized surface. The overall pH-dependent behavior of the PO_3H_2 shows the ionization steps $PO_3H_2 \rightarrow PO_3H^-$ and $PO_3H^- \rightarrow PO_3^{2-}$ which correspond to effective pK_a values of 4.7 and 11.6, respectively.

Thomas et al. [20] have measured adhesion forces between organic films over separations ranging from 10 nm to repulsive contact using interfacial force microscopy (IFM).

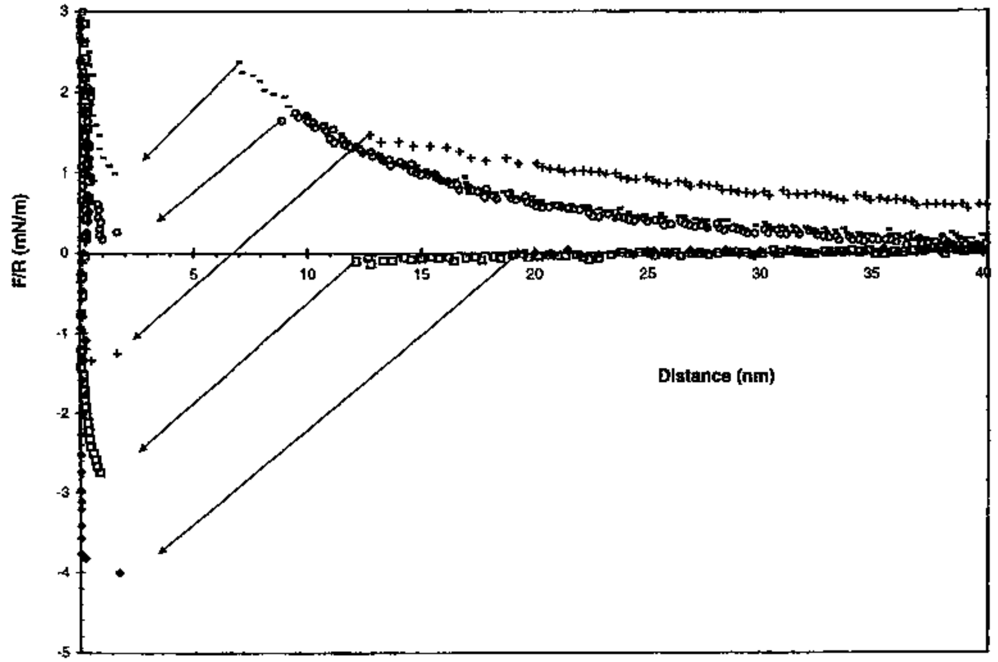

Figure 20 Normalized forces as a function of distance recorded between a 20 μm hydrophilic glass and a hydrophilic substrate in 3×10^{-4}–7×10^{-4} M NaCl as a function of pH: (◆) 2.0; (□) 3.8; (+) 4.7; (○) 8.2; (–) 9.7. (Reprinted with permission of the American Chemical Society from Ref. [179], E. Kokkoli and C. F. Zukoski, *Langmuir 16*: 6029 (2000).)

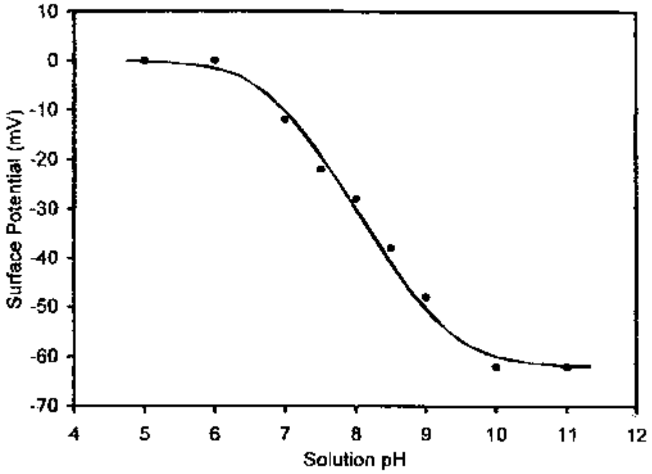

Figure 21 Measured (●) and theoretical (—) surface potentials of the carboxylic acid monolayer in 10^{-3} M KCl solutions at 25°C as a function of pH. The best theoretical fit gives surface pK_a at pH 7.7. (Reprinted with permission of the American Chemical Society from Ref. [180], K. Hu and A. J. Bard, *Langmuir 13*: 5114 (1997).)

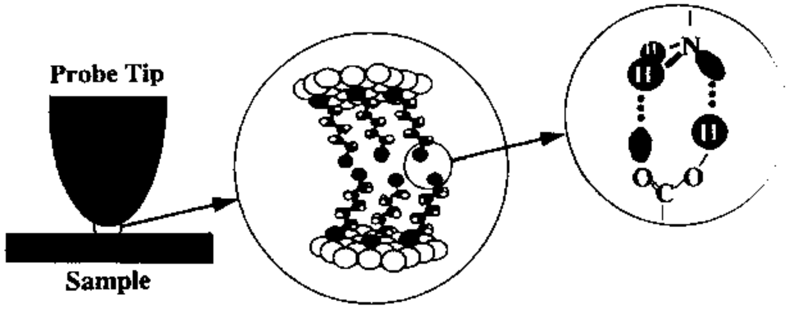

Figure 22 Schematic illustration of scanning probe studies of (acid–base) hydrogen bonding between functional group terminated self-assembled monolayers of n-alkanethiol molecules. The thiol monolayers self-assemble on gold substrates, thus both tip and sample are initially coated with gold. (Reprinted with kind permission of VSP Publishers from Ref. [181], A. R. Burns, J. E. Houston, R. W. Carpick, and T. A. Michalske, in Ref. [19], *Acid–Base Interactions: Relevance to Adhesion Science and Technology*, Vol. 2 (K. L. Mittal, ed.), VSP, Utrecht, 2000, pp. 223–234.)

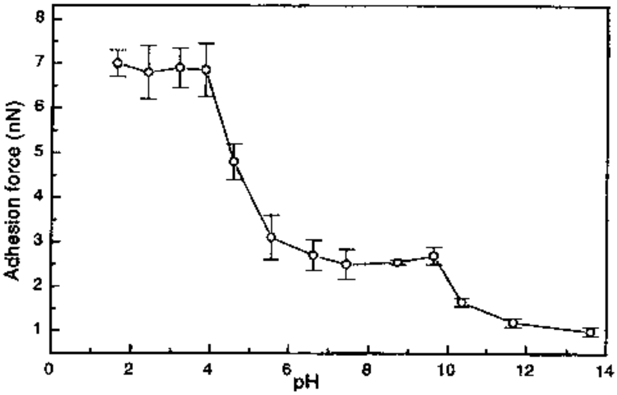

Figure 23 "Adhesion force titration curve" for a PO_3H_2 functional tip on a PO_3H_2 functional substrate at constant ionic strength. (Reprinted, in part, with permission of the American Chemical Society from Ref. [182], E. W. van der Vegte and G. Hadziioannou, *J. Phys. Chem. B 101*: 9563 (1997).)

This microscope uses a self-balancing force-feedback system to avoid the mechanical instability encountered in AFM or STM, due to the use of deflection-based force sensors. The quantitative measure of the adhesion forces between organic films was achieved by chemically modifying a gold substrate and a gold tip with organomercaptan self-assembled monolayers (SAMs) having either the same or different end groups (–CH_3, –NH_2, and –COOH). Figure 24 shows representative force profiles for some terminal group combinations. The arbitrary zero displacement represents the point where the interaction force goes through zero while the probe is in contact with the sample. The force axis is normalized to the probe radius and the same scale is used for direct comparison of the different chemical interactions. The peak value of the attractive force from the unloading

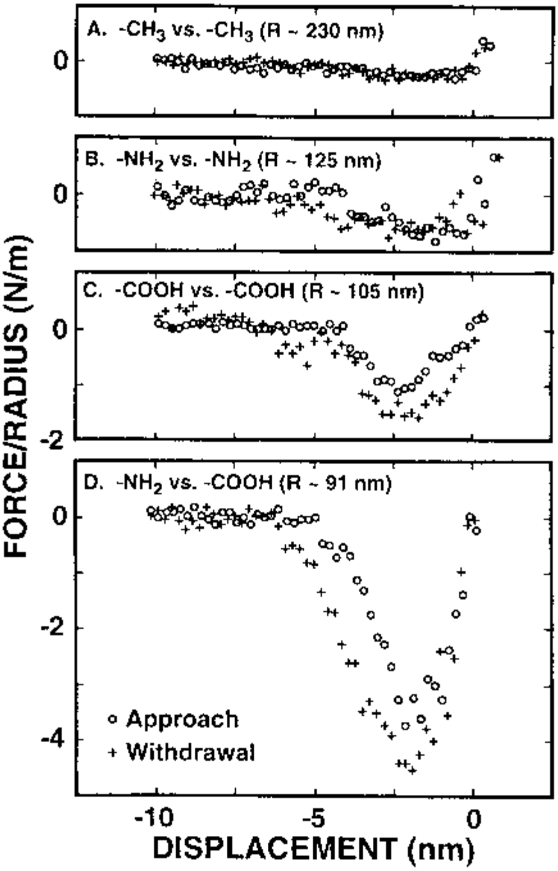

Figure 24 Force versus displacement curves taken between (A) two methyl-terminated SAMs, (B) two amine-terminated SAMs, (C) two carboxylic acid-terminated SAMs, and (D) an amine- and a carboxylic acid-terminated SAM. The force is normalized to R, the tip radius. (Reprinted with permission of the American Chemical Society from Ref. [20].)

curve (pull-off force) was used to evaluate the work of adhesion, W, for the various combinations using $W = F/2\pi R$, where R is the tip radius. The W values were found to be 60 ± 32, 100 ± 24, 228 ± 54, and $680 \pm 62\,\mathrm{mJ/m^2}$ for the CH_3 versus CH_3, NH_2 versus NH_2, COOH versus COOH, and NH_2 versus COOH combinations, respectively. These values qualitatively scale with those expected for van der Waals, hydrogen-bonding (for NH_2 versus NH_2 and COOH versus COOH pairs) and acid–base interactions. In the last case, the interfacial energy was found to be large and negative, and corresponded to a NH_2–COOH bond energy of 67 kJ/mol. High work of adhesion was obtained for such dissimilar materials.

SUMMARY

The background to acid–base interactions in adhesion science and technology has been reviewed with the emphasis on polymers, metal oxides, fillers, fibers, and pigments. When these specific exothermic interactions operate at interfaces they have a significant impact on adsorption, wettability, adhesion, and mixing as shown through some selected examples. The importance of such findings has resulted in the establishment of an impressive array of methods which enable an adhesionist to determine acid–base scales for materials. This task is, however, very delicate because it requires the determination of the heat or the free energy changes of acid–base interactions of reference acidic and basic chemical species with the material. The choice of reference test acids and bases is also crucial and usually depends on the nature of the material under investigation and the experimental conditions associated with the technique used for the assessment of acid–base properties.

Contact angle measurements (CAMs), IGC, XPS, and AFM are among the experimental techniques most used to interrogate the acid–base characteristics of polymers and other materials at the macroscopic and microscopic scales. CAM is very useful for the determination of acid–base contributions to the surface free energy and the determination of the interfacial free energies in a liquid medium such as water. This is of paramount importance when one has to deal with protein adsorption and cell adhesion. We clearly advocated the vOCG theory although it has met several criticisms in the recent literature, but in very different situations it was very effective in determining the mechanisms governing solubility, adsorption, adhesion, and deadhesion phenomena.

IGC remains one of the most versatile techniques for divided materials and fibers. However, whilst n-alkanes are universally used to determine the dispersive properties of materials, there is not a universal set of reference specific probes for the determination of acid–base properties of materials that differ markedly in nature (e.g., polymers and metal oxides). For example, metal oxides or clays are not amenable to characterization using specific probes such as alcohols, THF, or ethylacetate at temperatures in the 30–50°C range (real conditions). Consequently, it is very difficult to compare the acid–base properties of materials obtained at differing temperature ranges and using different sets of probes. We take this opportunity to point out that, at least, it will be very important that research papers report the temperature ranges in which acid–base constants were determined. This is not done systematically. Contrary to what is stated by Belgacem and Gandini [85], we believe that constants which are "temperature independent" determined at for example 80–100°C can hardly be representative of properties at room temperature (this is the case of metal oxides which can be more or less hydrated below or above about 100°C). To our knowledge this has never been checked experimentally.

The LSER theory combined with IGC should be applied more in the future because it permits distinction between London, Keesom, and Debye interactions in addition to the acid–base scales. This is not done in the traditional IGC studies in relation to adhesion.

XPS has been employed for many years to characterize the surface acid–base properties of catalysts and metal oxides by various methodologies including Fermi level monitoring. We have shown since the early 1990s the potential of XPS in characterizing acid–base properties of conventional polymers using the molecular probe technique. This approach has recently found application in characterizing commercial resins, photoinitiators, and plasma-treated polymers in relation to metallization.

Finally, AFM appears as an extraordinary technique to study acid–base interactions at the molecular scale. It enables the determination of pK_a for surface confined carboxylic and other Brönsted groups. With the systematic studies which have appeared over recent years using thiol-treated tips and surfaces, clearly AFM has become a very well established and powerful tool for fundamental and applied research studies on acid–base interactions in adhesion.

The importance of acid–base interactions in adhesion continues to attract several researchers, however, still there seems to be a lack of consistency in the approaches as stated by K. L. Mittal in the Preface of [19]. It is hoped that Round Tables will be organized in order to define common strategies for polymers, fillers, fibers, etc. which will permit inter-laboratory comparison.

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6

Interactions of Polymers in Solution with Surfaces

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I. INTRODUCTION

Polymers are involved in many practical adhesion problems. A polymer liquid can be present in the gap between the two media that adhere to one another in order to create strong attractive forces that strengthen the adhesion. In this context it is important to understand how polymer solutions interact with surfaces and how they create strong interactions between them [1]. The aim of this short review is to present rather qualitatively our understanding of the equilibrium thermodynamic properties of polymer solutions close to surfaces. This is clearly one of the important factors in understanding the adhesion between two surfaces mediated by polymers, but one must keep in mind that adhesion is a nonequilibrium process where energy dissipation plays a major role. This aspect will not be considered in this chapter.

There are three main modes of interaction between a polymer solution and a solid surface. The first interaction mode is depletion [2,3]. If the monomers are repelled by the surface (or in other words if the attractive interaction between the solvent molecules and the surface is larger than the interaction between the monomers and the surface), the polymer concentration in solution decreases as the surface is approached and a region depleted in polymer exists in the vicinity of the surface. The size of this region is the size of the polymer chain if the solution is dilute and the size of the correlation length of the solution if the solution is semidilute (if the polymer chains overlap). When two surfaces are brought in close contact, the density in the gap between the surfaces is smaller than the bulk concentration and the osmotic pressure in the gap is smaller than the bulk osmotic pressure. This osmotic pressure difference induces an attraction between the surfaces. The depletion interaction is not specific to polymers and exists with any particle with a size in the colloidal range [4]. It has sometimes been used to induce adhesion between particles of mesoscopic size such as red blood cells. The only limitation to this qualitative description of the depletion force is that at equilibrium the polymer chains (or any other particles) must leave the gap as the surfaces get closer. There is no attractive depletion force if they remain trapped in the gap. We will not consider further the depletion interaction.

In the opposite case where the surface prefers to be in contact with the monomers, the polymer chains strongly adsorb on the surface [5]. The specific polymer effect is that the adsorbed layer is much thicker than a microscopic size; its thickness is of the order of the polymer chain radius of about 10 nm [6,7]. This means that polymer adsorption can induce interactions between surfaces over a range of the order of the size of the polymers. Adsorbed polymer layers are fluffy in the sense that they are not dense, the monomer concentration decreases from a high value on the surface to a very low value at the outer part of the layer. This is due to the fact that a polymer chain can form long loops on the surface and that the size of the loops can fluctuate from a microscopic size to the size of the polymer chain. In addition to these loops an adsorbed polymer chain has two long tails which are the end parts of the chain that do not fold back on the surface. The important feature for adhesion is that a polymer chain can bind to two surfaces and form bridges between them. In many instances, the adsorption is irreversible and bridging strongly enhances the adhesion.

A last interaction mode between polymer solutions and surfaces is obtained by grafting the polymers on the surface by one of the chain ends. The grafting can be covalent and thus fully irreversible or physical; physical grafting is achieved by anchoring the chains on the surface with strongly dipolar groups or by using diblock copolymers where one of the blocks strongly adsorbs on the surface. The experimental difficulty is that there is a strong potential barrier against grafting owing to the repulsive interactions with already grafted chains and that the graft density within reasonable experimental time scale is often rather low. Tricks have been found [8,9] to increase strongly the graft density such as growing the grafted chains from the surface or grafting the chains from a dense solution where the excluded volume interactions are screened and very dense grafted layers (one grafted polymer every 2 nm on the surface) can be obtained. The thickness of grafted layers is very large and can reach hundreds of nanometers. Adhesion between surfaces carrying grafted polymer layers can be achieved if the chains bind onto both surfaces and form bridges or if the grafted layers on the two surfaces undergo a chemical reaction that allows the formation of a bridge at contact. In the study of the adhesion of rubbers to a hard surface, the adhesion is strongly increased if the hard surface is covered by a grafted layer that can be interdigitated with the rubber [10,11].

In the remainder of this chapter, we discuss theoretically the properties of grafted polymer layers in Section II and of adsorbed polymer layers in Section III. In each case, we first consider the equilibrium properties of a single layer and then discuss briefly the interactions between two surfaces.

II. GRAFTED POLYMER LAYERS

In this section we review the properties of grafted polymer layers or polymer brushes. We first consider a standard polymer brush on a solid surface and then discuss the bridging between two surfaces by a polymer brush [12].

A. Polymer Brushes

A sketch of a polymer brush is shown in Fig. 1. We call σ the graft density or the number of grafted chains per unit area of the surface. Each chain has N monomers. In a dilute solution the chain radius of gyration, R, is $R \sim N^{1/2}a$ for Gaussian chains in a θ solvent (a is the monomer size) and $R \sim N^{\nu}a$ in a good solvent with a swelling exponent $\nu = 3/5$. If the surface density is small ($\sigma R^2 \ll 1$) different chains on the surface do not see each other and behave as independent chains of size roughly equal to R on the surface. This is called

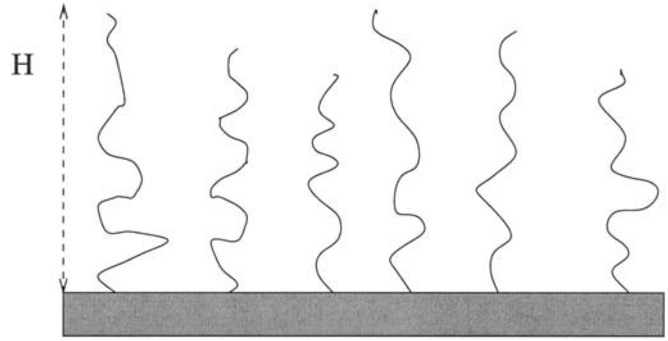

Figure 1 Polymer brush. The graft density is σ and H is the thickness of the brush.

the mushroom regime. If the surface density becomes larger, $\sigma R^2 > 1$, neighboring chains interact and repel each other in a good solvent. The chains stretch in the direction perpendicular to the grafting surface. In order to calculate the thickness of the polymer brush, we use a Flory type of argument. We assume that all the chain end points are located on the outside of the layer and thus all the chains have the same end-to-end distance H equal to the thickness of the brush. In a first approximation, we consider that the monomer concentration inside the grafted layer is constant and equal to $c = \sigma N/H$. The free energy of the chains is the sum of the Gaussian elastic free energy and the repulsive excluded volume interaction energy between the chains. The Gaussian elasticity measures the entropy cost due to the chain stretching. Polymer chains behave as springs and the elastic energy per unit area reads $F_{el} = (3/2)\sigma kT(H^2/Na^2)$ where T is temperature and k the Boltzmann constant. The interaction energy per unit area can be obtained from a virial expansion $F_{int} = (1/2)\,vc^2HkT$ where v is the positive second virial coefficient between monomers (the so-called excluded volume parameter); it is positive in a good solvent. The minimization of the total free energy $F_{el} + F_{int}$ gives the equilibrium thickness [13]

$$H \sim N(\sigma a^2)^{1/3} v^{1/3} \tag{1}$$

The thickness increases linearly with molecular weight and the polymer chains in a grafted layer are strongly stretched; this is consistent with the large thicknesses measured experimentally. The free energy per chain μ is proportional to $NkT\sigma^{2/3}$; it gives the energy barrier to insertion of one extra chain into the brush. This energy is much larger than kT and the rate of grafting of the chain must be very low in any experiment where the grafted layer is built up by adsorption from a dilute solution.

This Alexander–de Gennes model of polymer brushes gives a scaling description in good agreement with experimental results for the thickness of grafted polymer layers [14]. However, two of the starting points—the facts that the monomer concentration is constant over the layer and that the end points are all at the surface of the layer—are not consistent with experiments. These two constraints are relaxed in the more refined self-consistent field model proposed independently by Milner et al. [15] and Zhulina et al. [16]. The idea of this model is to consider in a mean field approach the conformation of one chain in an effective potential $U(z) = kTvc(z)$ where $c(z)$ is the local concentration at a distance z from the grafting surface. The potential is then calculated self-consistently to satisfy all the constraints of the problem using an elegant analogy to classical mechanics. The monomer concentration is found to decay parabolically from the grafting surface: $vc(z) = (3\pi^2/8N^2a^2)(H^2 - z^2)$. The other important result is that the chain end points are distributed throughout the layer. The density of end points vanishes on the grafting surfaces, it increases to a maximum at about three-quarters of the way into the layer and then decreases back to zero. These results are in good agreement with neutron scattering experiments [14].

When the grafted layer is built by physical adsorption of the chain end points on the surface either one or both end points may adsorb. If only one end point adsorbs, a standard grafted layer is formed and the end point graft energy monitors the chain graft density. If the two end points adsorb, a mixture between chains grafted by one end and chains grafted by both ends (loops) is obtained on the surface [17]. Within the self-consistent field approach a chain grafted by both ends can be cut at its midpoint and is thus equivalent to two grafted chains each containing $N/2$ monomers. The grafted layer can be considered as a polydisperse layer of chains of N and $N/2$ monomers. The fraction of chains grafted by both ends increases with the graft density E of the end points from zero if $E/\mu < 1$ to one if $E/\mu > 1$ where μ is the chemical potential of one chain in the brush (the energy per chain).

B. Interaction Between Surfaces (Bridging)

The interaction between two surfaces each carrying a grafted polymer layer of thickness H is repulsive [15]. If the distance h between the surfaces is larger than $2H$, the polymer layers do not overlap and the force between the surfaces owing to the polymer vanishes. If the distance h is smaller than $2H$, the two brushes interact. It can be shown that they do not interpenetrate but that they compress. The repulsive force is then due to the osmotic pressure opposing the compression. In the Alexander–de Gennes model, the concentration in the compressed layers is $c = 2\sigma/h$ and the osmotic pressure, π, which is the force per unit area between the surfaces is [6]

$$\pi \sim kT\left(\frac{2\sigma}{h}\right)^{9/4} \tag{2}$$

We have considered in this expression the polymer inside the layers as a semidilute solution and used the scaling expression for the osmotic pressure [18]. Note that we ignore here the variation of the monomer concentration at the edge of the grafted layer. Equation (2) thus overestimates the interaction between the two grafted layers when they are close to overlapping, $h \approx 2H$.

Bridging by grafted polymer chains can be induced by considering an irreversibly grafted polymer layer and by allowing the free end points to adsorb, with an adsorption energy δ per adsorbed end point [19], on a surface parallel to the grafting surface. The chains with adsorbed ends form bridges between the two surfaces. If the adsorbing surface is free with no applied force, the fraction of chains making bridges increases as a function of the reduced adsorption energy $\partial_r = \partial/\mu$ from zero to one. For most practical cases the chemical potential of the chains in a free brush is much larger than kT and the reduced adsorption energy is small which implies that the number of bridges is small. This is due to the fact that the end points of the chains are buried inside the layer and that in order to adsorb them one must stretch the chains to the adsorbing surface which costs elastic energy. A detailed calculation with the self-consistent field model shows that the fraction of chains forming bridges η increases linearly with δr. The grafted layer also shrinks upon bridging.

If a force is applied to the adsorbing surface, the fraction of bridges increases under compression (the repulsive osmotic force then dominates over the attractive bridging force); eventually, if the compression force is large enough, all the chains form bridges. Under extension, the number of bridges decreases (the bridging force dominates over the osmotic force) and eventually the system becomes unstable if the force is larger than a critical force. The interaction energy U between the two surfaces is plotted as a function of the distance h between the surfaces in Fig. 2; the reduced variables are $F_r = U/\sigma\mu$ and $d_r = h/H$. The curve has been calculated using the self-consistent field theory for a reduced attraction energy $\delta r = 0.2$. The equilibrium position is at the minimum of the curve (zero force); the critical force where the system breaks under extension is at the inflection point (maximum force) and the region with a downwards curvature is unstable; the point of complete bridging ($\eta = 1$) is indicated by the arrow. These results give a rather good description of experiments performed with polymer chains grafted on a sphere glued onto the tip of an atomic force microscope [20].

Another system where bridging is observed is a slab between two identical parallel solid plates with polymer chains that can adsorb by their end points on both surfaces. In the limit where the graft energy is large all end points are adsorbed and the slab is formed by loops on either plate and bridges between the two plates as sketched in Fig. 3. In this case also, the fraction of bridges at equilibrium has been found to be very low $\eta \sim (\sigma N^{6/5} a^2)^{-2/3}$ [21,22]. The interaction energy is repulsive at distances smaller than the contact distance $h = 2H$ and is attractive at larger distances. The equilibrium position is slightly shifted with respect to the contact distance; the interaction energy at the equilibrium position $U_{min} \sim -kT\sigma\eta$ corresponds to an attractive interaction energy of kT per bridge.

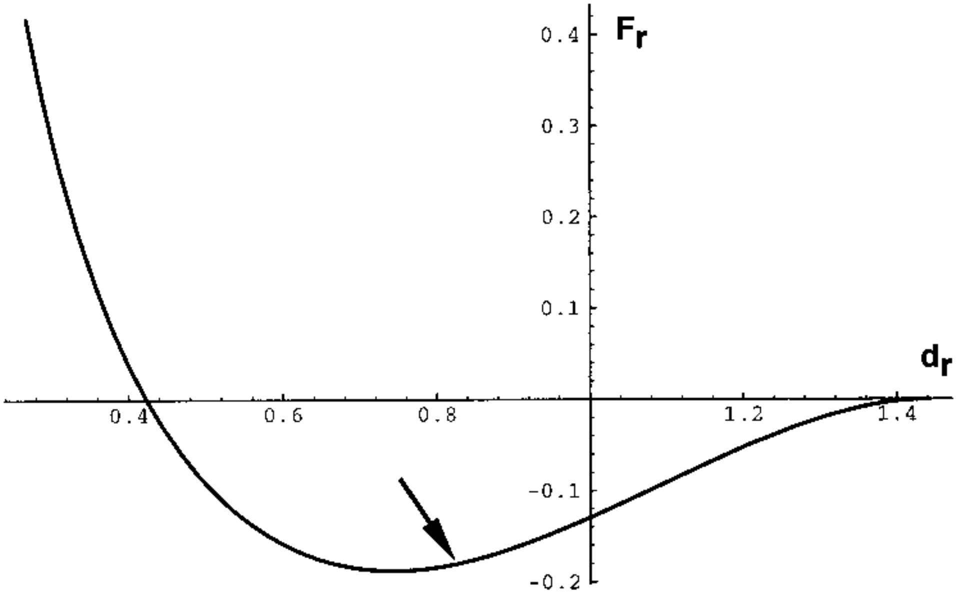

Figure 2 Reduced interaction energy between surfaces F_r as a function of distance between the surfaces d_r for a bridging brush.

III. POLYMER ADSORPTION

When all the monomers adsorb on a solid surface, a rather dense adsorbed layer is formed in the vicinity of the surface even if the bulk solution is dilute. This layer is rather thick due to the formation of large loops by the chains on the surface (although far thinner than a dense grafted layer). Some of the monomers belong to the tails of the chains. The structure of an adsorbed layer is presented in Fig. 4. In this section, we discuss the structure of an adsorbed polymer layer using first a mean field theory and then a scaling approach. In the last part, we present some results on the interactions between surfaces carrying adsorbed polymer layers.

A. Mean Field Theory (Tails and Loops)

In a mean field approach, the interaction between one chain and all the other chains of the adsorbed layer is approximated by a mean field potential proportional to the local concentration $U(z) = kTvc(z)$ and the average conformation of one chain is calculated in this potential. The conformation of one chain is characterized by the partition function

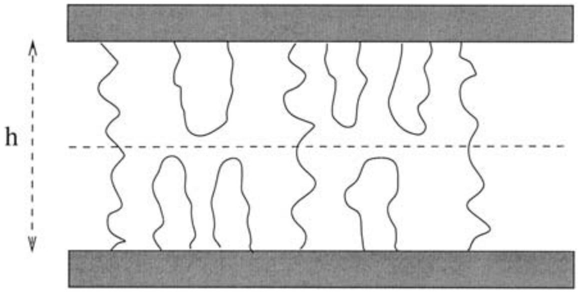

Figure 3 Two parallel plates bridged by end-adsorbed polymers.

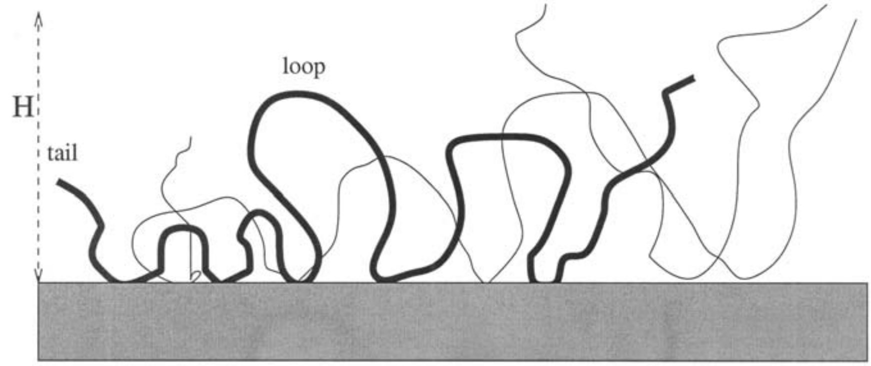

Figure 4 Structure of an adsorbed layer. Each chain is composed of two tails in the vicinity of the end points and forms loops on the surface.

$Z_N(z)$ which is proportional to the number of conformations of a chain with one end point fixed [18,7] at a distance z from the surface; the partition function satisfies a diffusion-like equation

$$-\frac{\partial Z_N}{\partial N} = -\frac{a^2}{6}\frac{\partial^2 Z_N}{\partial z^2} + U(z) Z_N \tag{3}$$

The interaction with the wall has a very short range and can be considered as a boundary condition to this equation on the surface ($z = 0$). The boundary condition is, in general, written as

$$-\frac{1}{Z_N}\frac{\partial Z_N}{\partial z}\bigg|_{z=0} = \frac{1}{b}$$

where the adsorption length b is inversely proportional to the energy gain of a monomer upon adsorption. If the energy gain is of the order kT, the adsorption length is of the order of the monomer size. This equation for the adsorption of a polymer solution must then be made self-consistent by recalculating the local monomer concentration from the chain conformation. A very powerful and useful numerical scheme was introduced some time ago by Fleer et al. [5] who were the first to point out the importance of the distinction between monomers belonging to the tail and loop sections of the chains. This scheme has been applied to many experimental situations and, in particular, to the calculation of the interaction between surfaces that we discuss in this chapter. We will consider here the limit of polymers with a very large molecular weight for which an asymptotic analysis is possible. It has been checked explicitly that the numerical approach is consistent with this asymptotic analysis [23,24].

In order to calculate the chain partition function, it is convenient to decompose the partition function into two parts. The partition function of an adsorbed chain (a chain that has at least one monomer in contact with the surface) is the first order parameter $\psi(z)$ [25]. The partition function of a free chain (a chain that is nowhere in contact with the surface) is characterized by a second order parameter $\varphi(z)$. The two order parameters satisfy equations very similar to Eq. (3). If a monomer belongs to a loop, the two subchains starting from this monomer are adsorbed chains and the statistical weight associated with this monomer is proportional to $\psi^2(z)$. If a monomer belongs to a tail, the two subchains are a free chain and an adsorbed chain; the corresponding statistical weight is proportional to $\psi(z)\varphi(z)$. By choosing a proper normalization of the partition function, the monomer concentration can be written as

$$c(z) = \psi^2(z) + B\psi(z)\varphi(z) \tag{4}$$

where B is a constant. The mean field potential can then be expressed as a function of the two order parameters which makes the problem self-consistent. The constant B is calculated by noting that the chain end point concentration is $c_e(z) = B\psi(z)$, and by writing the conservation of the end points (if the adsorbed layer contains Γ monomers per unit area the total number of end points per unit area is $2\Gamma/N$). The first term in the monomer concentration (4) is the concentration of monomers belonging to loops and the second term is the concentration of monomers belonging to tails.

An explicit solution of these mean field equations shows that an adsorbed polymer layer has a double layer structure: close to the wall the concentration of monomers belonging to loops dominates and $c(z) = a^2/3vz^2$. Further away from the surface, the concentration of monomers belonging to tails dominates and $c(z) = 10a^2/3vz^2$. One can note that the scaling of the monomer concentration with the distance from the surface is

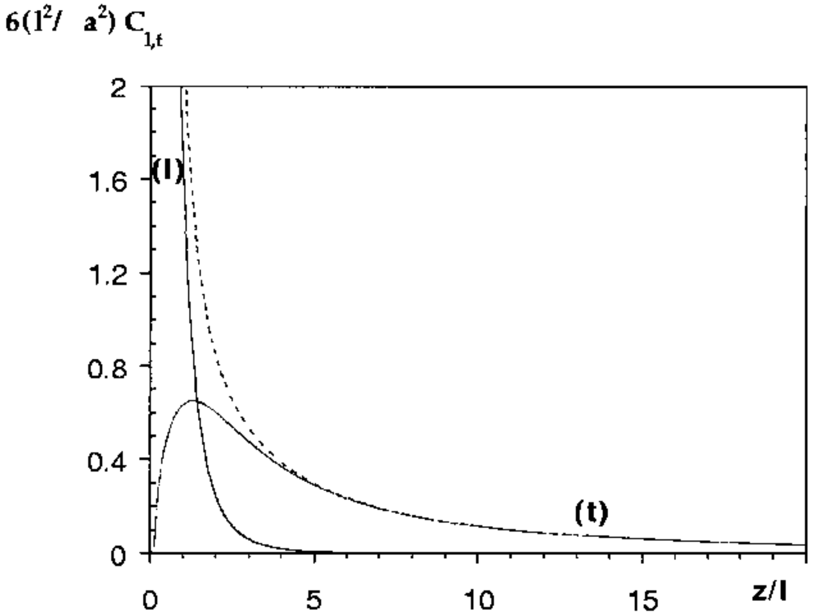

Figure 5 Concentration profiles of monomers belonging to loops (l) and tail (t), and total monomer concentration (dotted line).

the same in the tail and loop regions, but that the prefactor is different. The crossover between the tail and the loop regions occurs at a distance $\ell \sim N^{1/3}$. A plot of the loop and tail concentrations is given in Fig. 5.

The total thickness of the adsorbed layer is obtained by balancing the chemical potential of the chains in the adsorbed layer with that in the bulk. It is equal to

$$H = \left(\frac{Na^2}{6 \ln\left(1/c_b b^2\right)} \right)^{1/2}$$

where c_b is the bulk concentration and it is of the order of the bulk radius of gyration of the chains. The total number of adsorbed monomers per unit area is obtained by integration of the concentration profile and is equal to $\Gamma = a^2/3vb$ in the limit of very long chains; it depends only very weakly on the chain molecular weight and on monomer concentration at moderate polymer density.

B. Scaling Theory

The mean field theory allows the calculation of many physical properties of adsorbed polymer layers. For most experimental situations it gives a good qualitative description, but it is known not to be quantitative as it implicitly ignores the concentration fluctuations associated with the excluded volume interaction. A simple strategy is to assume that the mean field theory gives the correct picture and to take the concentration fluctuations into account using a scaling approach. The first scaling description of adsorbed polymer layers is due to de Gennes [26]. The starting point is to assume that the local structure of an adsorbed polymer layer is similar to that of a semidilute solution and can be described as a fluctuating network with a local mesh size $\xi(z)$. In a good solvent, the local correlation

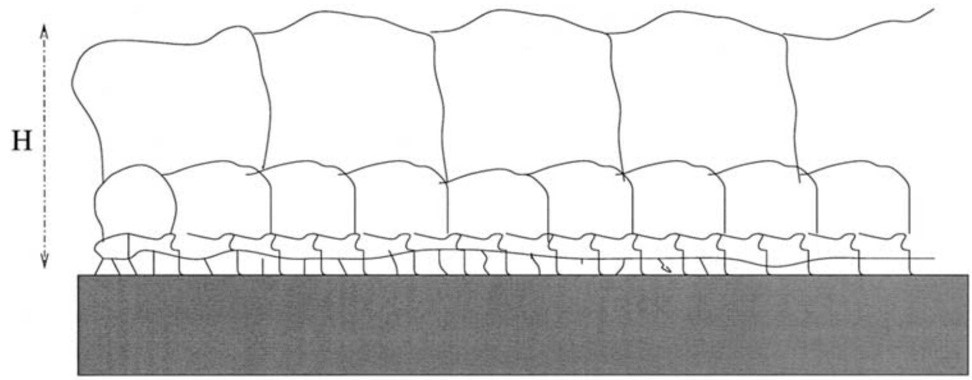

Figure 6 Self-similar concentration profile: at a distance z from the surface, the local mesh size of the temporary polymer network is proportional to z.

length varies as $\xi(z) \sim [c(z)]^{-3/4}$. At intermediate length scales between the adsorption length b and the polymer radius R the only relevant length scale is the distance to the surface z. The local mesh size must, therefore, be proportional to the distance z. This leads to a power law decay of the monomer concentration $c(z) \sim z^{-4/3}$ and to a concentration profile that is self-similar as represented in Fig. 6. The minimum size of the loops is the adsorption length b and the maximum size the chain radius R. Note that if the mean field expression for the correlation length is used $\xi \sim c^{-1/2}$, and the scaling argument is consistent with the mean field theory ($c(z) \sim z^{-2}$). The scaling approach is not refined enough at this level to distinguish between monomers belonging to loops or tails. It can, however, be improved in order to incorporate the differences between loops and tails [27]. As in the mean field theory, loops dominate close to the surface and tails dominate in the outer part of the layer. The crossover distance between these two regions is $\ell \sim N^{1/2}$. The probability of having a loop of g monomers is found to be $p_\ell(g) \sim g^{-(1+2\nu)}$ where $\nu = 3/5$ is the swelling exponent; the probability of having tail of g monomers is $p_t \sim g^{(\gamma-\nu)/2-1}$ where the exponent γ is roughly equal to 1.16. Note that the average loop length is very small (of order 1) and that the average tail length is very large (of order N). This scaling approach gives an accurate description of the structure of adsorbed polymer layers as probed, for example, by neutron scattering [28].

C. Nonequilibrium Adsorption (Pseudo-Brushes)

The whole discussion of polymer adsorption so far makes the fundamental assumption that the layer is at thermodynamic equilibrium. The relaxation times measured experimentally for polymer adsorption are very long and this equilibrium hypothesis is in many cases not satisfied [29]. The most striking example is the study of desorption: if an adsorbed polymer layer is placed in contact with pure solvent, even after very long times (days) only a small fraction of the chains desorb (roughly 10%); polymer adsorption is thus mostly irreversible. A kinetic theory of polymer adsorption would thus be necessary. A few attempts have been made in this direction but the existing models remain rather rough [30,31].

A simpler approach is to assume that polymer adsorption is an equilibrium process under constraint. In most experiments, the chains cannot diffuse outside the adsorbed layer and the total adsorbed polymer amount Γ is fixed, but the conformation of the chains can equilibrate (at full thermal equilibrium the chemical potential of the chains is fixed by the bulk solution). Even if the adsorbed layer is starved and has a low value of Γ, the structure of the layer at constant adsorbed amount is very similar to that at thermal equilibrium; the monomer concentration decays with the same power law. The thickness H of the layer increases with Γ.

In certain cases a higher degree of irreversibility is observed. This is the case for the so-called pseudo-brushes where the monomer adsorption on the surface is supposed to be irreversible and where the loop size distribution remains fixed under swelling. A pseudo-brush is obtained by placing the adsorbing surface in contact with a molten polymer (or a concentrated semidilute solution). All the chains within one Gaussian radius of gyration $R \sim N^{1/2}a$ adsorb on the surface and the adsorbance is $\Gamma \sim N^{1/2}a^{-2}$. The adsorption is irreversible and after washing with pure solvent, only the adsorbed chains remain attached to the surface; the adsorbed layer swells in the solvent forming the pseudo-brush. The pseudo-brush is thus equivalent to a polydisperse brush where the irreversibly adsorbed monomers play the role of the anchoring points; the equivalent graft density is $\sigma = \Gamma/N \sim N^{-1/2}a^{-2}$. Using the result given earlier for the thickness of a grafted layer (Eq. (1)) the thickness of the brush is $H \sim aN^{5/6}$. It is again a structure where the chains are highly stretched. A more detailed analysis of the pseudo-brush structure in terms of loop size distribution has been performed by Guiselin [32]. Pseudo-brushes have sometimes been used to coat surfaces in adhesion or friction experiments; they present the great advantage of being easy to make even though their properties are less understood theoretically than those of true brushes [33].

D. Interaction Between Surfaces, Bridging and Osmotic Repulsion

The equilibrium interaction between two parallel surfaces mediated by a polymer solution can be studied within the mean field approximation [34]. The polymer in the gap between the two surfaces is in equilibrium with a reservoir that fixes its chemical potential. One first determines the concentration profiles and then calculates the free energy. The interaction results from a competition between the osmotic repulsion and an attractive bridging contribution. The two contributions scale in the same way and one has to perform a complete calculation in order to determine the sign of the force. At large distances, when the two layers do not overlap, $h > 2H$, the force is exponentially small. At shorter distances, $\ell < h < 2H$, the force per unit area is repulsive and varies as

$$f = \frac{70kT}{6v}\frac{a^4}{h^4} \tag{5}$$

In this range of distances, only the tails are important and as in the case of the polymer brush the tails repel each other. The force is of the order of the osmotic pressure at the midplane between the two surfaces ($z = h/2$). At short distances $b < h < \ell$ the force still varies as $1/h^4$ but it is attractive. In this range, the loops on both sides overlap to form bridges and the bridging attraction dominates. This equilibrium force can be measured only in cases of reversible adsorption; this in general is not the case for adsorption on solid surfaces but it could be the case for adsorption on a liquid–liquid interface.

As explained above, on a solid surface the adsorption is irreversible. We will treat here the irreversibility by assuming that the adsorbed amount 2Γ in the gap between the surfaces remains constant. If the surfaces are saturated with polymer, that is if the adsorbance is equal to its maximum value $\Gamma = a^2/3vb$, the force is repulsive at all distances; at

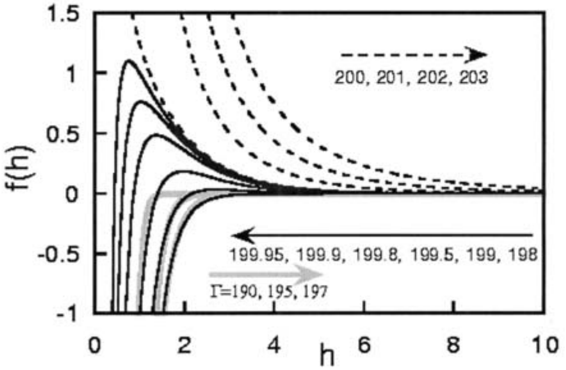

Figure 7 Force between two plates f as a function of the distance h between plates in a case of irreversible adsorption. The values of Γ are indicated on the arrows. The plotted quantities are made dimensionless using the units defined in Ref. [35]; the unit length is the crossover distance ℓ.

large distances it has the same dependence as in the equilibrium case, though with a higher numerical prefactor. If the surfaces are undersaturated, $\Gamma < a^2/3vb$, bridging becomes more important at short distances and the force is nonmonotonic, attractive at short distances due to bridging and repulsive at large distances due to the tails. Eventually, at lower values of Γ, the force is attractive at all distances [35,36]. A plot of the force as a function of distance calculated from the mean field theory is displayed in Fig. 7. In the figure, for the smallest values of Γ, the force is attractive at very short distances; this is not realistic as the dominant effect is the compression of a dense polymer layer. This is an artifact due to the virial expansion. A more realistic treatment including higher term in the virial series shows that at very short distances, the force is repulsive again. At intermediate values of Γ, the force is thus repulsive then attractive then repulsive when the distance h decreases.

The scaling theory does not provide the sign of the force but only the scaling behavior as a function of the distance. It is reasonable to assume that the mean field theory does provide the correct qualitative variation of the force and that only the scaling behavior is not accurate. A simple scaling argument shows that in all the regimes where the mean field theory predicts a force varying as h^{-4}, the force actually scales as $f \sim h^{-3}$ [37].

There is a whole body of experiments on polymer mediated interactions between solid surfaces performed using the surface forces apparatus (mostly by the group of J. Klein [38], but also by other techniques. The theoretical picture presented here is in good agreement with most of the results.

IV. CONCLUDING REMARKS

In this short review, we have presented some results on the behavior of polymer solutions close to surfaces in the context of adhesion phenomena. The emphasis has been placed on the interaction between two flat parallel solid surfaces induced by a polymer solution and more specifically on the bridging effect between the surfaces due to the polymer. Two types of interactions between the surface and the polymer have been considered: grafting and adsorption.

We have not discussed in detail experiments on interaction between surfaces mediated by a polymer solution. There exist now many experiments probing the interaction between two surfaces in a polymer solution both when the polymer adsorbs and when the polymer is grafted. The earliest experiments were performed using a surface forces apparatus and measuring the interactions between mica surfaces [38]. More recently, experiments have been performed using other techniques such as atomic force microscopy [39], thin film balance, or measuring the interactions between magnetic emulsion droplets [40]. The theories presented here give in most cases a rather accurate description of the experiments.

Some important effects are ignored by the theoretical models that we have presented. The most important approximation is the thermodynamic equilibrium assumption. All these surface interactions have very long relaxation times and this approximation is in many cases questionable (in some instances, the surface polymer layers are rather dense and become glassy, the thermodynamic description is then not meaningful). In some cases a description in terms of a constrained equilibrium compares favorably with the experiments but all these problems would require a kinetic description. Some steps towards a kinetic description have been taken for the structure of the surface layers but the description is far from being complete. For the interaction between surfaces and the bridging problem, only very few attempts have been made [41]. The important question here is the role of trapped entanglements that can have a strong influence on the interaction force in cases of both adsorption and grafting. So far this effect has not been included in the theories.

Another important aspect that we have not discussed in this paper is the dynamic properties of the polymer surface layers such as their behavior under steady shear [42] or under an oscillatory stress [43]. This is obviously essential for adhesion studies and theoretical work in this direction is certainly needed.

Finally, we have considered polymer solutions in good solvents only. For industrial applications, one tends to use more and more water as a solvent. Water soluble polymers have specific properties due to the character of the interactions between monomers in water. Most water soluble polymers, for example, carry ionic charges (they are polyelectrolytes); if the polymers contain hydrophobic groups, they have interesting associating properties. The surface behavior of polyelectrolytes and associating polymers is the subject of intense experimental and theoretical studies [44].

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Tailoring Adhesion of Adhesive Formulations by Molecular Mechanics/Dynamics

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I. INTRODUCTION

Molecular mechanics in the broader sense of the term is a computational technique which is, among other things, particularly suited for determining at the molecular level the interactions at the interface of well-defined polymers. It has already been used, in many fields, for instance, to calculate the most stable conformation, hence the conformation of minimum energy, of biological materials such as proteins, for the interactions of oxygen, carbon monoxide, and carbon dioxide on the functioning of the heme of respiratory proteins, for the design and activity forecasting of pharmacological drugs or other biologically active materials to fit the active sites of enzymes, for the determination of the structure of a variety of high-tech materials, to determine the structure and properties of a variety of synthetic and natural polymers, and even to model homogeneous and heterogeneous catalysis processes. The variety and number of applications of this technique in the past few years are indeed great and it has positively influenced many fields of science.

What exactly is molecular mechanics? It is the study of the interactions of non covalently bonded atoms in one or more molecules which determine the spatial conformation of such a structure or its change of conformation induced by a neighboring molecule. In short, it is the modeling of the structures of molecules, their structural interactions and modifications, and hence of their macroscopic and microscopic properties derived from the molecular level according to first principles in physics and physical chemistry. Its mundane appearance is that of a computational technique, and today extensive computation is always included. However, it is indeed much more than just a computational technique: it is the technique par excellence to explain our physical world from first, molecular, and atomic principles.

While it has now been used for almost thirty years in many other fields the application of this technique in the field of adhesion and adhesives, namely to theoretical and applied problems of adhesion and to the optimization of adhesion, is still relatively in its infancy. A few notable applications of this technique to adhesion and adhesives do, however, exist and this chapter is aimed at describing them, and their relevant consequences without pretending to be either exhaustive or limiting as to what regards any other future applications. As molecular mechanics and molecular dynamics are really "going back to basics" techniques aimed at explaining at molecular level the behavior of materials, there is no doubt that their use is also bound to grow in the field of adhesion just as rapidly and effectively as it has occurred in other scientific and technological fields, once the potential of such a technique is understood.

In the field of adhesion, in its broadest sense, several different pioneering trends are already on record, namely:

(i) studies of the adhesion of generalized particles to generalized surfaces, or of generalized particle to generalized particle
(ii) studies of the adhesion of polymers well defined at molecular level to surfaces equally well defined at molecular level
(iii) studies of the dynamic, differential, competitive adsorption, hence adhesion, of molecularly well-defined oligomers to an equally molecularly well-defined surface in the presence of solvents, such as, for instance, in the modeling of chromatography.

This chapter will address these three sectors of activity.

II. ALGORITHMS USED IN MOLECULAR MECHANICS

Different molecular mechanics systems and programs exist. There are programs that allow simultaneous variation of bonds and bond angles as well as allowing bond rotation, and there are programs in which instead all the covalent bond lengths and bond angles between covalently bonded atoms are fixed to specific values without allowance for their adjustment or modification during computation. It cannot be said that one system is better than the other as either of the two systems can be more apt at resolving a particular problem: it might then be necessary to choose the system according to the problem at hand.

The first type of program, based on an unconstrained force field approach is more comprehensive but suffers from the limitation of the size of molecules that can be investigated due to the extent of computations needed. It is thus very apt for the study of smaller molecules or systems of molecules up to 40–60 atoms, but this limitation is also fictitious because it really depends on the capacity and calculation rate of the computer used. Such unconstrained force field programs tend to suffer furthermore from the problem that the automatic search for the minimum of energy might lead the program to minimize on a local rather than total minimum, and if particular attention is not exercised completely false results can be obtained (the "black-box" syndrome).

The second type of program, based on a constrained force field approach, is generally taken to render computation more rapid. It is then particularly useful when big molecules, such as polymers are involved. All these programs are based on the finding that conformational studies in the field of biological macromolecules have shown that the conformational energy of a molecule can be represented with accuracy even when bond lengths and angles between covalently bonded atoms are prefixed [1], and is represented by a sum of four types of contributions namely

$$E_{\text{tot}} = E_{\text{vdW}} + E_{\text{H-bond}} + E_{\text{ele}} + E_{\text{tor}} \tag{1}$$

E_{tot} represents the total conformational energy of the molecule as a function of all the internal angles of rotation. E_{vdW} represents the contribution to the total energy due to van der Waals interactions between all the couples of unlinked atoms whose relative position depends on one or more internal bond rotational angles (ϕ^o, ψ^o) (in degrees). This contribution can be expressed by Buckingham-type functions

$$E_{\mathrm{vdW}} = \sum_{ij} \left[a_{ij} \exp(-b_{ij} r_{ij}) - c_{ij} r_{ij}^{-6} \right] \tag{2}$$

where the coefficients a, b, and c depend on the couple i, j of atoms, or by Lennard-Jones-type functions

$$E_{\mathrm{vdW}} = \sum_{ij} \left[\left(\frac{d_{ij}}{r_{ij}^{12}} \right) - \left(\frac{c_{ij}}{r_{ij}^{6}} \right) \right] \tag{3}$$

Both types of functions are commonly used. Several sets of a, b, c, and d, coefficients are available [1–3]. Equally good results can be obtained using Lennard-Jones-type functions alone or Buckingham-type functions alone or mixtures of Lennard-Jones and Buckingham functions [4]. The attraction coefficients c_{ij} in these expressions are generally but not always calculated with the formula of Slater and Kirkwood [5]:

$$\left[\frac{3}{2} \exp\left(\frac{h}{m^{1/2}} \right) \alpha_i \alpha_j \right] \Big/ \left[\left(\frac{\alpha_i}{N_i} \right)^{1/2} + \left(\frac{\alpha_j}{N_j} \right)^{1/2} \right] \tag{4}$$

where α_i and α_j are the values of the polarizability of the atoms i and j, and N_i and N_j are the numbers of effective electrons, respectively.

In Eq. (2), b_{ij} is fixed to a constant value [1,6–10] and a_{ij} is determined by imposing the minimum at the distance that is the sum of the van der Waals radii of the atoms or groups considered [1,6–10]. The van der Waals interactions are always calculated here as the sum of the single interactions between each couple of unlinked atoms.

E_{ele} describes the electrostatic contribution to the total energy. Dipolar momenta are here expressed, in the so-called monopolar approximation, by means of partial charges the values of which are fixed in such a manner as to reproduce the dipolar momenta of both bonds as well as the total dipolar momentum. Using partial charges, the dipolar interactions can be calculated with a Coulomb-type law of the form $E_{\mathrm{ele}} = \Sigma_{ij} (q_i\, q_j)/(\varepsilon\, r_{ij})$ where q_i and q_j are the charges of the two atoms i and j, r_{ij} is the distance between i and j and ε is the dielectric constant.

E_{tor} describes the contribution to the total energy due to hindered rotation around skeletal bonds. The formulas generally used for the torsional potentials are those of Brant and Flory [2,6–10] where the torsional barriers used can be of different values [2,6–10]. It is necessary to point out, however, the limiting condition that must be imposed on the rotational degrees of freedom. Rotations around bonds that have very high torsional barriers (C=C, C=O), and single bonds between them affected by their conjugation, as in the case of polypeptides, must not be considered [11].

$E_{\text{H-bond}}$ represents the hydrogen bond (H-bond) contribution between couples of noncovalently bonded atoms. Several functions, even very simplified and empirical ones, have been used, and often with good success. The H-bond, however, is at best a difficult interaction to describe through a function which is capable of both giving good results while really taking into account the physicochemical reality of the interaction. It is for this reason that there is a multitude of empirical simplified functions for its calculation. Where the H-bond is of little or no importance often the molecular mechanics calculations are just done on the basis of only the van der Waals interactions (and not with bad results, as in the earlier days of protein structure refinement). In systems in which the H-bond

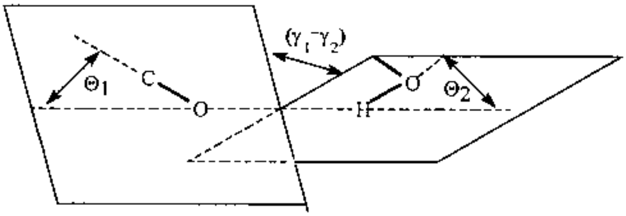


Figure 1 Dihedral angle ($\gamma_1 - \gamma_2$) of importance in the calculation of H-bond energy and showing the importance of directionality in this type of interaction. (From Ref. 8.)

contribution is important or determining to the results it is better to use a more complicated but more comprehensive function proposed by Stockmayer which has already been found to give very representative results in polypeptide sequences [11] and in cellulose systems [12]:

$$E_{\text{H-bond}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \left(\frac{\mu_a\mu_b}{r^3}\right) \times [2\cos\Theta_a\cos\Theta_b - \sin\Theta_a\sin\Theta_b\cos(\gamma_a^0 - \gamma_b^0)] \qquad (5)$$

which takes into consideration the angular dependence of the H-bond. The first term in Eq. (5) describes the interaction between the hydrogen atom and the oxygen atom participating in the H-bond, and it is nothing else than a Lennard-Jones potential with the expression in simplified form. The second term describes the H-bond as an electrostatic interaction between two point-like dipoles of magnitudes μ_a and μ_b centered on the oxygen and hydrogen atoms. The directional character of the H-bond is assured by the angular dependence of this function, and Θ_a and Θ_b are the angles that the C–O and O–H bonds form with the C–O- - -H–O segment linking the hydrogen and oxygen atoms (Fig. 1). The value ($\gamma_a - \gamma_b$) (in degrees) is the angle between the planes containing the H-bond and the O–H and C–O bonds (Fig. 1). The ε, σ, and μ are obtained by minimizing the first term of Eq. (5) at the van der Waals distance between the hydrogen and oxygen atoms, and the whole function at a H-bond distance of 2.85 Å with aligned C–O and O–H bonds.

Also in many of the unconstrained force field type programs today similar expressions for the H-bond based on a Lennard-Jones first term as above or a Buckingham first term [13] followed by a term describing the dipolar and angular dependence of the H-bond are used. However, there are also a number of programs in which the H-bond is described just as a Buckingham function without any consideration being taken of the directionality of the H-bond, or even by simpler expressions. There is nothing very wrong with these simplified approaches in cases where the H-bond is not of fundamental importance to the study, but they cannot be used reliably in cases where the H-bond is of determining importance.

III. GENERALIZED PARTICLE/SURFACE AND PARTICLE/PARTICLE MODELS

The mechanics of particle adhesion and the deformations resulting from the stresses generated by adhesion forces have now been studied both experimentally and theoretically for a long time. Most of the approaches taken on the subject stem from a thermodynamic rather than a molecular viewpoint, such as the use of the so-called Johnson–Kendall–Roberts (JKR) model [14]. The first time that such a type of problem was approached from a molecular viewpoint was the proposal by Derjaguin et al. of a new adhesion model (the Derjaguin–Müller–Toporov (DMT) model) [15]. Soon afterwards, the Müller–Yushchenko–Derjaguin (MYD) model was proposed by Müller et al. [16,17] by assuming that the adhesion forces, and hence the interaction between a particle and a substrate could be represented by Lennard-Jones potential functions. With this theory it is not possible as yet to speak of a molecular mechanics approach. Nonetheless, this is the first educated assumption and understanding that the interaction of generalized particles, atoms, and molecules can be described even for problems and theories of adhesion through Lennard-Jones functions, one of the classical type of potential functions used to describe interactions in molecular mechanics. This insight perhaps opened the way to the subsequent use of molecular mechanics in the field of adhesion. The JKR and DMT models have since been shown to be particular subsets of the more general MYD theory. They have been extensively studied [18–21] and models have been presented.

While all these theories have helped our understanding of particle adhesion, all of them suffer from the considerable drawback of treating the mechanical response of materials as something totally independent of the molecular level parameters influencing adhesion. As the intermolecular potential of a material determines, or at least strongly influences, both its mechanical properties as well as its surface energy the possibility exists that a more holistic adhesion model could be conceived by going back to the drawing board and starting from first principles. This, added to the fact that the theories briefly referred to above do not always predict the correct value of the power law dependence of the contact radius on particle radius prompted some attempts in this direction. Notable in this respect are two investigations, and only here for the first time in this chapter one can really speak of a molecular mechanics approach to some form of adhesion. The first investigation [22] was based on molecular mechanics calculations of the interaction of acrylic-type monomers with an idealized model surface composed of a rectangular parallelepiped of generalized, idealized atoms treated as spheres arranged at regular nodes of a square grid network and constitutes the first example ever of this type of approach. The second one followed four years later and went further [23–25]. It was a molecular dynamics study along very similar lines as the previous one, defining the interaction between the two surfaces of generalized, idealized atoms treated as spheres. It is this latter study which will be briefly presented and discussed, with all its advantages and limitations, because it is a more clear-cut case of a generalized model of particle adhesion based on molecular mechanics. The former and earlier model will not be discussed further as it really constitutes a hybrid case between the type of approach presented in the following section of this chapter dealing with examples of even earlier but conceptually more correct nongeneralized models, and the type of approach based on particle adhesion proper.

Before getting more involved in the finer points of particle adhesion studies by molecular mechanics it must be pointed out that such an approach suffers from considerable drawbacks. Molecular mechanics and dynamics by definition involve interactions between clearly defined types of atoms, with clearly defined atomic characteristics, placed in clearly defined molecular structures. Thus, a generalized, fictitious surface of only, let's say nitrogens, or even worse of generalized spheres, is a rather extreme physical approximation. It is by definition incorrect in a molecular mechanics and dynamics investigation. Such a drawback needs to be pointed out to put in perspective and understand the limitations inherent in a model pretending to describe atomic and molecular interactions in real systems by a molecular mechanics approach oversimplified at the physical level. Nonetheless, valuable information has been gathered by this type of approach. It is furthermore a very good approach for the description of particle/particle interactions when the particles themselves are composed of well-defined atom types interacting with each other both at the particle/particle interface and within the body of the particle itself.

The more advanced work today on particle adhesion [23–25] builds then on the assumption that particles interact through a Lennard–Jones-type potential function, namely

$$E = -4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right] \tag{6}$$

where ε is the binding energy between an atom and its nearest neighbor and σ is the distance between the two atoms when the value of the potential energy represented by the above function is neither attractive nor repulsive: namely at the crossover intersection point of the function with the axis. The authors of the theory recognized that the choice of this potential was purely empirical [25].

At first a flat surface of atoms was generated in a stepwise manner allowing the energetics associated with the creation of the surface to be determined, and then two of these surfaces were brought together and allowed to form a bond. The pairs of mated surfaces were then separated in a constrained tension test to form two fracture surfaces. The potential energy of the system and the axial stresses used to produce the displacements observed were monitored. The molecular mechanics computational modeling part consisted in assembling a parallelepiped of generalized atoms as spheres, arranged in a predetermined regular array. The computational model used in tension, compression, and shear modes allows examination of the stresses produced when free surfaces approach one another. The parallelepiped of atoms constituting each surface was composed of 768 atoms aligned parallel to the X, Y, and Z axes of a reference system. The parallelepiped of atoms was then constituted of 24, 8, and 8 layers of atoms in the X, Y, and Z directions, respectively. By the time the first 100 iterations were terminated the system temperature had fallen to half of its original value as a consequence of the equipartitioning of the energy into kinetic and potential contributions. The lateral dimensions of the surface that was about to be created were then fixed by putting back the atoms in their previous positions after each computation inducing, as a consequence, a gradual increase of the gaps between atoms without actual movement of the atoms. This effectively suppressed the usual atomic motions allowing the variation of the apparent potential energy of the system as the surfaces were separated be followed computationally. Once the size of the interatom gaps had increased to the size of the cut-off radius there was no further increase in potential energy with increasing gap size. Once the gap was established the atomic motions and temperature dependence were reactivated to allow the system to relax into its new state of equilibrium.

Once the free surfaces in equilibrium were computationally generated they were brought closer to one another by a very slow approach rate of 10,000 iterations to reduce the gap between the surfaces to one cut-off radius. The slow approach was necessary to minimize or eliminate complications arising from spheres' (atoms') impact energies. All this allowed changes in potential energy and the following of the resulting surface interactions which developed at constant temperature and constant dimensions. During the approach the mutual attraction increased monotonically until a certain critical stress level was reached. At such a critical stress the two surfaces lept into mutual contact as the strain energy increased because the rate of energy storage due to elastic deformation equated to the rate at which energy was provided by the attraction between the surfaces. Thus the model was able to reproduce, at least qualitatively, the leap-to-contact effect between a particle and a planar surface observed experimentally using atomic forces techniques [26–28]. In the cases where the surfaces were pulled, rather than lept, into contact the stresses were not uniform and traveling waves were generated. Additional traveling waves were also generated when the surfaces struck one another. These waves, which interacted with each other, correspond to atomic level kinetic energy and can be interpreted as an increase in temperature. As a consequence, the authors came to the interesting conclusion that in a real system this implied that energy loss occurred even if only elastic deformations resulting from the forces of adhesion were considered: hence, not all the energy is recoverable on surface separation as not all the energy of the system is stored elastically.

Study of the model during subsequent separation of the two surfaces, this corresponding to a tension, showed clearly the existence of hysteresis effects. This hysteresis might account for the effect of Young's modulus on particle adhesion, which is not predicted in the JKR model. In the simulation of the process of separation of the two surfaces and of the fracture mechanics of the model, fracture finally occurred only when the interatomic spacing of some regions exceeded the critical value to an extent that further separation reduced suddenly the energy. This occurred suddenly and over a very small number of iterations. Even in the case of surface separation, waves were generated which decayed as a function of time thus generating thermal energy which was then lost by the modeled system. Thus, even during elastic deformation, surface separation energy loss mechanisms exist. The maximum stress experienced in the leap-to-contact decreased with increasing temperature while the average stress, shortly after leap-to-contact, was much less sensitive to the temperature. Finally there was a distinct offset between the initial and final potential energies due to microstructural changes in the interfacial regions as the two layers of atoms near each of the two surfaces contained numerous site defects, namely atom sites which were empty.

IV. ADHESION MODELS FOR WELL-DEFINED POLYMERS TO WELL-DEFINED SURFACES

Contrary to the generalized approach already presented, models describing the adhesion between a polymer well defined at a molecular level and another, equally molecularly well-defined substrate also exist. These are models in which molecular mechanics and dynamics are applied in their more accepted role described in the Introduction. It must be realized that such models derive from a need different from what has prompted the development of the generalized models already described. They stem from the need to solve some applied problem of adhesion or to upgrade the performance of some adhesive systems in situations where the use of an experimental method would take too long, or is not able to give any clear results. It is for this reason that such models need to use the most precise and well-defined information possible or available on the molecules involved as well as using the sets of potential functions which describe in the most accurately conceptual manner the molecular behavior of the chemical species involved: all the research work that uses this approach is then applied to "real" case, not to idealized models, and is of considerable sophistication. Furthermore, all this type of research work is most commonly supported by direct or indirect experimental results which prove that molecular mechanics predicted well the improvements that needed to be implemented to upgrade adhesion or to upgrade an adhesive system. Notwithstanding their applied use, the sophistication of such a type of an approach has yielded very interesting results on the fundamental side of the science of adhesion and of the interface and it offers considerable promise and opportunities for more progress in the future.

The first of such studies [8] appeared in 1987 and thus preceded by a couple of years the first of the generalized approach studies [22]. It concerned the adhesion of phenol–formaldehyde (PF) polycondensates and resins to cellulose, hence to wood. It was followed later by other studies on the adhesion to crystalline and amorphous cellulose of urea–formaldehyde (UF) resins [7], of more complex PF oligomers [10], of water [29,30], of chromates [31], and finally of the more complex case of ternary systems in which two interfaces exist, namely in the situation of adhesion to cellulose and wood of an acrylic undercoat composed of a photopolymerizable primer onto which was superimposed an alkyd/polyester varnish [32,33]. The molecular mechanics algorithms used for all these studies were those already presented at the beginning of this chapter. The only difference was that for just the last of the studies mentioned the negligible importance of H-bonding to that particular system led to disregarding it in the calculations. Before the first of these studies, the understanding of the phenomenon of adhesion between a well-defined pair of adhesive and adherend had never been attempted by means of calculation of all the values of secondary interactions between the non covalently bonded atoms of the two molecules involved. This approach was rendered possible by the codification, again by molecular mechanics (or conformational analysis, as this technique was known in earlier days) from the data of earlier x-ray diffraction studies, of the spatial conformation of native crystalline cellulose (or cellulose I) [12], of the several mixed conformations possible for amorphous cellulose [12], and also of PF oligomers [34].

This initial molecular mechanics calculation was limited to the interaction with crystalline cellulose I of all the three possible PF dimers in which a methylene bridge links two phenol nuclei *ortho–ortho*, *para–para* and *ortho–para*. As not much was known as to how the system would react the investigation was very extensive. As cellulose constitutes as much as 50% of wood, where its percentage crystallinity is as high as 70%, this study also inferred applicability to a wood substrate. As even dried wood always contains a certain amount of water the influence of the water was taken into account by introducing into the calculations the effect of a parameter related to the dielectric constant of water.

The results obtained clearly indicated that adhesion of PF resins to cellulose was easily explained as a surface adsorption mechanism, a fact which, while very accepted today, was not evident in the wood gluing field and in the literature up to that time. This results also indicated that the interaction of the PF dimers with cellulose on all possible sites was more attractive than the average attraction by the cellulose molecule for the sorption of water molecules. In a few cases only, the interaction of water molecules with the few strongest sorption sites of cellulose was more attractive than that of PF dimers. This implied that in general even for the more difficult to wet crystalline cellulose the PF dimers, and by inference also higher PF oligomers, were likely to displace water to adhere to the cellulose surface. This was an important findings as it did show for the first time by numerical values that in wood bonding the adhesion of the polymer resin to the wood must be considerably better than the adhesion of water molecules to the wood. It is of importance first for "grip" by the adhesive of the substrate surface and secondly, in the cured adhesive state, in partly determining the level of resistance to water attack of the interfacial bond between adhesive and adherend. This result added a new dimension to the well-known water and weather resistance of PF-bonded lignocellulosic materials: it is not only due to the imperviousness to water of the cured PF resin itself, as believed up to then, but also to the imperviousness to water of the adhesive/adherend interfacial bond, a bond exclusively formed through secondary forces. A further deduction, with some applied inference, from the results was that a PF resin used to impregnate wood was likely to depress the water sorption isotherm of both wood and cellulose according to the number of substrate sorption sites which, on curing, have been denied to water, a deduction later confirmed experimentally.

The most important result, however, was that there were significant differences in the values of minimum total energy in the interaction of the three PF dimers with cellulose. It was possibly the more important conclusion, because it also had the more immediate industrial application. The *ortho–ortho* and *ortho–para* dimers had much greater average relative E_{tot} of interaction with the cellulose surface than the *para–para* dimer. In general the distribution of the methylene linkage in standard commercial PF resins at that time indicated a higher proportion of the ortho–para and para–para linkage over the *ortho–ortho* linkages. Experimental results confirmed this finding [35]. Maximization of the proportions of *ortho–ortho* and *ortho–para* linkages and decrease of the relative proportion of the *para–para* coupling is easily obtained in PF resin manufacturing by the addition of *ortho*–orientating additives [37–40]. As a consequence, the adhesion and performance improvement caused by a shift in the relative proportions of methylene bridge coupling renders possible the reduction by about 10% of the quantity of PF adhesive resins used in a product such as wood particleboard, at parity of performance. Alternatively, it does improve the performance at parity of quantity: not bad results if one considers that approximately 2 million tons of PF resins are used for wood bonding each year. It is not claimed here that the molecular mechanics result converted the PF resins industry to maximize *ortho*–coupling, but the theoretical justification it offered contributed to greatly accelerating the already existing empirical trend in such a direction. Maximization of *ortho*–coupling in commercial PF resins is now a much more common practice. Further confirmation of this was later obtained by studies of dynamic, differential, and competitive adsorption [9] which will be discussed in the next section of this chapter.

The findings also contributed to the visualization of the conformation of minimum energy of a resin on a substrate: the equivalent of a static, schematic photograph of the conformation of the two molecules at the interface. An example of this is shown in Fig. 2. It also contributed to the understanding, although this came from later work [7], that not only the energy at the interface but also the conformation of minimum energy of a molecule on a substrate was quite different from the conformation of minimum energy of the same molecule when alone, or when on a different substrate. This was confirmed later by x-ray studies determining the degree and/or lack of crystallinity of hardened UF resins in the presence or absence of cellulose [41]. It is also for this reason that idealized models are limited to never being able to complete with "real" models to solve adhesion problems.

Further molecular mechanics investigations in the same direction but for UF resins also followed, with equally interesting results. In these the efficiency of resin adhesion to both amorphous and crystalline celluloses was computed by following the synthesis of the resin. This was achieved by calculating by molecular mechanics the adhesive/adherend interactions with the two types of cellulose for each isomeride produced through the reaction of urea with formaldehyde. This was done up to the level of trimer. The adhesive/adherend interactions were calculated for urea, monomethylene diureas,

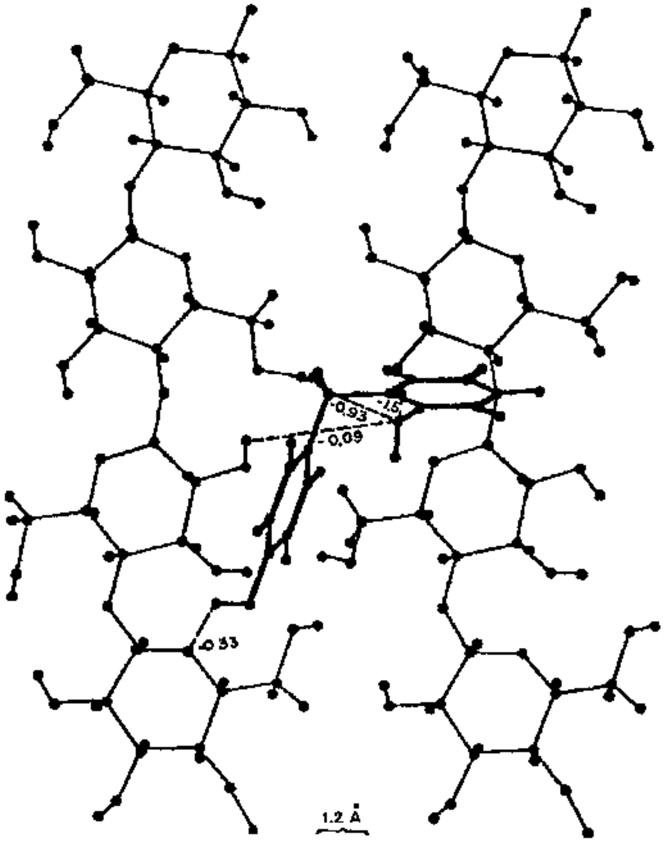


Figure 2 Example of planar projection of one of the configurations of an ortho–para PF dimmer on the surface of a schematic cellulose crystallite showing a phenolic dimmer (a dihydroxy diphenyl methane) conformation of minimal energy and main dimer–cellulose hydrogen bonding. (From Ref. 8.)

and dimethylene triureas, and their mono-methylolated, dimethylolated and trimethylolated species [6,7]. All the results found correspondence in already existing experimental results [42–44]. It was found, for example, that the lack of water- and weather-resistance of lignocellulosic materials bonded with UF resins did not appear to be due, to any large extent, to failure of their adhesion to cellulose. However, contrary to the case of PF resins exposed above, failure in the presence of water of UF resins to adhere to cellulose was also found to be only a minor contributory factor to their lack of water resistance. This confirmed that the lability to water attack of UF resins resided mainly in the hydrolysis of their amidomethylenic bond, a fact since confirmed experimentally. More important is the finding, later confirmed by x-ray diffraction [41], that when UF resins are interacting with cellulose some of the conformations that would be forbidden when the UF resin is cured alone become possible and are allowed. This same experimental study also confirmed that the secondary forces binding together linear chains, not cross-linked, of UF oligomers with cellulose were stronger than the intermolecular forces between the UF oligomers themselves. The molecular mechanics method used allowed the start of the polymerization of UF resins on the surfaces of cellulose be followed. This was achieved

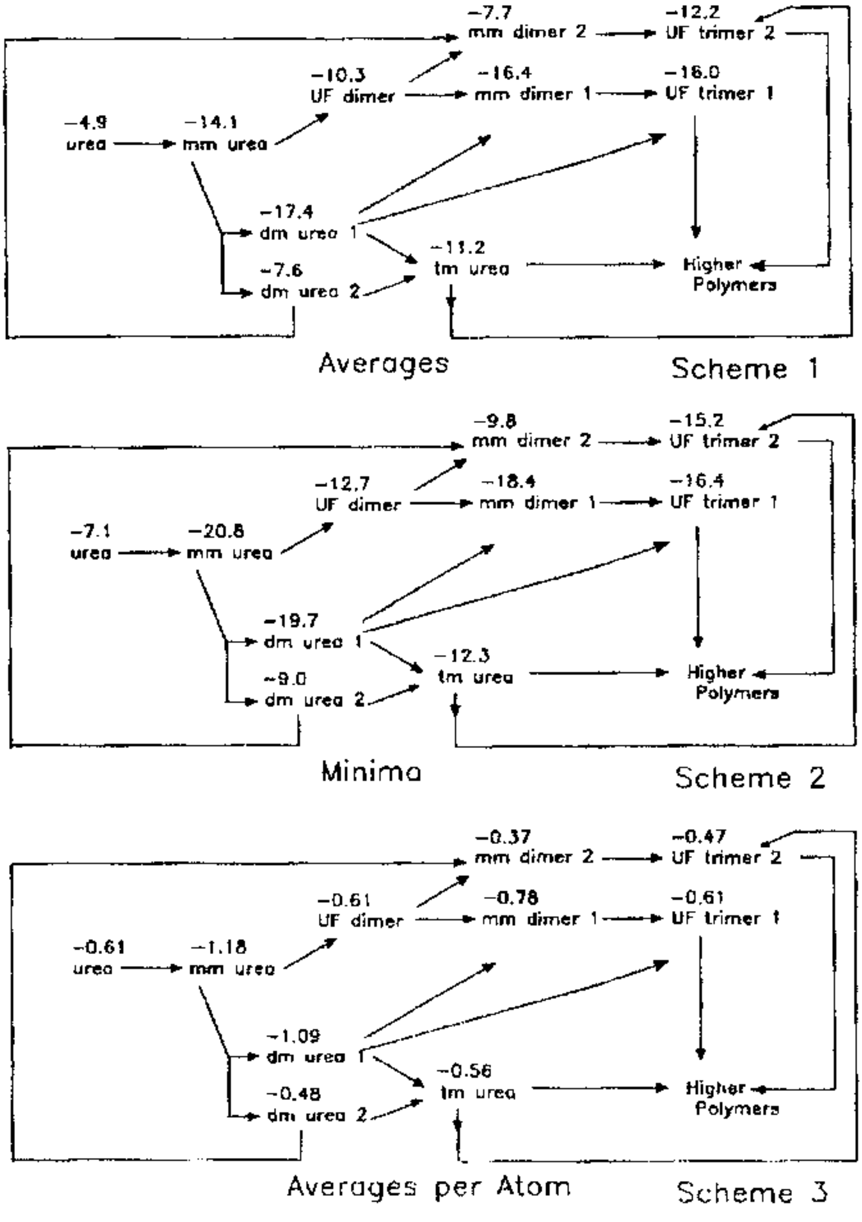


Figure 3 Averages, minima, and averages per atom of the interaction energy of UF oligomers with crystalline cellulose I (in kcal/mol) (negative signs indicate attractive interactions hence adhesion). (From Refs. 6, 7.)

by comparing the different energy levels of the different oligomers as the reaction proceeds from one oligomer to the next one (Fig. 3). The experimental consequence of this study was the development of a method to evaluate comparatively the applied performance of UF resin prepared according to different procedures just starting from the relative abundance of the various UF oligomers in each resin and their molecular mechanics calculated energy of interfacial interaction [6,7,45]. Similar results were also obtained with a more comprehensive investigation of the oligomers of PF resins [10].

It is however, with the more complex and comprehensive investigation of ternary systems that this molecular mechanics approach started to yield results of greater interest on the fundamental principles of adhesion [32]. Ternary systems present two interfaces because they are composed of three molecular species, namely the cellulose substrate, a photopolymerizable primer resin, and a top coat alkyd/polyester varnish [32]. This work was started mainly to address the concept of flexibility of a surface finish system on lignocellulosic materials but led to some unexpected and rewarding results on adhesion too. Examples of the visualization of the conformations of minimum energy of ternary systems are shown in Figs. 4–6.

Three photopolymerizable primer monomers, namely the linear hexanediol diacrylate (HDDA), the branched trimethylol propane triacrylate (TMPTA), and the linear tripropyleneglycol diacrylate (TPGDA), and a model of a linear unsaturated polyester/alkyd varnish repeating unit were used for the study. A model of the two top chains of an elementary cellulose I crystallite was used as a substrate, the refined conformation of which had already been reported [12].

The number of degrees of freedom for such calculations is considerable and particular techniques, already used in previous work [7–10], were used to facilitate the computation. At the end the total varnish/primer/cellulose assembly was allowed to adjust and minimize the energy of its configuration.

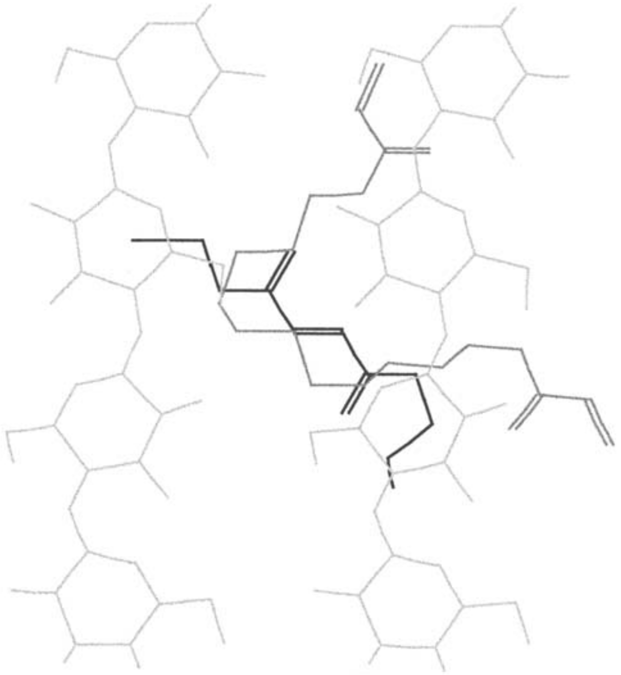


Figure 4 Example of planar projection of the minimal energy configuration of a ternary system composed of a cellulose I schematic elementary crystallite surface, the photopolymerizable acrylic primer tripropyleneglycol diacrylate (TPGDA), and a polyester finish. (From Refs. 72, 73.)

Figure 5 Example of perspective view of the ternary system in Fig. 4. (From Refs. 72, 72.)

Figure 6 Example of view along the cellulose crystallite axis of a ternary system similar to that in Fig. 4 but using a different photopolymerizable acrylic primer, namely trimethylolpropane triacrylate (TMPTA). (From Ref. 73.)

The applied part of this study relied on a standard peel test in which closely set vertical and horizontal cut lines had been incised on the specimen surface, and on a dynamic thermomechanical analysis of finish flexibility at constant temperature [32,33,46].

An equation correlating TMA deflection and interaction energy at the interface was found by its study:

$$E = \frac{-km}{\alpha f} \qquad \text{and conversely} \qquad f = \frac{-km}{\alpha E} \tag{7}$$

where α is the coefficient of branching by reactive sites, equal to both Flory's coefficient of branching for polycondensates [47] and a similar coefficient based on reactive carbons in each monomer for radical polymerization compounds. E is the interaction energy of the molecule of monomer with the substrate, hence the thermodymanic work of adhesion, calculated by molecular mechanics. f is the relative deflection obtained for the system by thermomechanical analysis (TMA), m is the maximum ideal number of internal degrees of freedom of the monomer once it is bound in the network. When m is measured experimentally by TMA it is the number-average number of internal degrees of freedom of the segments between cross-linking nodes. k is a constant. This equation can be used to determine the energy of interfacial interaction starting from a measure of TMA deflection, or vice versa. It is then a useful experimental tool.

The results and effectiveness of Eqs. (7) were checked also for other, quite different polymers, namely the polycondensates of resorcinol–formaldehyde, of melamine–urea–formaldehyde (MUF), of PF, and of quebracho and pine polyflavonoid tannins hardened with formaldehyde. The comparison of the energies of interaction obtained by measures of TMA deflection and the use of this formula compared well with the results already obtained for their energy of adhesion with crystalline cellulose in previous work [16–10]. It appears, then, that the formula works also for entanglement rather than just cross-linked networks.

It was also interesting to relate what was discussed above to existing models relating adhesion strength and adhesion energy. In the rheological model [48–53] the peel adhesion strength G is simply equal to the product of the adhesion energy E and a loss function Φ which corresponds to the energy irreversibly dissipated in viscoelastic or plastic deformations in the bulk materials and at the crack tip and which depends on both peel rate v and temperature T. Thus

$$G = E\Phi(v, T) \tag{8}$$

The value of Φ is usually far higher than that of E and the energy dissipated can then be considered as the major contribution to the adhesion strength G. It is more convenient in the above equation to use the intrinsic fracture energy G_0 of the interface in place of E to have $G = G_0\Phi(v, T)$. When viscoelastic losses are negligible, Φ tends to one and G must tend towards E. However, the resulting threshold value G_0 is generally a few orders of magnitude higher than E. Carre and Schultz [54] have concluded that the value of G_0 can be related to E for cross-linked elastomer/substrate assemblies through the expression

$$G_0 = Eg(M_c) \tag{9}$$

where g is a function of molecular weight M_c between cross-linked nodes and corresponds to molecular dissipation.

This lead to a few interesting considerations as regards the results obtained by molecular mechanics on the primer/cellulose interfaces. From the equation obtained to relate the flexibility at the interface to the interaction energy it is evident that $E \sim m/(\alpha f)$ (the negative sign of E obtained by molecular mechanics is a convention to indicate attraction rather than repulsion). The concept of M_c is intrinsic in the $(m/n)/\alpha$ ratio relating the number of degrees of freedom m per number of atoms n of the segments between cross-linking nodes as determined by α. This means that $g(M_c)$ can be represented by $m(\alpha f)$ and hence

$$G_0 \sim Em/(\alpha f) \qquad \text{thus} \qquad G_0 \sim E^2 \tag{10}$$

This is an important aspect and would at least partly explain in a manner somewhat different from the more accepted explanations why G_0 is generally 100 to 1000 times higher than the thermodynamic work of adhesion [48]. It indicates that $G \sim E\Phi(v, T)\, m(\alpha f)$, or differently expressed $G \sim E^2\Phi(v, T)$. Apart from this the interesting consideration still holds that the flexibility at the interface is inversely proportional to both the intrinsic fracture energy and to the peel adhesion strength at least where the effect of Φ is minimized.

This work also defined that the relation of G_0 to the thermodynamic work of adhesion W_A in tests varied according to the case considered. Thus, the molecular mechanics study showed in general $G_0 \sim W_A^2$ in tests in which viscoelastic dissipation of energy was eliminated or at least strongly minimized. This partly explains why G_0 is generally 100 to 1000 times higher than the thermodynamic work of adhesion [48]. This is not all, because it was shown that G_0 still included a component based on the viscoelastic properties of the material which it might not be possible to separate from G_0, then indeed $G_0 \geq W_A^2$. However, if the viscoelastic component is all transferred as it should be into the viscoelastic energy dispersion function $\Phi(v, T)$, then $G_0 = W_A^2$. It must be noted that it might not be possible to really separate completely the viscoelastic dispersion of energy component from G_0 as it is intrinsic to it. Conversely, it was also shown that the theoretical case in which the viscoelastic component characteristic of the material (not the effect of crack tip propagation within the material) had been minimized or eliminated the expression $G_0 \sim W_A^2$ really meant that $W_A \leq G_0 \ll W_A^2$ rendering acceptable also the alternative findings by other authors that under certain circumstances $G_0 \sim W_A$.

All the above, and the fact that by definition the molecular mechanics interaction energy is proportional to the thermodynamic work of adhesion, hence $kE_{\text{tot}} = W_A$, also brings the interesting consideration that

$$kE_{\text{tot}} \leq G_0 \leq kE_{\text{tot}}^2 \quad \text{where} \quad E_{\text{tot}} = k[E_{\text{vdW}} + E_{\text{H-bond}} + E_{\text{ele}} + E_{\text{tor}}]^2 \tag{11}$$

where the molecular mass M_c of Eq. (9) is represented by the combination of a number of parameters involved in Eq. (11). M_c is represented by the molecular degrees of freedom; the type of atoms involved; the coefficient of molecular branching/cross-linking; the atoms polarizability; the angle and direction of the interactions; the electrostatic charges; the number of effective electrons participating; and the dipolar momenta. The mass is then a parameter used, incorrectly, only as a simplified blanket parameter covering all this. Furthermore, to be conceptually correct even symmetrical and asymmetrical bond/angles stretching movements, and molecular translational movements, even if their contribution is quite small, should be considered.

All the calculations which have reported up to now were carried out by maintaining unaltered the structure of the elementary cellulose I crystallite in its conformation of minimum energy derived from x-ray diffraction data [55–60] refined and minimized in its atomic coordinates and charges [12,61–65]. The blocking of the cellulose crystallite surface in a fixed, predetermined conformation of minimum energy is a very acceptable assumption given the energetic stability of the crystallite itself. However, it is also of interest to investigate what influence the application of a primer or of a finish can have on the surface conformation of a cellulose crystallite as predicted by a molecular mechanics method. As the calculations involved are considerable, a simpler algorithm was used [66] for the calculations. Thus, the conformation variation of a system composed of the primer and of the finish superimposed on two parallel chains of the elementary crystallite of cellulose I was followed. All the component molecules were allowed to move. At the start the two cellulose chains were in their configurations of minimum energy already calculated. The results obtained were of two types:

(i) the stabilization obtained in terms of total energy of the system indicated that the longer was the segment which relied on secondary forces of adhesion to the cellulose surface the better was the stablization of the system by secondary forces: logically this result should have been expected
(ii) the conformation of the two chains of the cellulose changed, but what was unexpected was that it changed to the conformation of the crystallite of cellulose II [61], i.e. a different, more stable crystalline morphology!

This latter is an interesting result which infers that treatment of a lignocellulosic surface with a surface finish or other polymers might well alter irreversibly the conformation of the structure of some of the wood constituents. It implies that to discuss adhesion in terms of modification of the conformation of only the applied polymer without taking into account the variations induced in the substrate itself by the applied polymer might give only a very partial view of the process of adhesion at the molecular level. Previous, generalized but still very acceptable models [22] in which the substrate is taken as a homogeneous surface of hard or soft spheres can describe very well the cases in which the substrate is constrained in such a way that it cannot modify its configuration. However, these models cannot explain well the cases in which the substrate molecule changes its configuration as a consequence of the interactions exercised on it by another polymer species, at the interface: a far reaching conclusion. Notwithstanding this, the situation for crystalline cellulose I was found to be only partially one of these cases, due to the special limits and constraints to which such a rigid structure is subjected in its natural state.

It is also evident from the above that in the case of the primer substrate systems in which the primer is highly cross-linked and the cellulose crystallite is a highly crystalline solid no diffusion mechanisms at the molecular interface are likely. The situation might well be different when one deals with a molecular interface were reorganization of the substrate as a consequence of the interfacial interaction forces induced by the finish is indeed possible (see above). This is the case of a primer monomer, or even a primer of a low degree of polymerization or cross-linking, on amorphous cellulose or even on a sub elementary cellulose crystallites area. In this case the reported inverse dependence of the peel energy G of the system on, among others, the inverse of the molecular mass $(1/M)^{2/3}$ applies [48,167]. It appears again to be confirmed by the dependence on m and α, two parameters clearly linked to the molecular mass of the finish monomer, of the surface finish and of the segments between cross-linking nodes of the network when this exists. That m, n, and α are the key parameters representing the molecular mass is confirmed by the known dependence of peel strength on a 2/3 exponent of the molecular mass [48,67]. This clearly points out the constraints of rotational degrees of freedom (and rotational energy barriers) found for monomers the end atoms of which are constrained [32]. Furthermore, the apparent proportionality of the diffusion coefficient of the movement of reptation to M^{-2} [48,68–70] appears to be confirmed by the direct proportionality of the interfacial flexibility to the number of degrees of freedom m of the system. The more flexible is the system, hence the greater is the number of its degrees of freedom per unit mass (or per atom) the easier is interdiffusion. This shows again that it is not the molecular mass of the chemical species as such which will determine either the coefficient of diffusion or the relaxation time of reptation, but these two latter undoubted relation to the flexibility of the system which depends on the parameters m, n, α, and E, and especially the per atom values m/n and E/n.

V. DYNAMIC ADHESION MODELING OF MOLECULARLY WELL-DEFINED SYSTEMS

The molecular mechanics approach just described functions well, but the manner in which it has been used in the previous section is rather limited to static situations: dynamic situations can also be described well, although by a series of finite steps of ‘‘before and after’’ static calculations to ascertain the changes which have occurred or while they are occurring. Even the most modern molecular mechanics and dynamics programs still work in this manner. It might appear otherwise to a user, but every automatic molecular mechanics or dynamics computational program still works by a sum of small static situation steps, even if infinitesimally small. There is nothing wrong in such an approach of course, as it has been proven to work rather well even in the most complex situations. However, it is interesting to examine how such an approach works for systems in which movement at the molecular rather than atomic level is inherent in the definition of the system itself.

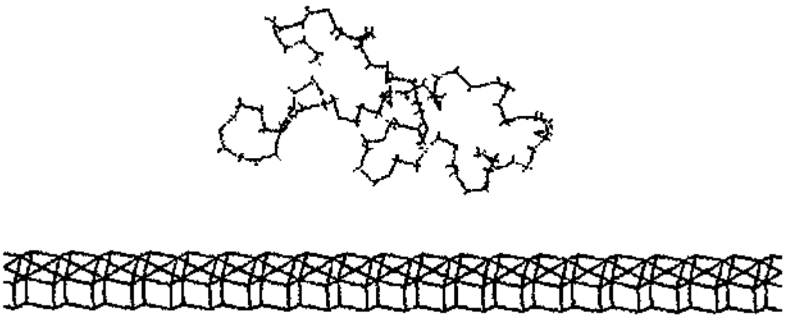
As regards adhesives proper only two series of studies fall in this category [9,71]. The first one of these models the process of chromatography [9]. There is no doubt that chromatography is a clear case of differential, competitive sorption, and hence a case of differential, competitive adhesion. Movement is inherent in the definition of the system, and predominance of secondary force interfacial interactions is inherent to the system too.

The study [9] concerns the achiral paper chromatography separation of three dihydroxydiphenylmethanes (the three PF resin adhesive dimers discussed earlier in this chapter) on crystalline cellulose, and checks whether the results, the relative R_f values obtained by experimental chromatography, correspond to the interaction energies calculated at the interface. The algorithms used were the same as used for the previous approach. The results obtained were excellent, showing not just a trend correspondence between experimental R_f values and calculated energy values but even very close numerical correspondence with the actual relative values of R_f for the three compounds. One of the most interesting findings was that in the case of the interaction with a substrate of a homologous series of chemical compounds, the solvent or mixture of solvents could be easily modeled by just varying the dielectric constant used in the model. Such a result is of importance because it spares in many ternary systems the need to model the third component of the system, namely the solvent or the water present either in the polymer or in the substrate (such as in wood and cellulose).

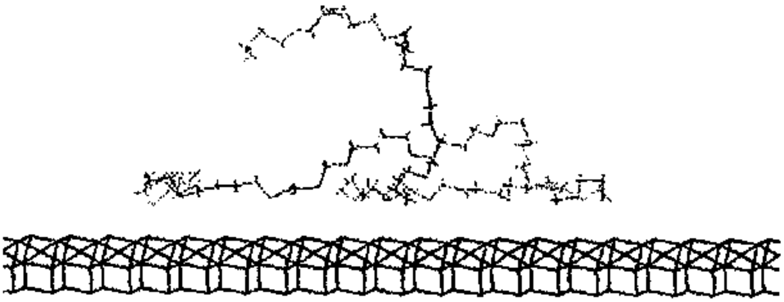
The work was continued on the paper chromatography modeling of UF oligomers [72]. In this series of experiments the limits of the molecular mechanics approach finally started to become apparent. While a good trend correspondence with experimental R_f values was again obtained within each of the two series of UF oligomers tested, correspondence was lost when one tried to compare the compounds within a series with the compounds of the other series. Thus, excellent correspondence existed within the homologous series urea, methylene-bis-urea and dimethylene-triurea, and within the second homologous series monomethylol urea, N,N′-dimethylol urea, trimethylol urea, monomethylol methylene-bis-urea, and N,N′-dimethylol methylene-bis-urea, but not between the two series. It became evident that to compare within two nonhomologous series of compounds it would be necessary to model the water in the system as a third group. Thus, the conclusion was that the wise use of the dielectric constant to spare modeling a ternary system was very valid, but only when the molecules to be compared belonged to a homologous series of compounds; If they were not, one needed to model the solvent too as a separate species [72]. There is no doubt that this can be achieved, either by a classical molecular mechanics method, or even better by modeling the solvent through a molecular dynamics approach in which a solvent layer is modeled as in Section III for the generalized system while the substrate and the polymer are still modeled by more classical molecular mechanics approaches. The study of the chromatography of UF adhesives on cellulose did not have such an industrial importance to warrant such an extensive, further investigation. Thus, the next investigation centered instead on the more difficult ternary systems but for a totally different set of molecules: this is the work on varnish/primer/cellulose systems reported earlier in this chapter.

The second study [71] is even more interesting and concerns the simulation of different polymers adsorbed onto an alumina surface. The alumina surface was modelled and a number of different polymers were modeled at the polymer–alumina interface. Among the adhesives modeled on the surface of alumina were polyolefins, several polyacrylates, polyoxides, polyols, and the polyphenyl bridges in epoxy resins, in diaminodiphenylsulfones and in diaminodiphenylmethanes (the same PF dimers modeled above on the surface of cellulose). The authors found that the method not only facilitated visualization of the preferred orientation of the adhesive chains with respect to the substrate surface (Figs. 7 and 8), but also indicated which groups were critical in determining such orientations. Their results again confirmed what was found in all previous studies that even in such a different series of adhesive/substrate systems the polymer structure which deformed easily was favorable to a more optimal orientation for adsorption on the substrate surface. The authors could identify which $-CH_2-$ groups and phenylenes in the backbone of the polymer were conductive to such deformations, and that the alkyl side groups found it more difficult to yield optimal deformation during the adsorption process, but were still able to produce strong adhesion once they had been adsorbed. Besides, the polyphenyl linkages revealed a wide low energy region in the rotations of torsional angles, this being favorable to deformation of the polymer chains with phenylene linkages in the backbone leading to large adsorption energies. Polar side groups instead were found to increase adsorption, confirming previous results, and in line with expectation. While the range of energy results reported was quite limited, as one could understand by the number of different cases approached, the study can be considered more as a purely comparative scan of the behavior of certain adhesives on an alumina surface rather than an in-depth investigation of the behavior of each adhesive/substrate system. Notwithstanding this, the calculated results once again could be qualitatively correlated with experimental observation, and the order of the energy interactions was shown to be the same. These results showed again how simulations by molecular mechanics/dynamics could potentially by used to facilitate the design of improved adhesives.

(a) 0 ps



(b) 0 ps (minimize)



(c) 10 ps (minimize)

(d) 20 ps (minimize)

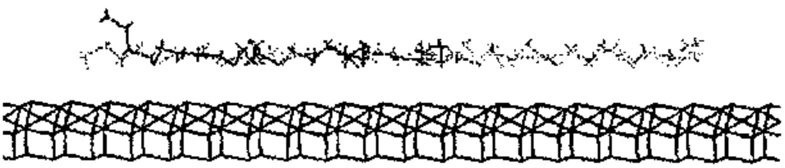


Figure 7 Simulation of the adsorption of poly(tetrahydrofuran) (PTHF) on an alumina surface for 20 ps. (From Ref. 71.)

VI. CONCLUSION

The material discussed in this chapter should give the reader a brief overview of what has already been achieved in the field of molecular mechanics to improve adhesion or to explain adhesion phenomena. More will surely be achieved in times to come by the application of such tools to adhesion problems. Molecular mechanics and dynamics then present a powerful tool which should not be ignored in the field of adhesion and adhesives.

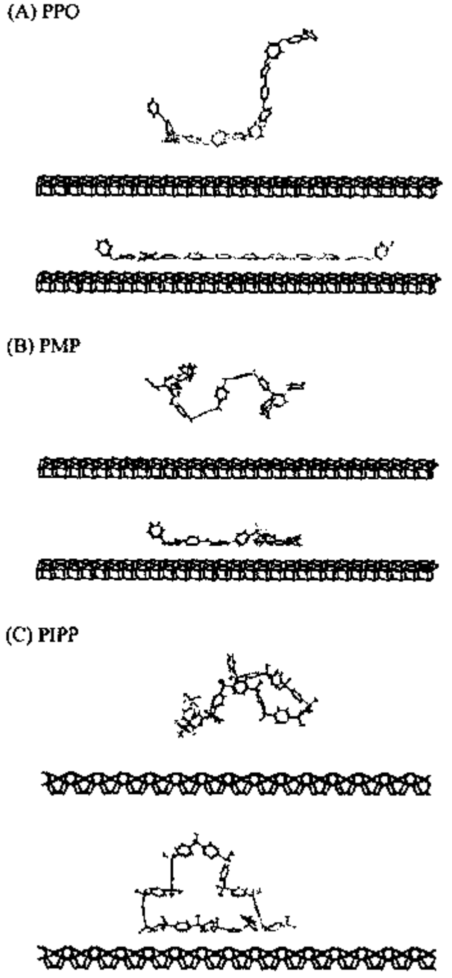


Figure 8 Simulated adsorption by molecular dynamics of (A) poly (*p*-phenylene) oxide (PRO), (B) poly(methyl-1,4-phenylene) (PMP) and (C) poly(iso-propyl-1,4-phenylene) (PIPP) on an alumina surface showing substantial structural changes during the adsorption process (upper figure: initial conformation; lower figure: = adsorbed conformation) (From Ref. 71.) Note the formation or absence of adsorption loops in the polymer chains for the different cases.

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8

Principles of Polymer Networking and Gel Theory in Thermosetting Adhesive Formulations

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I. INTRODUCTION

The study of adhesion and adhesives involves many scientific approaches and in particular many different scientific disciplines. From physics to applied engineering, from surface science to chemistry, be it analytical, organic, or physical, all have, and would have a contribution to make to the fields of adhesives and adhesion. Polymer science is, among others, one of the important ways to approach several fields of the science of adhesives. However, while polymer physics and perhaps the physical chemistry of polymers are extensively used in this field, not much work is found that reports the use of the principles of polymer chemistry and, in particular, of polymer networking and gelation theory in the applied formulation of adhesives, i.e. on how adhesives are made to achieve particular effects. While in many other fields this branch of science is used extensively, in adhesive formulation a variety of factors have contributed to the lack of its extensive use. The main cause of this is the relative unwillingness of this industry to abandon empirical research, this being an approach often successful in solving some applied adhesive problems. Notwithstanding this, important applicable results can be rapidly achieved from polymer gel theory if this science is properly applied to adhesive formulation, and these results are obtainable much more readily and with much less effort than by empirical research.

So, in this chapter the interest and importance of the polymer gel theory approach to the formulation of adhesives will be briefly shown and, in particular, we will limit this to thermosetting wood adhesives obtained by polycondensation such as phenol–formaldehyde-, urea–formaldehyde-, melamine–formaldehyde- and resorcinol–formaldehyde-based adhesives. The same approach is, however, very valid for other polycondensation resins, and also for adhesives obtained by routes other than polycondensation.

II. SOME PRINCIPLES OF POLYMER NETWORKING AND GEL THEORY OF IMPORTANCE TO THERMOSETTING ADHESIVES

Several theories and methods defining and modeling the formation of polymer networks exist [1–3]. The most useful of such theories, purely from an applied everyday use, are often the simpler and older ones [4,5]. More complex theories, although often excellent at describing to a much greater and thorough extent the molecular reality of gelation, suffer also from being rather difficult to use and unyielding for everyday practice. Thus, they often remain rather unapprochable to those who could benefit most from their application for the easy resolution of applied problems.

Many such theories concentrate on the determination, by different mathematical approaches and different physicochemical approximations, of the degree of conversion and hence of the advancement of polymerization at the point of gel formation and on the calculation of basic polymer parameters derived from the determination of the gel point. Two main approaches are used: statistical methods and kinetic methods. Combinations of the two have also been presented [1].

A. Statistical Methods

These methods generate structures by random combinations of reacting functional groups. This approach is thorough and the results are good when dealing with equilibrium-controlled reactions. The results are often a good approximation in kinetic-controlled reactions. Most of the formaldehyde-based polycondensations are equilibrium-controlled reactions, this being particularly true for urea–formaldehyde, melamine–urea–formaldehyde, phenol–formaldehyde and phenol–resorcinol–formaldehyde adhesive resins. Statistical methods are then ideal to describe these adhesive systems at the moment of gel formation and during formation of the hardened network.

Among the statistical method dealing with polymer networking and gelation in the field of polycondensation must be considered:

(1) The gel theory of Carothers [4] in which the critical degree of conversion at the gel point (p_{gel}) is defined as $p_{\mathrm{gel}} = 2/f$, with f being the average functionality of the monomers in the system.

(2) The probabilistic gel theory of Flory [5]–Stockmayer [6,7] in which p_{gel} is defined through the coefficient of branching $\alpha = 1/(f-1)$. In this theory f is taken as the functionality of the monomer of greater functionality. The main expression of this theory is the equation $\alpha = rp^2\rho/[1 - rp^2(1-\rho)]$ where p is both the degree of conversion and the probability that a certain reactive group type has in fact reacted, ρ is the proportion of such a reactive group type belonging to branching units, and r is the ratio of the types of reactive groups of the two monomers participating in the polycondensation.

(3) The cascade process theory of Gordon [8,9] based on more complex functions than the two preceding ones but also offering some further advantages over them.

(4) The Miller–Macosko [10] recursive method.

(5) The stochastic graphes theory of Bruneau [11] which is a more complete theory but very complex and complicated to use.

Even more complex theories can be found in the review literature [2,3]. Of the above theories the first two are of such a simplicity to be constantly used and the third and fourth ones are also used sometimes. They all suffer from some drawback: the Carothers theory, for instance, overestimates the numerical value of p_{gel} while Flory's theory underestimates it, but they are nonetheless extremely useful in solving applied problems. Furthermore, they do not describe what happens in the system between reaching the gel point and complete hardening of the network.

Percolation is another technique that is also used for structure growth simulation. Percolation techniques are only statistical methods of a slightly differently nuanced approach, and they appear not to be very suitable general methods to correlate structure and structure growth parameters but seem to be useful in examining structure growth near the gel point.

B. Kinetic Methods

Kinetic or coagulation theories develop all chemical species by the use of an infinite set of kinetic differential equations [1]. The resulting chemical species distribution can be obtained analytically only in the simplest case of random reactions; in some other cases distributions can be obtained numerically; and lastly the solution of the set of equations can also be obtained by Monte Carlo simulation methods. The application of kinetic methods has severe disadvantages: the gel is considered as one giant molecule, and hence cannot generate parts of the structures which are characteristic of the gel; and the equations and methods used are long, unyielding, and not very handy or practical to use. Combination of statistical and kinetic theories in some rare cases solves the problems inherent to the kinetic approach alone. Combination of statistical and kinetic theories also results in systems even more complex and unyielding that kinetic theory treatments alone. This field is not a very successful one. However, it is also in this field that the trend to ever more unwieldy mathematical treatment systems has led to approaches bordering on meaninglessness [12–14]. These are exercises removed from reality [12–14]. These have been developed for many years by groups [12–14] which have not understood that the aim of theories in this field is not to render more difficult but rather to solve everyday applied problems. Not only it is inconvenient to carry around equations half a page or longer as advocated by these groups, but their results cannot be believed either. Thus, these unwieldy methods are not worth further mention here.

C. Simple Statistical Gel Theories

The branching coefficient as defined by Flory is $\alpha =$ the probability that a certain branched unit will be joined to a second branched unit rather than to a terminal group. For example, for a trifunctional monomer if $\alpha = 1/2$ the molecule is a continuous chain equivalent in theory to a gel. In this case $\alpha = 1/2$ is the critical condition defining the start of the formation of an infinite tridimensional network.

When the monomer has functionality greater than or equal to 3 the system will gel when $\alpha(f-1) > 1$. The critical value of α is then

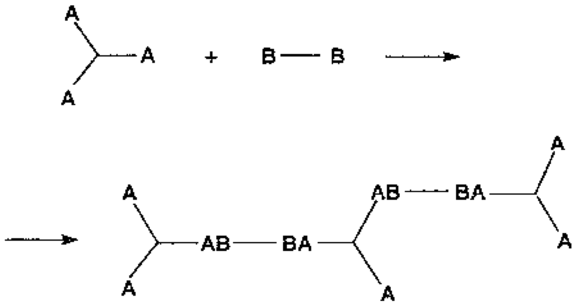
$$\alpha = \frac{1}{f-1} \tag{1}$$

where in Flory's statistical gel theory α is = the functionality of the monomer of higher functionality when there are only two monomers taking part in the polycondensation reaction. So if $f=3$ then $\alpha=0.5$. If $f=4$ then $\alpha=0.33$, etc. When $\alpha=0$ there is no reaction and when $\alpha \geq 1$ the system never gels. The gel point of a thermosetting resin, hence of an adhesive based on a thermosetting resin, depends on

1. the functionality of the monomers
2. the degree of conversion reached by the reaction
3. the ratio of the two monomers, or more exactly of the reactive sites/groups of the two monomers.

1. *Case 1: Case of Reaction of a Trifunctional Monomer with a Bifunctional Monomer*

In the polycondensation of a trifunctional monomer with a bifunctional monomer



the limiting condition to gelling is then that a bifunctional B–B monomer must be linked to two branched monomers, hence bound to two trifunctional monomers. Thus, if the proportion of B–B is limited, the extent of branching is also limited. The limiting condition to start branching, hence for the start of gelling, depends on the probability that segments –AB–BA– do indeed exist. In the theory all groups are considered as they cannot react with groups of the same kind (thus A can only react with B) and all groups have the same reactivity: the probability that the first group A (the one on the left) has then reacted with a group B is p_A, namely the fraction of all the groups A which have reacted. The probability that the second group B (the one on the right) has reacted with a group A is then p_B. The probability then that the segment –AB–BA– occurs is

$$p_A\, p_B$$

therefore

$$\alpha = p_A\, p_B \tag{2}$$

which is the probability of a joint between two branching sites. As the functionality of the monomer of higher functionality in this example has been taken as $f = 3$ then $\alpha = 0.5$. this means that at the gel point

$$(p_A\, p_B)_{\text{gel}} = \alpha \tag{3}$$

As the initial concentrations of reactive groups A and B are considered here to be the same, then $p_A = p_B = p$ and hence

$$p^2_{\text{gel}} = \alpha \qquad \text{and} \qquad p_{\text{gel}} = \alpha^{1/2} \tag{4}$$

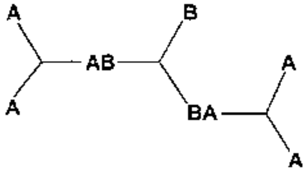
Which gives

$$p_{\text{gel}} = 0.707 \tag{5}$$

Where p_{gel} is the degree of conversion at the gel point which means that 70.7% of the reactive groups/sites of the system have reacted at the gel point.

2. *Case 2: Case of Two Trifunctional Monomers*

The polycondensation of two trifunctional monomers



In this case it is necessary that an –AB– joined segment exists between branching sites. This is equivalent to saying that

$$\alpha = p_A \quad \text{or} \quad p_B \quad \text{(depending which one is less)} \tag{6}$$

when A and B are at the same initial concentration. Thus, $p_A = p_B = p$, and the limiting condition for a gel to form will be

$$\alpha = p \tag{7}$$

Because here too $f = 3$ and $\alpha = 0.5$, the limiting condition for a gel to form will then be

$$p_{\text{gel}} = 0.5 \tag{8}$$

Where p_{gel} is the degree of conversion at the gel point which means that 50% of all the reactive groups/sites of the system have reacted at the gel point.

These two cases are valid also for monomers of higher functionality with the provision that higher functionality means a different value of f, hence a different value of α. Thus, in the case of polycondensations based only on two monomers there are only two possible cases to consider, one in which a bifunctional monomer is also present, and the other in which only monomers of functionality greater than or equal to 3 are present in the reaction medium. To take into account the cases in which the reactive sites of the two molecules are not equimolar one can define a ratio r as the ratio of the number of reactive sites A and B, with the proviso that r must always be smaller than or equal to 1 (so, if $A > B$ $r = B/A$ and vice versa if $A < B$ $r = A/B$; If r is greater than 1, absurd results are obtained and the theory cannot be used) [15]. The simpler form of the equations defined by Flory to describe the two cases above are then

$$p_{\text{gel}} = \left(\frac{\alpha}{r}\right)^{1/2} \qquad \text{with} \qquad r = \frac{N_A}{N_B}$$

and

$$p_{\text{gel}} = \frac{\alpha}{r} \tag{9}$$

These equations are in their simplest usable form. The original equations of Flory took into account also the density of the hardened polymer. It has been disregarded here as it is of no consequence in the formulation of thermosetting adhesives discussed later.

3. *Case 3: Case of Many Mono-, Bi-, Tri-, and Multifunctional Monomers*

The equations described in the previous two cases are not applicable to polycondensation systems in which either monofunctional monomers are present or a great number of branching monomers of a number of different functionalities of both type A and B are present. If one considers the most general case of a polycondensation system as

$$\mathrm{A} + \mathrm{A}_2 + \mathrm{A}_3 + \cdots + \mathrm{A}_i + \mathrm{B} + \mathrm{B}_2 + \mathrm{B}_3 + \cdots \mathrm{B}_j \rightarrow \text{polymer network}$$

in which are present: (1) monomers the functionality of which is between 1 and i for the reactive groups A, and (2) monomers the functionality of which is between 1 and j for the reactive groups B, the degree of conversion and advancement of the polycondensation reaction at the gel point is given by the following equation [15–17]:

$$p_{\mathrm{gel}} = \frac{1}{[r(f_{\mathrm{A}} - 1)(f_{\mathrm{B}} - 1)]^{1/2}} \tag{10}$$

where f_{A} and f_{B} are the weighted average functionalities of the reactive molecules A and B respectively, and where r is the same as above and represents the difference in stochiometric proportions of the reactive sites. f_{A} and f_{B} are defined as

$$f_{\mathrm{A}} = \frac{\Sigma f_{\mathrm{A}i}^2 N_{\mathrm{A}i}}{\Sigma f_{\mathrm{A}i} N_{\mathrm{A}i}} \qquad \text{and} \qquad f_{\mathrm{B}} = \frac{\Sigma f_{\mathrm{B}j}^2 N_{\mathrm{B}j}}{\Sigma f_{\mathrm{B}j} N_{\mathrm{B}j}} \tag{11}$$

where $N_{\mathrm{A}i}$ are the number of moles of Ai containing $f_{\mathrm{A}i}$ functional groups for each A-type molecule. The use of these equations is better shown by an example. Thus, for the following complex system of reagents

4 mol A	2 mol B
51 mol A_2	50 mol B_2
2 mol A_3	3 mol B_3
3 mol A_4	3 mol B_5

$$r = \frac{1(4) + 2(51) + 3(2) + 4(3)}{1(2) + 2(50) + 3(3) + 5(3)} = 0.9841$$

$$f_{\mathrm{A}} = \frac{[1^2(4) + 2^2(51) + 3^2(2) + 4^2(3)]}{[1(4) + 2(51) + 3(2) + 4(3)]} = 2.2097$$

$$f_{\mathrm{B}} = \frac{[1^2(2) + 2^2(50) + 3^2(3) + 5^2(3)]}{[1(2) + 2(50) + 3(3) + 5(3)]} = 2.4127$$

$$p_{\mathrm{gel}} = \frac{1}{[0.9841(1.2097)(1.4127)]^{1/2}} = 0.7711$$

This indicates that in such a complex polycondensation system gelling occurs when 77.11% of the reagents have in fact reacted. Equation (10) is then particularly useful when using Flory's statistical theory of gelation. Owing to its simplicity and ease of use, Flory's theory of gelation is the most useful theory to use for the formulation of thermosetting polycondensation adhesives. Flory's theory presents, however, a problem: it underestimates the degree of conversion at the gel point by around 10%. This means that an experimental value of $p_{\mathrm{gel}} = 0.770$ corresponds to a calculated value of $p_{\mathrm{gel}}(\text{Flory}) = 0.700$–$0.710$. This is due to not being able to take into consideration cyclization reactions, a fact established by Stockmayer, so this theory is often known today as the Flory–Stockmayer gelation theory.

Other theories, however, do exist, but the majority of these were published well after Flory's. These theories became increasingly complex and notwithstanding that they allowed perhaps a somewhat better precision in the determination of p_{gel}, the equations derived from them are so complex that in practice they are never used. This unnecessary complexity trend has gotten out of hand in certain cases to the level of a purely mathematical exercise rather removed from reality [12–14].

However, a second theory, older than Flory's, does indeed exist. This is the theory of Carothers. According to Carothers

$$\overline{\text{DP}}_n = \frac{2}{2 - \bar{f}p} \tag{12}$$

where $\overline{\text{DP}}_n$ is the number-average degree of polymerization and $\bar{f}$ is the average functionality of the system (a concept different from that of Flory's) which is equal to

$$f = \frac{[N_A f_A + N_B f_B]}{[N_A + N_B]} \tag{13}$$

where N_A and N_B are the numbers of moles of monomers A and B, and f_A and f_B are the functionalities, respectively, of monomers A and B. The degree of conversion in this theory is defined by the equation of Carothers

$$p = \left(\frac{2}{f}\right)\left[1 - \left(\frac{1}{\text{DP}_n}\right)\right] \tag{14}$$

Because DP_n becomes very large at the gel point as p tends to $2/f$, the critical condition for gelling is defined in the Carothers equation as

$$p_{\text{gel}} = \left(\frac{2}{f}\right) \tag{15}$$

While the theory of Flory underestimates the gel point, the theory of Carothers overestimates it. For example, for the case of a trifunctional and bifunctional reaction system presented above, at equimolar reactive groups, while Flory's theory forecasts $p_{\text{gel}} = 0.707$, Carothers theory forecasts a value of $p_{\text{gel}} = 0.833$, while the experimental p_{gel} is 0.765–0.775. Recently, however [18,19], thermodynamic reasons why the two formulas should be combined came to light. This led to the proposal of a very simple equation affording much higher precision than each theory alone. This simple equation also gave much better precision of all the very complex and difficult to use theories devised and presented since Flory's 1942 one:

$$p_{\text{gel}} = \frac{(2/\bar{f}) + (\alpha/r)^{1/2}}{2}$$

or

$$p_{\text{gel}} = \frac{1}{\bar{f}} + \frac{1}{2}\left(\frac{\alpha}{r}\right)^{1/2} \tag{16}$$

This equation is nothing other than the average of the equations of Carothers and Flory, and for instance yields a $p_{\text{gel}} = 0.770$, while the most exact of the complex theories yields a $p_{\text{gel}} = 0.800$ [18,19] for the simple case just shown above. The 1/2 operator is not there (but α/r is) in the case where no bifunctional monomer is present. This is valid also for the generalized Eqs. (17) and (18) which follow and which have been developed from Eq. (16) above. For two monomers, Eq. (16) can be developed to eliminate the presence in the equation of two different ways of expressing functionality [Carothers' average functionality of the system in the same equation in which appears (hiding in α) Flory's functionality]. Equation (16) can then be expressed in the same functionality, so as to eliminate such a discrepancy.

$$p_{\mathrm{gel}} = \frac{n_{\mathrm{A}} + n_{\mathrm{B}}}{f_{\mathrm{A}} n_{\mathrm{A}} + f_{\mathrm{B}} n_{\mathrm{B}}} + \frac{1}{2}\left(\frac{f_{\mathrm{B}} n_{\mathrm{B}}}{f_{\mathrm{A}} n_{\mathrm{A}}(f_{\mathrm{A}} - 1)}\right)^{1/2} \tag{17}$$

In the case of a system of more than two monomers where each monomer can react with the other but not with itself the general formula becomes

$$p_{\mathrm{gel}} = \frac{\Sigma n_x}{\Sigma n_x f_x} + \frac{1}{2}\left(\frac{\alpha}{\Sigma r_x + \Sigma r_{xy}}\right)^{1/2} \tag{18}$$

In the most common case in thermosetting polycondensation adhesives, namely a reaction system composed of three monomers in which two can both react with the third one but where the former two cannot react with each other (and no monomer can react with itself), the equation for higher precision determination of the degree of conversion at the gel point becomes

$$p_{\mathrm{gel}} = \frac{\Sigma f_x n_x}{\Sigma n_x} + \left(\frac{\alpha}{\Sigma r_x}\right)^{1/2} \tag{19}$$

It is easy to see from these equations that these higher precision equations become rapidly more difficult to use and to handle as the polycondensation system becomes more complex. Thus, Eq. (16) for two-reagent systems is used very easily, and Eq. (19) for three-reagent systems is still relatively easy to use, but for more complex systems Eq. (10) [15–17] is easier to use notwithstanding the 10% lower value it gives.

III. EXAMPLES OF APPLICATIONS TO THERMOSETTING WOOD ADHESIVES

A. Formulation of Phenol–Resorcinol–Formaldehyde Cold-Set Adhesives

Resorcinol-based adhesives are used extensively to bond structural grade, exterior laminated beams for building construction (see Chap. 29 on Resorcinol Adhesives). The cold-setting adhesives which dominate this field are based on phenol–resorcinol–formaldehyde (PRF) resins. The adhesive itself is composed of the PRF resin and a hardener that includes formaldehyde, often in the form of paraformaldehyde mixed with inert fillers. The performance of the resin is resorcinol dependent. The cost of the resin is also resorcinol dependent as this is a very expensive chemical produced industrially in only three locations in the world. The research work on these resins from their inception has then been based on the optimization of their bonding performance coupled with the decrease in the relative percentages of resorcinol used. It has the been a long and successful work of empirical research and development which still continues.

It is, however, simpler to calculate from basic principles of polycondensation gel theory, hence using polymer chemistry, the relative amount of resorcinol which needs to be used in the preparation of a certain PRF resin to optimize its performance. As a simplified real example of the approach, let us propose the following problem.

Let us assume that we have prepared a linear phenol–formaldehyde (PF) resol resin of number average degree of polymerization $\overline{DP_n} = 2$ and average content of hydroxybenzyl alcohol (methylol) –CH_2OH groups of 2. If one wants to prepare a PRF cold-set adhesive for wood laminated beams or fingerjointing, how can one determine the minimum quantity of expensive resorcinol which is needed to make sure that the addition does not gel the resin? Such a problem in short asks what is the minimum amount of resorcinol one needs to have a good performance resin which does not gel on resorcinol addition to the reaction. A resin that is taken as hardening only on addition of further formaldehyde hardener, but only in the glue mix.

According to Eqs. (1)–(4) to assure that the resin system does not gel on addition of resorcinol one imposes the limiting condition

$$p_{\text{gel}}(\text{experimental}) \geq 1 \tag{20}$$

As Flory's version of the polycondensation gel theory, which we will use for this problem, underestimates by approximately 10% the degree of conversion p at the gel point this means that the limiting condition expressed by Eq. (20) can be written using Flory's theory as

$$p_{\text{gel}}(\text{Flory's}) \geq 0.9 \tag{21}$$

As the functionality of resorcinol is 3 (three potential reactive sites) and of the PF resol resin is 2 (namely two reactive –CH_2OH groups) this means that Flory's branching coefficient $\alpha = 1/(f-1) = 1\,(3-1) = 0.5$, and because from Eq. (9) $p_{\text{gel}}^2 = \alpha/r$ one can write numerically the limiting condition defined by the problem as:

$$(0.9)^2 = \frac{0.5}{r} \tag{22}$$

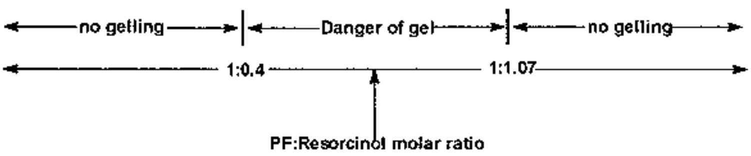
one obtains from this a value of $r = 0.617$. Consequently, because 1 mol PF = 2 mol –CH_2OH and 1 mol resorcinol = 3 mol reactive sites:

$$\left(\frac{2}{3}\right)x = r \tag{23}$$

hence $(2/3)x = 0.617$ and the unknown variable $x = 0.93$. This means then that 0.93 moles of PF are needed for each mole of resorcinol, which is the equivalent to saying that the PF: resorcinol molar ratio $\geq$ 1:1.07 is needed.

However, $(3/2)x = r = 0.617$ is an equally valid situation (as r is still maintained lower than 1). Solving this equation one obtains $x = 0.411$. This means that there will be no gelling of the resin system when adding less than 0.411 mol resorcinol to each mol PF resin, thus when the PF:resorcinol molar ratio is ≤ 0.411.

This means then

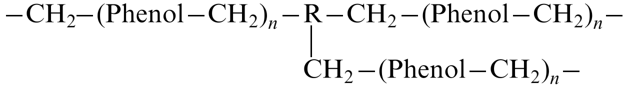


It is then easy to determine by polymer chemistry calculations what should be the most adequate amount of resorcinol which needs to be added to a PF resin to obtain a

PRF. Three types of back-checks are, however, needed, namely:

(i) To check mathematically that the assumption that has been imposed at the beginning, p_{gel} (Flory's) ≥ 0.9, is indeed correct. The 1.07 mol resorcinol is equal to $1.07 \times 3 = 3.21$ mol resorcinol reactive sites. According to Flory's Theory in the most simple form $p_{gel} = (\alpha/r)^{1/2}$, and as $\alpha = 0.5$ and $r = 2/3.21 = 0.623$, $p_{gel} = 0.896$. This is sufficiently close to the value of 0.9 which was imposed on the system at the beginning. It is then not necessary to repeat the calculation. Had this value been further from the initial 0.9 assumption a second iteration could have been done by imposing as a new starting hypothesis p_{gel}(Flory's) $\geq$ the new value found (here 0.896), until a sufficiently stable value and condition has been found by iteration.

(ii) Visual check: what does it really mean that amounts of resorcinol lower than 0.411 mol and greater than 1.07 mol stop the system from gelling (until a hardener is added), and how can this be visualized? When the amount of resorcinol is between 0.411 mol and 1.07 mol there is sufficient resorcinol for two or more $–CH_2OH$ methylol groups from separate PF resol chains to condense on the resorcinol nuclei. This leads to the formation of a three-dimensional network sufficiently large to yield a gel: the resorcinol functions then as the "hardener" for the PF resol resin, as shown by the following schematic figure:



$$-CH_2-(\text{Phenol}-CH_2)_n-\underset{\displaystyle CH_2-(\text{Phenol}-CH_2)_n-}{\overset{}{R}}-CH_2-(\text{Phenol}-CH_2)_n-$$

When instead the amount of resorcinol ≥ 1.07 mol the majority of $–CH_2OH$ methylol groups have each mainly (but not only) reacted with one resorcinol molecule. Thus, there are no more methylol groups available for reaction, if one had nearer to 2 mol resorcinol to 1 mol for the particular PF at hand. At best one methylol group reacts with one resorcinol, for example

$$R-CH_2-(\text{Phenol}-CH_2)_n-R \qquad \text{and} \qquad R-CH_2-(\text{Phenol}-CH_2)_n-R$$

In reality the situation that presents itself is as follows

$$-CH_2-(\text{Phenol}-CH_2)_n-R-CH_2-(\text{Phenol}-CH_2)_n-R$$

and

$$R-CH_2-(\text{Phenol}-CH_2)_n-R-CH_2-(\text{Phenol}-CH_2)_n-$$

This is closer to the real situation, in which PRF oligomers are formed but there is enough resorcinol present to stop the oligomers growing to too long a polymer, hence to gel. If viscosity is too high, some unreacted resorcinol is added to decrease the average molecular mass of the system. This brings the system viscosity down to a more acceptable level. No interactions are possible unless a hardener (generally additional formaldehyde) is added. This means that, in the absence of a hardener, bridges between two resorcinol nuclei grafted onto PF chains cannot form. Equally, the proportion of resorcinol is not sufficiently low for resorcinol to function as a bridge between two methylol groups of separate PF chains. In both cases formation of a very long, continuous polymer chain (the Flory equivalent of a gel) is severely inhibited. Thus, the system cannot gel unless additional formaldehyde hardener is added (which is only added in the glue mix just before use of the adhesive).

When instead the amount of resorcinol is ≤ 0.411 mol of PF there are not sufficient molecules of resorcinol to function as a bridge between two or three methylol groups of different PF chains. The proportion of resorcinol molecules to achieve this is then insufficient for the gel portion of the system to predominate. Only short linear structures of the type

$$\mathrm{HOCH_2-(Phenol-CH_2)}_n\mathrm{-R-CH_2-(Phenol-CH_2)}_n\mathrm{-OH}$$

are formed. Since the sol fraction is still in the majority, the resin system cannot gel.

(iii) Industrial formulation check: how much resorcinol is used in the best industrial PRF cold-setting adhesive formulations (most of which present a number average degree of polymerization of the original PF resol of approximately 2, and two reactive methylols)? It is interesting that the majority of the industrial PRF adhesives of this type use a PF : resorcinol : molar ratio of 1 : 1.15–1 : 1.17. This is an excess of just 0.08–0.1 mol resorcinol, thus just a small safety margin on what is really necessary to minimize the amount of resorcinol, maintain the adhesive's performance, and avoid gelling. This value has also been obtained over many years by empirical research. For different PRF adhesive formulations one can redo this calculation to account for the different characteristics of the formulation and arrive at an equally correct answer without spending years of empirical research to arrive at an optimized solution.

Exactly the same type of approach can be used for the formulation of other polycondensation adhesives. For example, the formulation of melamine–urea–formaldehyde adhesive resins for wood panel products can also be successfully approached in the same way as has been shown above for the cold-setting PRF adhesives.

B. Determining the Gel Point of an Adhesive Based on a Polycondensation Resin

In the case of the formulation of mixed resins for adhesives for which extensive formulation experience does not exist, the gel theory approach is also particularly useful. Le us examine, as an example, what would be the degree of conversion at the gel point of a resin based on the reaction of resorcinol (R) with acetaldehyde (A) and formaldehyde (F) in relative molar proportions of, respectively, R:A:F = 1:1:0.5. The two aldehydes can react and do react with resorcinol; while under the conditions used they are considered as not being able to react with each other (aldol condensation is indeed minimal under the conditions used to prepare adhesive resins). In short to avoid any gelling of our prereacted resin in the reactor, during manufacture, we want to know at what degree of conversion we can advance reaction of the resin without gelling it.

As the system is relatively complex and presents more than two reagents the simpler approach is to use the formula of Durand and Bruneau (Eq. (10)). This will tell us then that the functionality of resorcinol is 3; the functionality of the two aldehydes in the proportions given is 2 (they are both bifunctional, which simplifies matters), and thus $f_A = 3$ and $f_B = 2$, while $r = (1 \times 3)/(1 \times 2 + 0.5 \times 2) = 1$, to yield according to Eq. (10) $p_{gel} - 1/[1(3-1)(2-1)]^{1/2} = 0.707$ so according to Flory, gel intervenes at 70.7% of the reagent having in fact reacted.

As we know that Flory's and derived formulas such as Eq. (10) underestimate by approximately 10% the degree of conversion at the gel point one could also use the more exact but more complex Eqs. (18) and (19). In this case Eq. (19) is the one suitable to use. We will then have that $p_{\mathrm{gel}} = [(1+1+0.5)/(1\times 3+1\times 2+0.5\times 2)] + 1/2(0.5/1)^{1/2} = 0.770$. This indicates that the gel of the system intervenes when 77.0% of the reagents have in fact participated in the reaction, the latter formula yielding a precision of 99.5% while the previous one yields a precision of 91% only.

IV. CONCLUSION

In conclusion, the use of the simpler polymer networking and gel theories constitutes a very useful approach to focus more rapidly and within narrower limits applied formulation research for any polycondensation adhesive resin. This allows much faster adhesive formulation than just the empirical scan research approach still the favorite today for some of these resins. Final experimental verification and adjustments will, however, always be required.

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9

Application of Plasma Technology for Improved Adhesion of Materials

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I. INTRODUCTION

Adhesion, whether the bonding of polymers or the adhesion of coatings to polymer surfaces, is a recurring and difficult problem for all industries that use these materials as key components in their products. Designers must often select specially formulated and expensive polymeric materials to ensure satisfactory adhesion (albeit even these materials often require surface preparation). In some cases, entire design concepts must be abandoned due to the prohibitive cost of the required polymer or the failure of crucial bonds.

Historically, surface treatments to improve adhesion of coatings to plastics consisted of mechanical abrasion, solvent wiping, solvent swell that was followed by acid or caustic etching, flame treatment, or corona surface treatment. Each of these treatments has limitations, thus providing a strong driving force for the development of alternative surface preparation methods. Many of the common methods mentioned are accompanied by safety and environmental risks, increased risk of part damage, and expensive pollution and disposal problems.

Mechanical abrasion or sand blasting is operator sensitive, dirty, difficult to do on small parts, and often does not reach hidden areas of complex-part geometries. Although more effective than solvent-based methods, acid etching can easily result in overtreated and damaged parts in addition to serious hazard and disposal problems. For example, other than plasma treatment, the most effective method for improving the bonding of materials to fluoropolymers has been to etch the surface with a material commonly referred to as *sodium etch*. The process consists of a brief immersion of the component to be bonded in a solution of sodium naphthalene in tetrahydrofuran or other suitable solvent. Although sodium etch is quite effective in treating fluoropolymers, concerns with operator safety and the problems of disposal have caused many users to seek alternatives.

Flame and corona, although useful in oxidizing the surfaces of plastics, have limited utility in many applications. In addition, the transitory nature of these modifications prevents their widespread use in many applications. Corona treatment is limited to both the materials that are responsive to this method of surface preparation and the part configuration itself. Complex shapes cannot easily be treated, as the treatment quality is a function of the distance of the part from the electrode. Thus small-diameter holes and surfaces that are difficult to access in complex parts prove particularly troublesome when treating these parts with corona discharge. The result is an uneven surface treatment at best. Since corona discharge surface treatments are typically conducted in ambient air, the process is subject to change from day to day as the environment changes in the location where corona treatment is being conducted.

For many industrial applications of plastics that are dependent on adhesive bonding, cold gas plasma surface treatment has rapidly become the preferred industrial process. Plasma surface treatment, which is conducted in a vacuum environment, affords an opportunity to minimize or eliminate the barriers to adhesion through three distinct effects: (1) removal of surface contaminants and weakly bound polymer layers, (2) enhancement of wettability through incorporation of functional or polar groups that facilitate spontaneous spreading of the adhesive or matrix resin, and (3) formation of functional groups on the surface that permit covalent bonding between the substrate and the adhesive or matrix resin. Since plasma treatment is a process of surface modification, the bulk properties of the material are retained. The nature of the process also allows precise control of the process parameters and ensures repeatability of the process in industrial applications. Finally, several studies have demonstrated that these surface modifications can be achieved with minimum impact on the environment.

II. PLASMA PROCESSING EQUIPMENT

While most, if not all, plasma equipment consists of similar components, the design of the reactor chamber, the distribution of power, the excitation frequency, and the gas dynamics can all be critical parameters influencing the efficiency and properties of plasma reactions. An extensive amount of work has been published that shows a direct correlation between excitation frequency and plasma reactivity. Manufacturers of plasma equipment employing radio-frequency (RF) excitation use either low frequencies (i.e., less than 400 kHz) or the higher frequencies at 13.56 or 27.12 MHz as specified by the Federal Communications Commission. For applications involving the treatment of plastics, 13.56 MHz is the preferred frequency. Also important is whether the material being treated is in a primary or a secondary plasma. Older equipment using large cylindrical barrels typically comprises secondary plasma systems (Fig. 1). The plasma is created either between closely spaced, paired electrodes that may function as shelves or in the annulus between the vessel's outer wall and a ring electrode, when employed. Treatment of materials placed within the working volume depends on the diffusion of active species created in the primary

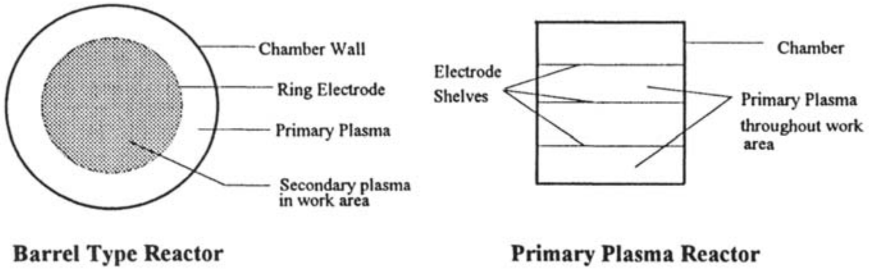

Figure 1 Typical reactor configurations.

plasma (i.e., within the RF field). Diffusion of these active species is very dependent on pressure; the higher the pressure, the shorter the mean free path. The mean free path is the distance that active species can probably travel before undergoing collisions that deactivate radicals or neutralize ions. Therefore, when using a secondary plasma, the concentration of active species varies either across the diameter of a barrel system or between electrode pairs, as the case may be. Thus, by the physical laws of nature, the treatment within the working volume of a secondary plasma system cannot be uniform. By contrast, when working within the RF field, or primary plasma, the gas is constantly being excited. Thus polymeric articles being treated are immersed in a constant concentration of active species. Further, since diffusion is not a mechanistic limitation, significantly higher operating pressures may be used. This allows higher process gas flow rates, assuring that off-gassing species from the polymer are sufficiently diluted, providing the full benefits of the desired process gas. In addition, the primary plasma is rich in ultraviolet (UV) radiation, which is often an important initiation step in polymer reactions. Since UV radiation is line of sight, uniform treatment of multiple parts can only be obtained when working within the primary plasma. Otherwise, any part in the shadow of another will receive different radiation, and therefore the effectiveness of the treatment is expected to vary.

The types of reactors used for the deposition of plasma polymers have been varied. Glass and/or quartz reactors or aluminum chambers with metal parallel-plate electrodes seem to predominate in the literature, although several investigators have used inductively or capacitively coupled systems with external electrodes. High rates of deposition are found in the glow area, with the rate of deposition decreasing as we move farther away from the glow discharge region. Consequently, primary plasma systems that use a 13.56-MHz RF source are favored. The RF excitation used by various equipment manufacturers can be as low as 2 to 4 kHz or can be the more typical 13.56 MHz (high frequency). Microwave plasma systems have also been used for the deposition of plasma polymers. Previous studies have shown that the densities of films deposited by low-frequency systems are significantly lower than those of films deposited by either the high-frequency or microwave plasma systems. The choice of equipment used for plasma polymerization and deposition is thus dictated by the rate of deposition desired, the film properties that can be obtained by the various systems, and practical considerations such as the size of the parts to be treated and processing rates that are feasible in any given system.

III. PLASMA TECHNOLOGY

A. Plasma Processes

There are many definitions of the term *plasma*, according to the various disciplines with which it is involved. It has often been referred to as the fourth state of matter; the generation of plasma being analogous to the transitions that occur when energy is supplied to a material, causing solids to melt and liquids to become gases. Sufficient additional energy supplied to a gas creates a plasma. In the case of cold gas plasma, typical of that used in this work, the process is excitation of a gas at reduced pressure by RF energy. Typically, a plasma is composed of a large concentration of highly excited atomic, molecular, ionic, and radical species. While on an atomic scale, plasma generation cannot be construed as a room-temperature equilibrium process, as the bulk of the material remains near room temperature. The plasma contains free electrons as well as other metastable particles, which upon collision with the surfaces of polymers placed in the plasma environment break covalent chemical bonds, thus creating free radicals on the polymer surface [1]. The free radicals will then undergo additional reactions, depending on the gases present in the plasma or subsequent exposure to gases in the atmosphere. The result is that these gas–radical reactions form a surface that is potentially very different from that of the starting bulk polymer. Since the process is conducted in a reactor under very controlled conditions, the end result is very reproducible.

Plasma processing is not one process but a "field of opportunities" that can be classified into three overlapping categories: (1) plasma activation, (2) plasma-induced grafting, and (3) plasma polymerization. Plasma activation is the alteration of surface characteristics by the substitution of chemical groups or moieties for groups normally present on the polymer chain being modified. The assumed mechanism is free-radical creation and coupling of these free radicals with active species from the plasma environment. Depending on the process gas selected, a large variety of chemical groups can be incorporated into the surface. These groups may be hydroxyl, carbonyl, carboxylic, amino, or peroxyl groups. Most important, the insertion or substitution of these groups in the polymer chain is under the control of the operation. In this manner, the surface energies and the surface chemical reactivity of plastics can be altered completely without affecting their bulk properties.

Plasma-induced grafting offers another method by which plastic surfaces can be modified. If a noble gas is employed to generate a plasma, a multitude of free radicals are created along the polymer backbone. If after the plasma is extinguished but prior to the introduction of air, an unsaturated monomer such as ally alcohol is introduced into the reaction chamber, it will add to the free radical, yielding a grafted polymer. The range of functional and reactive sites that can be incorporated onto a surface is increased significantly with this technique. This process differs from activation in that instead of functional modification of the surface polymer chains, material is added on to the polymer backbone.

The third category of plasma processes, plasma deposition, utilizes gases or vapors that fractionate and undergo polymerization under the influence of RF energy. For example, methane (CH_4) under the influence of plasma will deposit as a polyhydrocarbon that has a density approaching $1.6\,g/cm^3$. Any material that can be introduced into the process chamber is a potential candidate as a feed material for plasma polymerization. The properties of materials polymerized in this manner are very different from polymers obtained from these materials via conventional polymerization methods. These properties include a high degree of cross-linking and the ability to form pinhole-free films that adhere tenaciously to various substrates.

B. Factors Influencing Adhesion

The strength of an adhesive joint is influenced by several factors [2–4]. Removal of contaminants and process aids provides a means for the adhesive to interlock with the substrate surface rather than with a boundary layer that is merely resting on the surface. Increasing the surface energy of the substrate above the surface tension of the adhesive makes it possible for the adhesive to wet the entire surface of the polymer substrate. The increase in the apparent surface area of contact serves to increase the strength of the adhesive bond. Figure 2 illustrates this process.

Ablation of the surface layers of the exposed polymer can result in a microroughened surface that increases the area of contact between the adhesive and the substrate. Finally, modification of the surface chemistry in a manner that facilitates covalent bonding

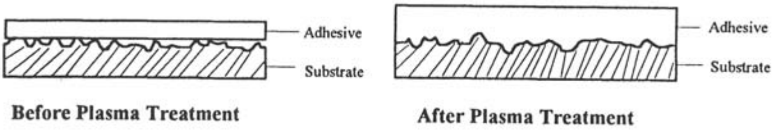

Figure 2 Effect of plasma treatment on surface wetting.

between the adhesive and the substrate surface further enhances adhesion strength. These changes are accomplished by competing molecular reactions that take place on the surface of a polymer substrate in a plasma.

1. *Ablation*: removal by evaporation of surface material. Ablation is the key process by which contaminants are removed from the surface of materials placed in a plasma. As the molecular weight of the contaminants is reduced due to chain scission, they become volatile enough to be removed by the vacuum system. Ablation of the surface layers of the polymer can also take place in a plasma and occur through a similar mechanism. If the substrate consists of a blend or alloy of materials that react differently in a plasma, differential ablation of these components can be used to create a microroughened surface.
2. *Activation*: act of substituting atoms in the polymer molecule with chemical groups from the plasma. The surface energy of the polymer placed in a plasma can be increased very rapidly by plasma-induced oxidation, nitration, hydrolization, or amination. The higher surface energy of the polymer surface increases its *wettability*, which describes the ability of a liquid to spread over and penetrate the surface. The increase in apparent bonded surface area that results serves to increase the strength of the bond. The process of activation can also be used to substitute surface polymer groups with those that facilitate covalent bonding between the polymer substrate and the adhesive.

C. Plasma Activation and Reactions on the Surface

The use of plasma surface treatment to improve adhesion is well known [5–19] and several literature sources provide an in-depth discussion of the nature of gas plasmas and their chemistries [1,5,7,10–12]. Although any gas can be ionized using RF excitation, gases such as O_2, N_2, He, Ar, NH_3, N_2O, CO_2, CF_4, and air or some combination of these gases are generally used for surface treatment.

One of the more common plasma processes used to enhance the adhesion of polymers is surface treatment in an oxygen plasma. An oxygen plasma is aggressive in its reactivity and forms numerous components. Within an oxygen plasma O^+, O^-, O_2^+, O_2^-, O, O_3, ionized ozone, metastably excited O_2, and free electrons are generally observed. The ionization of oxygen into the various species found in an oxygen plasma can be represented by the following reaction scheme:

$$O_2 + e \rightarrow O_2^- \rightarrow O + O^-$$

$$e + O \rightarrow O^+ + 2e$$

$$e + O_2 \rightarrow O_2^+ + 2e$$

$$e + 2O_2 \rightarrow O_2^- + O_2$$

$$O_2^- + O \rightarrow O_3 + e$$

These reactions represent a small sampling of those that occur in an oxygen glow discharge.

As the components formed during the ionization recombine, they release energy and photons, emitting a faint blue glow and much UV radiation. The photons in the UV region have enough energy to break the carbon–carbon and carbon–hydrogen bonds in the materials on the surface that are exposed to the plasma. In the case of contaminants, the net effect appears to be degradative, such that lower-molecular-weight materials are created. These lower-molecular-weight materials are subsequently removed by the vacuum. In this manner the surface that has been exposed to a plasma is cleaned. Lower-molecular-weight polymer fractions that comprise the weak boundary layers on the surface are also removed in this manner. Several reports documenting the efficacy of plasma surface cleaning have been published [1,13,15,20,21].

Once the contaminants have been removed, the virgin polymer surface is exposed to the plasma environment. The electrons, ions, and free radicals in the plasma act on this exposed polymer, creating free radicals in the molecular chains on the surface [1,22,23]. The free radicals that are created on the polymer surface by this process can then react with the various molecular and active species present in the plasma environment. In a low-pressure oxygen plasma, the following oxidation reaction scheme has been suggested:

$$\mathrm{RH} + \mathrm{O}^{\bullet} \rightarrow \mathrm{R}^{\bullet} + {}^{\bullet}\mathrm{OH}$$

$$\mathrm{R}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{RO_2}^{\bullet}$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{R'H} \rightarrow \mathrm{RO_2H} + \mathrm{R'}^{\bullet}$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{R'}^{\bullet} \rightarrow \mathrm{RO_2R'}$$

Here the $\mathrm{RO_2H}$ and $\mathrm{RO_2R'}$ indicate the formation of acids and esters. Not indicated in this reaction scheme are the possible formation of alcohols, ethers, peroxides, and hydroperoxides.

Thus in addition to the reactions resulting from the bombardment of the surface by photons, ions, and neutral particles, all of the active species in the plasma react with the polymer surface. The by-products, consisting of CO_2, H_2O, and low-molecular-weight hydrocarbons are readily removed by the vacuum system. The use of co-reactants can serve to modify the surface chemistry obtained with a single gas chemistry or to accelerate the reaction kinetics. For example, in an oxygen plasma, breaking of the carbon–carbon and carbon–hydrogen bonds is the rate-limiting step. When tetrafluoromethane is introduced as co-reactant, the O_2/CF_4 plasma yields excited forms of O, OF, CO, CF_3, CO_2, and F. Since fluorine or fluorine-containing species are more effective in breaking the carbon–carbon and carbon–hydrogen bonds, the reaction rate is accelerated. The permanent nature of these changes on the polymer surface has been confirmed by spectroscopic analyses and documented in several studies [24–27]. The use of other gases permits incorporation of other functional groups on the polymer surface. Examples include the use of ammonia, nitrogen, and oxides of nitrogen plasmas that are used to incorporate nitrogen in the surface and create nitrogen-based functional groups such as primary and secondary amines [28,29].

One result of such surface modification of the polymer surface is an increase in the surface energy of the polymer and an attendant improvement in surface wetting. As stated earlier, adequate wetting of the surface by the adhesive contributes to the improvement in bond strength by increasing the apparent area of contact over which the load is distributed. Published studies suggest that this improvement in wetting contributes directly to the observed improvement in the strength of the adhesive bond [30–32]. Another factor that contributes to improved adhesion is an increase in surface area of the polymer surface through microroughening. This occurs through the process of ablation of the polymer surface through exposure to a plasma. This is particularly the case when the plasma is highly reactive, as in the case when oxygen is used as one of the gas components that is being ionized. The nature of the gas being ionized to create the plasma is not the only factor that determines the extent of ablative etching. The nature of the polymer that is exposed to the plasma also plays a key role. Studies have shown that etching through ablation of surface polymer layers does occur in the case of polymers such as polyethylene (PET) and nylon 66 [11,33], whereas polyaramid materials such as Kevlar appear to be resistant to microroughening through ablation of the polymer chains [34].

Evidence has been presented in several studies which indicates that the strength of the adhesive bond is dependent on the particular functional group that has been created on the surface of the polymer. In some cases a direct correlation is drawn relating the nature of the chemical groups on the surface, the nature of the adhesive used, and the observed improvement in adhesion [11,32,35]. In other cases, the improvements are related to the effects of hydrogen bonding and specific surface chemical interactions that do not necessarily result in covalent bonding between the polymer surface and the adhesive [36]. The reader may infer these conclusions from the adhesion data presented along with the data describing the nature of the surface chemistry as determined by X-ray photoelectron spectroscopy (XPS) analysis [37,38].

As these examples illustrate, selection of the process gas determines how the plasma will alter the polymer. Very aggressive plasmas can be created from relatively benign gases. Oxidation by fluorine free radicals that are generated when tetrafluoromethane is included as one of the gases is as effective as oxidation by the strongest mineral acid solution. The primary difference is that the by-products of the plasma process do not require special handling since the active species recombine to their original stable and nonreactive form outside the RF field. In all cases, profound changes in the chemical nature of the polymer surface are implemented, changes that are permanent in nature. The stability of these surface changes is a function of the materials themselves and the storage conditions used [39]. For instance, plasticizers that can migrate to the surface or contaminants in the storage area that can be attracted to these high-energy surfaces will negate the effects of the chemical changes that have been created on the surface of these materials. Contact-angle measurements and electron spectroscopy for chemical analyses of plasma-treated surfaces have confirmed the permanent and long-lasting nature of plasma surface modification of polymers. For example, plasma-modified fluorinated ethene propene (FEP) was shown to retain its surface chemical characteristics over an 18-month observation period [40]. Similar phenomena have been observed by other investigators for other materials, such as polyethylene and polystyrene (unpublished data, HIMONT Plasma Science Applications Laboratory). These changes ultimately lead to significant improvements in adhesion strength, as the data in Table 1 suggest.

D. Plasma-Induced Grafting

As effective as these surface modification processes might be, they present limitations in terms of the extent to which the surfaces of polymers can be modified. Plasma-induced grafting offers another method by which chemical functional groups can be incorporated. In this process, free radicals are generated on the surface of a polymer through the use of an inert gas plasma. Because of the nonreactive nature of the inert gas plasma, surface chemical modification of the polymer does not occur. If the polymer surface that has been

Table 1 Lap Shear Strength of Untreated and Plasma-Treated Surfaces

Material	Plasma Chemistry	Adhesive	Bond Strength (psi)	Failure Mode	Ref.
Vectra	Control	Epoxy	939	Adhesive	8
A625	Oxygen plasma	Scotchweld	1598	Cohesive	
	Ammonia plasma	2216 (3M)	1240	Cohesive	
Noryl	Control	Epoxy	617	Adhesive	8
731	Oxygen plasma	Scotchweld	1485	Adhesive	
	Ammonia plasma	2216 (3M)	1799	Cohesive	
Ultem	Control	Epoxy	186	Adhesive	8
1000	Oxygen plasma	Scotchweld	1939	Cohesive	
	Ammonia plasma	2216 (3M)	2056	Cohesive	
Rynite	Control	Epoxy	683	Adhesive	16
530/935	Plasma treatment A		5875	Cohesive	
	Plasma treatment B		6067	Cohesive	
Tefzel	Control	Epoxy	10		12
	Ammonia plasma	Uniset	202		
	O_2/SF_6 plasma	D276	293		

treated in this fashion is exposed to vapors of unsaturated monomers, these monomers then get attached to the surface of the polymer. A variety of vinyl monomers are available and the possibilities for incorporating many different chemical functional groups are endless. Unlike surface modification, this is a two-step process that adds a degree of complexity. Few studies have appeared in the open literature, with the majority of such processes being used in proprietary applications [41,42]. This process is mentioned here as an option that is available to the surface engineer.

E. Plasma Film Deposition

In comparison to the processes described above, plasma polymerization offers an entirely new avenue for adhesion improvement when bonding different materials. For example, films deposited from a methane plasma have been shown to improve dramatically the adhesion properties of many materials when tested in both the dry and wet state [41]. The process of plasma film deposition is often called plasma polymerization, although the process that takes place is not polymerization in the classical sense. Gases in plasma may undergo polymerization, usually through a free-radical initiation process. When a gas is ionized by RF energy, the resulting plasma contains free electrons as well as other metastable particles. When the process gas mixture used consists wholly or in part of hydrocarbon gases, the hydrocarbon molecule is fractured into free-radical fragments. These free-radical fragments become the sites at which the polymerization process is initiated. As the molecular weight of the plasma polymerized product increases, it is deposited onto the substrate placed within the plasma chamber. Since the fragmentation of the feed gas in the plasma generates free-radical species for initiating the polymerization process, gases such as methane (CH_4), which have zero functionality, can be used to form plasma polymers. In addition to methane, plasma polymers have been formed from other hydrocarbon gases, such as ethylene or propylene, fluorocarbon monomers such as tetrafluoroethylene, and organosilicon compounds such as hexamethyldisiloxane (HMDSO) or vinyltrimethylsilane (VTMS). Due to the complex nature of the fragmentation process, the resulting polymer structure is unlike any that can be deduced from conventional polymerization mechanisms [43].

The physics of plasma polymerization processes has been described in depth elsewhere in sufficient detail for the interested reader [41,44]. The conditions used during glow discharge polymerization determine not only the structure of the resulting film but also the rate at which these films are deposited onto the target substrate materials [41,45,46]. The degree to which the monomer is fragmented is dependent on the amount of energy supplied per unit weight of monomer that is allowed to flow through the reactor. When sufficient energy is supplied to break all the bonds of the monomer molecule, the recombination or polymerization process becomes atomic in nature. In addition, the structure of the plasma polymers can be varied by changing reaction conditions, including the use of comonomers or the introduction of oxygen, nitrogen, or ammonia into the reaction chamber during the polymerization process. These studies have developed a correlation between the power input, type of monomer used, and monomer flow rate to the density and the type of active species in the plasma. These factors, in turn, determine the rate of deposition and the film structure [46,47]. Table 2 shows typical deposition rates for some common plasma-polymerized films.

While plasmas of ammonia, mixtures of hydrogen and nitrogen, and oxides of nitrogen have been used to incorporate nitrogen atoms into the surface layers of the polymer [28,29], the level of nitrogen incorporation has been less than 10 at.% [29]. In contrast, films deposited from allyl amine have been shown to contain up to 25 at.% nitrogen as measured by spectroscopic methods [48]. Despite this high nitrogen content, however, the authors report a lower than expected concentration of amino groups. Other studies have shown concentrations of up to 2 molecules/nm^2 of reactive amine groups on the surface of films deposited from allyl amine onto FEP substrates. These surface concentrations were determined by derivatization of the amine groups with fluorescein isothiocyanate and subsequent detection of the fluorescein chromophore by optical spectroscopic methods [49]. Since electron spectroscopy for chemical analysis does not always allow precise determination of functional sites, the earlier data may reflect limitations of the analytical methods used.

In a similar vein, hydroxyl and carboxylic acid functionalities can be incorporated by plasma-polymerizing acrylic acid [50] or ally alcohol [48]. Another technique commonly employed to incorporate specific atomic species is the use of co-reactants along with the primary monomer. In one such example, ammonia or acrylonitrile was used as the

Table 2 Deposition Rates for Various Compounds

Compound	Deposition Rate, D(Å × 10^8 g/cm^2 min)	D/D_0
Hexamethyldisiloxane	$233 = D_0$	1.00
Acrylic acid	28	0.12
Styrene	173	0.74
Tetramethyldisiloxane	191	0.82
Divinyltetramethyldisiloxane	641	2.75
Ethylene	42	0.18
Benzene	110	0.47

Source: Ref. 41.

co-reactant during the deposition of films from a methane plasma [51]. Two additional techniques that are available to the surface engineer interested in modifying plasma-deposited films are plasma surface modification of the deposited film in a second process step and wet chemical reaction methods. As an example, carbonyls formed during the plasma deposition of films from *N*-vinylpyrrolidone were reacted with lithium aluminum hydride and sodium borohydride to convert these carbonyls to hydroxyl groups [52]. It should be noted that the use of plasma-deposited films for adhesion enhancement is not limited to polymeric substrates. Such films have also been deposited onto inorganic materials such as mica [50] and metal substrates such as aluminum and steel in an effort to improve adhesion of these materials to polymers [41].

IV. CONCLUDING REMARKS

One hundred years ago, Sir William Crookes stated: "Investigation of the fourth state of matter—plasma—will be one of the most challenging and exciting fields of human endeavor." Plasma technology today is gaining increasing acceptance and recognition as an important industrial process for the surface modification of materials. Plasma processing is not one process but a "field of opportunities" that is poised to open up the development of complex new materials and products. By using this technology, the product designer is unlimited in the choice of materials at his or her disposal. That the surfaces of materials can be modified easily and effectively for a variety of end uses has become an established fact. The synthesis and deposition of ultrathin films with unique properties offers a means for cost-effective surface engineering in the quest for improved functionality of existing products and the development of products that were out of the realm of possibility just a few years ago.

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10

Silane and Other Adhesion Promoters in Adhesive Technology

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I. INTRODUCTION

It is axiomatic that the paramount property of an adhesive is adhesion to the substrate, but adhesion is also critical in the performance of surface coatings, which must adhere to protect and in obtaining optimum mechanical properties in particulate- and fiber-filled composites. Many surface preparation techniques have been employed to achieve high initial adhesion; these range from removal of surface contamination (solvent and vapor degreasing) to changes in substrate profile (grit blasting) to chemical modification (phosphating of steel, anodic treatments of aluminum). None of these methods solve the most critical problem in adhesion technology: that of the damaging effect of water on organic/inorganic bonds. Hydrolytic stability is essential in many technologies.

It has been shown by Walker that many types of organic coating lose up to 85% of their initial adhesion under water-soaked conditions [1], that adhesives show a marked loss of bond strength in water [2,3], and that glass-fiber-reinforced composites are readily degraded [4]. To improve the initial bond strength between adhesives and substrate, adhesion promoters may be used. These function by improving substrate wetting or by secondary bonding by van der Waals forces, dipole–dipole interactions, hydrogen bonding or acid–base reactions. Relatively weak forces in the range 5–8 kcal/mol are involved. If hydrolytic stability of the bond is to be achieved, use of a coupling agent that is capable of forming primary chemical bonds, 50–250 kcal/mol [5], is required. The important distinction here is that in the nature of the bond formed, only coupling agents form primary bonds and can therefore be expected to produce water-resistant bonding. A coupling agent is therefore defined as a compound capable of chemical reaction with both the polymer and the substrate, although there is some evidence that reaction with the polymer is not necessarily a prerequisite. It should be noted that a coupling agent can function as an adhesion promoter; the reverse is not true. Current views are that only a limited range of organometallic compounds are true coupling agents.

II. EVIDENCE FOR COUPLING ACTIVITY

Interfacial bonding studies have attracted the attention of many workers using a variety of spectroscopic techniques. Evidence for coupling activity has been demonstrated in the cases shown in Table 1.

III. MECHANISM OF ADHESION PROMOTION

Mechanistic theories of adhesion promotion have been described in detail by Rosen [11] with sole reference to silanes, but it is likely that many of the proposed theories apply equally well to coupling agents in general. The proposed mechanisms are described below.

A. Chemical Bond Theory

As applied to silanes, the theory postulates that trialkoxysilane groups chemically bond to silanols on the mineral substrate surface by reaction of the hydrolyzed alkoxy group forming interfacial bonds of 50–100 kcal/mol [12] to 50–250 kcal/mol [13]. The organofunctional groups of the silane bond chemically to the polymer molecules. Both reactions were considered to be essential if true coupling is to be achieved. Although originally postulated for silanes, it is equally applicable to other adhesion promoters, including titanates and zirconates. It has been pointed out that although covalent bonds may be formed between polymer and mineral surfaces, some covalent oxane bonds are easily hydrolyzed [12,14], and examples of hydrolytically stable bonding have been achieved in the absence of chemical reaction with the polymer [12,15].

B. Deformable Layer Theory

This theory postulates that the interface zone is plastic, allowing stresses between the polymer and mineral surfaces to self-relieve without bond rupture. Internal stresses are thus reduced. It has been suggested that in the case of a silane, the film is too thin to allow this [11]. However, it is possible that the presence of the coupling agent might cause preferential adsorption. Credence for this view is given by the number of

Table 1 Evidence for Coupling Activity

Bond	Coupling Agent/Substrate	Method[a]	Ref.
Si–O–Al	Silane/Al_2O_3	FTIR	6
Cr–O–Al	Volan/aluminium	ESCA	7
Zr–O–Al	Zirconate/aluminium		8
Si–O–Fe	Silane/iron	SIMS	9
Si–O–Si	Silane/SiO_2	NMR	10
Si–O–Pb	Silane/lead oxide	FTIR	11
Ti–O–Si	Titanate/SiO_2	FTIR	6

[a] FTIR, Fourier transform infrared; ESCA, electron spectroscopy for chemical analysis; SIMS, secondary-ion mass spectrometry; NMR, nuclear magnetic resonance.

workers who report that the amount of adhesion promoter used is critical and that excessive usage may result in adhesion failure [16,17].

C. Surface Wettability Theory

Erickson and Plueddemann suggest that particularly in filled systems, complete wetting of the mineral surface will improve adhesion by physical adsorption that would exceed the cohesive strength of the polymer. However, it is difficult to see how physical adsorption provides bond reinforcement when the polymer is in competition with water and possibly other weakly bonded surface layers, and where chemical bonding is also present [12].

D. Restrained Layer Theory

In effect, this theory postulates a chemical reaction between promoter, polymer, and mineral substrate as in the chemical bond theory but also suggests that the presence of a region of intermediate modulus between polymer and substrate which transfers stress from the high modulus surface to the relatively low modulus polymer. Adhesive technology has long recognized this principle in specially formulated primers for use when bonding rubbery polymers to metals.

E. Reversible Hydrolytic Bond Theory

Best regarded as a combination theory, it postulates the chemical reactions between coupling agent, substrate, and polymer of the chemical bond theory together with the rigid interface of the restrained layer theory and the plastic interface of the deformable layer theory. It allows for stress relaxation by the reversible breaking of stressed bonds without loss of adhesion in the presence of water. It also argues that when Si–O or Ti–O substrate bonds are broken by the intrusion of water, they may re-form with some recovery in adhesion. It is likely that hydrogen bonding is a particularly important aspect of this theory, especially in the case of silanes [18]. Recovery of adhesion between urethane and epoxide coatings and metal substrates on drying out after water immersion has been demonstrated by Walker [19–21]. It is now generally accepted that some silane coupling agents do not need to react with the polymer chemically to provide enhanced initial and wet adhesion [16,22].

F. Oxide Reinforcement

This theory postulates that a primary mechanism by which silane coupling agents improve initial and wet adhesion is by reaction with the oxide surface on a metal to increase the cohesive strength of the oxide [23] and certainly, in the case of aluminum oxide, increase the wet strength of the oxide by inhibiting hydration of the oxide [24]. This has the effect of causing any failure to occur in the new weakest layer (i.e., the adhesive or coating). This may also explain, in part, the differences in bond strength achieved with different coupling agents and different metals, as it may be the nature of the oxide film and the degree of reinforcement that varies rather than any intrinsic property of a particular metal–adhesion promoter combination.

It seems unlikely that any single theory can explain the mechanism of adhesion promotion for such diverse systems as particulate- and fiber-filled composites, surface coatings, and adhesives applied to the complete range of metallic and other mineral substrates. Plueddemann opines that all theories of adhesion describe factors that are involved in bonding through silane coupling agents [16], and this view is likely to apply generally to the entire field of adhesion promotion.

G. Other Mechanisms

In addition to the stated theories of adhesion promotion, there are other mechanisms that may be both operative and important and are of general application.

1. *Interpolymer Networks/Chain Tangling*

It has been suggested that in the case of silane coupling agents, interdiffusion of siloxanol segments with polymer molecules may be a factor in bonding thermoplastic matrices. Interpenetrating polymer networks (IPNs) need not necessarily involve cross-linking of the silane or other coupling agent and the polymer matrix. Plueddemann expresses the view that to establish a strong interpenetrating boundary layer involves a tricky interplay of mechanical and chemical interreaction at the interface [16]. A similar mechanism has been suggested for titanates [17].

2. *Acid–Base Reactions*

A comprehensive account of acid–base reactions is covered in detail in volumes 4 (No. 4), 5, and 8 (1990) and volume 5 (No. 1) (1991) of the *Journal of Adhesion Science and Technology* and a detailed account is beyond the scope of this chapter. Since different metal oxides have different isoelectric points in water and may therefore be regarded as acidic or basic, addition of material having acidic properties to adhesives to be used on basic substrates, or basic materials for use on acidic substrates, may improve adhesion [25]. Work with epoxide and polyurethane coatings of similar composition to adhesives have shown them to be basic in nature; the pH of water-soaked surfaces from which they were stripped is known to be 8–10. The aminosilanes APES and AAMS are strongly basic and when applied to oxide surfaces having isoelectric points in the range 9.1 (Al^{3+}) to 12.0 (Fe^{2+}) may be expected to produce a basic surface. Neither silane could therefore be expected to enhance the adhesion of a basic polymer by an acid–base reaction, although both have been shown to improve the initial and wet adhesion of epoxides and urethanes. This is not to argue that acid–base reactions are unimportant in adhesion promotion technology.

IV. METHODS OF USE IN ADHESIVE TECHNOLOGY

In general, adhesion promoters may be used as pretreatments or as additives. In the former case the promoter is used either as a solution in a suitable solvent or solvent mixture or as a formulated primer [26]; in the latter case they may be incorporated into the adhesive in a self-bonding concept [25]. The technique of filter treatment can be regarded as representing both approaches, although there is no evidence of this being used in filled adhesive systems. There are advantages and disadvantages inherent in both approaches: the pretreatment method allows a specific adhesion promoter to be used on a specific substrate to obtain optimum adhesion but has the disadvantage of introducing a process that is not under the control of the manufacturer. In theory the self-bonding additive concept is almost universally desirable, but in practice there are several critical parameters that need to be recognized, including potential polymer reactions, depletion by water, and shelf life. In adhesive technology as opposed to surface coating technology, the additive approach may not be as effective [27,28].

V. SILANES

Silanes of the general structure R–Si(OR′)$_3$, where R is an organofunctional group and R′ a hydrolyzable group, constitute the most technologically important group of adhesion promoters in use today and have a solid background of associated theory. Silane molecules are bifunctional, containing polar silanol groups and organofunctional groups capable of reaction with polymers. The range of silanes available commercially is large and continually expanding. Typical silane adhesion promoters are shown in Table 2. Other silanes that are attracting increasing interest are the fluoralkyl-functional silanes, the chemistry and uses of which have been reviewed extensively by Owen and Williams [29], cationic methacrylate, and cationic styryl silanes [30].

A. Silane Coupling Reactions

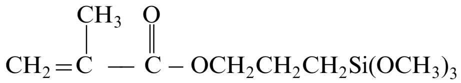
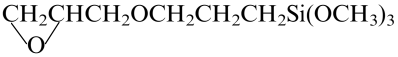
The reactions of interest in silane coupling are summarized below.

(a) Hydrolysis of the silane group:

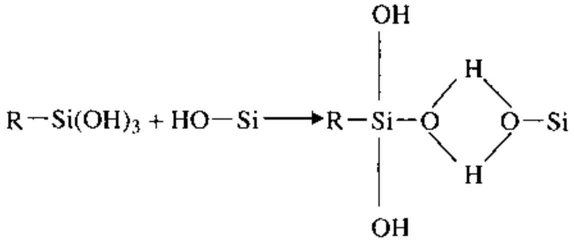
$$R{-}SiX_3 + 3H_2O \xrightarrow{\text{pH or catalyst}} R{-}Si(OH)_3 + 3HX \qquad (1)$$

where HX is usually an alcohol.

Table 2 Typical Silane Adhesion Promoters Commercially Available

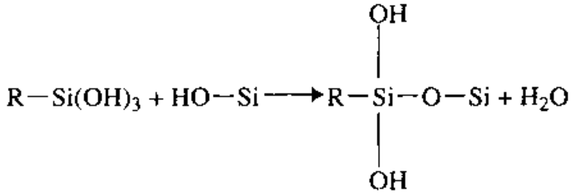
		Functional Group	
Chemical Description	Structure	With Polymer	With Substrate
3-Chloropropyltrimethyl oxysilane	$ClCH_2CH_2CH_2Si(OCH_3)_3$	Chloro	Methoxy
Vinyltriethoxysilane	$CH_2{=}CHSi(OC_2H_5)_3$	Vinyl	Ethoxy
γ-Methylacryloxypropyl trimethoxysilane	 $CH_2{=}\overset{\overset{CH_3}{\vert}}{C} - \overset{\overset{O}{\Vert}}{C} - OCH_2CH_2CH_2Si(OCH_3)_3$	Methacry-loxy	Methoxy
γ-Glycidoxypropyl trimethoxysilane	 $\underset{\diagdown O \diagup}{CH_2CH}CH_2OCH_2CH_2CH_2Si(OCH_3)_3$	Aliphatic epoxide	Methoxy
γ-Mercaptopropyl trimethoxysilane	$HSCH_2CH_2CH_2Si(OCH_3)_3$	mercapto	Methoxy
γ-Aminopropyltriethoxy silane	$NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$	Amino	Ethoxy
N-β-(Aminoethyl) aminopropyl trimethoxysilane	$NH_2CH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$	Amino diamino	Methoxy

(b) Hydrogen bonding to the surface:



(2)

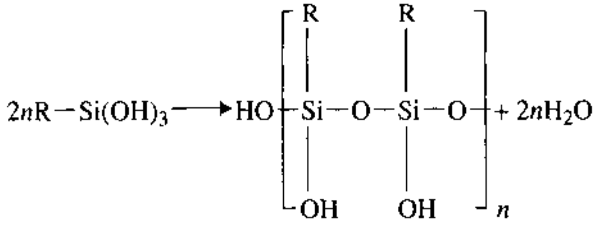
(c) Condensation with the surface:



$$R-Si(OH)_3 + HO-Si \longrightarrow R-\underset{\displaystyle OH}{\overset{\displaystyle OH}{Si}}-O-Si + H_2O$$

(3)

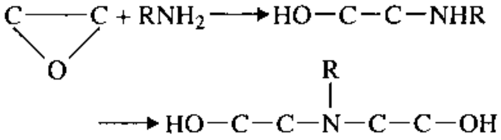
(d) Polymerization:



$$2nR-Si(OH)_3 \longrightarrow HO\left[\underset{\displaystyle OH}{\overset{\displaystyle R}{Si}}-O-\underset{\displaystyle OH}{\overset{\displaystyle R}{Si}}-O\right]_n + 2nH_2O$$

(4)

(e) Reaction with the polymer:



(5)

In this case reaction of the primary amine group in an aminosilane with an epoxide group.

Hydrolysis, Eq. (1), may take place on the surface by reaction with surface water or in solution prior to application, occurring rapidly in neutral or slightly acidic water solutions and only slowly in hydrocarbon solvents [31]. Aminosilanes are autocatalytic and do not depend entirely on hydrolysis for aqueous solubility [32]. Polymerization, Eq. (4), may occur not only on the surface as the silane triols, $RSi(OH)_3$, condense to form oligomeric siloxanes as in Eq. (3) via disiloxanols and trisiloxanols but also in solution before application. The speed at which this occurs and the oligomers become insoluble depends on silane concentration, solution pH, the presence of soluble catalytic salts [16], and the type of silane [33]. The pH factor is particularly important in silane technology.

The hydrolyzed silanol group will react with inorganic surface hydroxyl groups to form hydrogen bonds, Eq. (2), followed by condensation to form oxane bonds, Eq. (3). It should be noted that both hydrogen and oxane bond formation is reversible. Equation (5), reaction with the polymer, is a typical example of many possible reactions, depending on the functional groups on the silane and the polymer. In work with surface coatings, Walker [34] has postulated a variety of possible chemical reactions between silanes and the functional groups present in epoxide and polyurethane compositions.

B. Nature of Silane Films on Metals and Glass

Bascom [35] employed a variety of techniques in his study of the structure of silane films deposited on glass and metal substrates and concluded that vinyl-, amino-, and chloro-functional silane films were deposited as polysiloxanes, some of which could easily be removed from the surface by organic solvents or water. Contact-angle measurements on the remaining strongly retained material indicated it to be of an open polymeric structure since it was easily penetrated by the wetting liquids. That the critical surface tension of a silane film is not an important factor in adhesion promotion by silanes is indicated by many measured values below the minimum Y_c value of about 35 dyn/cm for polyesters and 43 dyn/cm for epoxides for optimum wetting to occur [16]. It is suggested that on glass the performance of reactive silanes parallels reactivity rather than polarity (as described by the solubility parameters) of the organofunctional groups [36]. Plueddemann concludes that reactivity of the silane in copolymerization is much more significant than polarity or wettability [16].

Films deposited from nonpolar solvents are relatively thick (>1000 Å) and resistant to desorption; films from polar solvents are generally thinner (<100 Å) and easily disrupted by polar solvents. An adsorbed silane film can consist of different strata: a silane interface with covalent bonding [10], a relatively cross-linked intermediate layer, and a superimposed layer of relatively un-cross-linked material. In practice, adsorbed films on both glass and metals are discontinuous and consist of discrete islands or agglomerates, called the button-down theory [37].

The molecular structure of silane films has been shown to depend to a great extent on the pH of the solution from which it was deposited. Using modified infrared spectroscopy to examine films of γ-aminopropyltrimethoxysilane (APS) adsorbed on iron and aluminum surfaces, Boerio and Williams [38] demonstrated that the nature of the film was highly pH dependent. When deposited from solutions of pH below 9.5, the films were of the structure indicated by the expected interaction with oxides with the amine functional groups uppermost and available for reaction with the polymer. When the solution pH was greater than 9.5, the film structure was reversed, suggesting a reaction between the amino groups and the surface. In this case the organofunctional groups were not available for reaction with the polymer. Further, this upside-down structure resulted in less hydrolytically stable bonds.

In an investigation of epoxide joints on iron and titanium using γ-APS as a primer, Boerio [39] concluded that although the film structures formed by γ-APS adsorbed onto the two metals were very similar, the performance of the films as adhesion promoters was very different. He concluded that the performance was determined by the orientation of the APS molecules at the oxide surface rather than by the overall structure of the film. The orientation was determined by the isoelectric point of the oxide and the pH at which the films were adsorbed onto the oxide [39,40]. A comprehensive account of the structure of APS silane films is provided by Ishida and co-workers [41].

C. Performance of Silanes in Adhesive Technology

Boerio and co-workers [32,39] showed that the average shear stress of epoxide/titanium lapshear joints primed with γ-APS at either pH 10.4 or 8.0 showed almost no decrease in strength after water immersion at 60°C for 60 days; unprimed controls lost 75% of their original strength. Epoxide/iron joints primed with APS at pH 8.0 retained 75% of their original strength after 60 days. Kaul and co-workers [24,42] investigated the strength of epoxide/aluminum single lapshear joints primed with γ-APS and showed that the use of γ-APS resulted in a lower dry bond strength than the unprimed control, and thicker films produced even lower bond strengths. The strength retention of unprimed joints after water immersion at 55°C was approximately 80% of the original, whereas the joints primed and standard dried (1 h at 25°C under vacuum) maintained only 50% of the dry strength. Joints primed and dehydrated (10 days at 110°C under vacuum) before bonding showed more than 95% retention.

In particularly useful paper, Gledhill and co-workers [43] investigated the effects of silane type, solution pH, solution age, and drying on the bond strength of a bisphenol A diglycidyl ether-based epoxide in a butt joint configuration. Several silanes were investigated. Unprimed joints showed a fall in bond strength from 37 to 5.8 MPa after 1500 h of immersion in water at 60°C. Joints treated with an aqueous 1% solution of γ-glycidoxypropyltrimethoxysilane (GPMS) aged for periods up to 24 days before application showed a retained bond strength of between 17.5 and 34.4 after the same immersion time, with a peak retention between 30 and 90 min of aging. In a similar experiment using a solution of 95 parts of ethanol and 4 parts of water there was no solution age dependency, the recorded joint strengths were lower, and there was no evidence of increased water resistance. Attempts to accelerate the drying of the aqueous γ-GPMS film resulted in a marked reduction in bond strength. In a study of bismaleimide adhesives the same authors showed that the use of an aqueous splution of γ-APS increased the bond strength of the unprimed joint from 9.7 MPa–23 MPa, but was highly dependent on solution pH.

Kerr and Walker [28] investigated the bond strength of a two-pack polyamide-cured adhesive and a diphenylmethane diisocyanate-cured polyester adhesive on mild steel, stainless steel, and aluminum in a butt tensile configuration using a range of silanes as pretreatment primers and additives. It was shown that not all silanes were effective adhesion promoters on all substrates. The most effective silanes were γ-mercaptopropyltrimethoxysilane (MPS) on stainless and mild steel and *N*-β-(aminoethyl)-γ-aminopropyltrimethoxysilane (AAMS) on degreased aluminum and stainless steel, with the urethane, where a 20% improvement in bond strength was achieved. AAMS was the most effective on degreased aluminum with the epoxide. On grit-blasted substrates, considerably higher bond strengths were achieved. In the comparative trials all the silanes were found to be more effective when used as pretreatments rather than as additives, a finding directly opposed to that found in the case of surface coatings, where the opposite was true. It was considered that this was a function of viscosity and curing time. After exposure to 100% relative humidity for periods up to 2 years, stainless steel specimens coated with MPS and γ-GPMS showed an equilibrium bond strength retention more than double that of the uncoated controls. On glass the retention values were four to five times greater.

Hong and Boerio described a particularly interesting practical use of silanes in obtaining good adhesion to mineral oil-contaminated steel substrates [44]. They showed that the addition of 5 wt% of γ-GPMS to amidoamine-cured epoxide adhesives [Epon 828 and V115 (both Shell Chemical Co.)] to oil-contaminated mild steel lapshear specimens increased the initial bond strength from 968 psi to 1556 psi. More surprisingly, the specimens immersed in boiling water for 12 h increased to 1681 psi, whereas the nonsilane control decreased to 665 psi.

VI. ZIRCONATES

Organometallic compounds based on zirconium are actively being promoted as adhesion promoters and are claimed to function as coupling agents. Zirconium compounds appear to have widespread potential for use in the polymer industries since they exist in both water and organic solvent–soluble forms. The aqueous chemistry is dominated by hydrolysis, depending on zirconium and hydrogen ion concentration and the nature and concentration of anions present. Depending on the ligand present the polymeric species in solution can be cationic, anionic, or neutral [17]. Simplified structural representations of polymeric zirconium species are shown in Fig. 1

Solvent soluble compounds include zirconium acetylacetonate, zirconium methacrylate, and the family of neoalkoxyl zirconates. Some commercially available zirconates are shown in Table 3. Wang [8] has described the synthesis of a soluble linear Schiff base zirconium-based coordination polymer (*N*, *N*′, *N*‴, *N*‴-tetrasalicylidene-3,3′-diaminobenzidene) zirconium, and other hybrid copolymers, and has demonstrated improved adhesion on glass and aluminum substrates for poly(methyl methacrylate), polyethylene, and polypropylene when used as hot-melt compounds.

Studies on a reactive PVA copolymer (commercial vinyl alcohol), vinyl acetate copolymers stabilized by *N*-methylol acrylamide, and unreactive PVA homopolymer emulsions have shown that the resistance of these materials to cold- and boiling-water immersion tests can be improved considerably by the addition of zirconium oxychloride, zirconium-hydroxychloride, and zirconium-nitrate. These improvements in water resistance are considered to occur in the former cases by interaction between polynuclear

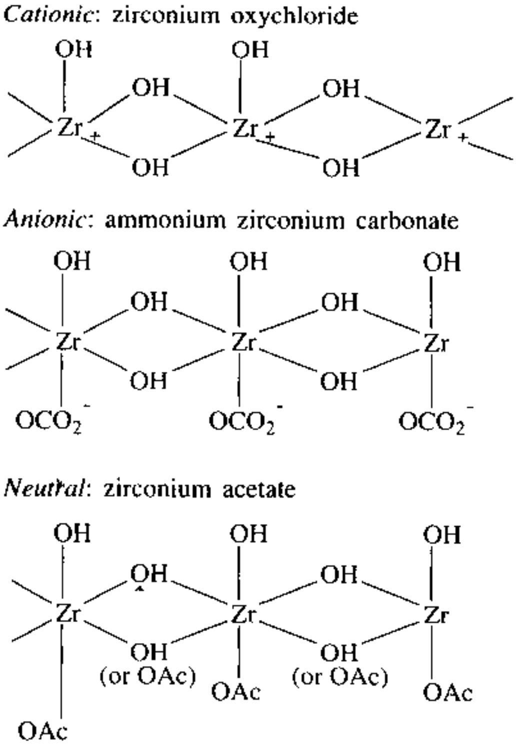
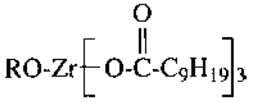
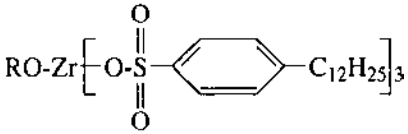
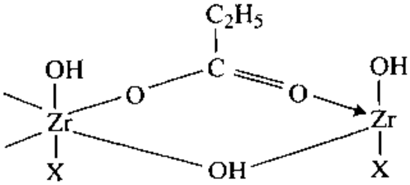


Figure 1 Structure representations of polymeric zirconium species.

Table 3 Typical Zirconate Coupling Agents

Chemical Description	Structure
Neoalkoxytrisneodecanoyl zirconate	 $RO\text{-}Zr\left[O\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}C_9H_{19}\right]_3$
Neoalkoxytris(dodecanoyl)benzene sulfonyl zirconate	
Neoalkoxytris(ethylenediaminoethyl) zirconate	$RO–Zr(–O–C_2H_4–NH–C_2H_4–NH_2)_3$
Neoalkoxytris(*m*-aminophenyl) zirconate	$RO–Zr(–O–C_6H_4–NH_2)_3$
Zirconium propionate	 $X = OH$ or $O_2CC_2H_5$

zirconium species and functional groups on the polymer and in the latter by reaction with the colloidal stabilizer. In these cases the zirconium compounds are functioning by an insolubilization process rather than as an adhesion promoter per se, but the end result is an increase in wet adhesion [45].

Other zirconium-containing coupling agents are the zircoaluminates, which are described in the technical literature [46] as inorganic polymer backbone materials of low molecular mass containing specific atom ratios of zirconium and aluminum with two organic ligands: one for overall molecular stability and the second to confer organo functionality; The commercial range includes amino-, carboxy-, and methacryloxy-functional compounds. It is claimed that the addition of these materials to adhesives and surface coatings improves their wet adhesion materially [47].

VII. TITANATES

A comprehensive patented range of titanates is marketed by Kenrich Petrochemicals, Inc. under the trade name Ken-React, and most of the published data on titanates emanates from this source. It is claimed that a typical titanate coupling agent provides six functions [17], although only three may be considered relevant to their use as adhesion promoters: the reaction of the alkoxy group of the titanate with free protons on the mineral surface to form an organic monomolecular layer on the substrate; transesterification resulting in cross-linking with carboxyl and hydroxyl groups in the polymer; and possibly chain entanglement. Titanate coupling agents are unique in that their reaction with free protons on the substrate surface results in a monomolecular layer on the mineral surface whether it be filler particle or metallic substrate. The reaction proceeds according to the equation

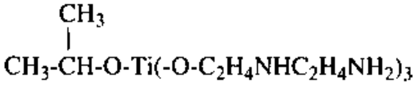
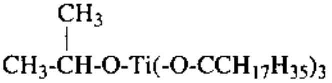
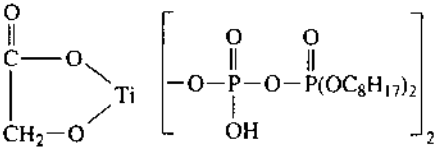
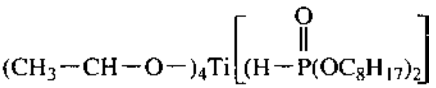
$$R'O = Ti(OR)_3 + M = OH \rightarrow MOTi(OR)_3 + R'OH \qquad (6)$$

where $R'O$ is a hydrolyzable moiety. Cassidy and Yager [48] speculate that ester linkages are hydrolyzed and coordination or condensation occurs between the resulting hydroxyl groups and substrate surface groups. Calvert and co-workers [49] infer the presence of strong bonds between isopropoxytitanium tristearate and SiO_2 and Al_2O_3 by the failure to remove the coupling agent by an extended hot-water treatment.

X-ray photoelectron spectroscopy studies by Yang and co-workers [50] showed that aluminum and steel surfaces treated with di(dioctyl)pyrophosphate were covered with the titanate coupling agent, and in the case of steel, the octyl groups of the titanate molecule were uppermost, confirming the view that titanates modify hydrophilic metal oxide surfaces with a hydrophobic organic layer. The possibility has been raised that acidic surface sites on glass may catalyze condensation with surface silanols when chelate titanium acetyl acetonate is used [8]. The range of chemical types include monoalkoxy, chelate, coordinate, neoalkoxy, and cycloheteroatom. A very few of the wide range of commercial titanate coupling agents available are shown in Table 4.

Although there are many references to the improvement in adhesion of surface coatings obtained by the use of titanates, numerical data are sparse [51] and few are available on their use in conjunction with adhesives. The literature contains conflicting evidence on the value of titanate adhesion promoters, and in an investigation of eight titanates tested with an acrylic resin only two titanates performed better than the nontitanate control, It has been claimed that alkyl titanates are effective coupling agents for polyethylene [52–54]. Using isopropyl triisostearoyl titanate as a primer

Table 4 Typical Titanate Coupling Agents

Chemical Description	Structure	Type
Isopropyl tri(*N*-ethylaminoethylamino) titanate	 $CH_3\text{-}\overset{\overset{CH_3}{\vert}}{CH}\text{-O-Ti(-O-}C_2H_4NHC_2H_4NH_2)_3$	Monoalkoxy
Isopropyl triisostearoyl titanate	 $CH_3\text{-}\overset{\overset{CH_3}{\vert}}{CH}\text{-O-Ti(-O-}CCH_{17}H_{35})_3$	Monoalkoxy
Titanium di(dioctylpyrophosphate)oxy acetate		Monoalkoxy
Tetraisopropyl di(dictylphosphito) titanate	 $(CH_3{-}CH{-}O{-})_4Ti[(H{-}\overset{\overset{O}{\Vert}}{P}(OC_8H_{17})_2]$	Coordinate
Neoalkoxytri[*p*-*N*-(β-aminoethyl)amino phenyl] titanate	$RO\text{–}Ti(OC_6H_4NHC_2H_4NH_2)_3$	Neoalkoxy

for polyethylene/Al_2O_3 joints, Sung and co-workers suggested that it was unlikely that this particular titanate functioned as an adhesion promoter in this system, notwithstanding the observation that heating the titanate above 70°C in vacuo resulted in a significant increase in peel strength [55].

Calvert and co-workers [49] have demonstrated the presence of isopropyl isostearate and isopropyl laurate in commercial isopropyl triisostearoyl titanate and conclude that this is the reason why the commercial product does not function as an adhesion promoter; treatment at 70°C in vacuo removes these fatty acid esters. It has been suggested to the author that failures to obtain improvements in adhesion using titanates can be remedied by isolating the pure compound (B. Nordenheim, private communication, 1988). It is possible that improvements in adhesion are more likely when commercial titanates are used as additives rather than as pretreatment primers.

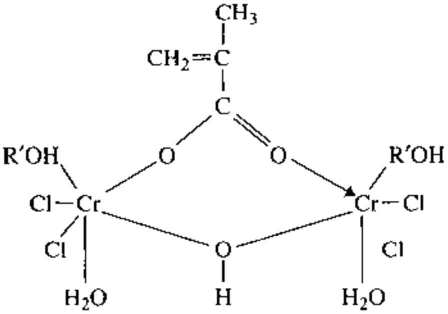
It is only fair to say that the trade literature [17] is emphatic that it is critical to use the correct amount of titanate coupling agent. The use of excessive amounts is probably the most significant factor in application failure tests. It is strongly recommended that selected titanates should be examined in a range of concentrations from 0.1 to 2.0% by mass in a filled system and even lower for unfilled systems. Excess titanate will result in unreacted alkoxy groups on the surface and in a loss of adhesion of the polymer. This could lead to the mistaken conclusion that a particular titanate was unsuitable or even harmful.

In general, titanates with the more polar organic moieties such as isopropyl tri(*N*-ethylenediamio)ethyl titanate and neoalkoxytri[-*P*-*N*-(β-aminoethyl)amino phenyl] titanate are recommended for adhesion promotion to polar substrates. Titanates with relatively nonpolar moieties, such as aliphatic carboxy titanates and isopropyl tri(dioctylphosphato)titanate, will adhere better to the nonpolar substrates.

VIII. CHROMIUM-CONTAINING PROMOTERS

Adhesion promoters containing chromium fall into two main classes: inorganic and organic complexes. Examples of the former are the chromate conversion coatings used extensively in the aerospace industries for pretreatment of aluminum and its alloys. Although acting as anticorrosion coatings in their own right, they improve paint adhesion substantially [56]. Chromium conversion coatings that may be of chromium phosphate (amorphous, accelerated, or nonaccelerated) may be applied by brush dip or spray. The crystalline chromium phosphate type is normally restricted to steel surfaces. In a simulated sterilization test using epoxide can coatings on an aluminum surface, Paramonov and co-workers showed that the use of a chromate conversion coating was essential for satisfactory adhesion [57].

Examples of the organic type are the coordination complexes of trivalent chromium chloride with carboxylic acids (Volan manufactured by Du Pont). The methacrylate–chrome complex is well known in fiberglass technology. In water solution the chromium chlorides hydrolyze to form basic salts that form oligomeric salts through solvation of hydroxyl groups on the adjacent chromium molecules. Hydroxyl groups also bond to silanol groups on the glass surface via hydrogen bonding and possibly covalent oxane bonds. The organic acid group develops a fairly stable bond to chromium by being coordinated to adjacent chromium atoms [8]. Other chromium complexes of functional carboxylic acids have been proposed [58]. Following is a typical structure:



A trivalent chromium fumarato-coordination compound, Volan 82, has been claimed to be an effective adhesion promoter for polyethylene coatings on aluminum. The toxicity of chromium compounds must place a question mark against their continued use as adhesion promoters.

IX. OTHER ADHESION PROMOTERS

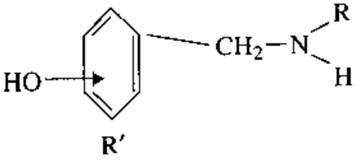
In addition to the organometallic adhesion promoters, a large number of inorganic, organometallic, and organic compounds have been investigated, usually in specific adhesives and coatings or on selected substrates. A comprehensive account of coupling agents in use prior to 1969 is provided by Cassidy and Yager [48]. Although much of the reported information on other adhesion promoters concerns their use with surface coatings or filled systems, it is likely that many would also be suitable for use with adhesives and have therefore been included in the interests of completeness.

A. Phosphorus-Containing Compounds

Tritolyl phosphate (TTP) has been examined as a pretreatment for E-glass in epoxide laminates and thermoplastic adhesives for bonding poly(vinyl chloride) to aluminum, steel to zinc, and acrylonitrile–butadiene styrene to aluminum [59]. Mono- and diphosphate esters have been claimed to be suitable adhesion-promoting primers for acrylic adhesives on metal [60,61], unsaturated acid phosphates have been suggested as primers for use on metals to be bonded with free radical initiated adhesives [42], and thiophosphate esters have been suggested for adhesives to be used on plastics, ceramics, and metals [62].

B. Amines

Hydroxybenzamines of the general formula have been claimed to improve the adhesion of a wide range of coatings to zinc and cadmium and other metallic substrates when used as either pretreatment primers or additives [63]. Ethylenically unsaturated hydroxy-functional amines have been claimed to improve the adhesion of water-based systems [64], and amines have been examined as adhesion promoters for aromatic isocyanate cured adhesives on glass and other substrates [65]. Primary aliphatic amines are claimed to improve the bondability of polyolefines [66] and an oxyethylated polyethylene polyamine claimed for polymer-to-polymer bonding [67].



4-Ethylpiperidine has shown promise as an adhesion promoter [68], aminoethylpiperidine has been shown to be beneficial in steel–epoxide systems [48], and primers based on piperidine derivatives improve the adhesion of adhesives to aluminum and stainless steel [69]. Pyridene derivatives such as 2-(2-methylethyl)pyridene are claimed to be effective primers for crystalline and nonpolar polymers to be bonded with cyanoacrylate adhesives [70].

C. Organic Resins

A wide variety of organic resins have been claimed to act as adhesion promoters on many different substrates Mahajan and Ghatge have reported that the use of a liquid epoxide resin (epoxide equivalent 260) materially improved the initial adhesion of polysulfide sealants to anodized aluminum alloy [71]. Abietate-terminated polysulfide polymers, epoxide-terminated polysulfide polymers; and abietate-terminated polyesters have also been claimed to improve the adhesion of polysulfide sealants [72]. Oxygenated fluorocarbon primers are claimed to improve the bonding of polyacetal and polyamide–imide substrates [73]. A primer based on an ethylene–vinyl mercaptoacetate copolymer has been shown to improve the adhesion of epoxide adhesives to steel [74]. Primers containing diorganopolysiloxanes are claimed to improve the adhesion to silicone elastomers [75], and aromatic polyether resins with aminophosphonic acid groups are stated to improve the adhesive bonding of steel, galvanized iron, and aluminum [76].

D. Miscellaneous Promoters

DeNicola and Bell report the use of bibenzoylmethane and 1-(O-hydroxyphenyl)-3-phenyl-l,3-propanediol as wet adhesion promoters for epoxide resin adhesives on low-carbon mild steel [77]. Metal chelating O-hydroxybenzlamine compounds are stated to produce adhesion-promoting films on metals [78], and improved adhesion to titanium is claimed for metal alkoxide primers. Oxazolidines containing trialkoxy or triaryloxysilyl groups are claimed to be adhesion promoters on metallic substrates [79]. Improved adhesion of epoxide resin adhesives to copper substrates can be achieved by pretreatment in a weak solution of a benzoheterocyclic(thiol) compound [80] and benzotriazole and derivatives have been claimed to improve the bond between vinyl polymers and steel [81] and the adhesion of photosensitive compounds to polymeric substrates [82]. Pesetski and Aleksandrova describe the use of dicarboxylic acids as primers for polyamide films on copper [83].

X. EFFECTS OTHER THAN ADHESION PROMOTION

It should be noted that side effects are possible when using adhesion promoters/coupling agents as additives in adhesives and coatings, usually beneficial but not invariably so.

Beneficial effects from the use of titanates include deagglomeration, improved wetting, improved corrosion resistance, increased hydrophobicity, electrical conductivity in conducting systems, and acid resistance. The overall rheology of filled systems may be changed by both titanates and silanes requiring products to be reformulated. Silanes, particularly amino silanes, may function as curing agents or accelerators in epoxide and urethane adhesives, thereby reducing the pot life of a mixed system. These side effects should be considered in the selection or rejection of an adhesion promoter even if adhesion is the primary concern.

XI. CONCLUSIONS

In attempting to cover such a wide and diverse topic as adhesion promoters in a short chapter, the author is aware of many gaps in the information presented and the omission of many aspects of theoretical and practical interest; it is hoped that the references quoted will fill many of these gaps. It has been demonstrated that adhesion promoters/coupling agents have a major role to play in the development of adhesive technology, but only if due regard is paid to the importance of matching the promoter to the substrate and the polymer, pH effects, solution age, dosage, and film thickness. Plueddemann concludes that the performance of coupling agents may depend as much on the physical properties resulting from the method of application as on die chemistry involved.

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11

Testing of Adhesives

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I. INTRODUCTION

The molecular mechanisms by which materials can adhere to one another have not been determined unambiguously. To date, no one has been able to predict reliably the strength of an adhesive joint based purely on the properties of the adhesives and adherends. Rather, to determine the strength of a joint, one must resort to testing. As will hopefully be made clear in this chapter, testing is not always as straightforward as it might appear superficially. Testing is, however, an important aspect of adhesive science and technology. Tests are conducted for a wide variety of purposes. There are a large number of different standard adhesive tests available to the technologist, engineer, or scientist, depending on his or her goals. It is essential not only that the proper test be selected (or designed) and that care be exercised in conducting the test, but also that the results be interpreted properly. The latter aspect often requires considerable background and insight.

II. STANDARD TESTS

In the United States, the American Society for Testing and Materials (ASTM) is the organization that has assumed the responsibility for the "development of standards on characterization and performance of materials, product systems and services, and the promotion of related knowledges." The testing specifications of other organizations (such as the military in their "Mil-Specs") often parallel those specified by ASTM. ASTM operates as a source of voluntary consensus standards. Most other countries (or groups of countries) have similar organizations, and there is considerable interaction and interchange between these groups from the various countries. For example, many of the standards adopted by European and Asian groups find their basis in ASTM, and vice versa. This is accomplished through coordinating committees from the various countries that meet frequently. While the standards of most of these countries could be cited in this chapter, the authors will rely almost exclusively on ASTM since these are the standards with which they are most familiar. The interested reader can usually find comparable standards in his or her own country. ASTM publishes an Annual Book of Standards that updates the test methods and other details on a yearly basis. The changes are seldom revolutionary but rather, evolutionary. New standards do appear, however, and all standards are reviewed periodically, at which time they may be eliminated or updated. The responsibility for developing new standards, revising existing standards, and approving standards for publication falls on ASTM volunteer committees. Of the more than 30,000 members of ASTM, nearly two-thirds serve on such committees. This is no small task. The 1990 Annual Book of Standards was composed of 68 volumes, divided among 16 sections. It is not uncommon for these volumes to be more than 500 pages long and some have nearly twice this many pages. The D-14 committee has the primary responsibility for adhesives. Volume 15.06 is the ASTM publication that covers most adhesive standards. Including indexes and the like, it has some 485 pages covering 116 standards.

To this point we have used the term s*tandard* in a very general sense. ASTM has a hierarchy of types of communications of this general nature, which are defined as follows:

1. *Classifications* are a systematic arrangement or division of materials, products, systems, or services into groups based on similar characteristics (origin, properties, composition, etc.) in which the instructions or options do not recommend specific courses of action.
2. *Guides* provide a series of options or instructions but do not recommend a specific course of action. The purpose here is to offer guidance based on a consensus but not to establish fixed procedures.
3. *Practices* outline definitive procedures for conducting specific operations or functions, that do not produce specific test results (comparative test methods).
4. *Specifications* are a precise statement of a set of requirements to be satisfied by a material, system, service, and so on, and the procedures to be used to determine if the requirements are satisfied.
5. *Terminology* is a document that helps standardize the terminology, their definitions, descriptions, symbols, abbreviations, acronyms, and so on. The relevant example here is D-907, Standard Terminology of Adhesives, which was originally published in 1947 and most recently approved by D-14 in 1990. This provides definitions for several hundred terms in common use in adhesive science and technology. Despite this very worthy effort, the use of many terms is somewhat ambiguous and a reader/researcher must seek to determine a word's exact meaning by looking at the context in which it is used.
6. *Test methods* are definitive procedures for identification, measurement, and/or evaluation of qualities, characteristics, or properties of materials, products, systems, or services. These will, in general, produce test results.

III. SOME SELECTED STANDARDS

Tests are performed for a wide variety of different reasons. Many tests have as a goal to compare different materials, procedures, products, and so on. For such comparisons to be meaningful, it is important that some type of standard procedure be used to obtain the information that will be used for comparison. This is, of course, one of the most important reasons for having standards. The goal is to separate, as much as possible, the results obtained from differences due to the laboratory or operator. In principle, one should be able to compare results from one operator (say, in Europe) with those in another place (say, in the United States).

Furthermore, all tests are not conducted with equa1 rigor. Quantitative testing is generally expensive and time consuming. Testing organizations have at times, therefore, developed qualitative tests that might be used to eliminate obvious unlikely candidates quickly. ASTM-D-3808, Spot Adhesion Test, is a good example of such a test. It is well established both theoretically and empirically that all adhesive–substrate pairs are not equally compatible. An adhesive that might tightly adhere to one substrate may form very weak bonds with other substrates with varying degrees between these extremes. To prepare and test standard quantitative test geometries (some of which will be described subsequently) for a large number of candidate adhesives for a given substrate could be prohibitively expensive. ASTM D-3808 suggests the following alternatives:

1. Prepare candidate substrates using techniques similar to those expected in service.
2. Mix a quantity of the candidate adhesive according to the procedures specified by the adhesive manufacturer.
3. Small spots of the adhesive (typically 5–10 mm in diameter) are placed on the substrates using application and curing techniques comparable to those expected in service or specified by the manufacturer.
4. The operator then uses a thin stainless steel spatula (or similar probe) to pry or lift the spot from the substrate. The operator then uses his or her senses to assess ease of separating the spot from the substrate.

Based on this operation, a decision is made as to whether this system is worthy of further quantitative analysis. Some quantitative tests are the subject of the next section.

A. Tests for Adhesive Joint Strength

A relatively large number of tests have been proposed and formalized for evaluating the strength of an adhesive. Although there are some important exceptions (some covered in the following sections), the majority of the long-standing adhesive joint strength tests fall in three categories: tensile, shear, and peel.

1. *Tensile Tests*

Given the choice, a designer seldom uses adhesives in a direct tensile loading mode. The primary reason for this is probably related to the fact that by overlapping, scarfing, and so on, the contact area of the adhesive may be markedly increased over that of a simple butt joint. The finger joints used to produce longer pieces of lumber or in other wood construction are a familiar example of such techniques. Figure 1 clearly demonstrates the difference in bond area between a butt joint and one of the types of finger joint assemblies

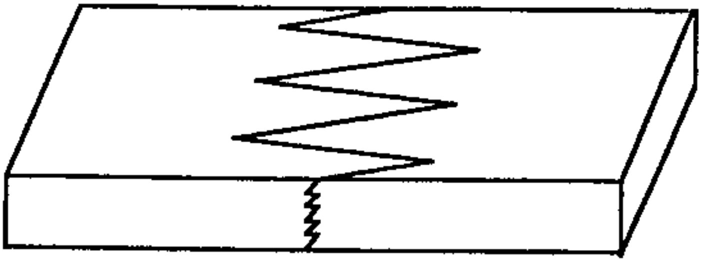


Figure 1 Typical finger joint.

described in ASTM D-4688. It is noted that this geometry also results in a change in the stress state. The butt joint appears to be dominated by tensile stresses (superficially at least). Differences in elastic–viscous–plastic properties between the adhesive and adherends induce shear stresses along the bond line even for the case of the pure butt joint, but the dominant "direct" stresses are tensile. (This is perhaps an opportune point to note that, as explained in more detail later, the stress distribution in joints is almost never as simple as it might first appear.) Clearly, for the tensile-loaded finger joint, shear stresses as well as tensile stresses are applied directly to the bond line. Another reason why tensile joints are avoided in design is because it has been observed empirically that many adhesives exhibit lower strength and high sensitivity to alignment when exposed to butt-type tensile stresses.

However, a variety of standard tensile tests are available. Sample geometries for some of the more common of these are shown schematically in Fig. 2. Figure 2a is a schematic representation of the configuration from ASTM D-897. It is used (with slight geometric alterations) for various adherends, ranging from wood to metal. It is often called the, "pi tensile test" because the diameter is generally chosen to yield a cross-sectional area of one square inch. Detailed specifications for U-shaped grips machined to slip over the collar on the bonded spool-shaped specimen, to help maintain alignment during loading, are given in the same standard. Our experience has been, however, that even with such grips, reasonable care in sample manufacture, and acceptable testing machine alignment, it is difficult to apply a really centric load. As a consequence, such experiments often exhibit quite large data scatter [1,2]. The specimens for ASTM D-897 are relatively costly to manufacture. To reduce this cost, ASTM D-2094 specifies the use of simpler bar and rod specimens for butt tensile testing. The D-2094 half specimens show in

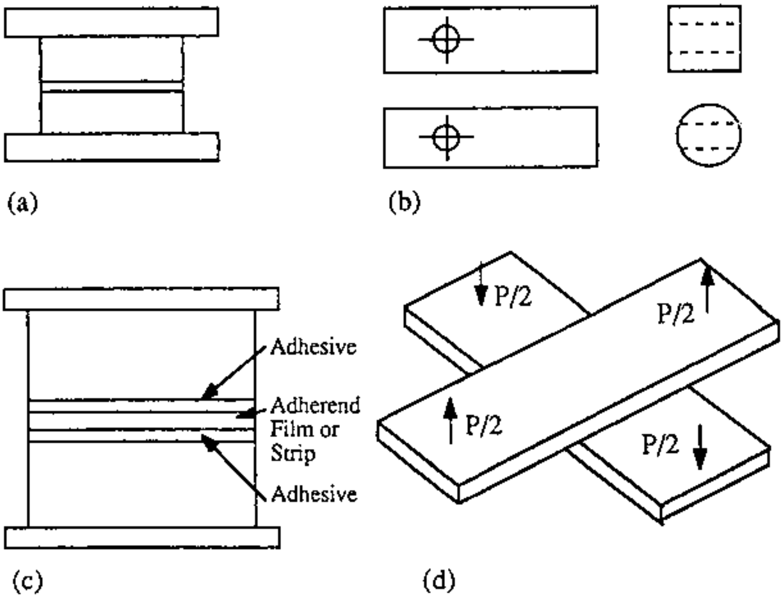


Figure 2 Tensile adhesion test geometries: (a) pi tensile test, ASTM D-897; (b) bar and rod tensile test, ASTM D-2094; (c) sandwich tensile test, ASTM D-257; (d) cross-lap tension test, ASTM D-1344.

Fig. 2b are loaded by pins through the holes. The testing specification also describes a fixture to assist in sample alignment, but this still remains a problem.

The specimens of both ASTM D-897 and D-2094 can be adapted for use with materials that cannot readily be manufactured into conventional specimen shapes, by the approach shown schematically in Fig. 2c. Such materials as plates of glass or ceramics and thin polymer films can be sandwiched between the spool-like sections made of materials that can be more readily machined such as metals. Obviously, to obtain meaningful results from this test, the strength of the adhesive bond to the spool segments must be greater than that to the thin film or sheet.

ASTM D-1344 describes a cross-lap specimen of the type shown in Fig. 2d for determining tensile properties of adhesive bonds. Wood, glass, sandwich, and honeycomb materials have been tested as samples in this general configuration. Even under the best of circumstances, one would not anticipate the stress distribution in such a case to be very uniform. The exact stress distribution is highly dependent on the relative flexibilities of both the cross beams and the adhesive. Certainly, caution must be exercised when comparing tensile strength from this test with data obtained from other tensile tests. Probably for these reasons, this test is scheduled by ASTM for discontinuation.

The results from these "tensile" tests are normally reported as the force at failure divided by the cross-sectional area. Such average stress information can be misleading. The importance of alignment has already been discussed. Even when alignment is "perfect" and the bonds are of uniform thickness over the complete bond area, the maximum stresses in the bond line can differ markedly from the average stress [3,4]. The distribution of stresses along the bond line is a strong function of the adhesive joint geometry. This is demonstrated in Fig. 3, which shows both the normal and shear stress distribution as a function of position for specimens of the general shape shown in Figs. 2a and b. These calculations assume an elastic adhesive that is much less rigid than the steel adherends and with a Poisson ratio of 0.49. The various curves in Fig. 3 represent differing diameter/adhesive thickness ratios, shown as the parameters listed for each curve. Note that both the normal stresses and the induced shear stress vary dramatically over the bonded surface. As described later, an understanding of stress and strain distribution in the adhesives and adherends is useful in fracture mechanics analysis. The average stress results commonly reported from standard tensile tests must be used with great caution in attempts at predicting the strength of different joints, even where the joints may be superficially similar. References 2 and 4 use numerical and experimental techniques to explore the effect of adhesive thickness on the strength of butt joints. The analysis and associated experimental results in these references illustrate that the strength of the joint and the locus of the point from which failure initiates are highly dependent on the adhesive thickness/diameter ratio.

2. *Shear Tests*

Some of the most commonly used adhesive joint strength tests fall under the general category of lap shear tests. Such samples are relatively easy to construct and closely resemble the geometry of many practical joints. The stress distribution for lap joints is far from uniform, but again the test results are commonly reported as load at failure divided by the area of overlap. The maximum stress generally differs markedly from this average value. More important, perhaps, failure of the joint is, in all likelihood, more closely related to the value of the induced cleavage stresses at the bond termini

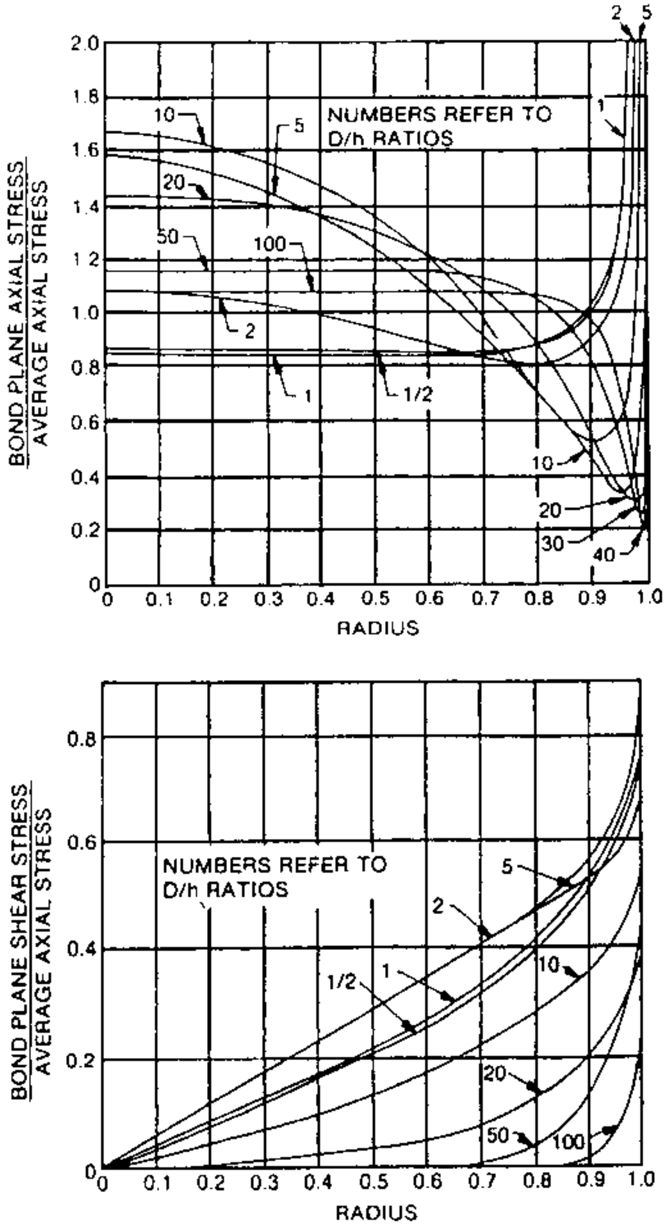


Figure 3 Axial and shear stress distributions in butt joints, $\nu = 0.49$. D/h is diameter/thickness ratio.

than to the shear stresses. Figure 4 shows several of the commonly used lap shear specimen geometries (i.e., those corresponding to ASTM D-1002, D-3165, and D-3528).

Because of flow of adhesive out the sides and edges as well as other difficulties in preparing and aligning the parts when preparing individual lap specimens, samples are frequently prepared from two relatively large sheets and the specimens are "saw" cut from the resulting laminated sheet. This is illustrated in Figs. 4b and 5 and described in ASTM D-3165. It has long been recognized that lap shear specimens such as those represented in

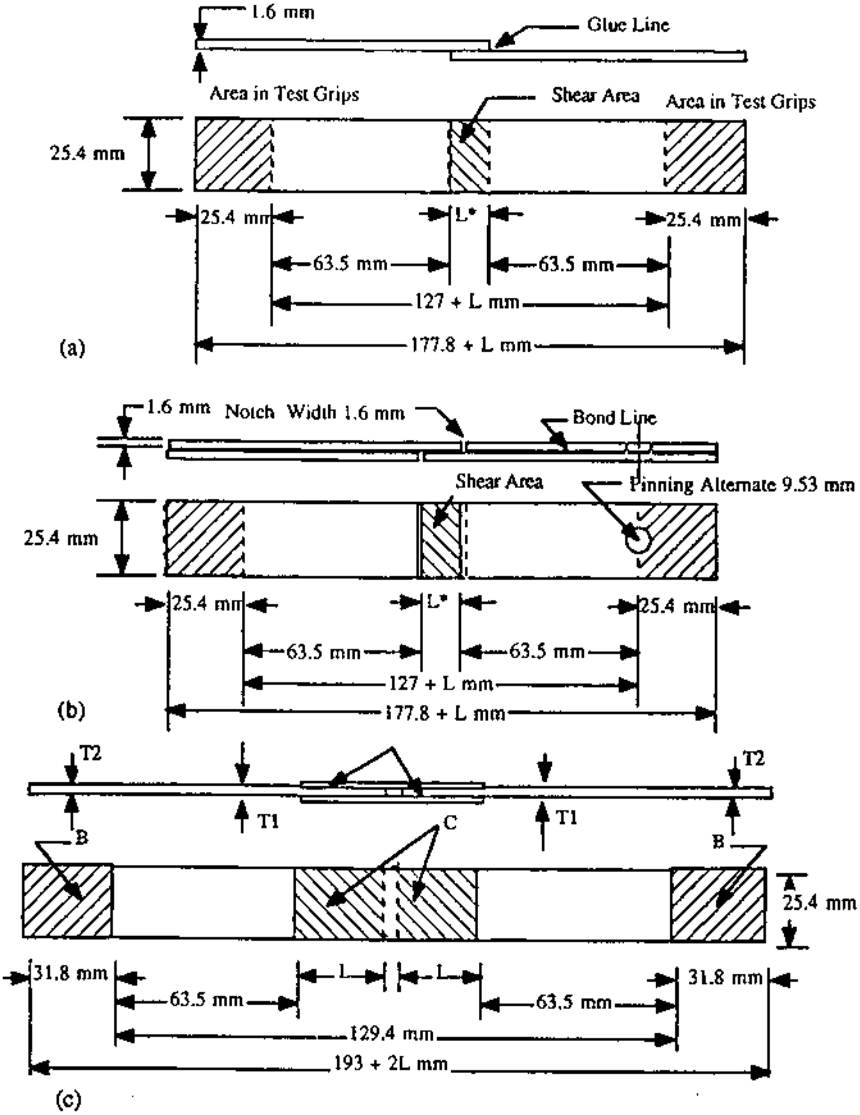


Figure 4 Standard lap shear geometries: (a) simple lap joint test, ASTM D-1002; (b) laminated lap shear joint test, ASTM D-3165; (c) double lap joint test, ASTM D-3528.

Fig. 4a and b must distort, so that the forces applied to the sample fall on the same line of action. This induces cleavage stresses in the adhesive near the bond termini. Double lap shear specimens described in ASTM D-3528 are proposed as a means of alleviating this problem (see Fig. 4c). However, based on our computer analysis and experimental studies, we feel that failure of double lap joints is still dominated by cleavage stresses [5].

As was the case for tensile specimens, the stress distribution in lap joints is intricately related to the details of the specimen geometry [2,6–16]. Such factors as amount of overlap, adhesive thickness, adherend thickness, relative stiffness (moduli) of the adhesive and adherend, and other factors critically influence the stress distribution. The maximum

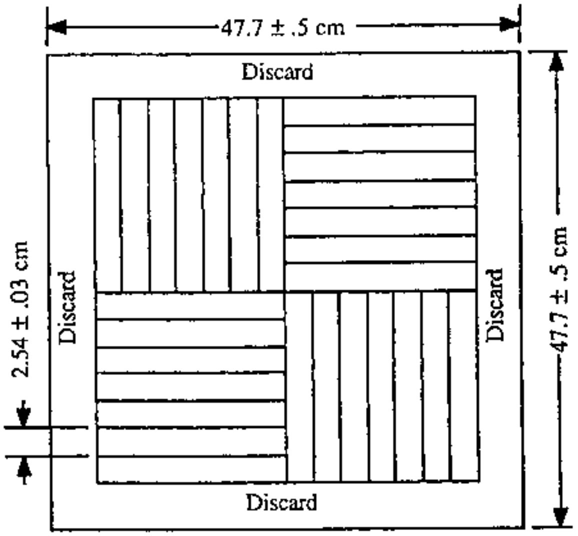


Figure 5 Large panel used to manufacture ASTM D-3165 specimens. The panel is cut into strips for testing.

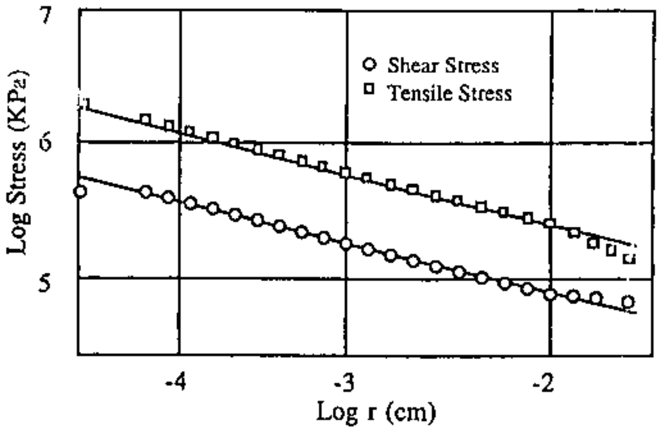


Figure 6 Log stress plot for the lap shear test.

stresses occur near the bond termini. Figure 6 shows the results of an elastic finite element analysis for the stresses in this region for a specimen of ASTM D-1002 geometry. Note that the tensile stresses are consistently higher than the shear. This fact, coupled with the fact that adhesives have typically been shown to be more susceptible to cleavage than shear failure, is consistent with the observation that cleavage rather than shear stresses usually dominate lap joint fracture.

A reason that one should be very cautious in attempting to use average shear stress criteria to predict failure of lap joints is illustrated in Fig. 7. This figure shows the force required to cause failure in ASTM D-1002 lap joint specimens using steel adherends of differing thicknesses. Note that for a given applied load, the "average shear stress" for all adherend thickness would be the same (i.e., the applied force divided by the area of

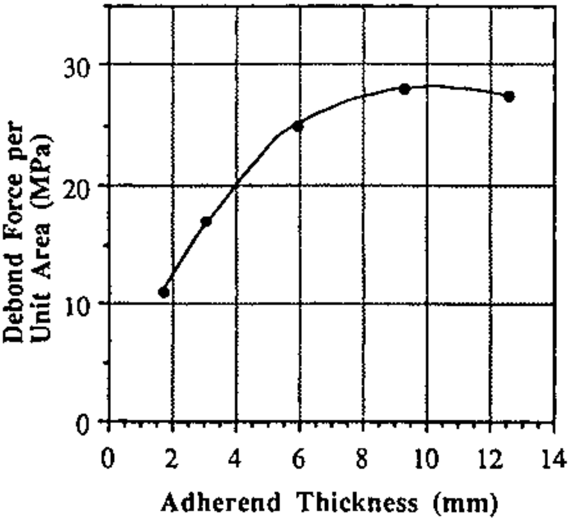


Figure 7 Force required to cause failure versus adherend thickness for ASTM D-1002 specimens using adherends of differing thicknesses.

overlap). If there was a one-to-one correspondence between this stress and failure, one would expect failure load to be independent of the adherend thickness. It is obvious from this figure that this is not the case. Similar results were obtained by Guess et al. [8]. The trends shown in Fig. 7 can be quantitatively explained using numerical methods and fracture mechanics [2,8]. Fracture mechanics is discussed later in the chapter.

A further indication of the popularity of lap shear tests is the number and variety of such tests that have been standardized as illustrated in the following examples. ASTM: D-905, Standard Test Method for Strength Properties of Adhesive Bonds in Shear by Compression Loading, describes test geometry, a shearing tool, and procedures for testing wood and similar materials. ASTM D-906, Standard Test Method for Strength Properties of Adhesive in Plywood Type Construction in Shear by Tension Loading, provides specifications for specimen shape and dimensions, grips and jaws, and testing procedures for testing plywood materials. ASTM D-2339 is a very similar test for plywood construction materials. ASTM D-3930 describes several adhesive tests, including a block shear test for wood-based home construction materials. D-3931 is similar to D-905, but for testing gap-filling adhesives; ASTM D-3163 and D-3l64 are similar to D-1002, except for use with plastics and plastic to metal instead of metal to metal. ASTM D-3983, Standard Test Method for Measuring Strength and Shear Modulus of Non Rigid Adhesives by a Thick Adherend Tensile Lap Specimen, describes a dual-transducer slip gauge, specimen geometry, and methods for determination of adhesive joint strength and modulus. ASTM D-4027 has a similar purpose but uses a more complex “modified-rail test” apparatus. ASTM D-4501 describes a shear tool and holding block arrangement for use in testing the force required to remove a square block of material bonded to a larger plate. D-4501 describes a shear test in which the specimen is a block bonded to a larger plate. D-4562 describes a shear test in which the specimen is a pin bonded inside a collar. The test uses a press to force the pin through the collar, which rests on a support cylinder. The test results in this case are the force required to initiate failure divided by the bonded area between the pin and collar. ASTM E-229 also uses a pin-in-collar type of specimen except that here torsional loading causes the failure. D-4896, Standard Guide for Use of Adhesive-Bonded

Single Lap-Joint Specimen Test Results, is intended to give insight into the interpretation of the results from all the lap shear tests. At other points in ASTM Vol. 15.06 and in this chapter, reference is made to other standard tests that use “shear-type specimens” to explore moisture, and other environmental, fatigue, and creep effects in adhesive joints.

3. *Peel Tests*

Another common type of test is the peel test. Figure 8 shows four common types of peel specimens. One can understand the test described in ASTM D-1876 by examining Fig. 8a.

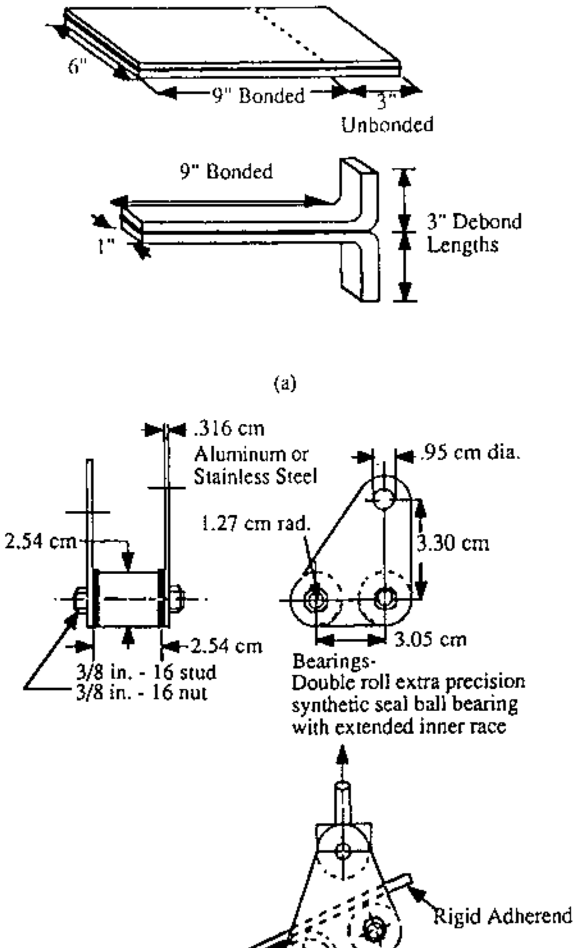


Figure 8 Some standard peel test geometries: (a) T-peel test specimen, ASTM D-1876; (b) typical testing jig used in ASTM D-1876; (c) climbing drum peel test, ASTM D-1781; (d) 180° peel test, ASTM 903.

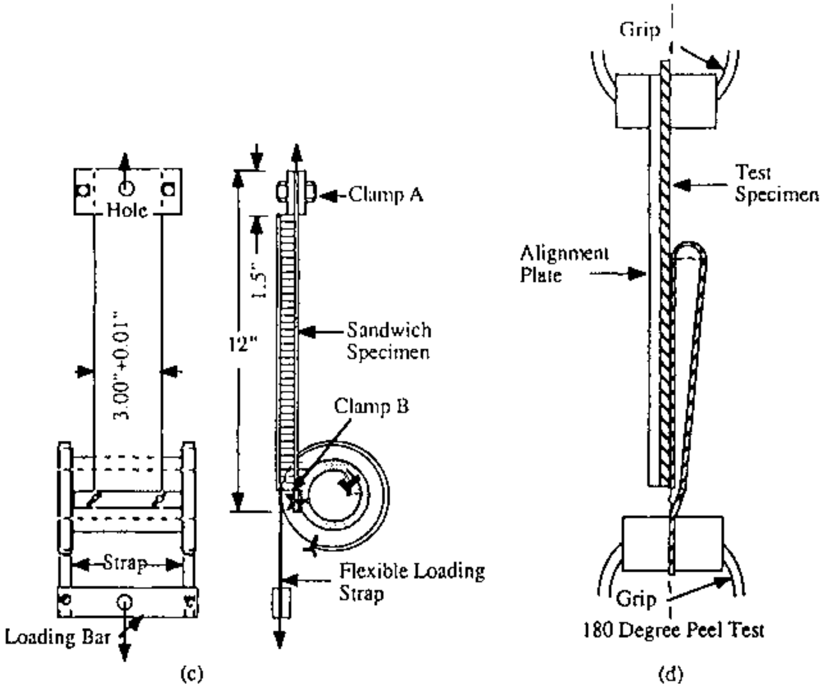


Figure 8 (Continued).

In this adhesive peel resistance test, often called the T-peel test, two thin 2024-T3 aluminum or other sheets typically 152 mm wide by 305 mm long are bonded over an area 152 mm wide by 229 mm long. The samples are then usually sheared or sawed into strips 25 mm wide by 305 mm long (at times, the sample is tested as a single piece). The 76-mm-long unbonded regions are bent at right angles, as shown in Fig. 8a to act as tabs for pulling with standard tensile testing grips in a tensile testing machine.

In a related test, one of the adhering sheets is either much stiffer than the other or is firmly attached to a rigid support. Various jigs have been constructed to hold the stiffer segment at a fixed angle to the horizontal and, by using rollers or other means, allow it to "float" so as to maintain the peel point at a relatively fixed location between the grips and at a specific peel angle, as show schematically in Fig. 8b (see, e.g., ASTM D-3167).

ASTM D-1781 describes the climbing drum peel test that incorporates light, hollow drums in spool form. The sample to be peeled is attached on one end to the central (smaller) part of spool. The other end of the sample is affixed to the clamp attached to the top of the crosshead of the tensile testing machine, as illustrated in Fig. 8c. Flexible straps are wrapped around the larger-diameter part of the spool and attached to the other crosshead of a loading machine. Upon loading, the flexible straps unwind from the drum as the peel specimen is wound around it and the drum travels up (hence the name "climbing drum peel test"), thereby peeling the adhesive from its substrate.

One of the simplest peel tests to conduct is the 180° peel test described in ASTM 903, Standard Test Method for Peel or Stripping Strength of Adhesive Bonds. In this test, one adherend is much more flexible than the other, so that upon gripping and pulling the two unbonded ends, the sample assumes the configuration shown in Fig. 8d.

Clearly, peel strength is not an inherent fundamental property of an adhesive. The value of the force required to initiate or sustain peel is not only a function of the adhesive type but also depends on the particular test method, rate of loading, nature, thickness of the adherend(s), and other factors [17]. Regardless, the peel test has proven to be a useful test for a variety of purposes.

The authors have been impressed with the interesting studies at the University of Akron [18,19], where Gent and his associates have used a peel test to measure the "work of adhesion." The work of adhesion is essentially synonymous with adhesive fracture energy, discussed in Section III.C. Gary Hamed has published an article reviewing some of the work at Akron [17]. This paper describes how peel tests have been used to, among other things, (1) verify the usefulness of WLF time–temperature superposition, (2) investigate dependence of the adhesive fracture energy on bond thickness, (3) study adherend thickness effects on adhesive strength, and (4) examine the effects of peel angle. J. R. Huntsberger has also written an interesting discussion on the interpretation of peel test results [20]. Others who have analyzed the stresses, energy dissipation, slip–stick phenomena, and other aspects of peel adhesion include Kaelble [21,22], Igarashi [23], Gardon [24], Dahlquist [25], Bikerman [26], and Wake [27].

Another type of test, somewhat related to both tensile and peel, are the cleavage tests, such as described in ASTM D-1062 and D-3807. This test uses a specimen that resembles the compact tension specimen used for fracture of metals except that there is an adhesive bond line down the sample center. The stresses for such a geometry are nonuniform, but typical test results are given as force per width (i.e., failure-loaded divided by bond width). ASTM D-3807 uses a specimen fabricated by bonding two narrow, long rectangular beams together to form a split double cantilever beam. The force required to initiate separation between the beams is measured and reported as average load per unit width of beam. ASTM 3433, 3762, and 5041 also make use of cleavage specimens. These are discussed in Section III.C because they are commonly used for determination of adhesive fracture energy. D-1184, Standard Test Method for Flexure Strength of Adhesive Bonded Laminated Assemblies, makes use of standard beam theory to calculate the interlaminar shear strength in laminated beams loaded to failure.

B. Environmental and Related Considerations

Adhesives are often used in applications where they are exposed to continuous or intermittent loads over long periods. It is difficult to duplicate such conditions in the laboratory. Neither is adhesive testing and/or observation under actual service conditions a very feasible alternative. The designer is not usually able or willing to await the results of years of testing before using the adhesive, and to tie up testing equipment and space for such long periods would be prohibitively expensive. There are, however, companies, universities, and other industry groups that have loading racks or other test systems where samples are exposed to dead weight or other loadings while exposed to "natural-weathering" conditions. It is advantageous, however, to have these backed up with (and an attempt made to relate them to) accelerated tests. These accelerated tests are generally experiments in which extreme conditions are used to increase the rate of degradation and deterioration of the adhesive joint. Although it is seldom possible to establish a one-to-one correlation between the rate of deterioration in the accelerated test and actual weather-aging conditions, it is hoped that the short-term tests will, at the very least, provide a relative ranking of adhesive–adherend pairs, surface preparation, bonding conditions, and so on, and/or provide some insight into relative expected lifetimes. As with all tests, the tester/designer should use all of his or her knowledge, common sense, and insight in interpreting the data.

Some accelerated tests are surprisingly simple and intended to give only highly qualitative information, while others have been formulated into standard tests intended to yield more quantitative results. Since heat and moisture, to which adhesive joints are commonly exposed, are environmental factors known to greatly influence adhesive durability, most accelerated tests involve these two agents.

As an example of a simple qualitative test we would like to cite a test devised by the late E. Plueddemann of Dow Corning [28]. Plueddemann was perhaps the world's foremost researcher in the area of silane coupling agents, bifunctional compounds with one end of the molecule designed to react with oxygen or similar molecules on the substrate (e.g., an oxide layer on a metal) and the other end designed to react with the polymer in the adhesive [29–31]. In this way, a covalent "bridge" is developed between the adherend and the adhesive. One of the main goals of these treatments is to reduce moisture deterioration of the bond line. Accordingly, Plueddemann had need for a test to access quickly this aspect of the wide variety of silanes produced and differing substrates. He devised the following simple test for this purpose.

In his test, a thin film of adhesive on a glass microscope slide or a metal coupon is cured and soaked in hot water until the film can be loosened with a razor blade. There is usually a sharp transition between samples that exhibited cohesive failure in the polymer and those which exhibited more of an interfacial failure. Since the diffusion of water into the interface is very rapid in this test, the time to failure is dependent only on interfacial properties and may differ dramatically between unmodified epoxy bonds and epoxy bonds primed with an appropriate silane coupling agent. The time to debond in the hot water for various silane primers differed by several thousandfold when used with a given epoxy. In parallel tests, a thick film of epoxy adhesive on nonsilaned aluminum coupon showed about the same degree of failure after 2 h in 70°C water as a silaned joint exhibited after more than 150 days (3600 h) under the same conditions.

The authors have, several times, heard Plueddemann express the opinion that he would be willing to guarantee that an adherend–silane–adhesive system that could withstand a few months of exposure to the conditions of his accelerated test would last many decades under normal outside exposure conditions. He was quick to point out that this guarantee does not cover other types of deteriorations of the adherends or adhesive (e.g., corrosion or polymer degradation) and that because of his age and health, he would not be around to honor the guarantee. Nevertheless, he was very convinced (and convincing) that his test was an "acid test" much more severe than most practical adhesive joints would ever experience in their lifetime.

Perhaps, the best known test of this type is the Boeing wedge test, a form of which is standardized in ASTM D-3762. Figure 9 shows this type of specimen and a typical plot of results reported by McMillan, and his associates at Boeing [32,33]. Theidman et al. [34] have also used the-wedge to investigate coupling agents.

Since adhesives have long been used in the wood/lumber business, where outdoor exposure is inevitable, many of the standard accelerated tests were originally developed for these materials. Such tests are increasingly finding uses for other materials. The most common accelerated aging tests are:

1. ASTM D-1101, Standard Test Method for Integrity of Glue Joints in Structural Laminated Wood Products for Exterior Use. Two methods are outlined in this standard for using an autoclave vessel to expose the joint alternately to water at

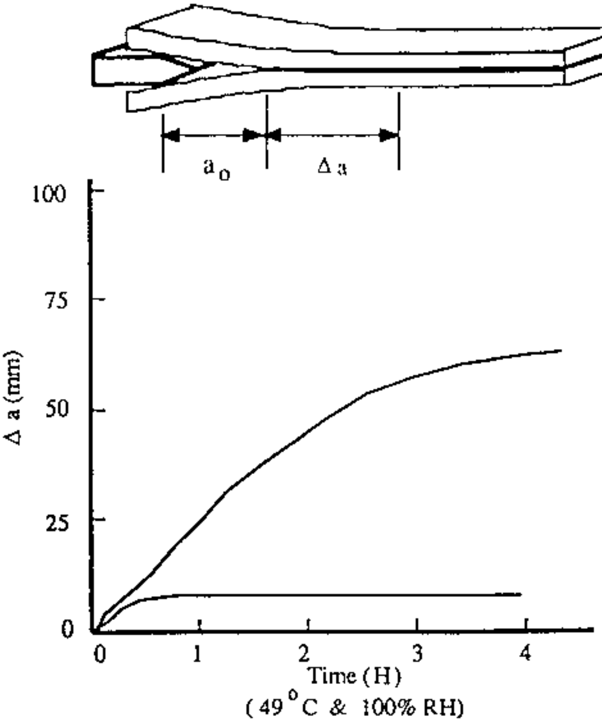


Figure 9 Boeing wedge test and typical results.

vacuum pressure (ca. 635 mmHg) and low temperature with a high-pressure stage (ca. 520 kPa), followed by a high-temperature drying stage (ca. 65°C circulated dry air). After the prescribed number of cycles (typically one or two), the samples are visually inspected for signs of delamination.

2. ASTM D-1183, Standard Test Methods for Resistance of Adhesives to Cyclic Laboratory Aging Conditions. This standard describes several different test procedures in which the joints of interest are subjected to cycles made up of stages at different relative humidities and temperatures, high-temperature drying cycles, and/or immersed in water for specified periods. The joints are then evaluated by standard strength tests (lap joint, tensile, or other) to ascertain the extent of degradation in strength.
3. ASTM D-2559, Specifications for Adhesives for Structural Laminated Wood Products for Use Under Exterior (Wet Use) Exposure Conditions. Like ASTM D-1101, this test makes use of an autoclave-vacuum chamber to impregnate specimens with water followed by drying in a hot (65°C) air-circulating oven. A more quantitative measure of degradation is obtained in this test by measuring lap shear compressive strength and measuring deformation as well as visual evaluation to determine the extent of delamination.
4. ASTM D-3434, Standard Test Method for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives. This standard describes the construction of apparatus to expose adhesive joints automatically to alternate boil/dry cycles. A typical cycle is composed of (a) submerging the specimen for 10 min in boiling water, (b) drying for 4 min with 23°C air

circulating at 1.75 m/s, and (c) exposing the specimen for 57 min to 107°C air circulating at 1.75 m/s. At a prescribed number of cycles, 10 specimens are withdrawn and their tensile shear strength measured and compared to tests on samples that have not been exposed to the accelerated testing conditions.

5. ASTM D-3632, Standard Practice for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method. This test is intended to explore degradation in elastomer based and other adhesives that may be susceptible to oxygen degradation. The practice involves subjecting specimens to controlled aging environments for specified times and then measuring physical properties (shear or tensile strength or other). The controlled environment consists of elevated temperature (70°C) and high-pressure (2 MPa) oxygen.
6. ASTM D-4502, Standard Test Method for Heat and Moisture Resistance of Wood–Adhesive Joints. Rather than using an expensive autoclave as in D-1101 and D-2559, moisture aging in this test is accomplished in *moist aging jars*. The samples are exposed to prescribed temperature–humidity cycles in the jars heated in ovens. The strength of the aged samples is measured by standard methods and compared to similar virgin samples.

There are tests that have been developed for use with solid polymer specimens that find some use with adhesives. Ultraviolet (UV) radiation (e.g., as present in sunlight) is known often to have detrimental effects on polymers. Accordingly, a popular accelerated weathering (aging) test, ASTM G-53, "Standard Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials," describes use of a "weatherometer" that incorporates UV radiation moisture and heat. These commercially available devices consist of a cabinet in which samples are mounted on aluminum panels, which in turn are stacked edgewise on a sloped rack along either side of the cabinet. These samples are then alternately exposed to two stages in periodic cycles: a condensation stage followed by a UV-drying stage. The first stage is accomplished by heating water in a partially covered tank below the specimens in the bottom of the cabinet. The specimens are maintained at a constant temperature (typically 30 to 50°C) which is lower than the water temperature. This results in moisture condensation on the specimens. This stage might last for 1 to 4 h as selected by the operator. This is followed by the UV-drying stage. An array of special fluorescent light tubes are situated along each side of the cabinet parallel to the rack-mounted samples. The operator selects a temperature higher than the condensation temperature (typically 40 to 70°C) that the system automatically maintains in the cabinet for a fixed period (usually 1 to 40 h) while the specimens are exposed to the UV radiation. The weatherometer is equipped with a timer, a float-controlled water supply for the tank, and other controls, so that it can continuously cycle through this two-stage cycle for months or even years with minimum operator care. Samples are removed periodically and their strength measured by standard techniques for comparison with virgin samples and aged and virgin samples of other materials. Many adherends are opaque to UV light, and hence one might question the use of this weatherometer to explore weathering aging of adhesives used with such adherends. However, even here, having such a commercial automated device might be very useful. Both the condensation and radiation-heat curing stages are very analogous to environmental exposures experienced by practical joints. This, along with the automated and "standard" nature of the equipment, often makes the technique quite attractive. More important, there are problems where the UV part of the aging may be critically important. An example would be the bonding of a thin transparent cover film to a thin sheet containing the reflective elements in sheeting used to make reflecting road signs. This device would have obvious advantages in such cases and, indeed, has become the standard for use in evaluating weather durability in that industry.

It is recognized that most accelerated tests do not duplicate or even closely approximate actual service conditions. As a case in point, most joints will, in all probability, never be exposed to boiling water. It is hoped, however, that resistance to boiling for a few hours or days may provide some valid evidence (or at least insight) into the durability of a laminated part after years of exposure to high ambient humidity and temperature. While such accelerated tests are never perfect, they may be the only alternative to observing a part in actual service for decades. The authors feel this philosophy is well stated in Section 1.1 of ASTM D-1183: "It is recognized that no accelerated procedure for degrading materials correlates perfectly with actual service conditions, and that no single or small group of laboratory test conditions will simulate all actual service conditions. Consequently, care must be exercised in the interpretation and use of data obtained in this test." ASTM D-3434 includes the following statement about its significance: "The test method assumes that boil/dry cycling is an adequate and useful accelerated aging technique." Evaluation of long-term durability of adhesives in wood joints under severe service conditions, including extended exterior exposure, is a complex field, and no entirely reliable short-term test is known to ensure that a new type of adhesive system will resist satisfactorily all of the chemical, moisture, microorganism, and solvent effects that such severe service may involve. Except for the effects of microorganisms and similar biological influences, this test method has proven very useful for comparison purposes to distinguish between adhesive systems of different degrees of durability to the usual temperature, moisture, and cyclic moisture conditions. It has proven very useful to distinguish between bond lines, made with adhesives of proven chemical and biological durability, that when properly used in production resist the mechanical and moisture effects that such joints must withstand in severe service over extended periods of exposure. It does not, however, in itself, assure that new types of adhesives will always withstand actual exterior or other severe service.

Other environmental related tests include ASTM D-904, Standard Practice for Exposure of Adhesive Specimens to Artificial (Carbon-Arc Type) and Natural Light; ASTM D-1828, Standard Practice for Atmospheric Exposure of Adhesive-Bonded Joints and Structures; ASTM D-1879, Standard Practice for Exposure of Adhesive Specimens to High Energy Radiation; and ASTM D-3310, Standard Test Methods for Determining Corrosivity of Adhesive Materials.

In practical joints, adhesives are not always loaded statically or loaded for short periods of time. To help evaluate the performance of stressed adhesive joints as a function of time, tests have been developed to determine the response of adhesive joints to creep and cyclic loading. ASTM D-1780, Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives, makes use of a deadload weight-lever loading frame to measure creep of lap shear specimens. ASTM D-2793, Standard Test Method for Creep of Adhesives in Shear by Compression Loading (Metal-to-Metal), describes the constructions and procedures for use of creep test apparatus in which the sustained loading is maintained by springs. ASTM D-2294 is similar to D-2293, except that here the spring-loaded apparatus loads the lap specimen in tension. ASTM D-4680, Standard Test Method for Creep and Time to Failure of Adhesives in Static Shear by Compression Loading (Wood-to-Wood), describes the construction of a spring-loaded apparatus and testing procedures for a creep apparatus for use with relatively large wood specimens. ASTM D-2918 and D-2919 describe tests to measure the durability of adhesive joints in peel and lap shear, respectively. The tests and recommended fixtures are intended to hold specimens under sustained loadings while exposed to environments such as moisture, air, vapors, water, or other environments.

ASTM D-3166, Standard Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal), provides procedures for testing and measurement of the fatigue strength of lap specimens. It makes use of conventional tensile testing machines capable of applying cyclic axial loads. Researchers have also made beneficial use of the concepts of fracture mechanics to evaluate the fatigue crack growth rate per cycle, da/dn, as a function of stress intensity factor. For this purpose, Mostovoy and Ripling [35], for example, have used fracture mechanics specimens similar to those described in ASTM D-3433. Fracture mechanics is discussed at the end of this chapter as well as in many books.

Adhesive joints are frequently exposed to sudden dynamics loads, and hence a knowledge of how adhesives react to impact loading is important for some applications. ASTM D-950, Impact Strength of Adhesive Bonds, describes sample configuration and testing apparatus for measuring the impact strength of adhesive bonds. The method is generally analogous to the Izod test method used for impact studies on a single material.

ASTM D-2295 describes apparatus that utilizes tubular quartz lamps to investigate failure of adhesive joint samples at high temperatures, and ASTM D-2257 outlines procedures for testing samples at low temperatures (−268 to −55°C). ASTM also provides specific standards to investigate failure-related properties of adhesives that are less directly related to mechanical strength. Such properties include resistance to growth and attack by bacteria, fungi, mold, or yeast (D-4300 and D-4783), chewing by rodents (D-1383), eating by insects (D-1382), resistance to chemical reagents (D-896), and so on. It is enough to make the adhesive designer or researcher paranoid. Not only are stresses, temperatures, moisture, and age working against him or her, but now it appears that microorganisms and the animal kingdom want to take their toll on any adhesively bonded structure.

Although the primary purpose of this chapter is to discuss mechanical testing and strength of adhesive joints, the reader should be aware that ASTM covers a wide variety of tests to measure other properties. ASTM, for example, includes standard tests to measure the viscosity of uncured adhesives, density of liquid adhesive components, nonvolatile content of adhesives, filler content, extent of water absorption, stress cracking of plastics by liquid adhesives, odor, heat stability of hot-melt adhesives, ash content, and similar properties or features of adhesives.

Of particular interest to the adhesive technologist are surface treatments. ASTM has adopted standard practices for treating surfaces to better adhesives. ASTM D-2093, Standard Practice for Preparation of Plastics Prior to Adhesive Bonding, describes physical chemical, and cleaning treatments for use on a wide variety of polymer adherends. D-2651, Standard Practice for Preparation of Metal Surfaces for Adhesive Bonding, describes techniques, cleaning solutions and methods, etchants or other chemical treatment, and so on, for metal adherends, including aluminum alloys, steel, stainless steel, titanium alloys, copper alloys, and magnesium alloys. ASTM D-2675 is concerned with the analysis and control of etchant effectiveness for aluminum alloys. ASTM D-3933 provides a standard practice for phosphoric acid anodizing of aluminum surfaces to enhance adhesion.

C. Fracture Mechanics Techniques

As noted earlier, the most commonly used standards for determination of adhesive joint properties and characteristics suggest reporting the results in terms, of average stress at failure. If average stress criteria were generally valid, one would anticipate that a doubling of the bond area should result in a proportionate increase in joint strength. Studies in our laboratory demonstrate that such criteria may lead to erroneous predictions [36]. This study involved leaving half of the overlap area unbonded. All of the samples had the same amount of overlap. Part of the samples (the control) were bonded over the complete overlap region. Part of the overlap area near one of the bond termini was without any adhesive and the other part had a 50% unbonded region centered in the overlap region. In neither case was the reduction in strength commensurate with the reduction in bond area. That is, for the end debonds, the reduction in load at failure averaged less than 25% and for the center debonds it was reduced by less than 10%. This is consistent with standards such as ASTM D-3165, Strength Properties of Adhesives in Shear by Tension Loading of Laminated Assemblies, which address the fact that average lap shear strength is dependent on different bond areas of the joint and that the adhesive can respond differently to small bond areas compared to large bond areas.

To determine failure loads for different geometries, other methods are required. This is due to the fact that the stress state in the bond region is complex and cannot be approximated by the average shear stress. A method that is gaining in popularity for addressing this problem is the use of fracture mechanics. With the use of modern computers, the stress state and displacement even in complex adhesive bonds can be determined with good accuracy. A fracture mechanic approach uses these stresses combined with the displacements and strains and conservation of energy principles to predict failure conditions. At least three ASTM standards are based on fracture mechanics concepts (ASTM D-3433, D-3762, and D-5041). The premise behind fracture mechanics is accounting for changes in energies associated with the applied load, the test sample, and the creation of new surface or area. Since fracture mechanics techniques are well documented in the literature (see, e.g., Refs. 37 and 38), only a brief review is presented here.

The methods suggested here are formulated using methods similar to those postulated by Griffith [39]. Griffith hypothesized that all real “elastic” bodies have inherent cracks in them. He hypothesized that a quantity of energy to make the most critical of these cracks grow would need to come from the strain energy in the body and work applied by loads. Conservation of energy dictates that a crack can grow only when the strain energy released as the crack grows is sufficient to account for the energy required to create the new “fracture” surface. In Griffith’s original work, he considered only perfectly elastic systems. He conducted his confirmation experiments on glass, which behaves as a nearly ideal elastic material. In this case the *fracture energy* is very closely associated with *the chemical surface energy*. Indeed, Griffith was able to establish such a correlation by measuring the surface tension of glass melts and extrapolating back to room temperature. Most engineering solids are not purely elastic and the energy required to make a crack grow involves much more than just the chemical surface energy. In fact, the energy dissipated by other means often dominates the process and may be several orders of magnitude higher than the chemical surface energy term. As explained in modern texts on fracture mechanics, this has not prevented the use of fracture mechanics for analysis of fracture in other quasi-elastic systems, where typically the other dissipation mechanisms are lumped into the fracture energy term G_c (discussed later). Techniques are also being developed to use the basic approach for systems that experience extensive viscoelastic and plastic deformation. These approaches are more complex. Here we confine our attention to quasi-elastic cases. Significant research and development work has gone into methods of increasing the dissipative processes required for a crack to grow, thereby, “toughening” the materials. As a consequence, another name for the fracture energy is *fracture toughness* G_c.

While Griffith's earlier fracture mechanics work was for cohesive fracture, the extension to adhesive systems is logical and straightforward. In the latter case, one must account for the strain energy in the various parts of the system, including adherends and adhesive, as well as recognizing that failure can proceed through the adhesive, the adherend, or the interphase region between them. Here too, energy methods can be useful in determining where the crack might grow since one might anticipate that it would use the path requiring the least energy.

In principle, the fracture mechanics approach is straightforward. First, one makes a stress-strain analysis, including calculation of the strain energy for the system with the assumed initial crack and the applied loads. Next, one performs an energy balance as the crack proceeds to grow in size. If the energy released from the stress field plus the work of external forces is equal to that required to create the new surface, the crack grows. A difficulty in performing these analyses is that for many practical systems, the stress state is very complex and often not amenable to analytical solutions. With the use of modern computers and computational codes, this is becoming progressively less of a problem. Finite element codes are refined to the point that very accurate stress–strain results can be obtained, even for very complex geometries (such as adhesive joints). Furthermore, it is possible to incorporate complex material behavior into the codes. The latter capability has not reached its full potential to date, at least in part, because the large strain deformation properties of the materials involved, at the crack tip, are not well defined.

A relatively simple example may help in understanding the application of fracture mechanics. First, let's assume that we have two beams bonded together over part of their length, as shown in Fig. 10a. Here we will make two additional convenient (but not essential) assumptions: (1) the adhesive bond line is sufficiently thin that when bonded as shown in Fig. 10b, the energy stored in the adhesive is negligible compared to that in the unbonded length of the beams *a*; and (2) the length *a* is sufficiently long that when loaded, the energy due to bending dominates (i.e., the shear energy and other energy stored in the part of the beam to the right of *a* is negligible).

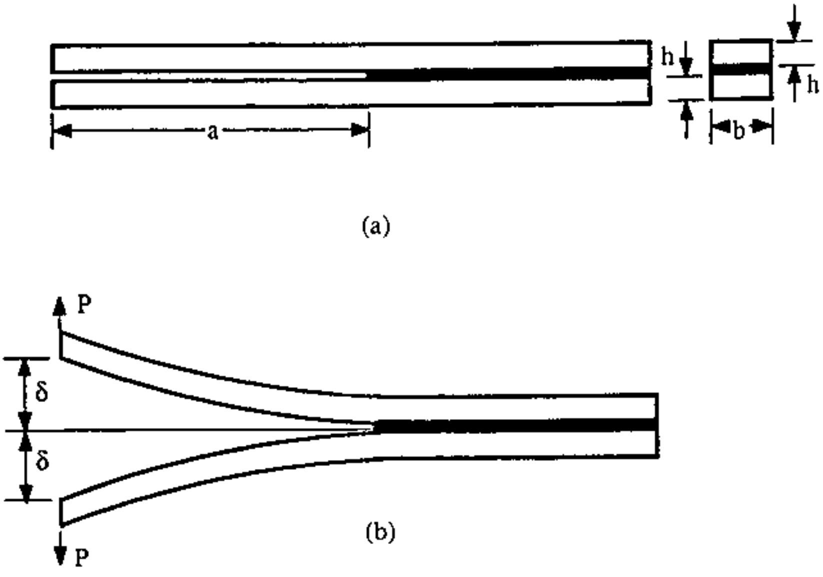


Figure 10 Double cantilever beam specimen showing nomenclature and specimen deflection.

The end deflection of the unbonded segment of each beam due to a load P is found in mechanics of material texts to be [40]

$$\delta = \frac{Pa^3}{3EI} \tag{1}$$

where a is the unbonded length, E the modulus of elasticity for the material from which the beams are manufactured, and I the moment of inertia for a rectangular cross-section. The work done by the forces P in deforming this double cantilever is therefore

$$W = \frac{1}{2}P(2\delta) \tag{2}$$

which for a conservative elastic system equals the energy U, where

$$U = P\delta = \frac{P^2a^3}{3EI} \tag{3}$$

If we assume Griffith-type fracture behavior, the energy released as the crack grows (a increases) must go into the formation of new fracture surface. The fracture energy G_c (sometimes called energy release rate) is therefore

$$G_c = \frac{\Delta U}{\Delta A} \tag{4}$$

Substituting Eq. (3) into (4) and taking the limit leads to

$$G_c = \frac{\partial U}{\partial A} = \frac{1}{b}\frac{\partial U}{\partial a} = \frac{P^2a^2}{EIb} = \frac{12P^2a^2}{Eh^3b^2} \tag{5}$$

where

$$\partial A \approx 2a(b) \tag{6}$$

We thus see that such beam systems could be used to determine G_c. Indeed, ASTM D-3433 makes use of such beams for this measurement. It should be noted that the equation given in Section 11.1.1 of D-3433 has a similar form:

$$G_c = \frac{4P^2(3a^2 + h^2)}{Eb^2h^3} \tag{7}$$

This equation can be used for smaller values of a since it includes effects of shear and other factors that, as noted above, were neglected in our simple analysis. Inspection of Eq. (7) shows that as a becomes large compared to h, this equation reduces to that derived above. By tapering the beams, ASTM shows how a related geometry can be used for G_c determination where the data analysis is independent of the crack length. The advantage here is that one need not monitor crack length. An advantage of double cantilever beam specimens is that measurement can be made for several different values of a for a given beam, making it possible to get several data points from a single sample. Conversely, if G_c is known, say from another test configuration, fracture mechanics can be used to determine the load required to initiate fracture.

The case described above is the exception rather than the rule. Most practical problems do not have stress and displacement fields easily obtained by analytical methods. Numerical methods can be applied to obtain the necessary stress and displacements needed to calculate the energy release rates. The basic consideration for calculating energy release rates is accounting for the difference in energy before and after crack extension dA. This condition can be approximated for a discrete system by using finite element methods (FEMs), that is, by using a computer to calculate the strain energy change as a crack area is incrementally increased.

Two different methods of calculating the energy release rate numerically are outlined briefly. The first, the *compliance method*, is readily applied using FEM [37]. This method requires only two computer runs for each energy release rate desired. The first computer run is used to calculate the total relative displacement, u^a, of the sample for the crack length a, under a constant force F^a. In the second computer run, a finite element node is released, extending the crack to a length of $a + \Delta a$. The second run allows calculation of the total relative displacement, $u^{a+\Delta a}$, of the sample for a crack length $a + \Delta a$ under the same constant load F^a. Using the discrete form of the energy release rate for a linear elastic body leads to

$$G = \frac{F^a(u^{a+\Delta a} - u^a)}{2\Delta A} \tag{8}$$

The discrete form of the energy release rate under constant displacement assumptions for the same crack length can easily be shown to be

$$G = \frac{F^a u^a \left(\dfrac{1 - u^a}{u^a + \Delta^a}\right)}{2\Delta A} \tag{9}$$

A third computer run can be used to extend the crack by releasing the next node in front of the crack tip. This increases the crack length to $a + 2\Delta a$. Letting $u^{a+\Delta a}$ equal the new relative displacement and u^a equal the total relative displacement from run 2, the energy release rate for the new crack length can be computed using Eq. (8) or (9) with the addition of only one computer run. This process can be repeated, each time determining a new energy release rate per single computer run, thereby producing a curve of energy release rate versus crack length. The crack length for which the energy release rate is equal to G_c is a critical crack length where failure should ensue.

A second method for calculating energy release rate is the *crack closure integral* (CCI) *method* [37,41–43]. This method uses FEM techniques to calculate the energy that is needed to close a crack extension. It is assumed that for an elastic system this energy is equivalent to the energy that is needed to create the crack's new surface, giving an alternative method of calculating the energy release rate from that just discussed.

The CCI method is also readily accomplished using FEM. The energy release rate calculated as outlined in the following is for a constant stress crack extension assumption. In general, this method requires four computer runs for each energy release rate calculated. The method can be shortened to three computer runs if verifying that the crack was closed is not necessary. In this case, only the second, third, and fourth steps explained below need to be performed.

The first computer run is used to calculate the displacements (or locations) of the finite element nodes near the crack tip for crack length a under constant load F^a. Let u^{BX1} and u^{BY1} represent the displacements of the first bottom node in the X and Y directions, respectively, from run 1. Let u^{TX1} and u^{TY1} represent the displacements of the first top node in the X and Y directions, respectively, from run 1. Since we have not yet released this first node for run 1, the top and bottom nodes are coincidental and should have the same displacement. This initial displacement indicates the point to which the nodes will have to be moved when the crack is closed in runs 3 and 4.

In the second computer run, a node is released extending the crack length to a length of $a + \Delta a$. This allows calculation of the new nodal positions of the same nodes that were

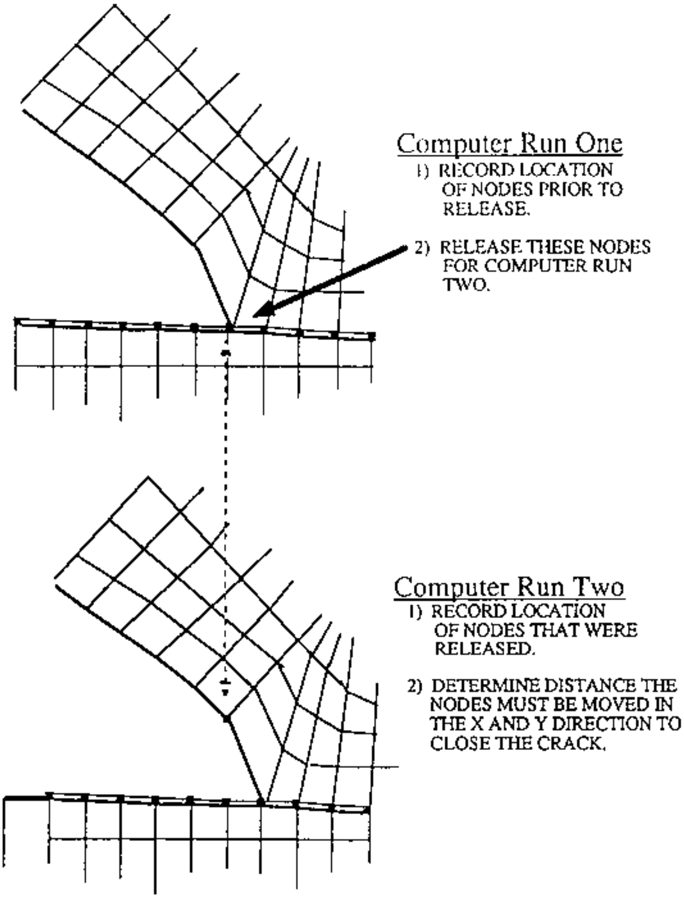
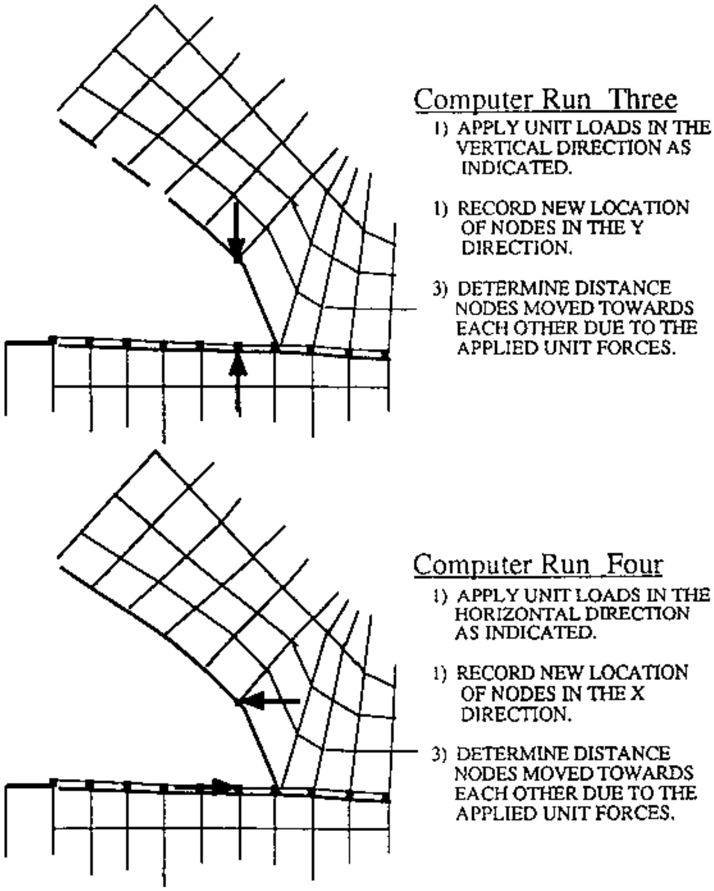


Figure 11 Pictorial of the first and second steps in the CCI method of determining energy release rates.

released from run 1 while under the constant load F^a. Let u^{BX2} and u^{BY2} represent the displacements of the bottom node in the X and Y directions, respectively, from run 2. Let u^{TX2} and u^{TY2} represent the displacements of the top node in the X and Y directions, respectively, from run 2. The distance between the top node and bottom node in the X and Y directions indicates how far the nodes will need to be moved in each direction to close the crack. Figure 11 shows computer runs 1 and 2 in a pictorial schematic and summary of the two steps.

In the third run, vertical unit forces are applied to the released nodes in the direction needed to bring them back to their original vertical positions. The nodal displacements of these released nodes of the sample for a crack length of $a + \Delta a$ under the same constant load F^a are noted. Let u^{BY3} represent the displacement of the bottom node in the Y direction from run 3. Let u^{TY3} represent the displacements of the top node in the Y direction from run 3. The difference between the node displacements from runs 2 and 3 indicates how far the vertical unit force moved each node toward its original position.

The fourth run is the same as run 3 except that the forces are now horizontal. Figure 12 shows computer runs 3 and 4 in a pictorial schematic and a summary of the two steps.



Computer Run Three

1) APPLY UNIT LOADS IN THE VERTICAL DIRECTION AS INDICATED.

1) RECORD NEW LOCATION OF NODES IN THE Y DIRECTION.

3) DETERMINE DISTANCE NODES MOVED TOWARDS EACH OTHER DUE TO THE APPLIED UNIT FORCES.

Computer Run Four

1) APPLY UNIT LOADS IN THE HORIZONTAL DIRECTION AS INDICATED.

1) RECORD NEW LOCATION OF NODES IN THE X DIRECTION.

3) DETERMINE DISTANCE NODES MOVED TOWARDS EACH OTHER DUE TO THE APPLIED UNIT FORCES.

Figure 12 Pictorial of the third and fourth steps in the CCI method of determining energy release rates.

Runs 3 and 4 provide a measure of how much each node is moved back toward each original position by unit forces. Since the material is modeled as linear elastic, the force required to move each node back to its original position can be determined simply by increasing these forces in proportion to the total displacements required to bring the nodes back to their original position. We will call these forces F^X and F^Y. The energies E^X and E^Y required to close the crack in the X and Y directions can now be calculated by determining the work of these forces on the crack closure displacements since for an elastic system, the work is stored as strain energy.

Based on this analysis, the energy release rates can be partitioned into the energy release rates associated with crack opening displacement (G_{I}) and shear displacement normal to the crack surface (G_{II}):

$$G_{\mathrm{I}} = \frac{\Delta E_1^X - \Delta E_2^X}{\Delta A}$$

$$G_{\mathrm{II}} = \frac{\Delta E_1^Y - \Delta E_2^Y}{\Delta A} \tag{10}$$

The total energy release rate can be determined from

$$G = G_{\mathrm{I}} + G_{\mathrm{II}} \tag{11}$$

In Eqs. (10) and (11), G represents the total energy release rate under constant-stress crack extension assumptions, G_{I} represents the portion of G in the mode I direction, and G_{II} represents the portion of G in the mode II direction. A couple of concluding comments to this section might be in order. Each of these methods of solving for the fracture energy has advantages. The compliance method is simpler and less expensive to perform. The crack closure method, on the other hand, facilitates calculation of crack growth analysis under different loading (i.e., crack opening or shear). There is evidence that cracks in materials behave differently under the various loadings. As a consequence, growth of a given crack may depend on the relative amounts of mode I and mode II stresses at its tip. It is also advantageous to have the two methods of determining G. Since they provide a systematic check on each other, that might be used to verify for code, programming, or other errors.

Computer-based energy release rates might be a very useful design tool. An example might be used to illustrate such use. Assume that nondestructive evaluation techniques are used to locate and determine the size and shape of a debond region in the interphase region of an adhesive bond in a structure. An example of such a bond might be between a rocket motor case and a solid propellant grain. A reasonable question would be: Is this “flawed” region “critical” in that it might cause failure under prescribed service load conditions? For many structures (e.g., the rocket case noted) this might literally be a million dollar question. A reliable answer could mean the difference between safely using the structure or needing to repair or discard it. Trying to answer the question experimentally would generally be very expensive. An alternative approach might make use of fracture mechanics. One might use FEM to model the structure, including the debond region that has been identified. Using the techniques outlined above, the energy release rate can be calculated for assumed increases in the size of debond. If the critical fracture toughness (G_c) is known (perhaps determined from independent tests with standard specimens), it can be compared with the value calculated. If the energy release rate calculated for the debond in the structure is equal to G_c, the debond is apt to grow. If it is larger than G_c, the crack should accelerate. Values of energy release rate significantly lower than G_c would indicate a noncritical region. Other types of irregularities, cohesive or adhesive, might be treated in a similar manner. Obviously, such an approach requires not only adequate FEM techniques and computers but also nondestructive means to identify and quantitatively measure potential critical regions.

As a final note in this section, a few examples taken from the research of the authors and their associates, on the utility of fracture mechanics in conjunction with numerical analysis, might be informative. Some of the research in the authors’ laboratory has centered on identifying the loci of failure “initiation” and the paths followed by cracks as they proceed through the adhesive in a joint.

Several rather different geometries have been investigated, some that were patterned after standard test configurations and one designed to simulate a specific application. The latter was a cone pull-out (or twist-out) specimen devised to simulate such dental adhesive applications as fillings, caps, and crowns [42,44]. In this test configuration material in the form of a truncated cone was bonded into a matching hole in a plate. Pulling (or twisting) could initiate failure of the cone while the plate was held fixed. If the cone had a zero degree cone angle, the test became a cylinder pull-out test. For the tests of interest here, the cone and the plate were fabricated from transparent poly(methyl methacrylate) (PMMA) and the adhesive was transparent polyurethane (Thiokol Solithane-113). The use of these materials allowed visual observation of the bond line of the adhesive joint. The lower 1.6 mm (at the truncated cone end) was left unbonded to act as a starter crack. Finite element analysis of this specimen, under stress, indicated that as the tip of this region was approached the stresses induced in the adhesive became very large (singular). Somewhat removed from this point, the stresses were finite and well behaved, independent of cone angle.

When samples with a zero degree cone angle were pulled to failure, it was always observed that the failure propagated from this starter crack. On the other hand, when the cone angle was increased slightly (e.g., to 5°), the initial failure was never observed to originate at this starter crack. Rather, the first signs of failure were observed further up in the joint—approximately halfway between the end of the starter crack and the other end of the bond line. This crack then grew from that point until ultimate separation occurred. The obvious question was, why did failure not occur at the point of "maximum stress," i.e., at the starter crack? The numerical analysis did indicate that there was a local maximum in the stress at the point where failure was first observed but the value of this maximum was significantly lower than that close to the singularity point. We feel the answer lies in the difference in the nature of the energy release rate (ERR or G) at the two points. A small (25 μm) "inherent" cracklike flaw was assumed to exist at the local "stress maximum" referred to above. The ERR was calculated for a crack proceeding from this point and compared with the value of the ERR for a crack emanating from the much larger starter crack. Even for such a small assumed inherent crack, the calculated ERR was larger at the point halfway up on the specimen. The conclusion was that failure is governed by the ERR and that failure initiation is at points of maximum ERR.

This same conclusion was substantiated by a series of tensile tests in which a butt tensile joint specimen was formed by adhesively bonding a PMMA rod to a PMMA plate with the polyurethane referred to above [42,44]. The specimens were set up in an Instron testing machine adapted with holes and a mirror arrangement that allowed the bond line to be observed and recorded with a video recorder. Finite element analysis indicated that for small assumed cracklike flaws, the values of the ERR and the location of maximum ERR were very strong functions of the ratio of the adhesive thickness to the joint diameter. As a consequence, the load required to propagate a crack should be a function of the thickness of polyurethane, even for constant size initial cracks. Furthermore, since the location of maximum ERR varied with this same thickness, one would anticipate the location of crack growth initiation to vary. Experimentally, both features were observed: (1) Variation in the value of the load required to propagate a crack was completely consistent with the calculated variation in ERR with thickness. (2) When the ERR for the assumed 25 μm inherent flaw was largest at the edge, cracks tended to start at the edge. When the ERR was greater in the center, that was the location from which the crack was observed to emanate. It is noted that, as with the cone test, finite element analysis indicated that the stresses at the bond line become singular as the outer diameter of the specimen is approached (e.g., as $r \rightarrow R_0$).

The final example involves fracture mechanics–finite element analysis of the double cantilever beam (nontapered) specimen (see Fig. 10 as well as the figures and descriptions in ASTM D-3433). The finite element analysis was very much as outlined above, leading to Eqs. (8) through (11). These results were compared with the equations in Section 11.1.1 of D-3433 (Eq. (7) in this chapter). Except for the longest cracks (i.e., very large a in Fig. 10), the FEM-determined ERR differed appreciably from the G_c value determined from Eq. (7). These differences might be attributed to the fact that the derivation of Eq. (7), similar to that for Eq. (5), assumes ideal cantilever boundary conditions at the point $x = a$.

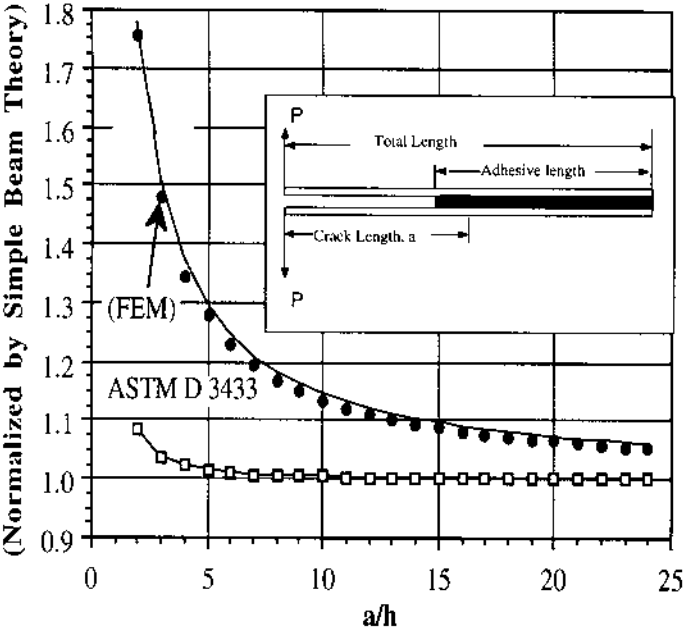


Figure 13 Comparison of the ERR determined by FEM with G values calculated using the equations from ASTM D-3433 as a function of the ratio of crack length, a, to couble Cantilever beam specimen depth, h.

The assumed conditions are that there is no deflection and zero slope (i.e., no rotation) at that point. Figure 13 (taken from [45]) illustrates that the differences in *G*, determined by the two methods, might be 50% or more for small values of *a*. The experiments described in ref. [45] demonstrate that much more consistent values of G_c are obtained when using the FEM to calculate G_c, from the experimental results over typical a/h values, than when they are calculated using the equation from D-3433. In the FEM case, the variation was typically less than ± 5%, while the variation using Eq. (7) could be ten times larger.

In addition to ignoring the energy associated with the nonideal cantilever conditions just described, the derivation of Eqs. (5) and (7) also neglects any energy stored in the adhesive. While this latter assumption might be valid for extremely thin adhesives, it is noted that for many adhesive–substrate combinations the modulus of the adhesive is only a few percent that of the adherends. As a result, for adhesives with thicknesses that are 5%, or so, of the adherend's thickness the contribution of the strain energy in the adhesive to the ERR (G_c) can be appreciable. This is also consistent with the experimental observations reported in ref. [44]. Inclusion of the strain energy in the adhesive in the total energy balance facilitated an additional calculation/observation. Adhesive engineers and scientists have long speculated on reasons for the common observation that cracks in adhesive joint generally follow paths somewhat removed from the so-called adhesive–adherend "interface" rather than along this bond line. It might reasonably be assumed that cracks would follow paths of maximum energy release rate, since this would be the path where the most energy would be dissipated. In the FEM analysis, various crack paths were assumed through the adhesive and the ERR determined [45]. By varying the adhesive and adherend(s) thicknesses, it was possible to design double cantilever beam specimens in which the path of Max-ERR was near the center of the adhesive, near one or other of the

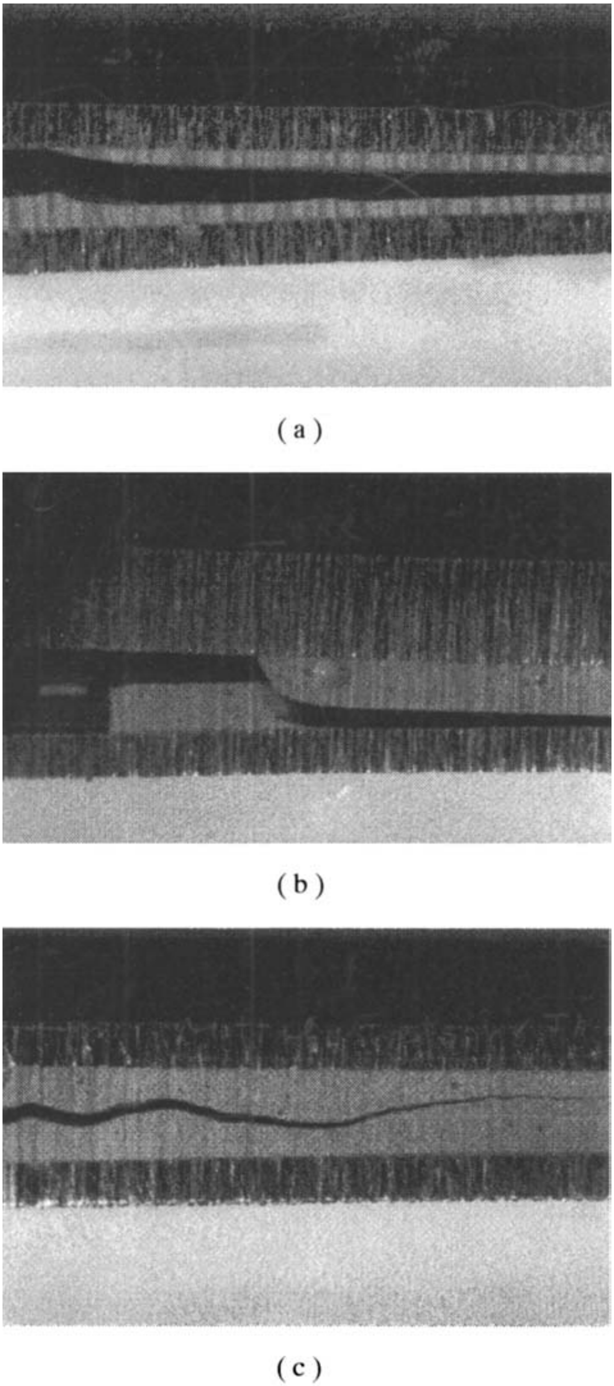


Figure 14 Photographs showing the loci of crack growth for different double cantilever beam adhesive joint specimens pulled to failure. (a) The ERR calculated by FEM for this specimen was largest down the center of the adhesive, (b) the ERR calculated by FEM for this specimen was largest near the lower edge of the adhesive, and (c) the ERR calculated by FEM for this specimen was essentially independent of position across the adhesive thickness.

edges of the adhesive, or relatively constant across the thickness. Samples of these differing geometries were constructed of aluminum and an adhesive (both of which exhibited relatively linear elastic behavior) to simulate the linear elastic finite element calculations. Starter cracks were introduced at different locations through the adhesive thickness. These samples were pulled to failure, the fracture load recorded, and the locus of the fracture path observed/noted. In every case, the experimentally observed fracture paths closely followed the planes of Max-ERR determined by the finite element analyses. If the starter crack was somewhat removed from this location, the ''running'' crack quickly moved to the path of Max-ERR. Figure 14 [45] shows photographs of some samples from these experiments. Photograph (a) was for a sample in which the FEM-determined ERR was maximum at the center and the starter crack was at the edge. The crack started at the starter crack and then moved to and ran nearly planar along the center. Photograph (b) is for a sample with different thicknesses of adherends. Here the FEM-determined ERR was at the lower edge of the adhesive and the starter crack was introduced at the upper edge. The crack started at the starter crack but again quickly moved to and ran along the path of Max-ERR. In (c) the FEM-determined ERR was relatively insensitive to the exact path in the adhesive. Here, there was no ''mechanical'' reason for a preference for a specific path and the crack wandered as apparently chemical or physical differences in the adhesive dictated the exact path followed.

These analyses and associated experiments demonstrate that fracture mechanics can be used to provide information and insight into the value of the failure load, the locus of likely crack growth, and the path along which the crack will then grow. Where analytical analyses of stress, strain, and energy release rates are difficult or impossible, modern numerical methods can be very useful. In the opinion of the authors, the utility of these combined tools has hardly been exploited. The inclusion of nonlinear, nonelastic effects in the analyses is feasible is such materials are carefully characterized and/or properties become available.

IV. CONCLUSIONS

There are a great many properties that affect adhesive quality. One of the more important is the strength of joints formed with the adhesive and adherends. We have discussed a number of standard tests commonly used to ''measure'' adhesive joint strength. These methods are valuable and serve many purposes. In this chapter, however, we point out that the use of the ''standard'' results from these tests to predict the strength of other joints that differ in even seemingly minor details is questionable. A more reliable comparison between adhesives and joints might be to compare more fundamental properties, such as moduli, adhesive fracture toughness, and so on. This is a basic premise of fracture mechanics. With improved computation facilities and codes, these methods show promise for using results from standard tests to predict the performance of other (perhaps more complex) practical adhesive joints. As such, they should become very powerful design tools.

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12

The Physical Testing of Pressure-Sensitive Adhesive Systems

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I. INTRODUCTION

It is assumed in almost all cases, that any pressure-sensitive adhesive to be tested has already been applied to a flexible carrier, which is either in tape form, or which can be cut into tapes for testing, virtually all test methods making this assumption. If this is not the case, then it would be necessary to coat the adhesive onto a suitable flexible carrier, usually 25 μm polyester film, which may need to be suitably pre-primed, the prime coat used depending on the adhesive type. The coat weight chosen should be that used for the practical application of that adhesive, or if this adhesive is still under development, then a series of coat weights can be run, to determine which provides optimum performance. An exponential relationship will be found between coat weight and resulting adhesion.

The need for the physical testing of a pressure-sensitive adhesive can vary considerably; such reasons include the determination that a given pressure-sensitive adhesive will perform satisfactorily for its intended use, that it meets a specific standard, that uniformity exists within a given population, or between populations, or that it could be to compare one system to other similar systems—all of which demand that any test method must be accurate and reproducible. The thermoplastic nature of pressure-sensitive systems can make this objective very difficult to achieve, without a full understanding of their behavior and without observing a number of precautions.

Recognizing that the behavior of a pressure-sensitive system varies according to temperature and to rate, and that a pressure-sensitive adhesive easily deforms under pressure, which affects the degree of contact, then the conditions under which any pressure-sensitive adhesive is both prepared for testing, then tested, must be rigidly controlled. Otherwise considerably different values will be found for each uncontrolled evaluation of the same adhesive system. This also applies to the geometry of the test, where the bending of a flexible adhesive carrier plays a key part, as in peel adhesion testing, the relative stiffness of the backing altering the intended angle of the test.

The nature of the bond that is formed with a specific adhesive depends both on the adhesive design and on the nature of the surface to which it is adhered. This not only applies to its material of construction, but also whether it is porous or nonporous, the degree of surface roughness, and from this, the contact that can be obtained, 100%

contact during testing being a rarity. So now we must add to our protocol for standardization of Testing, standardized test surfaces both in material and in surface roughness, recognizing that nonporous and porous substrates will behave quite differently, keying into the micro-irregularities of a porous surface being one means of attachment.

The internationally recognized standard material chosen for a nonporous test surface is stainless steel [1–5], both the European and United States Adhesive Tape Councils agreeing on Type 304, although there are differing opinions as to surface roughness. For a porous test surface, in the United States, a standardized cardboard, Standard Reference Material 1810A from the National Institute of Standards and Testing, is used, other testing authorities again having their own choice. Since any result obtained using a standardized test surface will be applicable to that surface only, accurate data for alternative surfaces will require a retest with that new surface.

The application of any stress that a pressure-sensitive adhesive encounters in practical use ranges from a very rapid rate, as in unwinding a pressure-sensitive tape on an automatic application machine, to a continuous slow stress as would be the case with a packaging tape in use, or with a double-sided tape used as a mounting tape. In the very rapid rate case, the viscous component of the adhesive has little or no time to respond and under excessively rapid rates, separation may even be in the form of a brittle fracture. This behavior would be duplicated if the adhesive were stressed at extremely low temperature, due to the time/temperature relationship [6]. In the case of a continuous low stress, there is ample time for viscous response, and resultant molecular disentanglement and failure may well be cohesive, again with a corresponding behavior if tested at high temperature. For the most part, both in use and in testing, there is a simultaneous elastic and plastic response to stress by pressure-sensitive adhesives, each to a greater or lesser extent, depending on the rate and/or temperature.

Regarding test panels, it is common practice to reuse standard test panels over and over again, and the need for a contamination-free surface at each test is essential to obtain reliable data. While it appears that a specific pressure-sensitive test leaves no residue on removal, and the panel may appear perfectly clean, a simple dusting, as is done for fingerprint identification, will show that there is indeed an adhesive residue remaining after each test, and further, this micro-trace can be quite difficult to remove. There are standard procedures as to the correct solvent for test panel cleaning [7], but with the variety of pressure-sensitive systems now available, the correct method is the one that removes the last applied adhesive system most satisfactorily, and leaves the test panel clean and dry. It may well involve the need for two solvents, one to remove the adhesive then another to remove the last traces of the first solvent. Because of this inherent adhesive micro-contamination, even following the standard cleaning procedures, there are those who prefer to restrict the use of a series of test panels to a specific adhesive system, to further standardize their test surfaces and to prevent any cross-contamination, and others who use microscope slides as their standardized surface, the slides being discarded after each test. Other possible sources of contamination of both the panel and the sample under test are perspiration from the fingers, dust, and moisture, all of which can act as a weak boundary layer between the adhesive and the test panel. Although care in handling and panel cleaning can correct the perspiration and dust, the humidity of the air controls the moisture, and so testing must be in a controlled humidity environment, normally 50% relative humidity, and at a temperature of 23°C (73.5°F) [8], to restrict the testing to a known condition.

If all of the foregoing is appreciated, then not only will the observed behavior of a pressure-sensitive adhesive during testing be better understood, but it will also be possible either to adapt existing test methods, or to devise others, which are more appropriate to the practical application of a specific adhesive.

Finally, it should be recognized that, when a stress is applied to a pressure-sensitive adhesive, it is either a tensile stress, a shear stress, or a combination of both. In the specific end use of a given pressure-sensitive adhesive system, a clear understanding should exist as to what type of stresses can be encountered, to ensure that the test methods applied bear a relationship to use. The various standard test methods can now be considered.

II. ADHESION

Although slight differences occur here and there, the universally recognized method to determine how well a pressure-sensitive system adheres is to apply the adhesive, which has been pre-coated onto a flexible carrier, to a rigid standardized test panel under very controlled conditions and environment, using a roller of standard weight, dimensions, and construction, in order to apply a controlled application pressure. Then the force required to separate the two is found out by peeling the flexible carrier at a controlled rate, at either 180° [9] or 90° [10] (Figs. 1a and b), the rate of both roll-down and peel usually being at 12 in. (300 mm) per minute, with various dwell times between roll-down and testing, from immediate to 20 min. The 90° test is usually chosen when the thickness of the backing prevents a 180° peel, but these two angles of peel tell a different story, the 90° peel being one of tensile stress, while the 180° peel is a combination of tensile and shear stress [11]. Also, it is to be noted that, while, both the 90° and 180° tests are being peeled at the same tester rate, the peel front of the 90° test is moving at twice the rate of the 180° test, and so the adhesion results of the two angles of peel are not truly comparable.

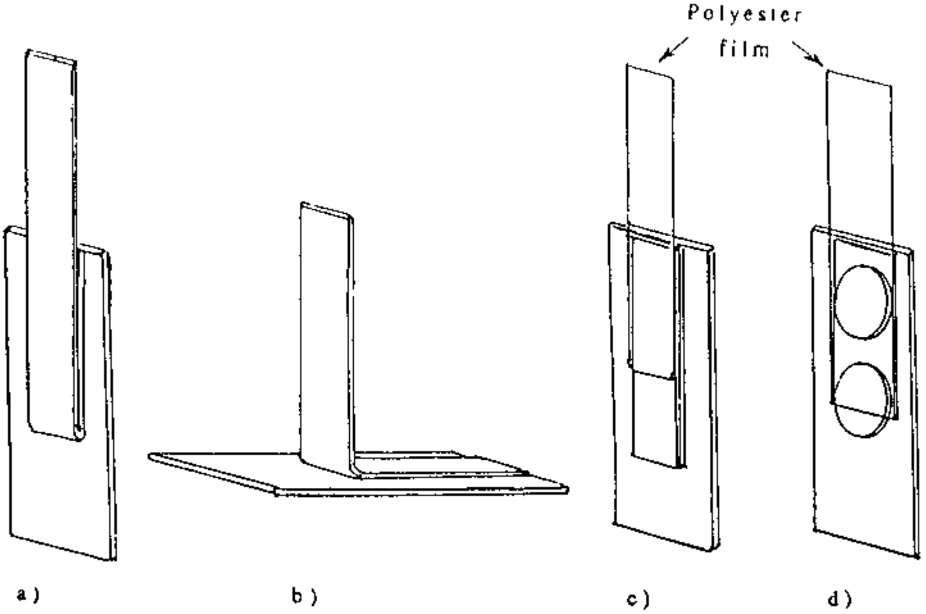

Figure 1 Peel adhesion testing: (a) 180° peel; (b) 90° peel; (c) reverse 180° peel; (d) adhesion of irregular shapes.

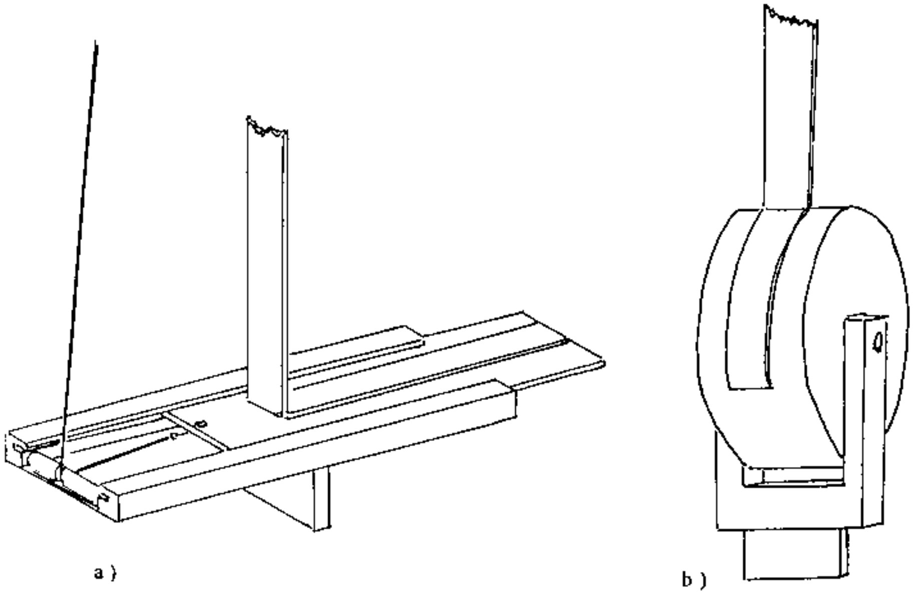

Figure 2 90° peel adhesion testing: (a) controlled 90° peel adhesion; (b) drum peel.

To maintain a constant 90° angle during peel, a special jig is necessary that moves the test panel at the same rate as the tape is being stripped (Fig. 2a). An alternative method [9] is to apply the tape to a free-rolling drum, which automatically maintains 90° by rotating during the stripping process (Fig. 2b).

The work done in peeling is divided between that necessary to separate the adhesive from the test surface, and that required to bend the backing, and the latter value can be a significant component [12]. Further, the basic assumption is that the geometry of the peel process is constant. With more rigid backings this is not the case, the backing both creating a restrictive action to the intended angle of peel, and also requiring a considerable amount of energy to bend. The resulting adhesion with the same coat weight adhesive using various backings over a range of backing thickness can be seen in Fig. 3. There are two ways that the effect of the backing can be investigated and/or overcome. One is to use the same backing in a series of thicknesses, each coated with the adhesive under evaluation at a constant desired coat weight. By plotting the adhesion values obtained, then extrapolating, an adhesion value can be obtained that eliminates the effect of the backing. An alternative method is to attach the adhesive-coated strip, adhesive side exposed, to a test panel, using a high adhesion double-sided tape, then applying to this a strip of 25 µm polyester film very slightly wider than the test tape, following the same standard preparation and test procedures as if the polyester strip were the tape under test, and the exposed adhesive surface were the test panel (Fig. 1c). This would then enable tapes of backings of various stiffnesses to be compared without the backings interfering with the test geometry. This method is also applicable to irregularly shaped pressure-sensitive coated pieces, the recorded adhesion values obtained being correlated with the changes in dimensions of the piece, and brought to that of a standard width by calculation (Fig. 1d).

Adhesion testing of double-sided tapes is achieved by applying a 25 µm polyester film of suitable width to one side of the tape, then carrying out a standard adhesion test on the

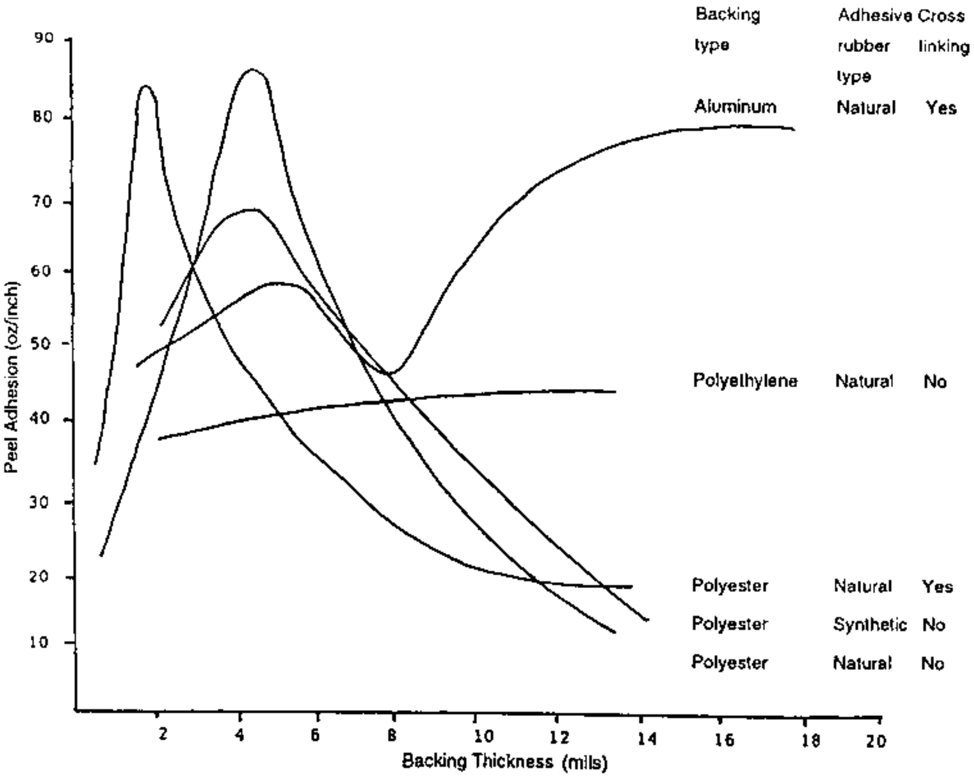

Figure 3 Effect of backing on nominal 180° peel adhesion.

other side, recognizing that the polyester film will add to the value obtained as work done in peeling.

A. Tack

Tack is an indication of how quickly an adhesive can wet out, and so come into intimate contact with, a particular surface, and eventually reach its optimum adhesion. In effect what is attempting to be measured is a rate of change of adhesion with time. This rate of change is exponential in character, can be manipulated by the degree of applied pressure, and much of the event can occur in fractions of a second. The methods of measuring tack are many [13], with considerably different techniques and geometries, often being unique adhesion test methods, but they can be divided into three broad categories: those using a rolling ball, those using a modification of the peel test, and those using some form of probe.

There are three major methods of tack test using a rolling ball method, each with its own variations, to suit a specific need, all involving rolling a small ball down a ramp and over the adhesive surface. The Douglas method (Fig. 4a), useful for adhesives with a high tack value, uses a 12 in. (300 mm)-radius ramp and a $1\frac{1}{8}$-in.-diameter steel ball, but different sizes and types of ball are also used, depending upon individual preference, one method using a table tennis ball, to create the minimum of pressure. The tack value is proportional to the reciprocal of the distance rolled, which also implies that the further

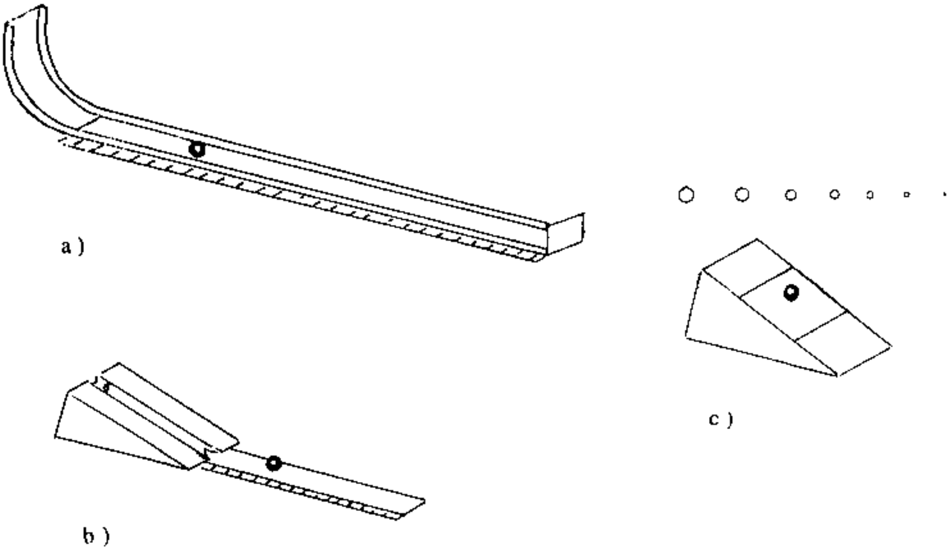

Figure 4 Rolling ball tack testing: (a) douglas; (b) PSTC; (c) dow.

the ball rolls, the less reliable the method becomes, useful to 15 in. or so of ball travel. It has its problems, such as the contact area of the adhesive on the ball differing with the softness of the adhesive, the tendency of the tape to climb up the receding side of the ball, and the fact that after one revolution of the ball, the surface is now contaminated by adhesive. However, it is a useful comparative test for similar adhesive systems. The PSTC Test Method, No. 6 for Rolling Ball Tack (Fig. 4b) uses a 6 in. (150 mm) ramp at 21.5° with a slight curve at the exit, and a 7/16-in.-diameter steel ball. It is useful for adhesives with a lower tack value, with the same relationship and problems as the Douglas method useful for only the first few inches of travel. The Dow method (Fig. 4c) uses a 30° ramp, the adhesive-coated material being secured to the ramp face up with 3 in. of adhesive exposed. Then a series of steel balls each differing in diameter from the next by 1/32 in., are rolled individually in decreasing order, over the 3 in. (75 mm) section of adhesive on the ramp, until one ball is stopped in the 3 in. (75 mm) section. The tack value is taken as the numerator of the diameter of that ball. In all cases, the need for controlled conditions, and thorough cleaning and drying of the balls used, is essential.

The commonest modified peel test, known as the "Quick-stick" or Chang test [14], uses the same equipment as for 90° peel (Fig. 2a), but the tape is laid on the test panel without any applied external pressure, then peeled immediately at 90°. The flaws in this method are that the adhesive continues to wet out the test panel with time, as it remains in contact, the precise time from application to testing being variable, but of much greater significance is that a zone of pressure follows the peeling action, governed somewhat by the flexibility of the backing, so that the tape effectively applies itself to the panel with pressure immediately following the peel zone [15] (Fig. 5a). In effect, it becomes a 90° adhesion test. One other well-known method, known as the loop tack method [16] (Fig. 5b), makes a loop of a 1-in.-wide sample of the tape, adhesive exposed, then this exposed adhesive is touched to a horizontal test panel with minimal pressure, to bring a definite area into contact. The force required to remove the loop, which is tested as for a

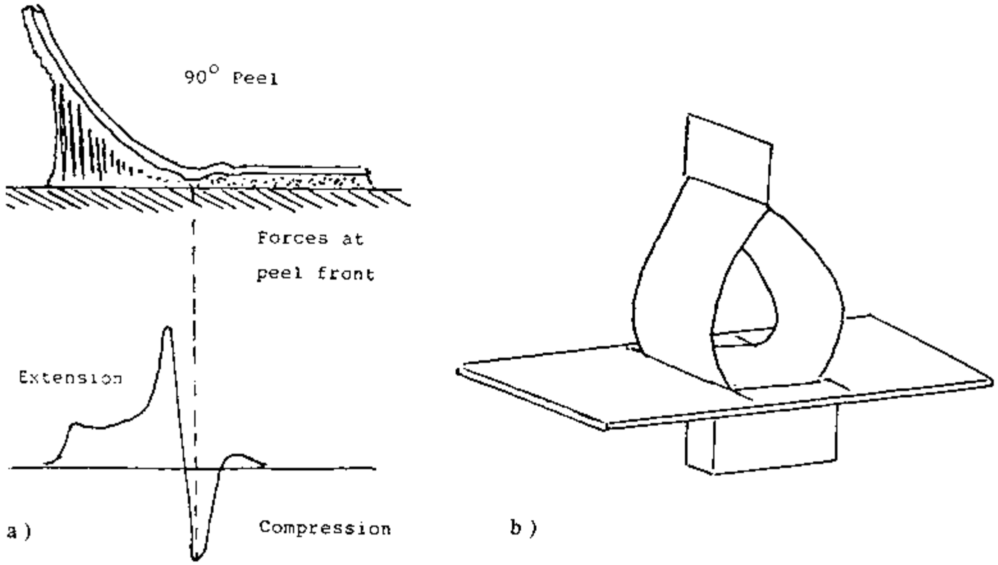

Figure 5 Quick-stick tack testing: (a) compressive effect of 90° peel; (b) loop tack testing.

90° peel, is recorded as the tack value. This is essentially two Quick-stick tests, back to back, and therefore has the same flaws.

There have been various methods of probe tack testing, which have included using a ball bearing with supporting ring [17], or a large hemispherical probe [18], but one method now dominates, which is the Hammond or Polyken probe tack tester [14] (Fig. 6a). This method has the latitude of a variable pressure, a variable dwell time, a variable rate of removal of the probe, probes of various construction, and even the option of a heated probe. Bringing the probe and adhesive surface together to ensure uniform contact can be difficult, even when using a probe of small diameter, the standard being a flat surface stainless steel probe of 0.5-cm^2 area, as there is a tendency to trap a very small air bubble. A slightly domed probe can overcome this [19]. Too low an application pressure will give nonuniform contact; too great a pressure causes the value obtained to plateau out, as will too great a dwell time before separation of the probe. The standard test conditions are 100-g/cm^2 loading, with a 1-s dwell time and 1-cm/s removal, but this can be adjusted to suit certain adhesive systems. The separation mechanism is in actuality a very low angle circular peel (Fig. 6b) at very high speed, as has been shown by high speed photography [20]. While the probe tack method has not yet been fully adopted, when understood, it gives the most meaningful data.

Variations in test results for tack from test to test for a given sample are common, possibly because such a small area of the adhesive surface is under examination at each test, and for this reason, whatever test method is used for tack testing, a number of checks are necessary to obtain a statistically meaningful result.

B. Shear

The universally accepted method for testing adhesion under shear is a static load test [21], where a known surface area of the adhesive-coated product is applied under controlled

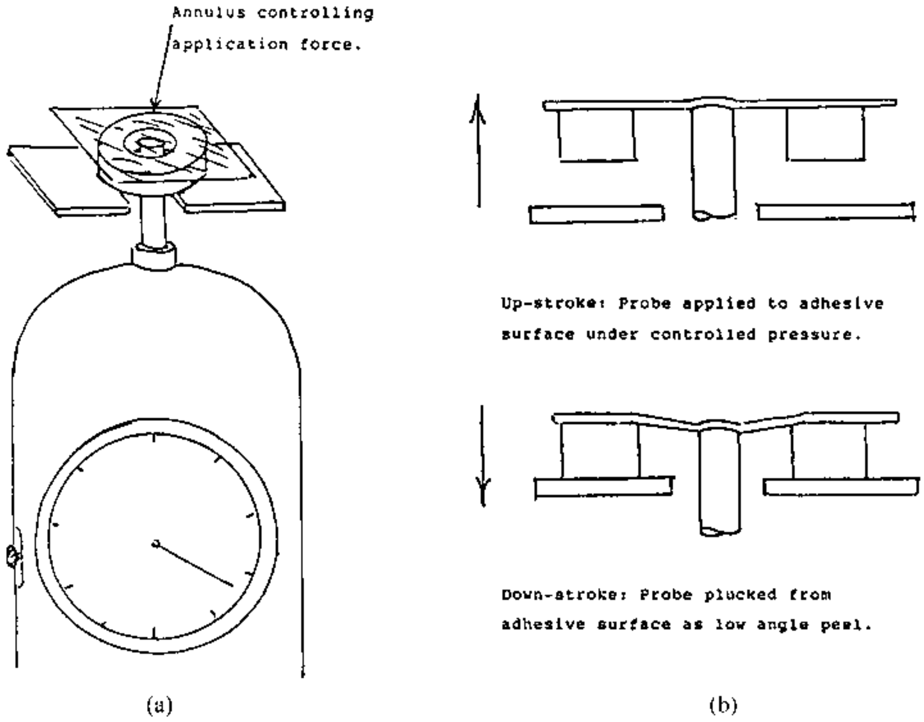

Figure 6 Kendall probe tack testing.

conditions to a standard test surface, usually stainless steel or a standard cardboard, or even the product's own backing. Then this is secured vertically, plus a 2°tilt-back, to prevent any possible low-angle peel. A fixed load is then applied (Fig. 7a), and the time taken for failure is recorded or any slip that occurs in a given time measured. A trip mechanism can be set up so that the falling weight stops a stopclock to denote the failure time. This test can be carried out at elevated temperature; variations of the basic concept exist, such as mounting the test surface horizontally [22] with a small radius of curvature at the edge of the test panel to redirect the tail of the tape under test to the vertical, in order to hang a suitable load (Fig. 7b). A further variation, used in the electrical industry to measure adhesive thermoset characteristics, is a high temperature shear test [23], where a controlled area overlap bond is formed, usually 0.5 in. (12 mm) by 0.5 in. (12 mm), either face to face, or face to backing. The adhesive is then given a thermoset cycle, followed by a high temperature shear test (Fig. 7c).

While a static load test is the commonly accepted procedure, in practice many variations in areas and weights are used, to compensate for the various qualities of adhesive evaluated, so that the test results will fall into a similar time frame, so it becomes difficult to compare different adhesive systems from accumulated data. It has the disadvantage of giving variable results for the same adhesive system, and is essentially a pass/fail test, as many products remain in place at the end of the test period. Experience has shown that the shear properties of pressure-sensitive adhesives to porous and nonporous substrates can be quite different, and each must be judged on its own merits.

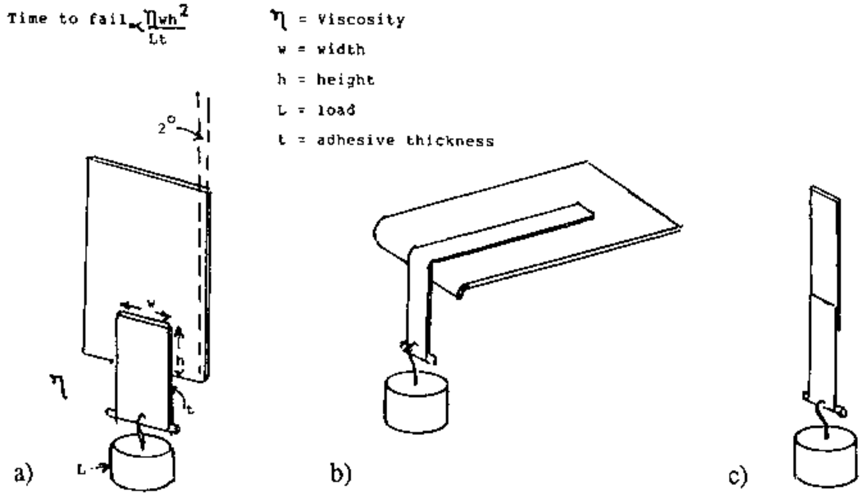

Figure 7 Shear testing: (a) 178° shear; (b) horizontal shear; (c) overlap shear.

C. Adhesion to Release Liner

The test methods presently used to evaluate the adhesion of pressure-sensitive adhesives to release liners are modified adhesion tests, such as the 180° or 90° peel test, with the liner adhered to a test panel, or a T-peel test, where the sample is freely suspended while the tape is peeled at a controlled rate from the release liner. The values obtained by the latter method are affected considerably by the stiffness of the liner, which alters the angle of peel.

One method occasionally used evaluate the relationship of silicone release liners or other materials of very low surface energy to a pressure sensitive, is to bring a coated pressure sensitive into contact with the liner under pressure, to carry out an adhesion test. This is of little value, as the adhesive is unable to wet out and so come into intimate contact with the release liner. The adhesive must first be coated onto the liner, dried, or cooled in the case of a hot melt, and then a carrier laminated to it, as is standard practice for transfer coating. As low values of adhesion can be expected, the force required to bend the backing may dominate, and so a thin flexible backing should be used, to maintain a constant peel angle, 25 μm polyester being satisfactory. Then a standard 180° peel test can be carried out with the release liner secured to a test panel.

III. AGING TESTS

The usual function of an aging test should be to challenge the product artificially in an accelerated manner in one or more environments that can be expected, so that either after prolonged storage or after long periods of use its behavior can be predicted.

The popular accelerated aging temperature used to predict natural aging is 65°C (150°F), with the adhesive-coated products either in roll or sheet form independently supported in a controlled humidity environment, such that they occupy less than a quarter of the available space to ensure ample circulating air. Typical commercial products are exposed to an 80% humidity using a saturated reagent grade ammonium sulfate bath [24], while for electrical products this is taken up to 90% using a bath of 37% by weight solution of glycerin [25]. The time period to predict behavior after 1 year of natural aging varies from 4 to 7 days at 65°C (150°F), depending on the authority, the change in physical characteristics before and after high temperature aging being compared. A reduction in physical characteristics of less than 10% after the aging test is normally considered a satisfactory performance.

The chemical makeup of many pressure sensitives makes them prone to oxidation, and while antioxidants can compensate for this, it is still necessary to evaluate whether the antioxidant is functioning satisfactorily. Any test to evaluate resistance to oxidation becomes a comparative test in change of performance, usually of adhesion and tack, the severity of the test depending on individual requirements for the finished product. One simple but effective test is to expose the adhesive to 120°C (250°F) in a forced-air oven for various periods of time, evaluating samples before and after heat exposure, a 1-hour exposure being a good starting point. A more severe test is the use of an oxygen bomb, at lower temperatures, with high pressure oxygen. Again, a good starting point is an overnight (16 hour) test at 38°C (100°F) and 300 psi.

Exposure to ultraviolet (UV) light can have similar degrading effects, either from sunlight or even from exposure to fluorescent lighting. The need for stability to UV light will depend on the adhesive end use, many adhesives never encountering such conditions. Similar to the oxidation test, the adhesive should be exposed to a controlled source of UV light, typically around 300 periods, with the samples under test mounted on a slowly rotating turntable to ensure uniform exposure, the adhesion and tack exposure being compared [26]. Commercial UV light sources are available. The source should be far enough away from the samples, usually around 18 to 30 in. (450 to 750 mm), to eliminate a possible secondary exposure to excessive heat from the light source; certainly exposed to no more than 50°C (120°F). The UV intensity at the test surface should be determined with a suitable UV light meter, adjusting the UV source location if necessary to ensure the same UV exposure for each test cycle. One proposed intensity is 2250 $\mu W/cm^2$ at 12 in. (300 mm) from the source with the samples at 18 in. (450 mm). As the UV source will deteriorate with time, it will be necessary to replace it periodically. The time of exposure is dependent upon the marketing objectives for that product, but one can expect the test period to be as prolonged as 180 h.

An alternative UV exposure test method is the use of a commercial weatherometer [27], in which carbon arcs are used as the UV source, the samples being mounted on a carousel rotating around the source. The carbon arcs need changing frequently, to provide the necessary exposure time, again the time of exposure depending on individual preference. The weatherometer has the added advantage of being able to provide in addition a water spray at chosen intervals, to simulate outdoor exposure.

Degradation by heat, resulting in breakdown of the various polymer structures is another cause of loss of properties, as can occur during the processing of hot melt systems, or in adhesive systems intended for high temperature applications. Here, the effect will not be seen so much in a change of tack or adhesion (these characteristics maybe even improving), but in deterioration of the ability of the adhesive to resist shear forces, which can be dramatic. The actual change in molecular weight and its distribution can be determined by gel permeation chromatography [28]. The lower-molecular-weight polymer systems as used in hot melt pressure-sensitive adhesives can be handled with conventional equipment and technology, but the much higher molecular weight of other natural and synthetic rubber-based systems will require more sophisticated equipment, including the use of heated columns.

IV. LOW TEMPERATURE TESTING

Low temperature testing can be to determine whether the adhesive can be applied effectively at that low temperature, or whether it functions satisfactorily when in use at that temperature. Both require the use of a cold box with access to manipulate the samples and test equipment, the test equipment being either totally or partially enclosed within the cold box. The sample to be tested and all materials needed to set the test up must be in the cold box at the chosen temperature for at least 4 h before testing begins. Test panels will need to be washed with acetone to remove any condensate, then thoroughly dried with a lint-free wipe just prior to application of the adhesive. Testing can then proceed as normal, using whatever test methods are felt appropriate, usually including a peel adhesion test. In a functional test which involves adhesive separation from a test surface, if the adhesion value obtained is sufficiently high to reflect a satisfactory bond, any adhesive transfer due to brittle fracture that occurs under these conditions is usually discounted.

V. HIGH TEMPERATURE TESTING

Here the adhesive is applied under standard conditions to whatever test surface is felt appropriate. The test, usually adhesion or shear, is then carried out in the high temperature environment, after allowing sufficient time for the assembly to reach the test temperature before beginning the test. Visual examination for signs of cohesive failure is a necessary part of high temperature adhesion testing.

One method used to evaluate the upper working temperature of block copolymer systems is to measure the shear adhesion failure temperature (SAFT), a useful method to discover exactly what has been gained in the upper working temperature limits when resins are added to the styrene domain of polystyrene end-block systems to increase the effective glass transition temperature. Typically the test is set up as a standard shear test, either to the standard stainless steel panel or to polyester, with a 1 in. by 1 in. (25 mm by 25 mm) area and a load of 1 kg. The set-up is placed in an oven that can be accurately controlled so that the temperature is increased by 2.0°C (3.6°F) per minute, the temperature at which failure occurs being recorded as the SAFT.

The above tests are general in nature. Specific products may call for specific tests aimed at the needs of that market.

VI. PACKAGING

Packaging in industry is universal; the need in most cases is the ability of a pressure-sensitive adhesive that will hold well to cardboard surfaces under stress. A simple introductory test would be to determine whether the adhesive wets out the surface well enough to delaminate the cardboard. Although this is a subjective test, it can be used very satisfactorily to rate the cardboard-keying ability of various systems. This test can be performed both initially and after allowing the adhesive to remain in contact at ambient conditions for a prolonged period, usually overnight. An estimate is made of the percentage fiber tear. A cardboard surface is not random; the cellulose fibers lie in a definite direction and at an angle, predetermined by the paper-making machine. Because of this, any cardboard used should be examined initially to determine which way the fibers lie. This is discovered by stripping an adhesive tape from the cardboard surface in each of the four directions. The cross direction of the card will show little or no fiber tear in either direction, while fiber tear should occur to some degree at right angles to this, denoting the machine direction of the cardboard. Because the fibers lie at an angle, the degree of fiber tear in the machine direction can be different, depending upon the direction of stripping. Testing should be carried out in the machine direction, stripping both ways, and recording the estimated fiber tear in each direction.

There are various box closure tests in use, some proprietary, all of which naturally call for the standard cardboard. If the cardboard used in the final package is available, the tests should be repeated with this specific material as many are coated or treated and the behavior on such surfaces can be quite different from that obtained with the standard cardboard.

One conventional packaging tape test is an inverted 90° peel test [25], using either standard cardboard or a cardboard of choice as test surface. The time taken to strip a 1 in. (25 mm) length of a 1 in. (25 mm)-wide sample using a 200-g load is measured (Fig. 8a). By using a window of silicone-coated release paper to define the 1 in. (25 mm) length, only that section of cardboard is contacted, and the sample falls away at the completion of the test.

By using a piece of equipment arranged to create a synthetic box closure, a stress can then be applied to a 2 in. (50 mm) length of packaging tape placed equally across two cardboard surfaces, one or both of which can be variously loaded, and can pivot, as for a conventional box closure (Figs. 8b and c). In Fig. 8b, the stress is one of shear to the tape on the moving surface and low-angle peel to the tape on the fixed surface. In Fig. 8c, they are both shear. The time taken to fail is recorded. Both testing techniques are used commercially. There are also those who prefer a static 20° peel from cardboard in place of either of these methods, measuring the time taken to strip a given length (Fig. 8d).

Then there are the pragmatists who use a new box, then apply 2 in. (50 mm) lengths of packaging tape as L-clips to hold the box flaps in place, 1 in. (25 mm) on the flap and 1 in. (25 mm) on the body of the box, allowing the spring action of the new cardboard to

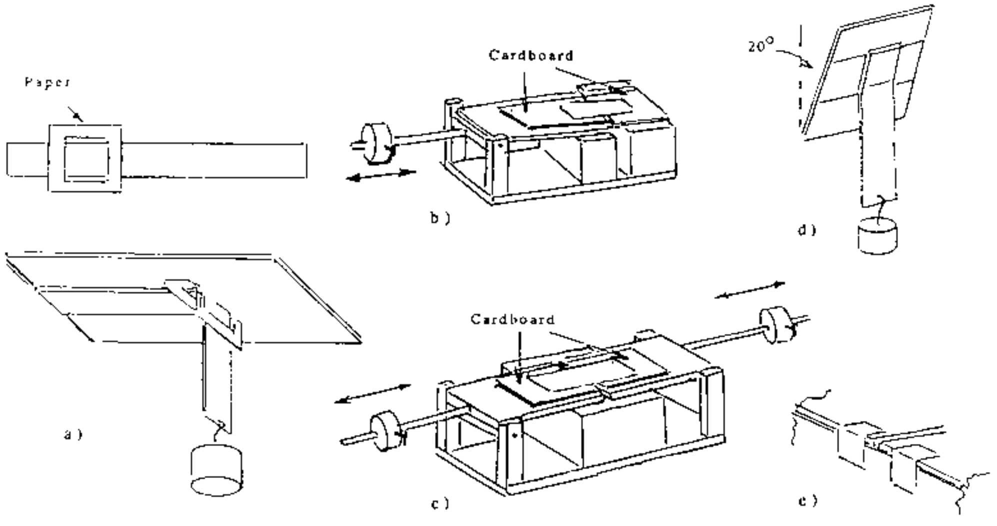

Figure 8 Cardboard box testing: (a) 90° inverted peel; (b) single-arm closure test; (c) double-arm closure test; (d) 20° peel; (e) L-clip.

create the stress (Fig. 8e). The boxes are then aged for 1 week under various conditions, finally rating the success or failures. A variation of this is the use of boxes overstuffed with latex foam to create the stress. A further commercial method is to fill the boxes suitably, as would be expected in practice, then arrange them on a vibration table such that the flaps are vertical rather than horizontal, and carry out a standard container shipping test.

A. The Appliance Industry

While packaging needs remain a major concern of the appliance industry, one other cause for concern with pressure-sensitive adhesives is the potential for staining on painted surfaces. A pressure-sensitive adhesive system may come into contact with a painted surface, either temporarily during the manufacturing process or for prolonged periods of storage, following which, on removal of the adhesive tape, slight discoloration may be observed. This may be either apparent immediately or it may not become apparent until some time later.

One suitable test to evaluate staining [26] is to use freshly painted test panels using the paint under consideration, and to these are applied strips of the tape being considered in precise locations, plus a control known to be satisfactory, marking the reverse side of the panels as to the exact location and type of each sample under evaluation. Sufficient areas of the panels are left exposed to provide a good comparison later. These panels are then aged. For the evaluation of in-process adhesive systems, the temperatures which the system can encounter during processing are used, at double the exposure time. For long-term storage evaluation, 1 week at 65°C (150°F) is usually sufficient. The adhesive tapes are then removed and any adhesive residue cleaned off with a suitable solvent ensuring that the solvent chosen does not also affect the paint. This can be a low-boiling-point aliphatic hydrocarbon, but isopropyl alcohol may be adequate. The panels are then examined carefully under both daylight and artificial light for signs of color change. A Macbeth light box can be a useful source of light. For latent staining [27] using these same stripped and clearly identified panels, one half of the previous location of each adhesive tape is obscured with small metal plates or other suitable coverings. The panels are then exposed to UV light for several hours, 4 h being typical, then examined for any latent staining. The UV set-up can be as previously outlined on aging, taking care to prevent any temperature build-up from the heat of the light source.

VII. HIGH TEMPERATURE MASKING TAPES

This testing is in addition to the high temperature testing described previously. High temperature masking tape can be applied to a variety of surfaces—plain, primed, or painted; metal, glass, rubber or chrome finished—and testing must include them all. The simplest test is to apply the tape to the appropriate surface, subject it to the heat and for the time period that the tape can expect in practical use, then strip the tape from the surface at various rates, both immediately, while the panel is still hot, and after 1 h, when the panel has been allowed to return to ambient temperature, visually examining the surface for any signs of cohesive failure.

Masking tapes, however must conform to curves, and the adhesive must hold at high temperatures under these stressed states. Also, it is common practice to use paper or plastic drapes to cover other areas which may accidentally receive the applied paint. These drapes or “aprons” are set into place by the same masking tape and quite often adhered to the backing of masking tape already applied directly to the surface to be painted. Using a high velocity, high temperature oven samples of the masking tape under evaluation should be set in the oven at the evaluation temperature in a manner duplicating this use: that is, in curves of various radii and applied to its own backing in similar curves, with apron paper attached, both in slight and excessive curves, and to its own backing. These test panels should be mounted vertically in a manner such that they are under the effect of the high velocity hot air. After the test cycle, the samples are carefully examined for signs of lifting. All of the previous tests can be duplicated to include applying the various paints that the masking tape may encounter in use, then investigating any effect that the paint has had on the adhesive.

VIII. ELECTRICAL TAPES

Almost all electrical tapes have thermosetting adhesive characteristics, and a suitable test to measure satisfactory thermosetting has been described in Section II.B. Many electrical tapes are used to wrap coils of various diameters, and there may be a tendency for the end of the tape to lift away after application, known as *flagging*. This can occur either after the coil is taped and held in storage awaiting the next process, during a thermoset cycle in preparation for a varnish dip, or in the varnish dip process itself. Any flagging test must cover all eventualities. How much challenge the tape receives will depend upon the diameter of the coils wrapped; the smaller the diameter the greater the stress and therefore the greater the tendency to flag. One suitable test is to use a 0.5 in. (12 mm)-diameter mandrel and wrap the tape around the mandrel with an exact 0.5 in. (12 mm) overlap. These should be set aside and examined 1 week later for any tendency to flag. While the storage conditions for this 1-week period would be expected to be ambient, temperatures of as high as 30°C (85°F) and humidities of 80 to 90% can be expected in a coil manufacturer's working environment, and so must be brought into the evaluation study. The test assemblies, or others set up simultaneously, are then subjected to the manufacturer's recommended cure cycle for that adhesive, or if unknown, 1 h at 150°C (300°F), and again examined for flagging. The cured assemblies are then dipped for 20 min in the commercial varnish that the adhesive would normally encounter and reexamined for flagging. When sufficient experience has been gained, including comparative studies, this may be modified to a 5-min dip in the solvent system used in the varnish.

In the case of an electrical tape used as a harness wrap, the flagging test can be modified [28] by using a 0.125 in. (3 mm) diameter rod, spiral wrapping the rod with the tape under test, ensuring a 50% overlap, then examining for any tendency to flag after an aging cycle.

Electrical tapes may come into contact with current-carrying fine bare copper wires, a potential condition for electrolytic corrosion. While the tendency for electrolytic corrosion can be, and is, estimated indirectly from the reciprocal of the insulation resistance of an adhesive tape, insulation resistance is determined using the total cross-section of the tape, whereas electrolytic corrosion is related to the adhesive only. A more reliable estimate can be made directly by attaching two 32-gauge fine bare copper wires, 0.25 in. (6 mm) apart, along the adhesive surface of a 6 in. (150°mm)-length of tape, using the standard roll-down application method. Care should be taken to avoid any kinks in the wire. With 250 V DC applied across the wires, this assembly is placed in an enclosure that provides a saturated atmosphere and then aged at 50°C (120°F) for 20 h. After removing the applied voltage and allowing to cool, the wires are carefully removed and the tensile test performed on each wire. The direct electrolytic corrosion is reported as the ratio of the tensile strengths of the two wires, no corrosion giving a factor of 1.

A much simpler version of this test, which can be used as a screening test, is to apply the adhesive tape to a freshly polished soft copper panel using a 100-grit aluminum oxide polishing wheel or 150-grit paper, then heat-age this at 100°C (212°F) for 72 h. After allowing to cool, the tape is removed and the panel inspected for any indication of staining.

Electrical tapes can also encounter various solvents as used in varnishes, or oils as used in transformers, and here a test can be devised that is specific to the end use by immersing a test panel on which the adhesive tape under consideration has been applied, as for an adhesion test, in the liquid in question, the time period being relevant to that which would be encountered in practice. After removal of the panel from the liquid, the excess liquid is removed carefully using an adsorbent, and a standard adhesion test carried out, the result being compared to the original value. In most cases, some adhesive edge transfer is permissible. There are other tests relating to electrical properties such as dielectric strength and insulation resistance, but these are more related to the backing and as such will not be discussed here.

IX. SPECIAL TESTS

There may be a tendency, with time, for a pressure-sensitive adhesive tape to slowly curl away from the surface to which it is applied, usually owing to a prolonged slight stress coupled with stress relaxation within the adhesive. Conventional testing may not indicate this weakness. One way to study this is to use a modified form of the 90° inverted peel test shown in Fig. 8a. The surface under evaluation should be marked into equal units, as for example, six 1 in. (25 mm) divisions. The adhesive tape under evaluation can be applied along this marked area, as for a conventional adhesion test, together with a control product known to adhere satisfactorily. Then in place of the usual 200-g loading, a much lighter load is applied, sufficient to apply a very slight stress. This will be in the area of 10 or 20 g, depending on the adhesive. Any adhesive system that has a tendency to slowly release from a surface will gradually peel away, sometimes within minutes, while a satisfactory product will hold indefinitely.

An alternative method that has provided interesting data is to run a 90° peel test but begin this test at 0.1 in. (2.5 mm)/min, then stop the tensile tester under stress but allow the recorder to continue. It will be necessary to reduce the speed of the recorder, as the test may take minutes. Stress relaxation will be shown by the rate of drop of the peel value obtained when the tester was stopped. A useful value of stress relaxation time is that time taken when the applied stress has been reduced to 40% of its original value.

The degree of initial contact that can be obtained from a given pressure-sensitive adhesive-coated material depends not only on the surface to which it is applied, but also on the roughness of the adhesive surface itself, which may come from its prolonged contact with its own irregular backing, such as a glass cloth or embossed or heavily creped paper or plastic facing or carrier. One simple method to evaluate surface contact is to apply the adhesive-coated product to a piece of plate glass as for a standard peel test, then examine the degree of contact area as seen by the degree of light reflection difference at the adhesive/glass interface, observing from the reverse side of the glass. A further method is to use carbon paper. By applying the adhesive-coated product to the carbon paper with a standard roll-down, then carefully removing it, the degree of ink removed and the pattern seen is a measure of the potential contact. The carbon paper may need reinforcement to prevent tearing on removal of the tape.

A. The Butt Tensile Test

The work done in testing pressure-sensitive adhesives in the 0.01 in. (0.25 mm)/min area has yielded an interesting new research test method, given the name of the butt tensile test. The standard 90° peel test is one of tensile stress, but there is a continuous change in the adhesive under examination as the peel front recedes. By rearranging the geometry so that a limited fixed area of adhesive is under a continuous tensile stress, a new and informative test can be performed on the adhesive. For this test, a tensile tester with the ability to accurately record values covering the 2.0 lb (1000 g) range is necessary, test results by this method typically falling into this range. First, the adhesive-coated tape under evaluation is prepared for testing by securing it, adhesive out, to a microscope slide in such a manner that a narrow strip of exposed adhesive at the end of the slide can be evaluated (Fig. 9a). The opposite end of the microscope slide is wrapped to give the tester jaws a better grip. This assembly is then mounted in the upper jaws of the tensile tester. With the tester set on the 2.0 lb (1000 g) scale and the return speed of the tester set at a suitably low value, starting at 5 in. (125 mm)/min, the narrow strip of exposed adhesive at the end of the microscope slide is then brought into contact with a polished horizontal test surface that has been mounted in the lower jaw of the tester, adjustments being made to the slide if necessary to ensure that the two surfaces are parallel (Fig. 9b).

Slight pressure is then brought to bear to ensure intimate contact. One way this can be achieved is the use of a tester fitted with an extension/compression strain gauge, setting

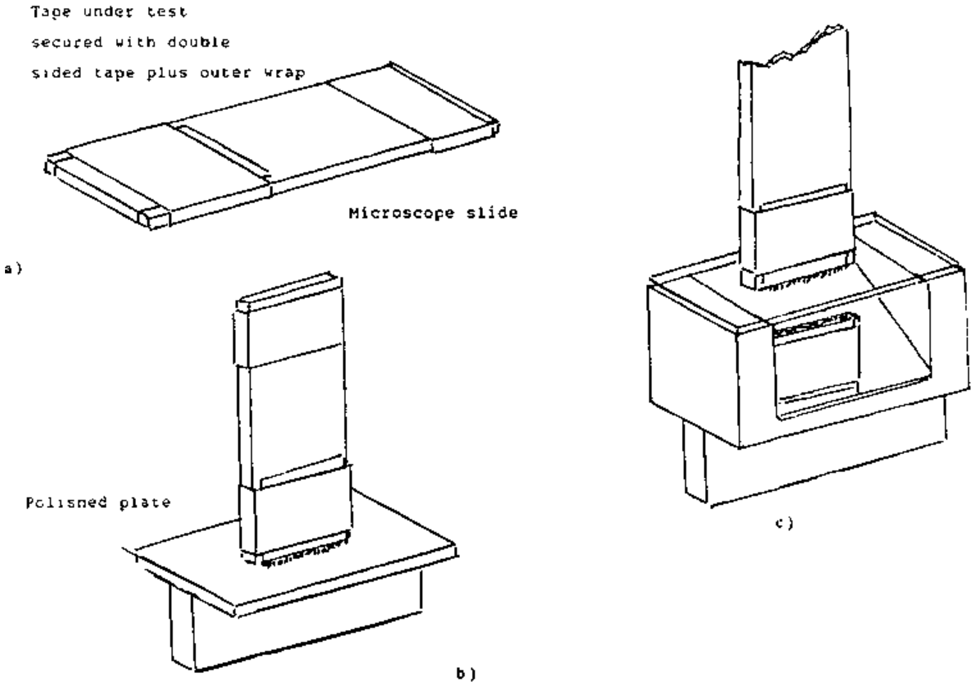

Figure 9 Butt tensile test: (a) sample preparation; (b) tensile tester set-up; (c) 45° mirror set-up.

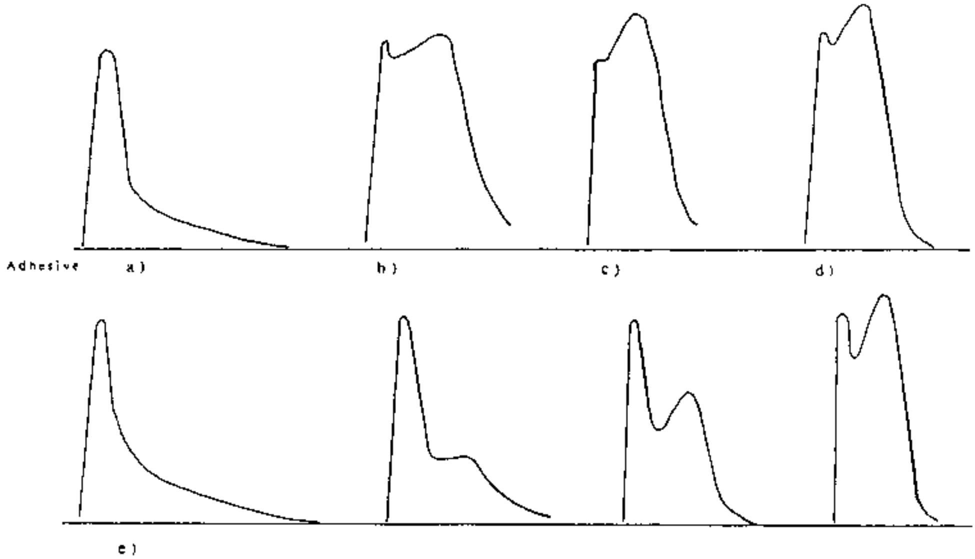

Figure 10 Typical butt tensile test graphs: (a) undercured, (b) cross-linked, (c) overcured, and (d) block copolymer adhesives; (e) stages in the cross-linking of a pressure-sensitive adhesive.

the zero of the recorder at a position 5% from the zero of the full scale deflection, followed by recalibration of the scale. The lower jaws are slowly raised until sufficient compression is applied to the bond to return the recorder pen to zero. The drive is then stopped and the application force held for 10 s. The lower jaw is then slowly lowered until the applied stress returns to zero. The set-up is allowed to relax for 2 min to relieve any stress within the adhesive. A tensile test is now carried out on the bond at 0.01 in. (0.25 mm)/min with the recorder set at 1.0 in. (25 mm)/min. Typical curves that can be generated are shown in Fig. 10. The shapes of the curves obtained are independent of width, which affects only the amplitude, and so compensation can be made for the sample width available by calculation, as for adhesion testing. As the fibers are delicate, the equipment should be made as vibration free as possible.

Another variation in the test surface is to use a second microscope slide and, using a suitable set-up, mount a 45° mirror below. Then it can be ensured visually that adequate contact is being achieved (Fig. 9c), and further, the mechanism of failure can be studied. This method was used successfully initially to ensure the viability of the test method.

A description of these curves, and a possible interpretation follow. The very slow speed of testing allows for cavitation, molecular disentanglement, and the formation of adhesive fibers which are then drawn out until adhesive failure at the polished surface takes place. The length of these fibers is many times the original thickness of the adhesive. One can make the analogy that the adhesive consists of a broad spectrum of polymer structures. At one end of this spectrum, fibers are formed that require a considerable force to elongate, but the degree of elongation is low. At the other end of the spectrum, fibers are formed with a very high elongation, which it takes little effort to extend. The former fibers are those that contribute to adhesion, while the latter contribute to tack. If the adhesive polymer structure is chemically cross-linked, or has pseudo-cross-links, as in a block copolymer, then the fiber extension process is restricted and orientation occurs, resulting in the formation of a secondary peak. The ratio of the primary to the secondary peaks is a measure of the cure level for that adhesive. If a series of tests are carried out on an adhesive at various stages in its cure cycle, not only will the secondary peak gradually build, but the tail of the curve is also gradually lost, no doubt due to the lower-molecular-weight components, the most mobile, being taken up in the curing process (Fig. 10).

Adhesive systems showing high adhesion levels by conventional methods naturally show a high value of the primary peak, the area under the curve denoting the work done in separation. Un-cross-linked systems show no secondary peak (Fig. 10a). Adhesives with a high degree of cure show a high value secondary peak (Figs. 10b and c), the pseudo-cross-linking of block copolymers showing the highest, and depending on adhesive design, often higher than the primary peak (Fig. 10d).

This technique can therefore provide various pieces of information in a single test. It can be used to evaluate the degree of cure of a given system once a standard has been determined and evaluated (Fig. 10e). The tail is a reflection of the low-molecular-weight component; adhesives with a low-molecular-weight plasticizer will show an exceptionally long tail. Such systems in practical use would be expected to show a tendency to lift after application. The method can thus highlight the cause of failure and identify poor design. Other potential uses for this test method will present themselves as the user becomes more familiar with its operation.

B. Dynamic Shear

One major cause of adhesive tape failure is the gradual disentanglement of the adhesive polymer system under slight but prolonged shear stress. While the standard shear stress test under static load (see Section II.B) is the accepted test method to evaluate this, the nature of the results, which could be in tape movement, time to fall, or no movement whatsoever, make it difficult to compare one adhesive with another.

By converting the static shear test into a dynamic test, and running the test at a slow enough rate to allow polymer disentanglement, more meaningful and comparable data can be generated. For the butt tensile test, this rate is around 0.01 in. (0.25 mm)/min. While the width of the test sample is proportionate to the result obtained, the height of the sample on the test surface should be limited in order to limit the energy applied to the backing and so prevent adding a tensile test into the test mode. A satisfactory value is 0.25 in. (6 mm).

With increasing applied stress, the rectangular cross-section of the adhesive under stress will become increasingly trapezoidal until eventually disentanglement occurs (Fig. 11). The test is now terminated, having provided that force necessary to initiate disentanglement. The test also provides secondary information in that, if the adhesive thickness is known accurately and the distance moved before disentanglement is also known from the recorder chart, then the ratio of these two dimensions is a measure of the deformability of the adhesive, a key factor in pressure-sensitive adhesive behavior.

X. CONCLUSIONS

In conclusion, anyone testing pressure-sensitive adhesive systems should not only be fully acquainted with the fundamental characteristics of pressure-sensitive adhesives and the pitfalls in testing to ensure that the data gathered in whatever test method being used are meaningful, but the tester should also develop the skill to manipulate these test methods to meet specific needs.

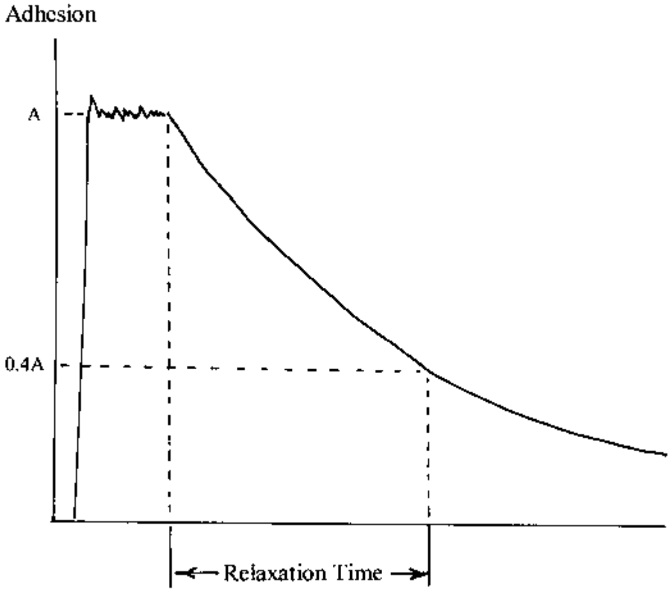

Figure 11 Relaxation time.

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Durability of Adhesive Joints

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I. INTRODUCTION

Although obtaining high initial bond strength is relatively easy, maintaining good bond durability in aggressive environments is comparatively more difficult. The most important factor leading to bond degradation of most materials is moisture. Moisture is pervasive over much of the world and is responsible for the vast majority of bond failures, both in the field during service and in the laboratory during research and development.

The importance of adhesive bond durability will vary depending on the particular application and environment. One of the most critical cases is military and civilian aircraft, especially those that operate in tropical, coastal, or marine locations. At the other extreme, less critical applications include those subject to low stresses and protected from harsh environments, such as interior furniture in temperate climates [1] or even wrapped gift packages. Increased durability generally requires additional initial cost through more expensive materials or processing. Consequently, it makes little sense for a bond to have a significantly longer lifetime than the item or system of which it is a part. In this chapter, we will concentrate on applications where durability is a critical issue, such as the aerospace industry—an emphasis natural to the topic.

The rate of bond degradation depends on a number of variables that can be grouped into three categories: environment, material, and stress. The environment is dominated by temperature and moisture. It can also include the concentration of aggressive ions, such as chlorides, and the presence of fuels, deicers, and other fluids. Electrochemical potential, either directly applied or created by galvanic couples, and extreme pH can also promote degradation. The material grouping is all-inclusive and includes the adherend, the adhesive, and the interphase between them. Finally, the stresses to which the bond is subject either during or after exposure also influence its lifetime or residual strength.

Each of these factors will be discussed in more detail. We also review the means to enhance durability. Entire books can and have been written on durability; in this short chapter, we can only touch on the subject. For more details, the reader is referred to the many reviews in the literature [1–13].

II. ENVIRONMENT

As already mentioned, moisture is the bane of most adhesive bonds. It is nearly impossible to keep water from a bond exposed to the outside environment [14]. Water can readily diffuse through the adhesive or the adherend, if it is permeable, as a composite might be. Moisture can also wick or travel along the interface and it can migrate via capillary action through cracks and crazes in the adhesive. Once moisture is present, it can attack the bond by [14]

reversibly altering the adhesive, e.g., plasticization
swelling the adhesive and inducing concomitant stresses
disrupting secondary bonds across the adherend/adhesive interface
irreversibly altering the adhesive, e.g., hydrolysis, cracking, or crazing
hydrating or corroding the adherend surface.

The first three of these processes are reversible to one extent or another. Provided that bond degradation has not proceeded too far, if the joint is dried out (which may be a long process), the bond can regain some of its lost strength [10,15]. There appears to be a critical water concentration, below which either no weakening occurs [1,16], or whatever weakening that does occur is reversible [15,17]. This critical water concentration is dependent on the materials used in the joint and is likely to be dependent on the temperature and stress as well. At higher moisture levels, some strength may be recovered upon drying, but at a certain point, the failure becomes near catastrophic and is beyond recovery.

Upon moisture penetration, the locus of failure almost always switches from cohesive within the adhesive to at or near the interface. Because metal oxide surfaces are polar, they attract water molecules that can disrupt any dispersive (van der Waals) bonds across the interface. This disruption can be seen thermodynamically by the work of adhesion in an inert medium, W_{A}, which can be represented as [1]

$$W_{\mathrm{A}} = \gamma_{\mathrm{a}} + \gamma_{\mathrm{s}} - \gamma_{\mathrm{as}} \tag{1}$$

where γ_{a} and γ_{s} are the surface free energies of the adhesive and substrate, respectively, and γ_{as} is the interfacial free energy. In the presence of a liquid such as water, the work of adhesion, W_{Al} becomes

$$W_{\mathrm{Al}} = \gamma_{\mathrm{al}} + \gamma_{\mathrm{sl}} - \gamma_{\mathrm{as}} \tag{2}$$

where γ_{al} and γ_{sl} are now the interfacial free energies of the adhesive/liquid and substrate/liquid interfaces, respectively. In an inert environment, the work of adhesion for a bonded system will be positive indicating a stable interface, whereas in the presence of water, the work of adhesion may become negative, indicating an unstable interface that may dissociate. Table 1 shows, in fact, that moisture will displace epoxy adhesives from iron (steel), aluminum, and silicon substrates and promote disbonding [1]. In contrast, although moisture weakens epoxy/carbon fiber bonds, these remain thermodynamically stable. Industrial experience with both metal and composite joints confirms these predictions [1].

The data presented in Table 1 illustrate the potential disastrous results when relying solely on dispersive bonds across the interface between an epoxy adhesive and metals or ceramics. To illustrate this danger, demonstration specimens can be produced that exhibit good initial strength, but fall apart under their own weight when a drop of water is placed at the crack tip.

Table 1 Work of Adhesion for Various Interfaces

Interface	Work of Adhesion (mJ/m^2) In Inert Medium	Work of Adhesion (mJ/m^2) In Water	Interfacial Debonding After Immersion in Water
Epoxy/ferric oxide (mild steel)	291	−255	Yes
Epoxy/alumina	232	−137	Yes
Epoxy/silica	178	−57	Yes
Epoxy/CFRP	88–99	22–44	No

CFRP, carbon fiber reinforced plastic.
Source: Ref. 1.

III. MATERIALS

The adherend, adhesive, and interphase between them are major factors in determining bond durability. For example, the simple disruption of the dispersive forces already described indicates that joints made with composite adherends will be inherently more stable than those made with metallic adherends. To increase durability, most metallic and many polymeric adherends undergo surface treatments designed to alter the surface chemistry or morphology to promote primary covalent chemical bonds and/or physical bonds (mechanical keying or interlocking) to maximize, supplement, or replace secondary dispersive bonds. These treatments are discussed elsewhere [1,3,12,18–24]. An intent of each treatment is to provide interfacial bonding that is resistant to moisture intrusion.

Formation of durable chemical bonds is an obvious means to stabilize the interface and has been demonstrated for phenolic/alumina joints [25] and for silane coupling agents [26,27]. However, for most structural joints using epoxy adhesives and metallic adherends, moisture-resistant chemical bonds are not formed and mechanical interlocking on a microscopic scale is needed between the adhesive/primer and adherend for good durability. In these cases, even if moisture disrupts interfacial chemical bonds, a crack cannot follow the convoluted interface between the polymer and oxide and the joint remains intact unless this interface or the polymer itself is destroyed.

The scale of the microscopic surface roughness is important to assure good mechanical interlocking and good durability. Although roughness on any scale serves to increase the effective surface area of the adherend and, therefore, to increase the number of primary and secondary bonds with the adhesive/primer, surfaces with features on the order of a few nanometers exhibit superior performance to those with features on the order of micrometers. Several factors contribute to this difference in performance. The larger scale features are fewer in number and generally are smoother (even on a relative scale) so that interlocking is less effective. Depending on the particular treatment used, there may also be loosely bound detritus that prevents bonding to the integral adherend surface [28]. In addition, the larger scale roughness frequently allows trapped air and surface contaminants to remain at the bottoms of troughs and pores [28,29]. These unbonded regions limit joint performance by reducing both chemical and physical bonds and serving as stress concentrators. In contrast, smaller scale microroughness tends to be more convoluted in morphology and generates strong capillary forces as the primer wets the surface, drawing the polymer into all the "nooks and crannies" of the oxide and displacing trapped air and some contaminants to form a microcomposite interphase [29]. Indeed, cross-sectional micrographs show complete filling of the micropores [4,6,12,18,28,30].

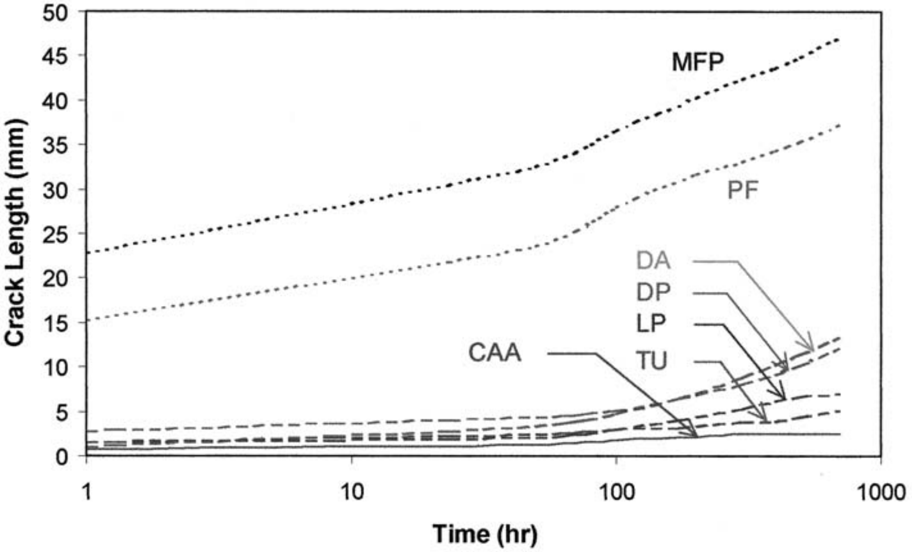

Figure 1 Wedge test results for Ti adherends with several different surface treatments having differing degrees and scales of roughness. Specimens were exposed to 100% relative humidity at 60°C. (Data from Ref. 31.)

This dependence on the degree and scale of roughness is illustrated in Fig. 1, which shows wedge test results of titanium bonds with several surface preparations [31]. Because the titanium surface is stable under these conditions (see below), differences in the joint performance can be attributed solely to differences in the polymer-to-oxide bonds and correlate very well with adherend roughness. The poorest performing group of pretreatments [Class I: phosphate fluoride (PF) and modified phosphate fluoride (MPF)] produced relatively smooth surfaces. The intermediate group [Class II: Dapcotreat (DA), dry Pasa Jell (DP), liquid Pasa Jell (LP), and Turco (TU)] exhibited macrorough surfaces with no microroughness. They had significant improvements in durability over the smooth adherends, but not as good as the Class III pretreatment [chromic acid anodization (CAA)] which provided a very complex microroughness. Subsequent Class III tests using sodium hydroxide anodization (SHA) and plasma spray provide further evidence of this correlation [32–34]. Both of these give very good durability performance and exhibit high levels of microroughness.

A. Adherends

The adherend often establishes ultimate joint durability. The morphology of its surface determines the degree of physical bonding (mechanical interlocking) with the polymer and its chemistry, in part, determines the degree and type of chemical bonding. Furthermore, the stability of the adherend and its surface determines the ultimate limit of durability. Once the adherend becomes degraded, the bondline is reversibly damaged and the joint fails.

Each material exhibits its own form of degradation and conditions under which the degradation occurs. For aluminum adherends, moisture causes hydration of the surface, i.e., the $A1_2O_3$ that is formed during the surface treatment is transformed into the

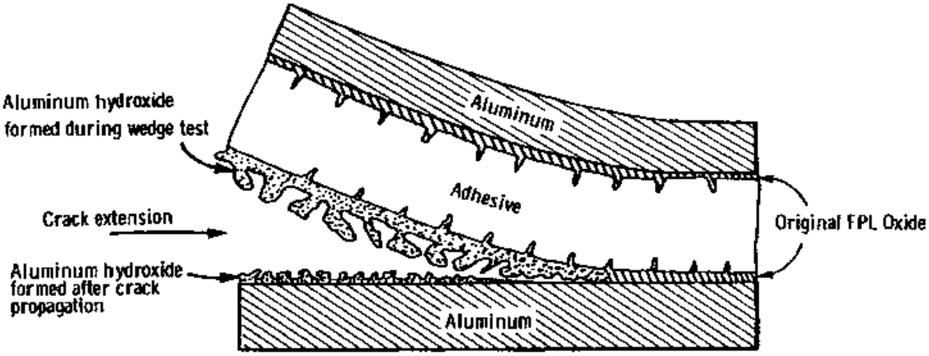

Figure 2 Schematic representation of hydration causing crack propagation in a wedge test specimen. The increase in volume upon hdyration induces stresses at the crack tip that promote crack growth. (From Ref. 4.)

oxyhydroxide AlOOH (boehmite) or trihydroxide $Al(OH)_3$ (bayerite). The transformation to the hydroxide results in an expansion of the interphase (the volume occupied by the hydroxide is larger than that originally occupied by the $A1_2O_3$). This expansion and the corresponding change in surface morphology induce high stresses at the bondline. These stresses, coupled with the poor mechanical strength of the hydroxide, promote crack propagation near the hydroxide/metal interface, as shown schematically in Fig. 2 [1].

The rate of hydration of the aluminum oxide depends on a number of factors, including surface chemistry (treatment), presence of hydration/corrosion inhibitors in the primer or applied to the surface, temperature, and the amount of moisture present at the surface or interface. One surface treatment that provides an oxide coating that is inherently hydration resistant is phosphoric acid anodization (PAA) [30]. Its stability is due to a layer of phosphate incorporated into the outer Al_2O_3 surface during anodization; only when this phosphate layer goes into solution does the underlying Al_2O_3 hydrate to AlOOH [35]. The hydration process is illustrated in the surface behavior diagram of Fig. 3 [35,36]. It shows hydration to occur in three stages: (I) a reversible adsorption of water, (II) slow dissolution of the phosphate layer followed by rapid hydration of the freshly exposed Al_2O_3 to AlOOH, and (III) further hydration of AlOOH to $Al(OH)_3$.

Another means of providing a hydration-resistant surface is its treatment with a hydration inhibitor [37]. Figure 4 shows wedge tests results for a Forest Product Laboratory (FPL) bond, [38] an FPL bond pretreated with nitrilotrismethylenephosphonic (NTMP) acid [39–41], and a PAA bond. The monolayer coverage of NTMP stabilizes the surface against hydration and provides wedge test bond performance similar to that of PAA-treated adherends.

Although the evolution of surface chemistry depicts the hydration of bare surfaces, the same process occurs for buried interfaces within an adhesive bond. This was first demonstrated by using electrochemical impedance spectroscopy (EIS) on an adhesive-covered FPL aluminum adherend immersed in hot water for several months [42]. The EIS, which is commonly used to study paint degradation and substrate corrosion [43,44], showed absorption of moisture by the epoxy adhesive and subsequent hydration of the underlying aluminum oxide after 100 days (Fig. 5). At the end of the experiment, aluminum hydroxide had erupted through the adhesive.

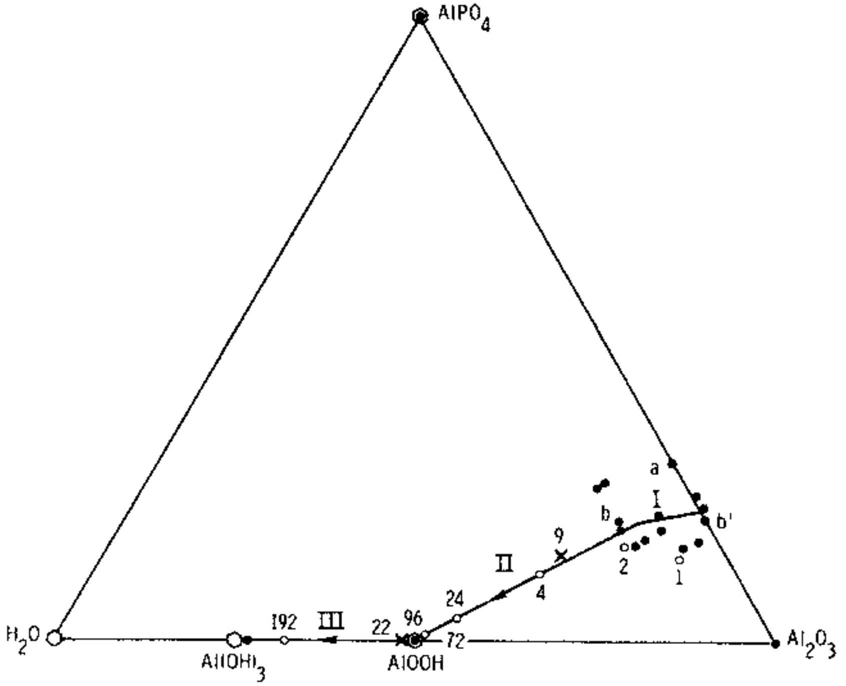

Figure 3 Surface behavior diagram showing hydration of the PAA Al_2O_3 surface. Hydration occurs in three stages: I, reversible adsorption of moisture; II, hydration of the Al_2O_3 to AlOOH; and III, further hydration to Al(OH)3. The numbers represent hours of exposure to high humidity. (From Refs. 29 and 35.)

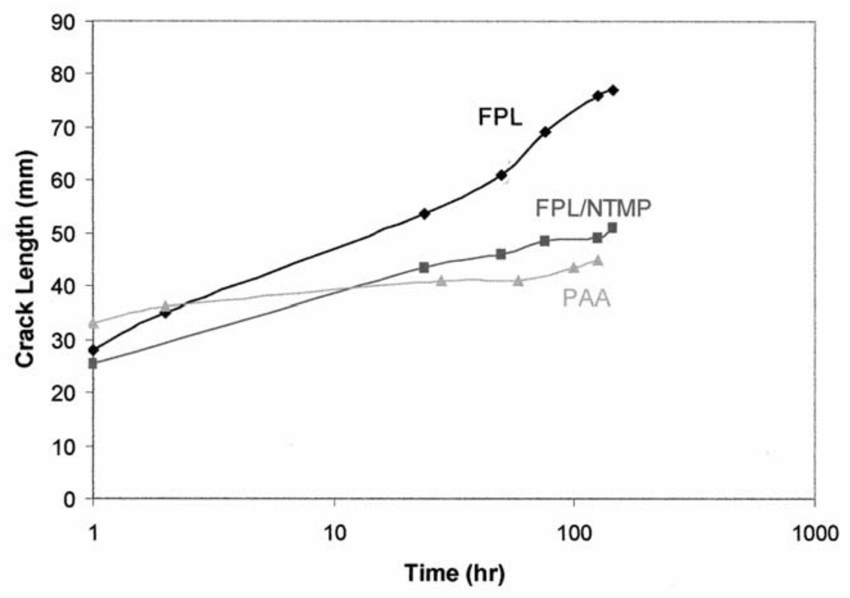

Figure 4 Wedge tests results of aluminum adherends with the following surface preparations: FPL, PAA, and FPL followed by an NTMP treatment. (From Ref. 40.)

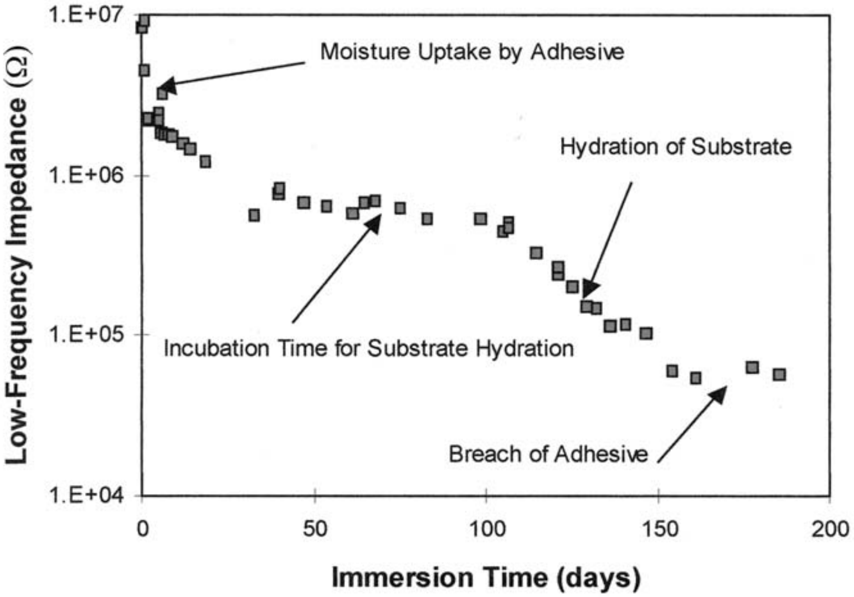

Figure 5 Low-frequency electrochemical impedance of an epoxy-coated FPL aluminum adherend as a function of immersion time in 50°C water. (From Ref. 42.)

Subsequent investigations showed that identical hydration reactions occurred on both bare aluminum surfaces as well as bonded surfaces, but at very different rates of hydration [45]. An Arrhenius plot of incubation times prior to hydration of bare and buried FPL surfaces clearly showed that the hydration process exhibited the same energy of activation (~82 kJ/mol) regardless of the bare or covered nature of the surface (Fig. 6). On the other hand, the rate of hydration varies dramatically, depending on the concentration of moisture available to react at the oxide/polymer interface or the oxide surface. The epoxy-covered surfaces have incubation times (and rate constants) three to four orders of magnitude longer than bare, immersed specimens, reflecting the limited amount of moisture absorbed by the epoxy and free to react with the oxide.

Steel adherends are also subject to corrosion in moist environments. Unfortunately, no general etch or anodization treatment has been developed that provides superior bond durability [12,18,46]. In part, this is due to the lack of a coherent, adherent stable oxide—iron oxides do not protect the underlying substrate from the environment. Equally important, the different steel metallurgies react to chemical treatments differently—a procedure that may give good results for one steel alloy may give very poor results for another, similar steel alloy.

In contrast to aluminum and titanium structural bonds where performance can be optimized for most aerospace applications, steel bonds are often designed to minimize cost as long as certain performance standards are met [47]. If feasible, many manufacturers prefer to select adhesives or primers that provide adequate strength and durability with untreated steel rather than to prepare the surface for bonding.

The most common surface treatments are grit blasting or other mechanical abrasion processes that clean the surface and provide a more chemically reactive oxide. Although the result is not as good as that of the common aluminum and titanium treatments,

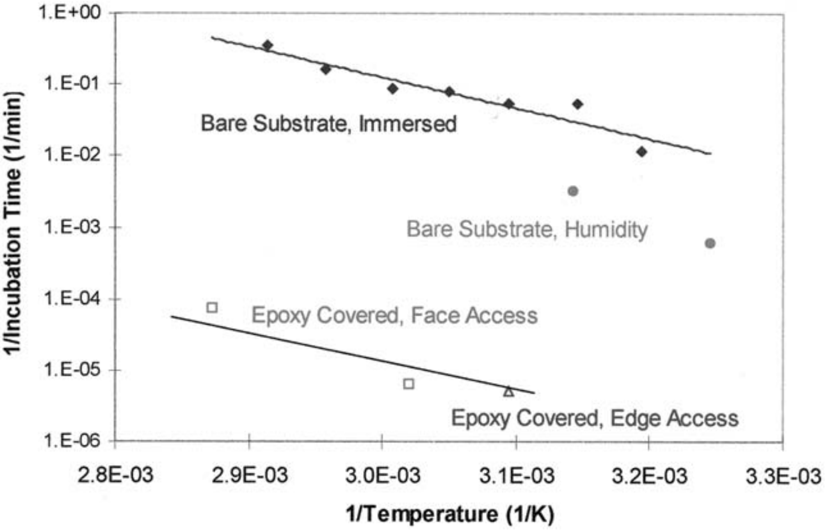

Figure 6 Arrhenius plot of incubation times prior to hydration of FPL aluminum under various conditions. (From Ref. 45.)

performance is frequently adequate. Improvements to grit blasting, based on either performance or cost, have been reported for individual steels [48–54]; however, rankings of different treatments commonly vary from researcher to researcher because of different steels or exposure/test conditions.

Deposited coatings often provide better bond durability than native surface treatments. For example, optimized conversion coatings can provide a microscopically rough surface that is resistant to corrosion [55–59]. They serve to stabilize the surface from degradation and to form physical bonds with the adhesive/primer. Smaller-grain coatings tend to be preferred over larger-grain coatings as they provide better physical bonding and greater resistance to fracture. Again, differences in the adherend metallurgy can cause differences in the coating morphology and chemistry. Nonetheless, such conversion coatings and other deposited coatings provide the best durability for steel bonds.

Alternative deposited coatings involve thermal spray, such as plasma spray or two-wire arc [60]. Substrate alloy effects are minimal and coating chemistry and morphology can be designed for specific applications. Corrosion protection and good adhesive bond strength can be provided and maintained [61–64].

Joints made with steel and other metals can also be subject to cathodic disbondment if they are immersed in an electrolyte and subjected to a cathodic potential, such as that created when the adherend is in electrical contact with a more electrochemically active metal [65]. Although corrosion of the adherend is suppressed via cathodic protection, the rate of bond failure is increased. After an induction period that depends on the imposed cathodic potential and temperature [65], interphasal debonding occurs [66,67]; such disbondment does not occur in the absence of a cathodic potential. Several mechanisms have been proposed to explain this phenomenon. These include hydrogen evolution at the steel substrate [65], degradation and weakening of the polymer in the high pH environment generated at the interface [66–69], osmotic pressure resulting from lead chlorides formed at the interface by dehydrohalogenation of the polymer [68], and breaking of secondary and primary bonds at the interface [1].

Bond failure can also occur if the surface is anodic relative to another joint component. An example would be clad aluminum adherends where a thin layer of pure aluminum overlays the base alloy. Such a surface layer is designed to be more corrosion resistant than the alloy, but to act as a sacrificial anode should corrosion occur. Although this approach works well for corrosion protection of the substrate material, it can be a disaster for bonded material if the adherend surface/interface corrodes. As a result, American companies tend to use unclad aluminum for bonding and provide other means of corrosion protection, such as painting [1,70]. On the other hand, European companies commonly use clad adherends, but with a thicker oxide (CAA) [6,18,71–73] that provides bondline corrosion protection.

In contrast to aluminum and steel, titanium adherends are stable under conditions of moderately elevated temperatures and humidity. Although moisture has been shown to accelerate the crystallization of the amorphous oxide of titanium adherends anodized in chromic acid (CAA) to anatase [74], the crystallization, along with the resulting morphology change, is very slow relative to the changes observed with aluminum and steel. In the wedge test results of Fig. 1, the adherend surfaces underwent no change in morphology or crystallinity. Failure of the CAA specimens remained within the adhesive, with the physical bonds provided by the microscopically rough oxide remaining intact [74]. Identical results were also observed for wedge tests performed in boiling water, i.e., crack propagation for CAA adherends was entirely within the adhesive [75]. For moderate conditions, the key requirement for a titanium treatment is a convoluted microrough surface to promote physical bonding. Critchlow and Brewis extensively reviewed reported results of different surface treatments for titanium [76].

At elevated temperatures where titanium alloys would be the adherend of choice, a different failure mechanism becomes important. Because the solubility of oxygen in titanium increases with temperature, the oxygen in a CAA or other oxide diffuses or dissolves into the metal, leaving voids or microcracks at the metal–oxide interface and embrittles the metal near the interface (Fig. 7). Consequently, stresses are concentrated over small areas at the interface and the joint fails at low stress levels [75,77]. Such phenomena have been observed for adherends exposed to 600°C for as little as 1 hour or 300°C for 710 hours prior to bonding [75] and for bonds using a high-temperature adhesive cured at 371°C [78] or 400°C [75].

To prevent this failure mode, thick oxides, such as those grown by CAA, must be avoided in high-temperature applications. Two types of surface treatments that show some

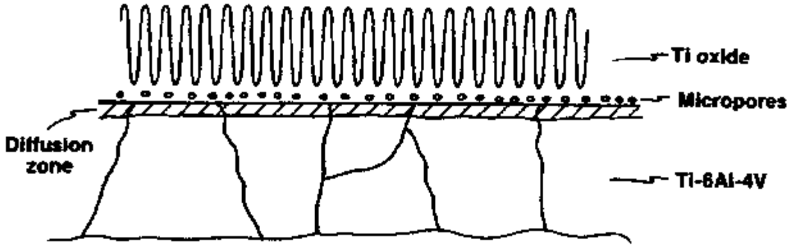

Figure 7 Schematic representation of oxygen diffusing or dissolving from the oxide into the titanium metal at high temperatures. The interphase is weakened with the formation of voids, porosity, and microcracks and with the embrittlement of the interphasal metal region. (From Ref. 75.)

compatibility with high temperatures have been proposed but both have had problems with consistency under long term testing. Plasma-sprayed metallic titanium coatings were proposed at first and showed promising initial results [75,79]. By properly controlling the deposition parameters, a fractal-like microrough coating is obtained that provides physical bonding with the adhesive. Only a thin native oxide is present and this is apparently insufficient to cause the type of failure described above. Plasma-sprayed adherends have been heated to 450°C for 165 hours prior to bonding and tensile testing and have been bonded with a 400°C-curing adhesive and wedge-tested at 230°C for 1000 hours [18,75]. In both cases, failure occurred within the adhesive, indicating a stable interphase. In later tests, cohesive failure within the coating during wedge tests showed that additional development was needed.

Another titanium treatment that has been evaluated for high-temperature applications is sol–gel coatings [78,80,81] (see below). Specimens retained 50–60% of their initial single lap tensile shear strength after 10,000 hours at 177°C although interfacial failure increased to about 60%. Improvements have been slow because of the long duration tests to distinguish between different variations and the failure of more accelerated tests to give reliable, consistent results. These investigations illustrate the difficulty in designing materials and processes for extreme conditions that cannot be accelerated without introducing new degradation mechanisms.

Another means by which temperature can influence bond durability is through stresses that develop when different parts of a joint have different coefficients of thermal expansion (CTEs). This consideration is especially important when different classes of materials are being bonded together. Typical CTE values for selected materials are given in Table 2 [82]. Polymer CTEs usually are 10–100 times those of other materials. Stresses begin to develop across the interphase once the adhesive cures to a solid (rubbery) state and the joint begins to cool [82]. As long as the adhesive is above the glass transition temperature (T_g), it will generally be compliant enough to relax and accommodate these interphasal stresses. However, once T_g is reached, the adhesive is less compliant and stresses begin to build up. Thus the thermal stresses in a joint will depend on the CTE differences between the substrate(s), adhesive, and any overlying layers or films and on the

Table 2 Coefficients of Thermal Expansion

Material	CTE (10^{-6}/K)
Epoxy (above T_g)	190
Epoxy (below T_g)	68
Poly(methyl methacrylate) (above T_g)	530
Poly(methyl methacrylate) (below T_g)	260
Low-density polyethylene	100
High-density polyethylene	130
Polystyrene	700
Aluminum	29
Steel	11
Titanium	9
Soda-glass	8.5
Wood (along grain)	3–5
Wood (across grain)	35–60

Source: Ref. 82.

degree of cooling below T_g. One way to minimize these stresses is to blend low and high CTE polymers to match the CTE of the substrate—a procedure most relevant to polymeric substrates [83]. Another is to incorporate mineral fillers into the adhesive to reduce its CTE [82]. In cases of mismatched adherends, e.g., composite to aluminum, a near room-temperature-curing adhesive may be the best solution [84,85].

B. Adhesives/Primers

The effects of water and temperature on the adhesive itself are also of utmost importance to the durability of bonded structures. In the presence of moisture, the adhesive can be affected in a number of ways, depending on its chemistry and how rapidly the water permeates through and causes significant property changes [51,86–88]. The potential efficacy of moisture penetration on the locus of failure of bonded joints has been discussed in the previous section. As expected, elevated temperature conditions tend to degrade joint strength at a faster rate.

Of primary importance in moist environments is the plasticization, or softening, of the adhesive, a process that depresses T_g and lowers the modulus and strength of the elastomer [89–91]. Plasticization of the adhesive may also allow disengagement from a microrough adherend surface to reduce physical bonding and thus reduce joint strength and durability [37]. On the other hand, it may allow stress relaxation or crack blunting and improve durability [92].

Brewis et al. studied the effects of moisture and temperature on the properties of epoxy–aluminum joints by measuring changes in the mechanical strength properties of the soaked adhesive [90]. The T_g of the wet adhesive and relative strengths of wet and dry joints were evaluated for up to 2500 hours. They concluded that the joint weakening effect of water was due to plasticization of the adhesive that, in turn, was dependent on the rate of water diffusion within the adhesive.

The softening behavior has also been observed with Cytec FM 1000–Al single lap joints exposed to 100% relative humidity at 50°C for 1000 hours [91]. As shown in Fig. 8, wet and dry joints exhibited similar strength–temperature relationships, but with the former being shifted to a lower temperature by 30–50°C, a quantity close to the water-induced depression of the T_g. Hence, in this case, the T_g depression acts as a shift factor that defines the strength–temperature relationship between the dry and wet adhesive so that at a given temperature, a wet joint exhibits lower strength than a dry one.

Water entering a joint can also cause swelling, which tends to introduce stresses to weaken the bonded system. Weitsman has shown that normal stresses resulting from swelling (3%) of an epoxide adhesive are manifested at the edges of the joint; however, after an initial rise, the stress concentration decreases with time, suggesting that they do not contribute to long-term structural weakening [93].

As discussed earlier, chemical bonds between the adhesive and adherend help to stabilize the interface and increase joint durability. Aluminum joints formed with phenolic adhesives generally exhibit better durability than those with epoxy adhesives [1,92,94]. This is partly attributable to strongly interacting phenolic and aliphatic hydroxyl groups that form stable primary chemical bonds across the interface [25,95,96]. Nonetheless, epoxy adhesives are more widely used due to their greater toughness and lower temperatures and pressures required during cure.

Silanes and other coupling agents can be applied to various substrates or incorporated into an adhesive/primer to serve as hybrid chemical bridges to increase the bonding between organic adhesive and inorganic adherend surfaces [97–100]. Such bonding

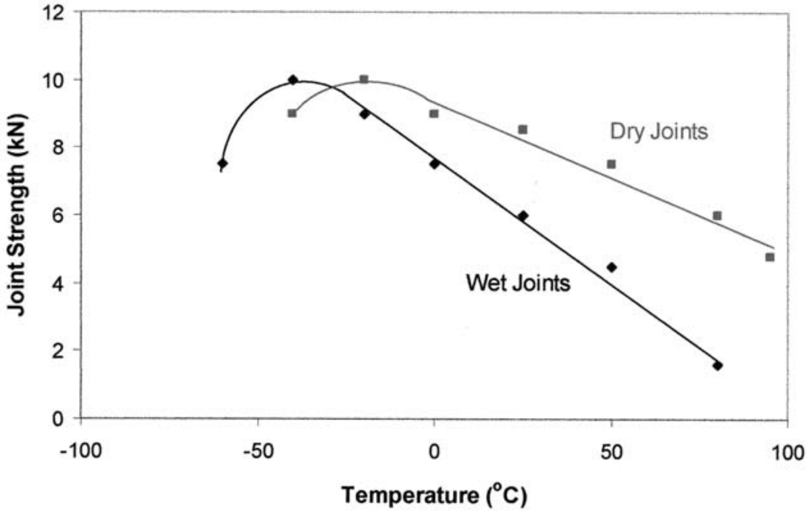

Figure 8 The strength of wet and dry lap joints with FM-1000 adhesive as a function of temperature: (■), dry joints; (♦), joints preconditioned for 1000 hours at 50°C and 100% relative humidity. (Data from Ref. 91.)

increases the initial bond strength and stabilizes the interface to also increase the durability of the resulting joint. Silanes and other coupling agents are discussed in Chapter 10 in this book. Silane-based primers have been shown to be effective in increasing the environmental resistance of joints prepared from aluminum [101] and titanium [102] alloys. Plueddemann has shown that the resulting interphase can be designed for maximum water resistance by employing hydrophobic resins and coupling agents and by providing a high degree of cross-linking [103].

Corrosion-inhibiting adhesive primers are commonly applied onto bonding surfaces soon after the surface treatment [99]. Their primary function is to wet the adherend and penetrate the "nooks and crannies" to form both chemical and physical bonds. They also perform other functions essential for durable bonds: creation of a stable surface, prevention of contamination or mechanical damage of surfaces that have been chemically etched or anodized, and corrosion inhibition to the bonded and nonbonded areas of the assembly. Primer systems are normally pigmented with chromates, such as calcium, strontium, or zinc, which provide corrosion inhibition. More recent, environmentally safer primers have replaced chromates with other corrosion inhibitors. The mechanism of inhibition by chromates and some other inhibitors in the presence of moisture involves the passivation of the aluminum surface and the prevention of cathodic evolution of hydrogen by the reduction of hexavalent chromium to the trivalent state [104]. Figures 9 and 10 illustrate the improvement in joint performance using a corrosion preventative primer (Cytec BR-127) and a hydration inhibitor [12,18].

A hybrid surface treatment/primer sol–gel process has been developed that provides a graded interphase between the metal and the adhesive [78,80,81,105,106]. The sol–gel coating is typically 0.5–2 μm thick and consists of an inorganic component, an organic component, and, in some cases, a coupling agent. The inorganic component is concentrated at the metal surface (aluminum, titanium, and steel adherends have been used) while the organic component and the coupling agent are concentrated at the adhesive

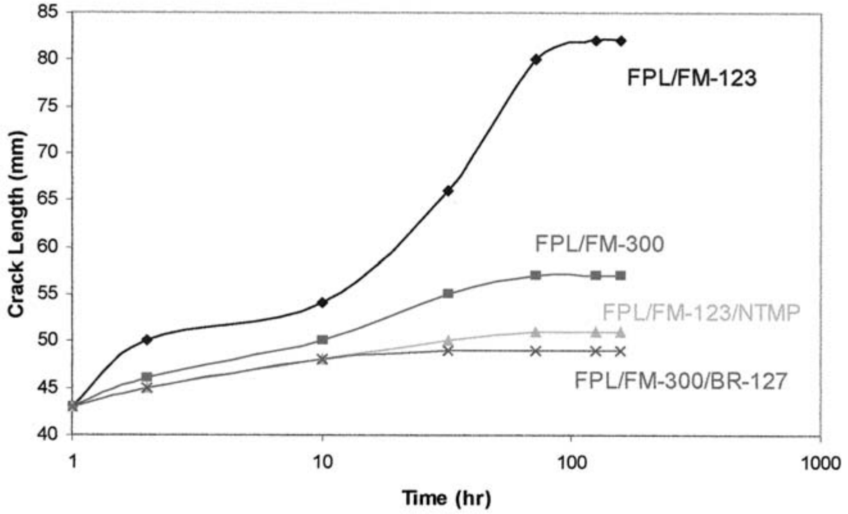

Figure 9 Wedge test results for FPL-etched aluminum adherends: with FM-123 (moisture-wicking) adhesive, with FM-300 (moisture-resistant) adhesive, with an NTMP treatment and FM-123, and with BR-127 primer and FM-300.

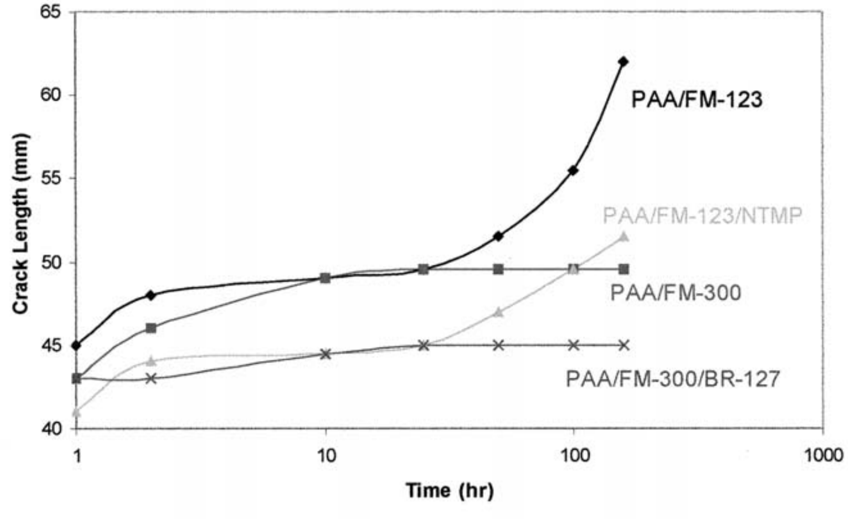

Figure 10 Wedge test results for PAA aluminum adherends: with FM-123 (moisture-wicking) adhesive, with FM-300 (moisture-resistant) adhesive, with an NTMP treatment and FM-123, and with BR-127 primer and FM-300.

or conventional primer (if used). Both abraded and otherwise cleaned metal surfaces and surfaces with conventional surface treatments, such as described above, have been used. In this system, strong covalent bonds that are resistant to moisture attack are formed between the metal and the inorganic component and between the polymer and the organic component. Accordingly, physical bonding (mechanical interlocking) is less important and these surfaces tend to be smoother than the intentionally microrough oxides normally grown on the metal surfaces. Excellent bond durability results have been reported under moisture conditions and elevated temperatures (titanium). Because the sol–gel process does not involve toxic materials, such as hexavalent chromium, or strong acids or bases, it has the potential to be an environmentally friendly surface treatment.

IV. STRESSES

The stresses that a joint experiences during environmental exposure also influence its durability, i.e., it exhibits either decreased lifetime or decreased residual strength [1,7,10,107]. As with moisture, there may be a critical stress level below which failure does not occur [108,109] or is not accelerated (depending on the moisture level). The type of stress is also important. For example, cyclic stresses degrade the bond more rapidly than constant stresses [5,7].

The stresses on a joint make primary and secondary chemical bonds, both within the polymer itself and across the polymer–oxide interface, more susceptible to environmental attack by lowering the activation energy for bond breaking [1,14,92]. The stresses can also increase the rate of transport of moisture in the adhesive, possibly via crazing or the formation of microcracks [1,14,92,110] or increasing the free volume of the polymer to allow more moisture ingress. Joints subjected to thermal "spikes" or cycling, such as those present in high-speed military aircraft, are particularly vulnerable to this type of aging. Thus, weight gains in bonded composite systems that encountered one to four spikes (0°C–150°C–0°C) per day were proportional to the total number of spikes [111,112], suggesting that water was entering the microcracks formed during thermal cycling. Additionally, studies of the chemical hydrolysis of epoxides by water (80°C) indicated that although unstressed samples were unaffected for up to 3 months, stressed systems induced hydrolysis of ester groups within days [113,114].

The stress at the crack tip of a wedge test specimen, together with the presence of moisture at the tip, serve to make this test specimen more severe than soaked lap shear specimens or similar types and a better evaluation of relative durability. In fact, Boeing has correlated the results of wedge tests from actual aircraft components with their in-service durability [5,115]. Wedge test specimens fabricated from components that had exhibited service disbonds showed significant crack growth during the first hour of exposure whereas those fabricated from good components showed no crack growth during this time period. In contrast, lap shear specimens and porta shear specimens all demonstrated high bond strengths regardless of the service conditions.

V. MEANS TO IMPROVE DURABILITY

Although the degradation of a bond is likely to be inevitable, there are means by which to slow down the process; some of which were discussed above. For convenience of the discussion, these methods can be classified as environment, materials, and design related.

Changing the environment to which a bond is exposed is probably the most effective means of ensuring good durability; bonded structures are not likely to degrade at moderate temperatures and in low humidity. Unfortunately, this usually is not a viable option. However, it may be possible to protect the bond from its external environment, at least for a period of time. Ways to design a joint to do this are discussed below.

Material selection and preparation are perhaps more feasible options than changing the environment. Although not an economical solution, substitution of titanium for aluminum would solve many moisture-related problems. Selection of more water-resistant adhesives and/or corrosion-resistant primers is more common and was illustrated in Figs. 9 and 10 [12,18]. Here, selection of a water-resistant adhesive (Cytec FM-300) decreased the final crack length in the wedge test by 1–2 cm for both FPL and PAA surfaces compared to a water-wicking adhesive (FM-123). The use of a chromate-containing (corrosion-resistant) primer (Cytec BR-127) further decreased the final crack length (Section III.B).

Surface preparation is another commonly used means to increase durability. We have already seen that the durability of microrough surfaces is superior to smooth surfaces or to surfaces with only larger-scale roughness (Fig. 1) and that hydration-resistant aluminum surfaces provide further improvements (see Section III.A). Figures 9 and 10 also illustrated this enhancement. For a given adhesive, PAA surfaces that are more hydration resistant show less crack growth than FPL surfaces and, for both FPL and PAA surfaces, treatment with a hydration inhibitor (NTMP) gives superior durability over untreated surfaces. This improvement of PAA surfaces over FPL surfaces has also been demonstrated in the field, most notably in Vietnam, where FPL-treated joints suffered a large number of disbonds whereas PAA-treated joints were significantly more reliable [10].

Proper design of a joint or structure is also necessary to maximize durability. Although moisture cannot be prevented from reaching a bondline, it can be slowed or reduced in quantity. One way is to prevent pooling or other accumulation of water by designing the geometry to promote runoff, or including adequate drain holes. Maintenance is then required to ensure that the holes do not become plugged. Sealants are also used to slow down moisture ingress from joint edges and seams [116]. Again, proper application is necessary to prevent moisture accumulation and to ensure the absence of an easy path to the interface. One category of sealants, water-displacing corrosion inhibitors (WDCIs), can even creep under existing water films, displacing the moisture and eliminating the corrosive environment [116].

Another approach to improve durability involves overdesigning the bond so that the actual stresses experienced are a small fraction of the stresses that the joint is capable of withstanding. Stresses are thereby reduced to below any critical level and the load can be carried even if moisture creates a disbond over a portion of the joint. Of course, this approach may not be feasible from a cost or weight standpoint. Alternatively, the bond can be designed so that moisture has a long diffusion path to reach a critical area—the same general principle by which sealants work.

VI. SUMMARY

Long-term durability is one of the most important properties of many adhesive bonds. Although it can be difficult to achieve in aggressive environments, modern materials and processes have proven successful in increasing durability. Moisture is the cause of most environmentally induced bond failures. It can weaken or disrupt secondary (dispersion-force) bonds across the adhesive–adherend interface, especially those involving high-energy surfaces such as metals; as a result, the joint may need to rely solely on primary (covalent or ionic) or physical (mechanical interlocking) bonds. More severe degradation can subsequently occur with hydration or corrosion of the adherend surface. At this point, the joint will fail regardless of the type of bonding at the interface.

Most means of improving durability involve slowing down the degradation mechanisms or providing additional bonding schemes, e.g., primary and/or physical bonds that are less susceptible to degradation. Surface preparations that provide physical bonds and a hydration-resistant surface are typical examples. The use of coupling agents, phenolic-based adhesives (with aluminum adherends) and sol–gel treatments are other examples where stable chemical bonds are formed in the interphase and slow down bond degradation.

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14

Analysis of Adhesives

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I. INTRODUCTION

Adhesives now form an inextricable part of modern life. In fact it is difficult to imagine our everyday existence without these bonding substances. Consider packaging, building, automobiles, dentistry, medicine, consumer goods, and food industries—all these activities rely heavily on adhesive materials. Use of adhesives in today's technology continues to grow at a rapid pace throughout the world and research in polymer science continues to mushroom, producing a plethora of new adhesives.

For a successful application of an adhesive to a substrate (adherent), to reach a maximum adhesion, it must be able to flow, penetrate, wet, and set. The adhesive in its final state must be a solid, high-molecular-weight polymer that is able to carry and transfer mechanical forces. In order to meet these four criteria, there are three ways in which adhesives are prepared: (1) A polymeric adhesive can be dissolved or dispersed in a solvent; after application, the solvent is allowed to evaporate, leaving behind the high-molecular-weight polymer. (2) If the adhesive is a thermoplastic polymer, it can be heated to melt and apply in a molten state; after application, it is allowed to cool and solidify in the glueline. (3) An adhesive can be prepared by chemical reactions via a polymerization process to convert monomer (low-molecular-weight starting unit) into polymer (high-molecular-weight material). Many natural adhesives are prepared based on the first method, and most of the synthetic adhesives are prepared by the third method.

In essence, an adhesive is any substance, inorganic or organic, natural or synthetic, that is capable of bonding substances together by surface attachment. The bonding power of an adhesive depends heavily on its molecular weight or size of the molecules. Under a proper bonding process, the adhesive with higher molecular weight provides a stronger bond. Hence the adhesive is a high-molecular-weight substance, commonly known as a *polymer*.

A polymer is composed of repeating units (i.e., monomers) that are linked together into long chains that can be linear, branched, or cross-linked. If a polymer contains two different types of monomers, it is a copolymer. A linear polymer is a thermoplastic. At elevated temperatures it melts and flows as a liquid. In a cross-linked polymer, the repeat units are actually linked into a three-dimensional network of macroscopic size. It is a thermoset. Once the polymerization is completed, the cross-linked polymer cannot be softened or melted. It is hard, infusible, and insoluble. Hence a thermoset adhesive is the most durable but is also difficult to characterize as compared to a thermoplastic one.

Adhesives are a very diverse and complex group of materials. They can manifest themselves in many shapes and forms—they can be viscous liquids, powders, or cured products. Analysis or characterization is an essential step in working with adhesives. As a rule, such efforts are directed toward a specific purpose that may focus on structural determination, curing reaction, size of the molecule, material design at a molecular level, process control, or failure analysis. In this chapter we provide a general review of several physical methods frequently used for analysis of adhesives. In view of the prolific literature on the subject as well as the space constraints, it is not intended to give a comprehensive treatment of the theory and experimental aspects. The examples chosen for this review are illustrative and not exhaustive.

II. TECHNIQUES FOR ANALYSIS AND CHARACTERIZATION

Perhaps the most apt definition of analysis of adhesives is their qualitative and quantitative characterization. Since the early days of adhesive development, the elementary chemical analysis of adhesives has provided valuable information on the structure and purity of materials. Chemical methods of analysis are simple and cheap but labor intensive. The use of such techniques for analysis has been decreasing over the past 30 years. This is due to the complexity of the polymeric structures of adhesives as well as the development of much powerful and sophisticated instrumentation. More recently, advances in computer technology have been combined with analytical instruments to give speed, resolution, simplicity, and minimal sample requirements that were unimaginable two decades ago.

Adhesives may be synthesized by many processes; very often the precise conditions used have an effect on the structure of the product. Because of the statistical nature of the polymerization process, most polymers show a distribution of molar mass or molecular weights, which may be averaged in several different ways. Any physical or performance property of a polymer may be related to one or more average molecular weights, the type of average being determined by the physical averaging process inherent in the method used to measure the property. Thus, a complete description of the molecular weight distribution of a polymer is important to understand its physical, rheological, and mechanical properties. Hence a separation technique, gel permeation chromatography (GPC), which has proven to be useful for determination of molecular weight and molecular weight distribution, is discussed. The use of spectroscopic methods for the characterization of adhesive systems has provided important molecular level descriptions of these systems. Thus Fourier transform infrared (FTIR) and Raman spectroscopy and nuclear magnetic resonance (NMR) are described. Many adhesives are network polymers that are insoluble and as a result are not as easily characterized by the conventional methods, including GPC, which require dissolution. For these adhesives, thermal techniques have been used popularly to study chemical kinetics of curing reactions, curing behavior, degradation reactions, and transition of molecules. Thus three thermal analysis techniques, namely, differential thermal analysis (DTA), differential scanning calorimetry (DSC), and dynamic mechanical thermal analyzer (DMTA) are described.

A. Average Molecular Weight and Molecular Weight Distribution

The molecular weight of an adhesive is of prime importance in its preparation, application, and performance. The effect of molecular weight on the tensile strength or bonding power of an adhesive is illustrated in Fig. 1. At very low molecular weights, the ultimate tensile

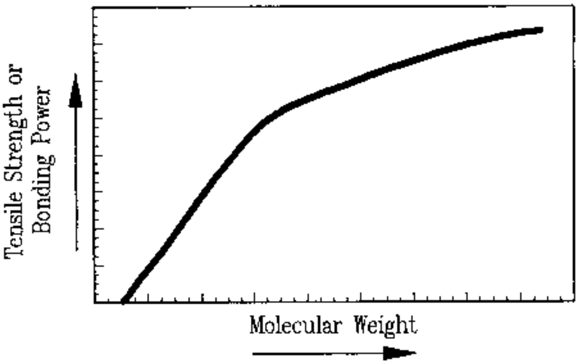


Figure 1 Effect of molecular weight on tensile strength or bonding power of adhesives.

stress is near zero. As the molecular weight increases, the tensile strength rapidly increases, then gradually levels off. Hence, the useful bonding and mechanical properties of an adhesive are heavily dependent on its molecular weight. Normally, bonding power does not begin to develop in adhesives until a minimum molecular weight above 5,000 is achieved. Above that size, there is a rapid increase in the mechanical performance of adhesives as their molecular weights increase.

For analysis or characterization of adhesives, the first step is to determine the molecular weight or degree of polymerization. The molecular weights of adhesives can be determined by chemical or physical methods of functional group analysis or by measurement of the colligative properties, light scattering, ultracentrifugation, or dilute solution viscosity [1]. With the exception of some types of end-group analysis, all molecular weight methods require dissolution of the adhesive. This requirement is sometimes difficult to meet, particularly for very-high-molecular-weight or cross-linked adhesives. Hence, normally the average molecular weight is a property that can be measured only for linear and branched adhesives.

Unlike low-molecular-weight compounds where the molecular weight in the sample is uniform, polymer samples are usually polydisperse. They are composed of polymer chains of varying length and hence exhibit a distribution of molecular weights. Therefore, in expressing polymer molecular weights, various average expressions are used. These averages are defined in terms of the molecular weight M_i and the number of moles n_i or the weight w_i of the component molecules by the following equations:

Number-average molecular weight:

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum w_i/M_i} \tag{1}$$

Weight-average molecular weight:

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum w_i M_i}{\sum w_i} \tag{2}$$

Z-average molecular weight:

$$\overline{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i} \tag{3}$$

(*Z*+1)-average molecular weight:

$$\overline{M}_{z+1} = \frac{\sum n_i M_i^4}{\sum n_i M_i^3} = \frac{\sum w_i M_i^3}{\sum w_i M_i^2} \tag{4}$$

Viscosity-average molecular weight:

$$\overline{M}_v = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}\right)^{1/a} = \left(\frac{\sum w_i M_i^a}{\sum w_i}\right)^{1/a} \tag{5}$$

Equation (5) is an important practical molecular weight average derived from viscometry. In order to calculate this average, the exponent *a* of the Mark–Houwink relationship relating intrinsic viscosity [η] to molecular weight must be known:

$$[\eta] = KM_v^a \tag{6}$$

where *K* and *a* are the characteristic parameters predominantly determined by the combination of polymer and solvent at a constant temperature. Extensive tables of constants *K* and *a* are available in the literature [2].

A typical molecular weight distribution (MWD) is depicted in Fig. 2. The M_n, M_v, M_w, M_z, and M_{z+1} are labeled. It is obvious that

$$\overline{M}_n < \overline{M}_v < \overline{M}_w < \overline{M}_z < M_{z+1} \tag{7}$$

It is clear from these equations that for M_w, M_z, and M_{z+1} the molecules of greater mass contribute more to the average than do less massive molecules. Conversely, M_n is very sensitive to the presence of low-molecular-weight tails. In the study of polymerization kinetics, M_n is a critical parameter. The glass transition temperature (T_g) of an adhesive is also particularly sensitive to low-molecular-weight species. Knowledge of M_n is also necessary for evaluating the level of functionalization in adhesives with specific end groups. In studying rheology, various average molecular weights and the shape and breadth of the distribution are important. Polydispersity ratios such as M_w/M_n and M_z/M_w can give some insight into the latter problem. Adhesion, toughness, tensile strength, brittleness, and environmental stress-crack resistance are a few of the many properties affected by the MWD. For many adhesives, a narrower molecular distribution yields

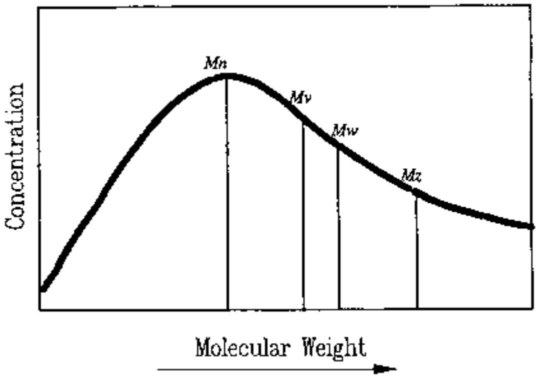


Figure 2 Typical polymer molecular weight distribution and corresponding average molecular weight.

better properties. An elegant way of determining the MWD is by gel permeation chromatography (GPC) or size-exclusion chromatography (SEC).

B. Gel Permeation Chromatography and Size-Exclusion Chromatography

The technique of GPC or SEC is introduced for determination of the molecular weight and MWD of adhesive polymers, separation of small molecules, and preparation of molecular weight fractions. This technique is possibly the most widely used chromatographic technique in polymer analysis. It is capable of characterizing very high-molecular-weight polymers up to 10^6, thermoset resins of molecular weight 10^3 and 10^4, and oligomers or prepolymers in which only a few monomer units are joined. Several valuable texts are available on this subject [3,4].

Gel permeation chromatography or SEC is a liquid column chromatographic technique in which an adhesive solution is introduced onto a column packed with a rigid porous gel and is carried through the column by a solvent or solvents (mobile phase). Ideally, size separation is achieved by differential pore permeation. Under the influence of the solvent stream passing down the column, the smaller molecules in the adhesive go into and out of more pores in the packing than do the larger molecules. Hence larger molecules are eluted from the column earlier than smaller ones and are detected by means of some suitable instruments. A more detailed discussion on the separation is available [5]. The separation is based on the hydrodynamic volume of a polymer molecule. This hydrodynamic volume is converted to a molecular weight or equivalent molecular weight compared to the hydrodynamic volume of a calibrated polymer by means of a calibration curve (see Fig. 3a). Specific molecular weights in GPC can be determined only from a calibration curve. Calibration requires chromatographing several samples of the specific polymer type that have narrow molecular weight distributions and known molecular weights covering the entire range of interest. For example, a gel permeation chromatogram of polystyrene standards with various molecular weights is shown in Fig. 4. The peak retention volumes of the sample are then plotted graphically against the known molecular weight average. The molecular weight average of the unknown is determined from the calibration plot and the peak retention volume and is in the units of the calibration curve, M_w, M_n, or M_v.

In GPC or SEC the distribution coefficient of a solute species is defined [6] in terms of the fraction of the intraparticle volume, V_s, which is accessible to the solute so that

$$K = \frac{V_t - V_m}{V_s} \tag{8}$$

and

$$V_t = V_m + KV_s \tag{9}$$

For large, totally excluded molecules, $V_t = V_m$ and hence $K = 0$. For small solute molecules which can enter all the pores, $V_t = V_m + V_s$ and hence $K = 1$. Separation therefore occurs only where solute molecules obey the condition $0 < K < 1$. Figure 3b is a typical gel permeation chromatogram. Notice that the first peak to be eluted corresponds to the largest molecular weight species in the sample. It should be noted that GPC requires the polymer sample to be dissolved in a solvent. For this reason, cross-linked adhesives cannot be analyzed by the GPC technique.

The essential components of the instrumentation (Fig. 5) are a solvent reservoir, a solvent delivery system (high pressure pump), sample injection system, packed columns,

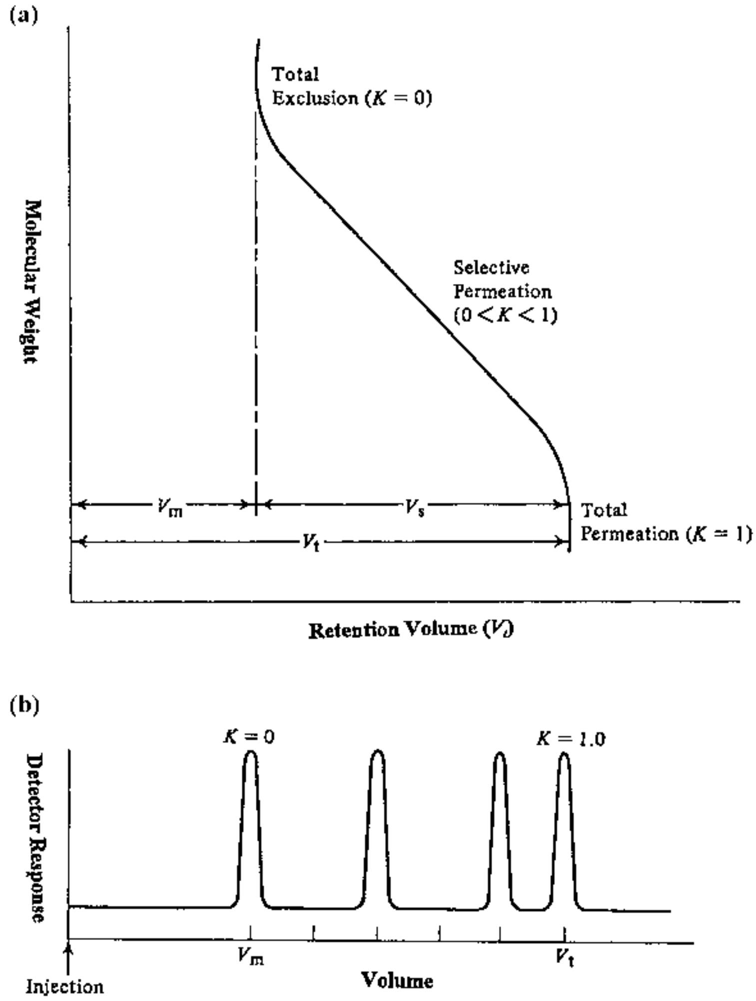


Figure 3 Relationship between molecular weight and retention volume for gel permeation chromatography: (a) calibration curve; (b) chromatogram.

detector(s), and a data handling system. The heart of the instrumentation is the fractionation column where the separation takes place. The most common packing material used has been a semirigid cross-linked polystyrene gel. The concentration of the polymer molecules eluting from GPC columns is monitored continously by a detector. The most widely used detector in GPC is the differential refractometer, which measures the difference in refractive index between solvent and solute. Other detectors commonly used for GPC are a functional group detector and an ultraviolet detector. Chromatograms obtained on a phenolic resin to determine the oligomers and on a phenol–formaldehyde (PF) prepolymer adhesive are shown in Figs. 6 and 7, respectively. As discussed earlier, the various fractions of the polymer can be estimated from a calibration curve. Determination of the MWD and kinetic investigations of PF adhesives have been reported [7–10]. Resorcinol–

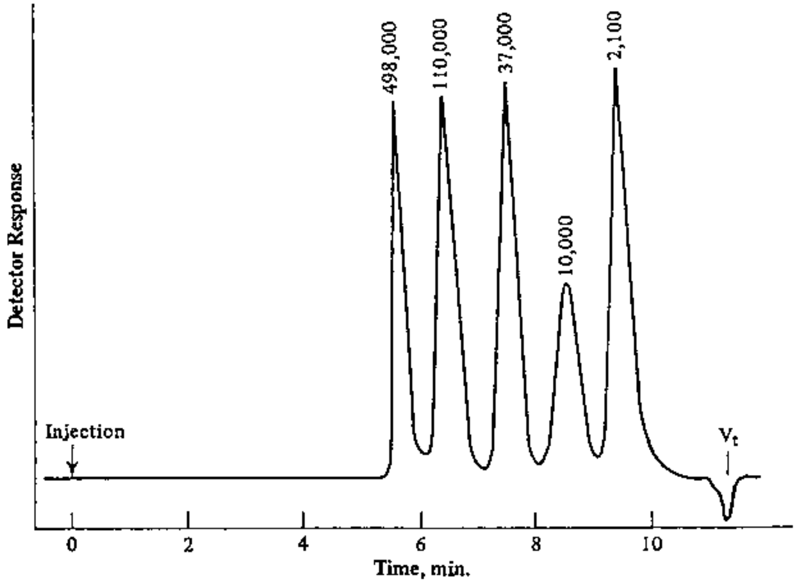


Figure 4 Gel permeation chromatogram of polystyrene standards with various molecular weights.

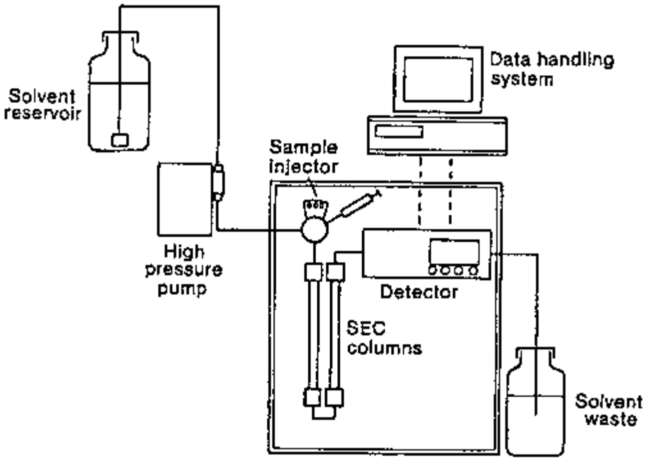


Figure 5 Equipment schematic for a typical gel permeation chromatograph.

formaldehyde condensates have been characterized [11]. The use of *N*,*N*-dimethylformamide (DMF) as a solvent with Poragel/Styragel columns allows analysis of PF melamine–formaldehyde condensates [12]. Epoxy resins have been characterized by GPC under various conditions depending on their molecular weights. Typically, tetrahydrofuran is used as the solvent and ultraviolet absorption as the detection mode. For low-molecular-weight resins, less than 1,000, the uses of Biorad SX-2 and combinations of Styragel and Biorad SX-2 for higher-molecular-weight materials have been reported [13].

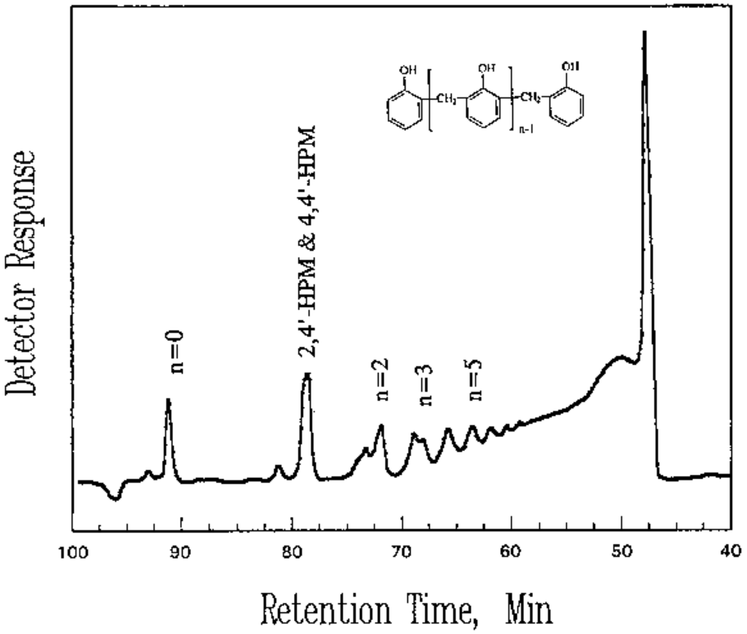


Figure 6 Determination of oligomers in a phenol–formaldehyde adhesive. HPM, dihydroxydiphenyl methane.

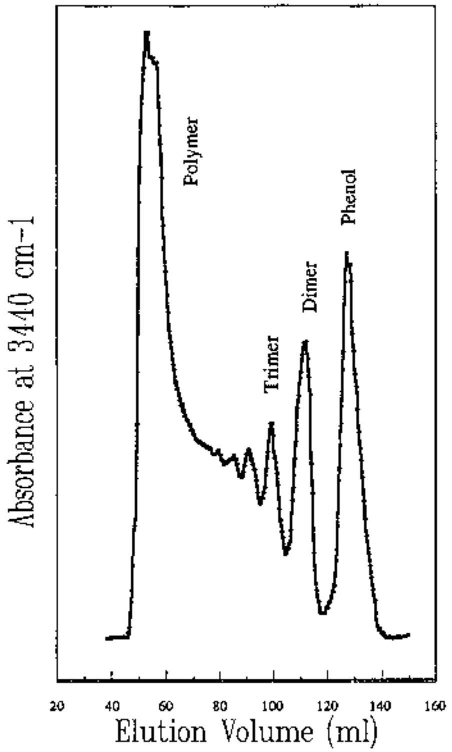


Figure 7 Gel permeation chromatogram of a phenol–formaldehyde prepolymer adhesive.

C. Vibrational Spectroscopy

Vibrational spectroscopy has been widely used to identify polymers, to quantitatively analyze chemical composition, and to specify configuration, conformation, branching, end groups, and crystallinity. Chemical reactions including polymerization, curing, cross-linking, degradation, and weathering have been studied using vibrational techniques.

Light, which is a form of electromagnetic radiation, can interact with matter in a number of different ways. The interaction of light of a given wavelength with a particular object depends on the molecular structure of the object. Incident light may be transmitted, reflected, *absorbed*, or *scattered* by the molecules. Infrared (IR) spectroscopy is a particular type of *absorption* spectroscopy whereas Raman spectroscopy arises via the inelastic *scattering* of photons by molecules of the object. Both the structure and the electronic distribution of the molecule determine the intensity of a vibrational transition for each technique. In this sense, the methods may be considered to be complementary, and in some cases a combination of both may prove to be especially useful [14,15].

Infrared spectroscopy is the fastest and cheapest of the spectroscopic techniques used by organic and polymer chemists. As indicated, it is the measurement of the absorption of IR frequencies by organic compounds placed in the path of the beam of light. The samples can be solids, liquids, or gases and can be measured in solution or as neat liquid mulled with potassium bromide (KBr) or mineral oil. Recent developments in attenuated total reflection (ATR) and diffuse reflectance techniques have made the analysis of solid adhesives possible. In fact, for bulk samples or powders, the reflectance technique is probably more suitable than transmission.

Infrared radiation is electromagnetic radiation in the wavelength range that is adjacent to and of less energy than visible radiation. The IR region starts at a wavelength of about 0.7 μm and ends at a wavelength of about 500 μm. Many chemists refer to the radiation in the vibrational IR region in terms of a unit called wavenumbers (ν), which is the number of waves of the radiation per centimeter (cm^{-1}).

While molecules absorb radiation, some parts of the molecule (i.e., the component atoms or group of atoms) vibrate at the same frequency as the incident radiant energy. After absorbing radiation, the molecules vibrate at increased amplitude. When molecular vibrations result in a change in the bond dipole moment, as a consequence of a change in the electron distribution in the bond, it is possible to stimulate transitions between energy levels by interaction with electromagnetic radiation of the appropriate frequency. In effect, when the vibrating dipole is in phase with the electric vector of the incident radiation, the vibrations are enhanced and there is transfer of energy from the incident radiation to the molecule. It is the detection of this energy absorption that constitutes IR spectroscopy. The complex motions of the atoms in a molecule due to the twisting, bending, rotating, and vibrating actions produce an absorption spectrum that is characteristic of the functional groups comprising the molecule and of the overall molecular configuration as well. Thus, IR spectroscopy readily distinguishes between aliphatic and aromatic compounds. Table 1 gives characteristic IR absorption bands for some functional groups.

Several collections of spectra are available [17–21]. The total structure of an unknown may not be readily identified from the IR spectrum, but perhaps the type or class of compound can be deduced. Once the key functional groups have been established as present (or, equally important, as absent), the unknown spectrum is compared with spectra of known compounds. As an example, consider polyethylene. There are at least three types of carbon–hydrogen groups in polyethylene: methyl, $-CH_3$; methylene, $-CH_2-$; and tertiary carbons, $-CHR-$. The methyl groups appear at the ends of a chain and its

Table 1 Simplified Correlation Chart

	Type of vibration	Frequency (cm^{-1})	Wavelength (μm)	Intensity[a]
C–H	Alkanes (stretch)	3000–2850	3.33–3.51	s
	$-CH_3-$ (bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$ (bend)	1465	6.83	m
	Alkenes (stretch)	3100–3000	3.23–3.33	m
	(out-of-plane bend)	1000–650	10.0–15.3	s
	Aromatics (stretch)	3150–3050	3.17–3.28	s
	(out-of-plane bend)	900–690	11.1–14.5	s
	Alkyne (stretch)	ca. 3300	ca. 3.03	s
	Aldehyde	2900–2800	3.45–3.57	w
		2800–2700	3.57–3.70	w
C–C	Alkane (Not interpretatively useful)			
C=C	Alkene	1680–1600	5.95–6.25	m–w
	Aromatic	1600 and 1475	6.25 and 6.78	m–w
C≡C	Alkyne	2250–2100	4.44–4.76	m–w
C=C	Alkyne	1740–1720	5.75–5.81	s
	Ketone	1725–1705	5.80–5.87	s
	Carboxylic acid	1725–1700	5.80–5.88	s
	Ester	1750–1730	5.71–5.78	s
	Amide	1670–1640	6.00–6.10	s
	Anhydride	1810 and 1760	5.52 and 5.68	s
	Acid chloride	1800	5.56	s
C–O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	7.69–10.0	s
O–H	Alcohols, phenols			
	Free	3650–3600	2.74–2.78	m
	H-bonded	3500–3200	2.86–3.13	m
	Carboxylic acids	3400–2400	2.94–4.17	m
N–H	Primary and secondary amines and amines (stretch) (bend)	3500–3100 1640–1550	2.86–3.23 6.10–6.45	m m–s
C–N	Amines	1350–1000	7.4–10.0	m–s
C=N	Imines and oximes	1690–1640	5.92–6.10	w–s
C=N	Nitriles	2260–2240	4.42–4.46	m
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1950	4.40–5.13	m–s
N=O	Nitro ($R-NO_2$)	1550 and 1350	6.45 and 7.40	s
S–H	Mercaptans	2550	3.92	w
S=O	Sulfoxides	1050	9.52	s
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375–1300 and 1200–1140	7.27–7.69 and 8.33–8.77	s s
C–X	Fluoride	1400–1000	7.14–10.0	s
	Chloride	800–600	12.5–16.7	s
	Bromide, iodide	< 667	> 15.0	s

[a] s, Strong; m, moderate; w, weak.

Source: Ref. 16.

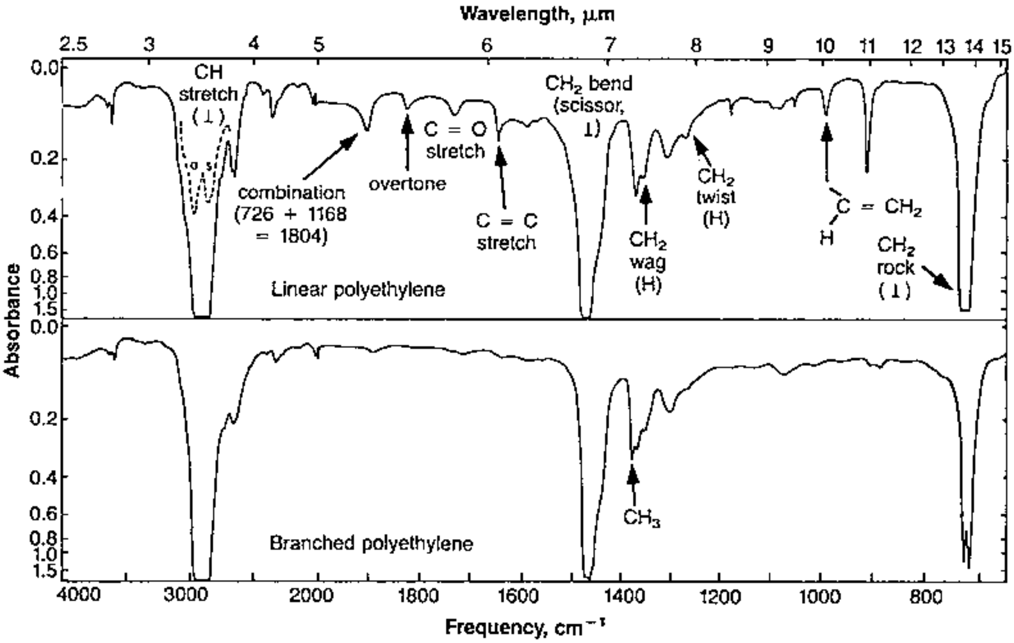


Figure 8 Infrared spectra of (top) linear and (bottom) branched polyethylene.

branches, the methylenes in the middle of a chain, and the tertiary carbons at the connecting points of chain branches. Each of these groups produces spectral bands that appear at different wavelengths in vibrational spectrometries. Figure 8 illustrates the difference IR absorbance between linear and branched polyethylene. If the baseline is accounted for, then the absorbance of the 1374 cm^{-1} band reflects the methyl content of the specimen.

Infrared instrumentation is divided into *dispersive* and *nondispersive* types. Before the advent of the Fourier transform infrared (FTIR) spectrophotometer, a dispersive instrument that depends on gratings and prisms to disperse the IR radiation geometrically was necessary for IR spectroscopy. Most dispersive spectrometers are double-beam instruments. The dispersed IR radiation is passed over a slit system, by means of a scanning device, and thus the frequency range falling on the detector is isolated. The data indicate the amount of energy transmitted through a sample as a function of frequency, and as a result, an IR spectrum can be obtained. However, the sensitivity of the technique is relatively low, because a large percentage of the available energy from the source of radiation does not fall on the open slits and is lost to the technique. Fortunately, the energy limitation can be minimized by using interferometers of the Michelson type rather than the conventional prism and grating instruments. This technique is called FTIR spectroscopy [22].

The Michelson interferometer is shown schematically in Fig. 9. It consists of two mutually perpendicular plane mirrors, one of which can move at a constant rate along the axis and one of which is stationary. Between the fixed mirror and the movable mirror is a beam splitter where a beam of radiation from an external source can be partially reflected to the fixed mirror and partially transmitted to the movable mirror. After each beam is reflected back to the beam splitter, it is again partially reflected and partially transmitted.

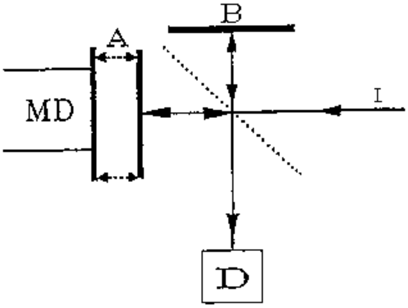


Figure 9 Diagram of a Michelson interferometer: I, unmodulated incident beam; A, moving mirror; B, stationary mirror; D, detector; MD, mirror drive; broken line, beam splitter.

Thus a portion of the beams that traveled in the path to both the fixed and movable mirrors reach the detector. If the two path lengths are the same, no phase difference between the beams occurs, and they combine constructively for all frequencies present in the original beam. For different path lengths, the amplitude of the recombined signals depends on the frequency and the distance the mirror moved. For example, low frequencies interfere destructively (they have a phase shift of 180°) for relatively large movements of the mirror, whereas high frequencies require relatively small movements for this condition to occur. The resulting interferogram contains information on the intensity of each frequency in the spectrum. These data can be calculated by a mathematical operation known as the Fourier transform to yield the IR spectrum.

Fourier transform infrared spectroscopy offers a dramatic improvement in the signal-to-noise ratio over dispersive IR spectroscopy due to the multiplexing (or Fellgett) advantage and the throughput (or Jacquinot) gain. The multiplexing advantage arises because all of the resolution elements are observed all the time. The large sampling area and the absence of narrow slits in the interferometer produce the throughput gain. The accuracy of frequency determination (Connes' advantage) in FTIR, which is made possible by the use of the He–Ne laser interferometer to reference the position of the moving mirror, is another advantage. In addition to the advantages inherent in the interferometric acquisition of the data, the computer, which is an integral part of the system, offers many possibilities for manipulation of the stored data (such as spectral subtraction or addition) to improve the capabilities for rapid and accurate quantitative measurements. Detailed discussions of the principles of FTIR have been given by Bell [22] and Griffiths [23]. The application of FTIR has been popularly used for charcterization of adhesives. Sojka et al. [24] used FTIR to study the reaction of phenol with hexamethylenetetramine (HMTA) at 100°C. Pearce et al. [25] analyzed cured novolak and resol adhesives. Figure 10 shows an IR spectrum of resol. The curing kinetics and mechanism, degradation processes, and chemical reactions of epoxies with coupling agents have also been studied by FTIR [26]. The completeness of the cross-linking reaction for a mixture of epoxy resin and curing agent immediately after being mixed and after being cured at 160°C for 2.5 h has been studied by Yorkgitis et al. using FTIR [27].

When a beam of radiation encounters an interface between two media, approaching it from the side of higher refractive index, total reflection occurs if the angle of incidence is greater than some critical angle, the value of which is given by

$$\alpha = \sin^{-1}\frac{n_2}{n_1} \tag{10}$$

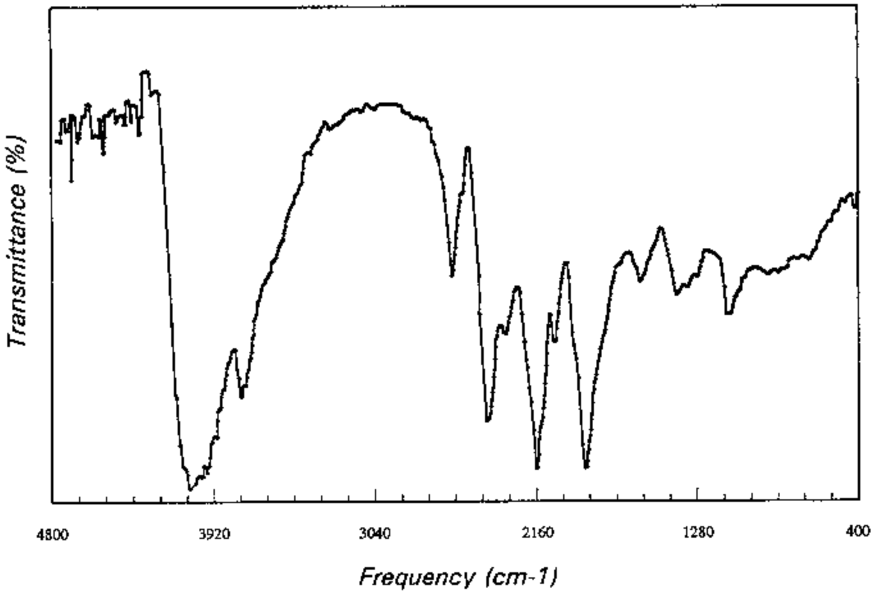


Figure 10 The infrared spectrum of a phenol–formaldehyde (resol) adhesive.

when n_1 and n_2 are the two indices of refraction, with $n_1 > n_2$. Not so generally realized, although predicted by electromagnetic theory, is the fact that in total reflection, some portions of the energy of the radiation actually cross the boundary and return. If the less dense medium absorbs at the wavelength of the radiation, the reflected beam will contain less energy than the incident, and a wavelength scan will produce an absorption spectrum. This principle has been found useful in the IR. The distance to which the radiation appears to penetrate in internal reflection depends on the wavelength but is on the order of 5 μm or less in the mid-IR region. This phenomenon is generally known as ATR [28,29]. This method enables a reflection spectrum to be obtained which is superficially very similar to an absorption spectrum with the only difference being the higher intensities of absorption bands at longer wavelengths. To obtain measurable absorption spectra, it is a normal practice to use multiple reflection prisms (Fig. 11), and these are available as standard spectrometer accessories. A common material for the prisms is thallium bromoiodide (KRS-5). A trapezoidal prism having an angle of incidence of 45° giving 25 reflections is useful for adhesive materials. The sample is clamped securely to provide good optical contact with the prism and, where possible, the sample should be placed on both surfaces of the prism to give optimum sensitivity (see Fig. 11). Attenuated total reflection has been found most useful with opaque materials that must be observed in the solid state. Applications include studies of polymeric materials, adsorbed surface films, paints, and adhesives. Infrared spectra of polystyrene in transmission and by ATR are shown in Fig. 12.

Like IR spectroscopy, Raman spectroscopy can provide qualitative, quantitative, and structural information about a variety of materials. The potential of laser Raman for distinguishing critical structure differences in cured urea–formaldehyde (UF) resins has been demonstrated from studies made on model compounds [30]. Fourier transform-Raman studies of thermally and photochemically induced epoxy curing reactions have been reported [31].

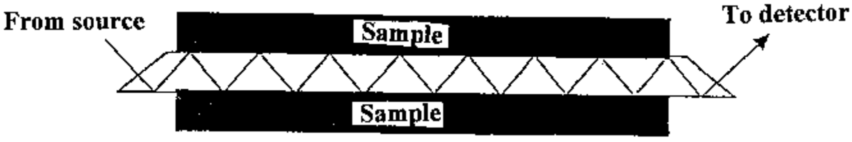


Figure 11 Multiple internal reflection setup.

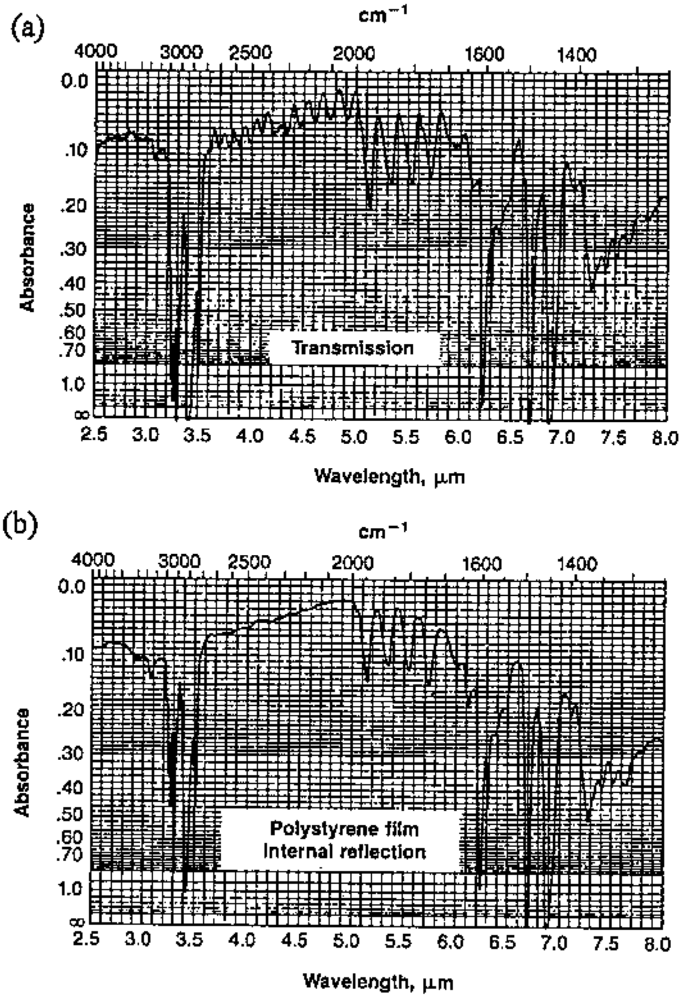


Figure 12 Infrared spectra of polystyrene (a) in transmission and (b) by internal reflection.

Infrared spectroscopy and Raman spectroscopy are complementary analytical techniques. Both provide vibrational information about the molecule, but different data are conveyed in the absorption and scattering spectra analyzed, respectively, by IR and Raman spectroscopy. In general, the IR spectrum arises from the absorption of radiation the frequency of which is resonant with a vibrational transition, while the Raman effect results from inelastic scattering of photons to leave a molecule in a vibrationally excited state. The shift in frequency of the scattered photon corresponds to the frequency of the normal mode that has been excited. A particular molecular vibration may be observable in both spectra, but different in intensity. The lower the symmetry of a molecule, the greater the overlap of its IR-active and Raman-activated vibrations. Polar compounds and asymmetric vibrations are more readily observed in IR spectroscopy, whereas Raman spectroscopy favors nonpolar compounds and symmetric vibrations. Furthermore, the Raman-scattered light occurs in the visible and ultraviolet regions of the electromagnetic spectrum and the detection systems in this range are far superior to those in the infrared region. However, the intensity of a Raman spectrum is usually quite weak—it is about one-thousandth of the intensity of the light that is scattered at the same frequency as the incident beam (Rayleigh scattering). Generally, IR spectroscopy yields more useful information for the identification of polar groups, whereas Raman spectroscopy is especially helpful in the characterization of the homonuclear polymer backbone. Thus, the application of both techniques is highly desirable in order to extract the maximum amount of information from an adhesive specimen. The complementarity of the two techniques is illustrated by Fig. 13, which shows the IR and Raman spectra of poly(vinyl acetate). Comprehensive reviews of these techniques are available [14,15,32,33].

D. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is now well established as one of the most useful instrumental techniques for characterization of adhesives and for the study of polymeric adhesive structure–property relationships [34]. The reasons are that (1) individual chemical groups in adhesive often give signals that can be resolved, (2) the NMR signals are sensitive to environment, and (3) the theory is well understood and the relationship between spectral parameters and the information of interest (such as concentration or structure) is relatively straightforward. Polymer scientists and technologists have been

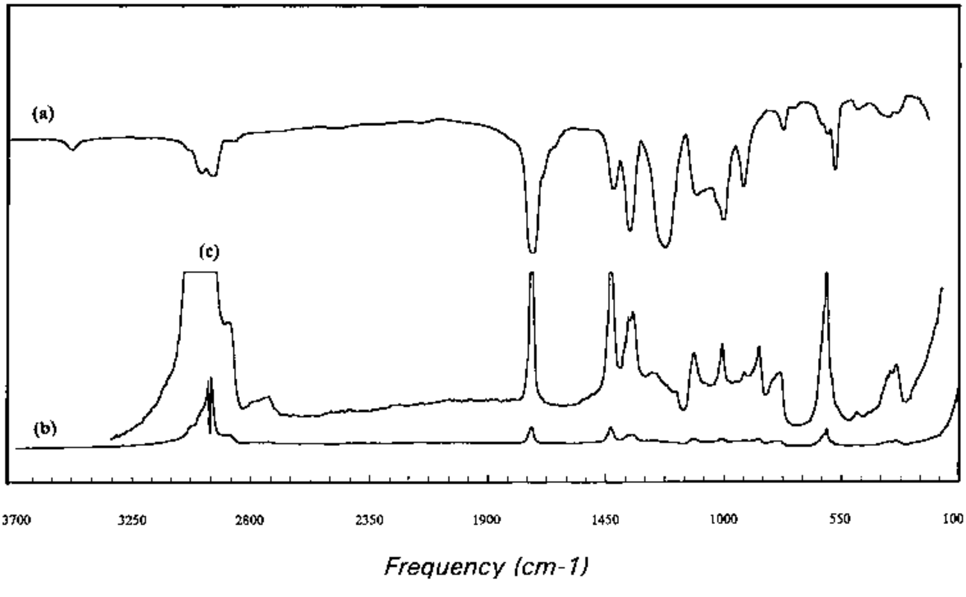


Figure 13 (a) Infrared and (b) Raman spectra of poly(vinyl acetate). (c) The expansion of (b).

using NMR to study the detailed chain structure of polymers and copolymers and the morphology and transition in the solid state. It has also provided a means for identifying intermediate structures formed during polymerization reactions so permitting more detailed reaction mechanisms to be proposed.

Nuclear magnetic resonance involves the interaction of radio waves and the spinning nuclei of the combined atoms in a molecule. The nuclei of certain isotopes, such as ^1H, ^{19}F, ^{31}P, ^{13}C, ^{15}N, ^{29}Si, and others have an intrinsic spinning motion around their axes, which generates a magnetic moment along the axis of spin.

For the vast majority of polymeric materials, only ^1H exists in high concentration and it has been the subject of the majority of applications of NMR to date. However, recent advances in instrumentation and computer capabilities, coupled with pulse techniques and Fourier transformation, have greatly enhanced the sensitivity of NMR spectroscopy. Thus, NMR spectra may be obtained from solutions of very low concentration, nuclei may be observed that have very low natural abundance (i.e., ^{19}F, ^{31}P, ^{13}C, ^{15}N, ^{29}Si), and resolution of spectral lines is greatly improved. Until recently, high-resolution NMR spectra could be obtained only on samples in solution; however, new spectrometers have become available which utilize special techniques to provide solid-sample capability [35,36].

The simultaneous application of a strong external magnetic field H_o, and the radiation from a second and weaker radio-frequency source H_1 (applied perpendicular to H_o) to the nuclei results in transitions between energy states of the nuclear spin. The NMR phenomenon occurs when these nuclei undergo transition from one alignment in the applied field to an opposite one. This process is illustrated in Fig. 14 for a hydrogen nucleus.

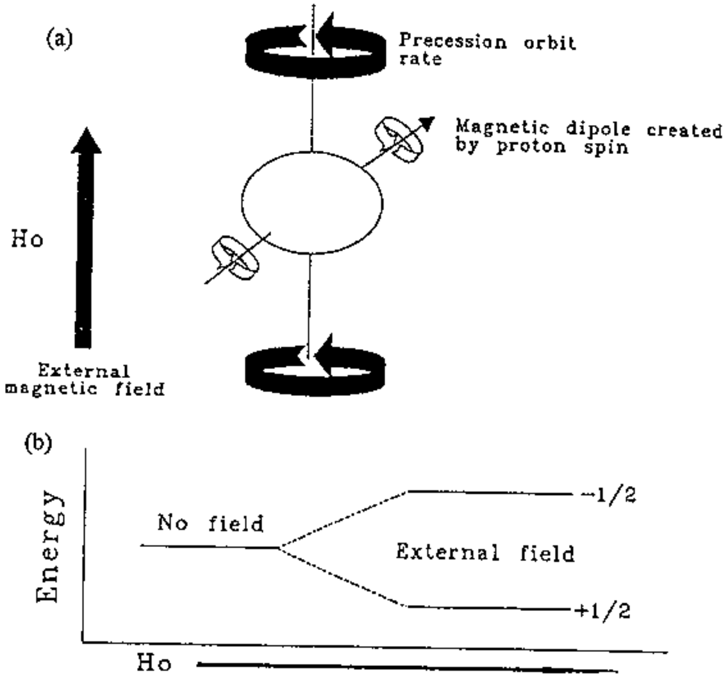


Figure 14 Relation between precession and the exciting field ^1H: (a) precession of a proton's magnetic dipole in a magnetic field; (b) splitting of energy levels for a hydrogen nucleus in a magnetic field.

The energy absorption is a quantized process, and the energy absorbed must equal the energy difference between the two states involved:

$$\Delta E_{\text{absorbed}} = (E_{-1/2} \text{ state} - E_{+1/2} \text{ state}) = h\nu \tag{11}$$

In practice, this energy difference is a function of the strength of the applied magnetic field, H_o. The relationship between these energy levels and the frequency ν of absorbed radiation can be calculated as follows:

$$E = -M\left(\frac{\mu}{I}\frac{h}{2\pi}\right)B_o \tag{12}$$

where M is the magnetic quantum number, μ the nuclear magnetic spin, B_o the applied magnetic field, and I the spin angular momentum.

At a given radio frequency, all protons absorb at the same effective field strength, but they absorb at different applied field strengths. It is this applied field strength that is measured and against which the absorption is plotted. The NMR spectrum consists of a set of resonances (or spectral lines) corresponding to the different types of hydrogen atoms in the sample. There are six basic measurements that can be obtained from a set of resonances: (1) the number of signals, which is related to the number of protons presented in the molecule; (2) the intensity or area under the resonance, which is proportional to the amount of species present in the sample; (3) the position of the resonance or chemical shift, which is indicative of the identity of the species; (4) the line width of the resonance, which is related to the molecular environment of the particular ^{1}H; (5) the multiplet structure, which is related to the spin–spin coupling constant (J); and (6) a relaxation time (T_2) which is related to the line width. These parameters used in adhesive characterization are shown in Fig. 15. The fact that the resonance area is proportional to the concentration of the

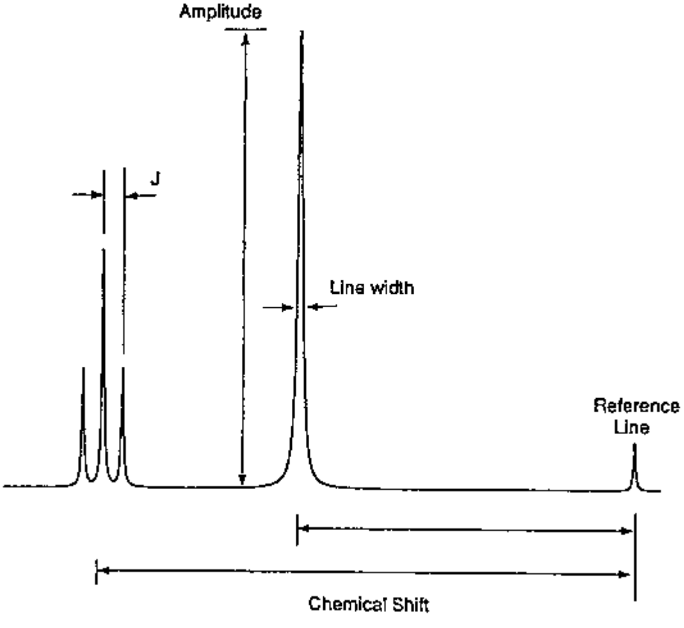


Figure 15 A NMR signal is characterized by several parameters: number of signals; intensity or amplitude; line width; multiplet structure and coupling constant, J; and chemical shift.

species is the basis of quantitative NMR. By taking the ratios of different resonances corresponding to different species, the composition of multicomponent systems can be obtained.

In a given molecule, protons with the same environment absorb at the same applied field strength; protons with different environments absorb at different field strengths. A set of protons with the same environment is considered to be equivalent; the number of signals in the NMR spectrum shows how many sets of equivalent protons a molecule contains. The position of the signals in the spectrum indicates the types of protons (primary, secondary, tertiary, aromatic, benzylic, acetylenic, vinylic, etc.) in the molecule. These protons of different kinds have different electronic environments, which determine the number and location of the signals generated. When a molecule is placed in a magnetic field, circulation of electrons about the proton itself generates a field that acts against or reinforces the applied field. In each situation, the proton is to be shielded or deshielded. Shielding or deshielding thus shift the absorption upfield and downfield, respectively. For example, the proton attached to the carbonyl carbon of acetaldehyde (CH_3–CHO) is more deshielded, due to the electron-withdrawing properties of the carbonyl oxygen, than the protons of the methyl group of an alkane (R–CH_3), which are surrounded by a higher electron density since there is no electron-withdrawing group. The carbonyl proton absorbs downfield from the methyl protons. The reference point from which chemical shifts are measured is not the signal from a naked proton, but the signal from a reference compound, usually tetramethylsilane, $(CH_3)_4Si$ (TMS).

The position of the absorption relative to TMS is called the chemical shift; its designation is δ and its units are ppm (parts per million). Thus

$$\text{chemical shift (ppm)} = \frac{\text{chemical shift from TMS (Hz)}}{\text{spectrometer frequency (Hz)}} \times 10^6 \tag{13}$$

For protons there is an alternative scale that expresses the chemical shifts in ppm on a τ (tau) scale, so that

$$\tau = 10 - \delta \tag{14}$$

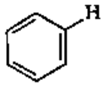
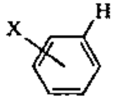
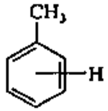
Most chemical shifts have δ values between 0 and 15. A small δ value represents a small downfield shift, and vice versa. A simplified correlation chart for proton chemical shift values is shown in Table 2 [37].

The real power of NMR derives from its ability to define complete sequences of groups or arrangements of atoms in the molecule. The absorption band multiplicities (splitting patterns) give the spatial positions of the nuclei. These splitting patterns arise through reciprocal magnetic interaction between spinning nuclei in a molecular system facilitated by the strongly magnetic binding electrons of the molecule in the intervening bonds. This coupling, called spin–spin coupling or splitting, causes mutual splitting of the otherwise sharp resonance lines into multiplets. The strength of the spin–spin coupling or coupling constant, denoted by J, is given by the spacings between the individual lines of the multiplets. The number of splittings of a multiplet adjacent to n equivalent spins is given by

$$s = 2nI + 1 \tag{15}$$

where s is the number of lines and I is the spin of the nucleus causing the splitting. Since ^1H has a spin of 1/2, this reduces to $n+1$ for proton spectra. The intensities of the multiplets also have a predictable ratio and turn out to be related to the coefficients of the binomial expansion $(a+b)^n$. These are given by Pascal's triangle, where each coefficient is the sum of the two terms diagonally above it (Table 3). For simple spectra, then, we can predict the

Table 2 Approximate NMR Chemical Shifts of Protons

CH_3– Protons		–CH_2– Protons		–CH– Protons		Other groups	
Proton	δ (ppm)	Proton	δ (ppm)	Proton	δ (ppm)	Proton	δ (ppm)
CH_3–C	0.9	–C–CH_2–C	1.3	–C–CH–C	1.5	–C=CH	5.3
CH_3–C–C=C	1.1	–C–CH_2–C–C=C	1.7	–CH–C–Br	1.9	–C=CH–	5.1
CH_3–C–Cl	1.4	–CH_2–C–Cl	1.8	–CH–C–Cl	2.0	–C=CH–(cyclic)	5.3
CH_3–C–O	1.4	–CH_2–C–Br	1.8	–C–CH–C–O	2.0	R–C≡CH	3.1
CH_3–C=C	1.6	–C–CH_2–C–O	1.9	–C–CH–CO–R	2.7	–C=CH–CO	5.9
CH_3–C–NO_2	1.6	–C–CH_2–C–NO_2	2.1	–C–CH–N	2.8	–CH=C–CO	6.8
CH_3–C–Br	1.8	–C–CH_2–CO–O–R	2.2	–CH–Ar	3.0	R–CHO	9.9
–C=C(CH_3)–CO	1.8	–C–CH_2–C=C	2.3	–C–CH–O–R	3.7	Ar–CHO	9.9
CH_3–CO–N–R	2.0	–C–CH_2–CO–O–R	2.2	–C–CH–O–H	3.9	H–CO–O	8.0
CH_3–C=C–CO	2.0	–C–CH_2–C=C	2.3	–CH–Cl	4.0	H–CO–N	8.0
CH_3–CO–R	2.2	–C–CH_2–CO–R	2.4	–CH–Br	4.1	$CHCl_3$	7.25
CH_3–Ar	2.3	–C–CH_2–C=C–CO	2.4	–C–CH–NO_2	4.7	H_2O	∼5
CH_3–N	2.3	–C=C(CH_2)–CO	2.4	–C–CH–O–CO–R	4.8		
CH_3–CO–O–Ar	2.4	–C–CH_2–N	2.5				
CH_3–CO–Ar	2.6	–C–CH_2–Ar	2.7	Aromatic Protons			
CH_3–Br	2.7	–C–CH_2–O–R	3.4		7.2		
CH_3–Cl	3.0	–CH_2–Cl	3.4				
CH_3–O–R	3.3	–CH_2–Br	3.4				
CH_3–O–Ar	3.8	–C–CH_2–O–H	3.6				
CH_3–O–CO–R	3.7	–C–CH_2–O–CO–R	4.1		7.0–9.0		
		–C–CH_2–O–Ar	4.3				
		–C–CH_2–NO_2	4.4		2.3 7.1		

R = Alkyl group; Ar = Aromatic group.
Source: Ref. 37.

Table 3 Relative Intensities of the Lines of a Multiplet

n	Multiplicity	Intensity
0	singlet	1
1	doublet	1 1
2	triplet	1 2 1
3	quartet	1 3 3 1
4	quintet	1 4 6 4 1
5	sextet	1 5 10 10 5 1

number of splittings and their intensities from the multiplicity and intensity rules given above.

An NMR instrument normally has a strong magnet with a homogeneous field, a radio-frequency transmitter and receiver, and a computer to store, compile, and integrate the signals. A sample holder positions the sample relative to the magnetic field so that the sample will be exposed continously to a homogeneous magnetic field. The sample holder may also have a variable temperature control. Instruments for NMR are built with different magnetic field strengths. They are listed according to the radio frequencies required for the proton to resonate. They can have magnetic fields that require protons to absorb from 60 to 600 MHz to resonate.

A few words about sample preparation. The typical NMR spectrum is obtained from a sample in a 5-mm thin-walled glass tube containing about 0.4 mL of sample. Sample concentrations for routine work can be as low as 0.01 M, but concentrations greater than 0.2 M are preferred for good signal-to-noise ratio. Liquid samples are seldom run as neat liquids, since their greater viscosity will lead to broader lines. Instead, the liquids and solids are dissolved in a suitable solvent that does not show any peaks in the region of interest. Common solvents include CCl_4, $CDCl_3$, D_2O, acetone-d_6, and DMSO-d_6.

Many studies have been done for polymer systems with respect to monomer composition and the average stereochemical configuration present along polymeric chains [38,39]. Both solid-state and conventional solution NMR techniques provide information on molecular motion, chain flexibility, and in some cases, crystallinity and network formation due to chain entanglement or cross-links [40–42]. The use of NMR spectroscopy for solid polymers has been reviewed by McBrierty [43–45], who has covered molecular motion studies in addition to the structural characterization of these systems in great detail. Jelinski [46] addressed the subject of chemical information and problem solving for both solution and solid-state polymer studies. In addition to elucidating chemical structure, NMR can also be used for a particular facet of a structure, such as chain length or number of moles of a branched polymer, and in the study of polymer motion by relaxation measurements. Kinetic studies of curing reactions at temperatures in the range -150 to $+200$°C are another application. Useful information can also be obtained from complex mixtures, such as the total methylene linkage of a PF adhesive. The NMR technique has also been used to distinguish the structure of transient molecules involved in resin formation [47], structures of species involved in HMTA cure, and the final structure of phenolic oligomers [48]. Figure 16 is the NMR spectrum of a PF resol in acetone-d_6 solution. The resonances of the protons in various structures are identified.

As mentioned earlier, one of the low-sensitivity nuclei which has become a routine analytical tool for polymer chemists since the advent of Fourier transform NMR is ^{13}C.

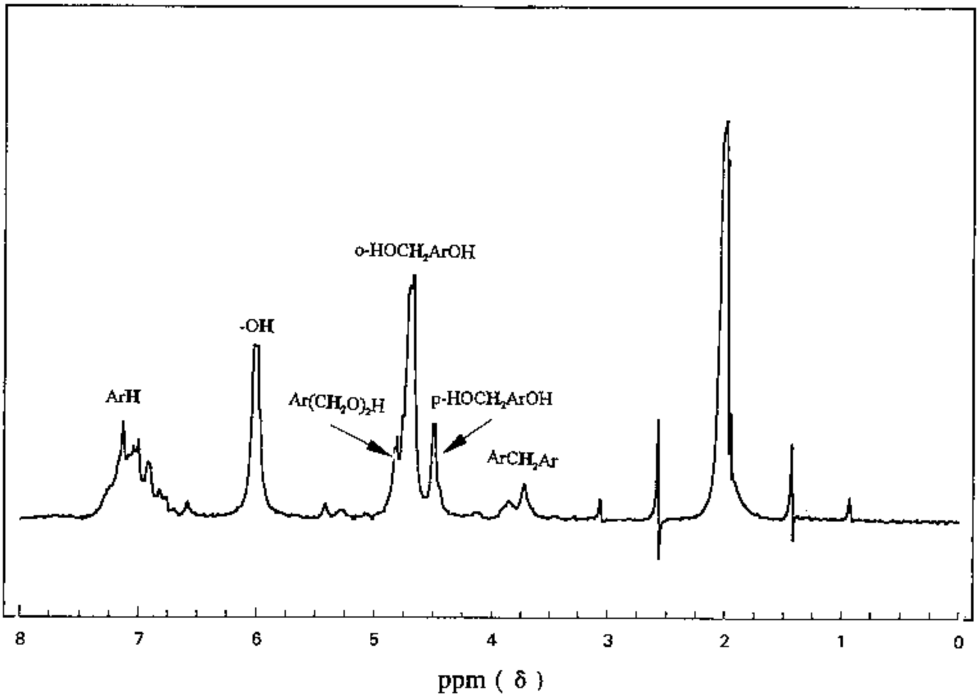


Figure 16 The NMR spectrum of a phenol–formaldehyde (resol) adhesive.

The magnetic moment of ^{13}C is about one quarter of that of ^{1}H, but its natural abundance is only 1.1%. The rare occurrence of the isotope greatly simplifies ^{13}C NMR spectra by eliminating the spin–spin coupling (^{13}C–^{13}C) which is so dominant in ^{1}H NMR spectra. The other advantage of ^{13}C NMR is that the chemical shifts are dispersed over 200 ppm rather than the 10 ppm typically observed for ^{1}H NMR. A ^{13}C NMR spectrum of a reaction mixture of UF concentrate with phenol under acidic conditions is shown in Fig. 17, in which the presence of co-condensed methylene carbon was confirmed.

E. Thermal Analysis

Heat or temperature has a considerable effect on curing, working life, and stability of adhesives. Several structural transitions can occur in adhesives during heating. Thermal analysis techniques can provide a detail road map of curing, properties, and stability of cured adhesives that has predictive utility. They also provide the ability to assess degree of cure and composition.

Thermal analysis refers to any technique for the study of materials which involves thermal control [49–52]. The techniques include the measurement of temperatures at which changes may occur, the measurement of the energy absorbed (endothermic transition) or evolved (exothermic transition) during a phase transition or a chemical reaction, and the assessment of physical changes resulting from changes in temperature. Measurements are usually made with increasing temperature, but isothermal measurements or measurements made with decreasing temperatures are also possible. Hence thermal analysis has provided important contributions in the characterization of adhesives, and a great deal has been

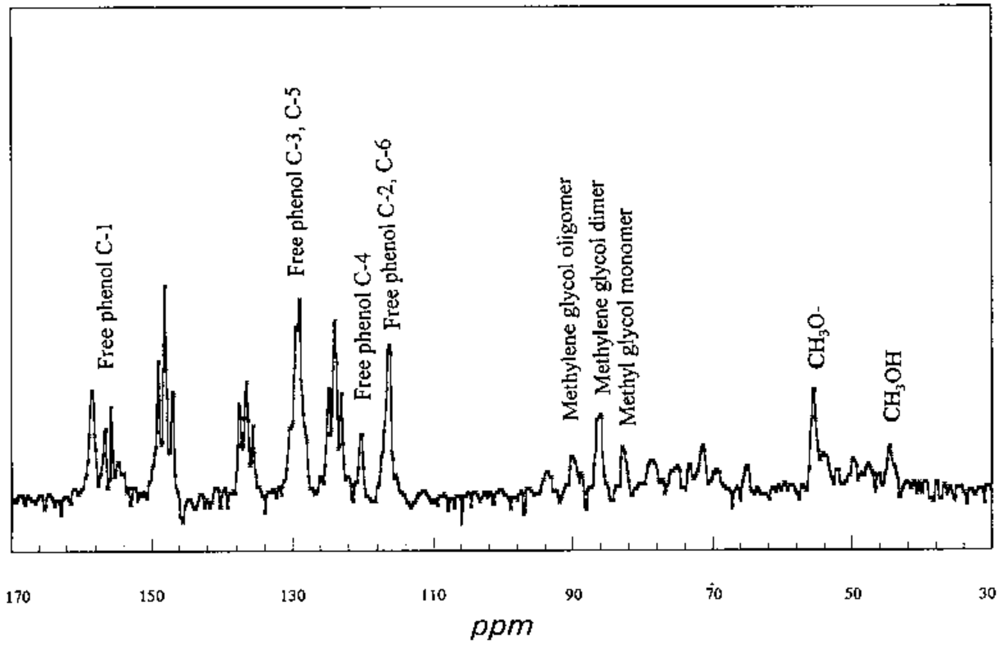


Figure 17 The ^{13}C NMR spectrum of the reaction mixture of urea–formaldehyde concentrate with phenol under acidic conditions.

written on this subject. It yields a ‘‘fingerprint’’ that may uniquely characterize the adhesive and assess its thermal stability. Thermal analysis data may also permit the evaluation of the kinetic parameters for the chemical changes that may have taken place during the heating process. For insoluble network adhesives, thermal techniques have been used to establish the degree and rate of cure, to study the chemical kinetics of curing reactions and the curing behavior itself, and to study degradation reactions.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are techniques that monitor either the heat evolution or absorption for any reactions that are occurring in a sample. Thus, DTA/DSC thermograms reflect changes in the energy of the system under investigation—changes that may be chemical or physical in origin. The technique is particularly useful for adhesives because polymerization or structural changes are almost invariably accompanied by energetic effects so that curing, crystallization, melting and other reactions all show characteristic DTA/DSC thermograms (see Fig. 18). The use of dynamic mechanical thermal analysis (DMTA), however, is not involved in heat change; it is a technique that measures molecular motion in adhesives to obtain a temperature/modulus relationship. These thermal analysis techniques are discussed below.

1. *Differential Thermal Analysis*

Differential thermal analysis is a technique by which phase transitions or chemical reactions can be followed through observation of heat absorbed or evolved. It is especially suited to the study of structural changes within a solid adhesive at elevated temperatures. The temperature difference between a sample and an inert reference material is monitored while both are subjected to a linearly increasing environmental temperature. Figure 19

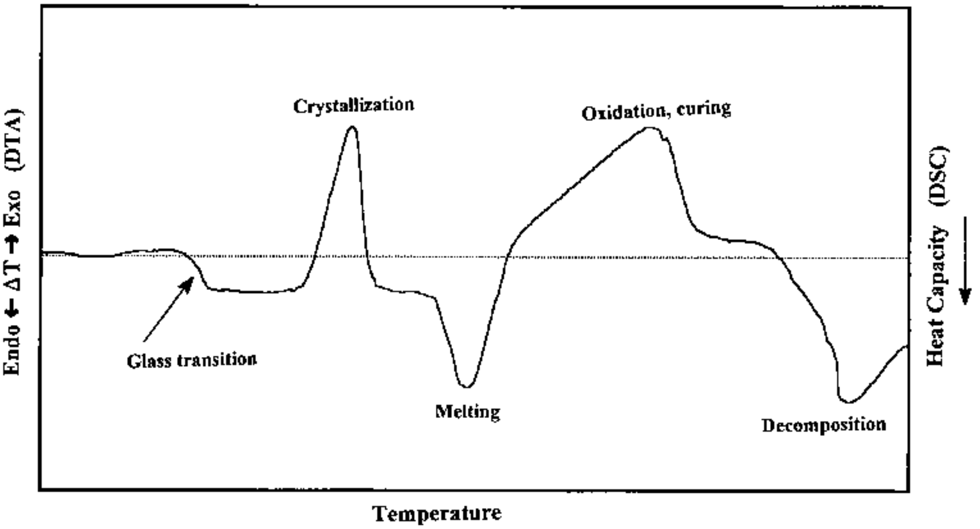


Figure 18 Schematic DSC or DTA curve.

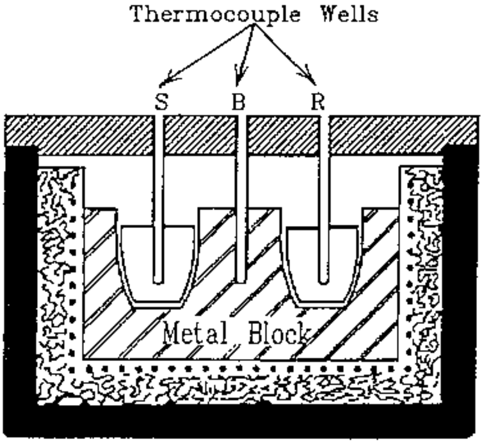


Figure 19 The construction of a DTA apparatus.

illustrates the principle. Two small crucibles, placed in suitably shaped cavities in a metal block, contain the sample (S) and the reference (R). The two junctions of a thermocouple are inserted into the crucibles so as to give directly the temperature difference between them. A separate thermocouple is placed in cavity B to measure the temperature of the block. The entire assembly is then heated under the control of a linear programmer. With constant heating, any transition or thermally induced reaction in the sample will be recorded as a peak or dip in an otherwise straight line. An endothermic process will cause the thermocouple junction in the sample to lag behind the junction in the reference material, and hence develop a voltage, whereas an exothermic event will produce a voltage of an opposite sign. It is customary to plot exotherms upward and endotherms downward.

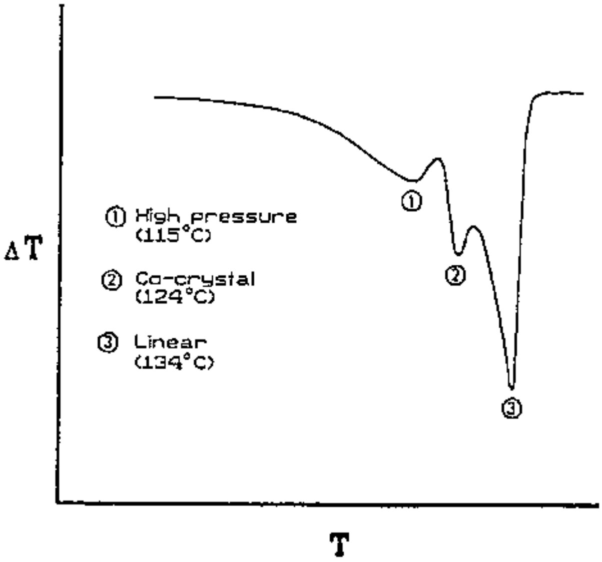


Figure 20 Typical DTA thermogram of a linear high-pressure polyethylene blend.

Conventional DTA can give good qualitative data about temperatures and signs of transitions, but it is difficult to obtain quantitative information about the sample or the heat of transition. Figure 20 shows a typical DTA thermogram of a linear high-pressure polyethylene blend [53]. This polymer, upon heating, undergoes three phase changes from its high-pressure form (115°C) to co-crystalline form (124°C) to a linear form (134°C). The 115°C peak was associated with the high-pressure polyethylene, whereas the 134°C peak was shown to be proportional to the linear content of the system. Recently, it was shown that there is reasonable correlation between the gelation time and the temperature corresponding to the peak of the isotherm on curves for an epoxy resin system [54]. The DTA method has yielded accurate kinetic results for a PF resin system, in addition to providing an insight to the actual chemistry of the curing process [55]. Orrell and Burns [56] used DTA to investigate phenol HMTA and novolak HMTA reactions.

2. *Differential Scanning Calorimetry*

Quantitative results can be obtained by converting the sample compartment of a DTA apparatus into a differential calorimeter. The instrument, a differential scanning calorimeter, is built based on this principle. In this setup, the sample and reference are heated directly with separate heating coils as shown in Fig. 21. A heating coil makes the temperature of the reference material increase at a constant rate. A second heating coil is placed in the sample. The sample and the reference are kept at equal temperature. When a phase change or weight loss occurs, the sample and reference temperature become slightly different, which generates a current in the thermocouple system measuring the temperature difference between the two cells. The current activates a relay, causing extra power to be directed to the cell at the lower temperature. In this manner the temperatures of the reference and sample cells are kept virtually equal throughout. The quantity of electrical energy used in heating the sample and the reference is measured accurately and

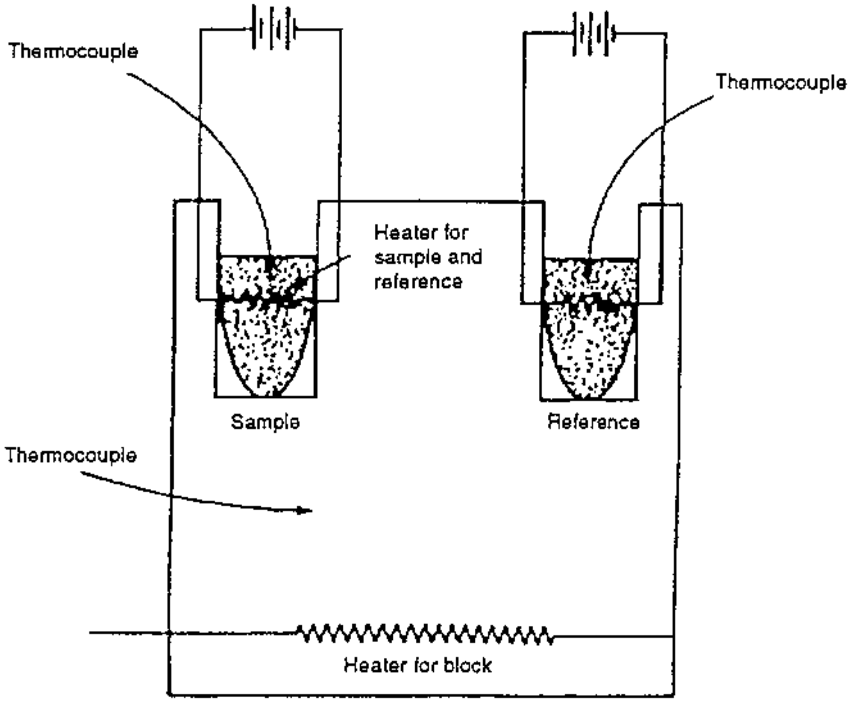


Figure 21 The construction of a DSC apparatus.

continuously. In turn, the electrical energy is an exact measure of the number of calories used in heating the cells.

The resultant thermogram is similar to a DTA trace but more accurate and reliable. Endothermic changes are recorded as heat input into the sample, and exothermic changes as heat input into the reference. The area of the peaks is an exact measure of heat input involved. Differences in heat capacity or thermal conductivity do not affect the results. From the data, accurate quantitative analytical results can be obtained.

Much information about molecular ordering can be obtained from DSC, including the glass transition temperature (T_g), melting temperature (T_m), heat of fusion, and entropy of fusion (see Fig. 18). The melting behavior in DSC permits a determination of the extent of crystallinity. In the measurement of heats of reactions for the types of polymerization under discussion DSC is the more frequently used technique because it gives a quantitative measure of the heat and the rate of the curing reaction. All thermosetting adhesives liberate heat during cure:

$$\text{Reactants} \xrightarrow{-\Delta H} \text{Products} \tag{16}$$

where $-\Delta H$ is the exothermic heat per mole of the reacting groups. Since DSC measures heat flow (dH/dt) directly it is ideally suited to measure not only the heat of reaction but also the rate of heat evolution. If the cure reaction is the only thermal event in the curing process, the reaction rate $d\alpha/dt$ is directly proportional to dH/dt:

$$\frac{d\alpha}{dt} = \frac{(dH/dt)}{-\Delta H} \tag{17}$$

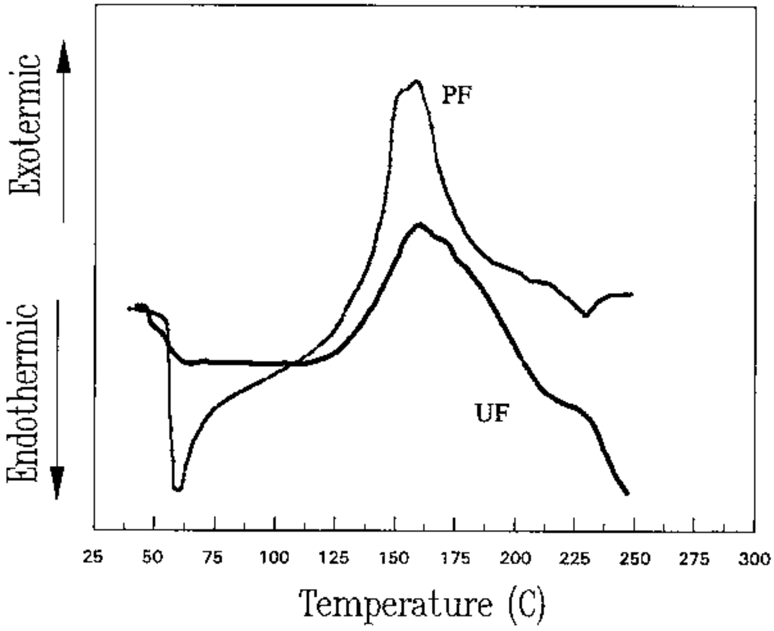


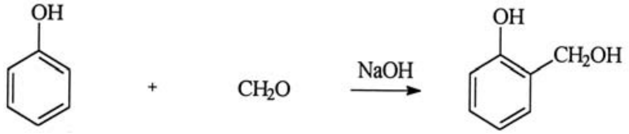
Figure 22 Typical DSC thermograms of PF and UF.

During isothermal DSC runs, the degree of conversion is:

$$\alpha_t = \frac{\Delta H_t}{\Delta H} \tag{18}$$

where α_t is the extent of reaction and ΔH_t the heat evolved up to time t [57].

Figure 22 illustrates typical DSC thermograms for UF and PF resins. The PF resin had larger exothermic heat of curing as compared to the UF resin. For illustration purposes, the reaction between phenol and formaldehyde in alkaline conditions to form PF adhesives is briefly discussed here. The first step is an exothermic addition reaction forming methylol derivatives at the ortho or para positions:



(19)

This change or transition can be monitored by DSC as shown in Fig. 23. Detailed study of curing of PF by DSC was performed by Sebenik et al. [58].

Fava [59] described kinetic measurements involving the heat of reaction for measuring the extent of cure in an epoxy resin. The three methods for obtaining isothermal cure curves using the DSC technique are isothermal operation, analysis of thermograms with different scan rates, and scans on partly cured resins. From DSC curves, the state of cure can be monitored and the kinetic parameters of cure can be determined. Using this technique, kinetic studies have been made of polymerization of vinyl acetate and PF, and curing of epoxy resins. A kinetic study of isothermal cure of epoxy resin has been carried out [60,61]. Kinetic parameters associated with the cross-linking process of PF and melamine–formaldehyde copolymers have been obtained from exotherms of a single DSC

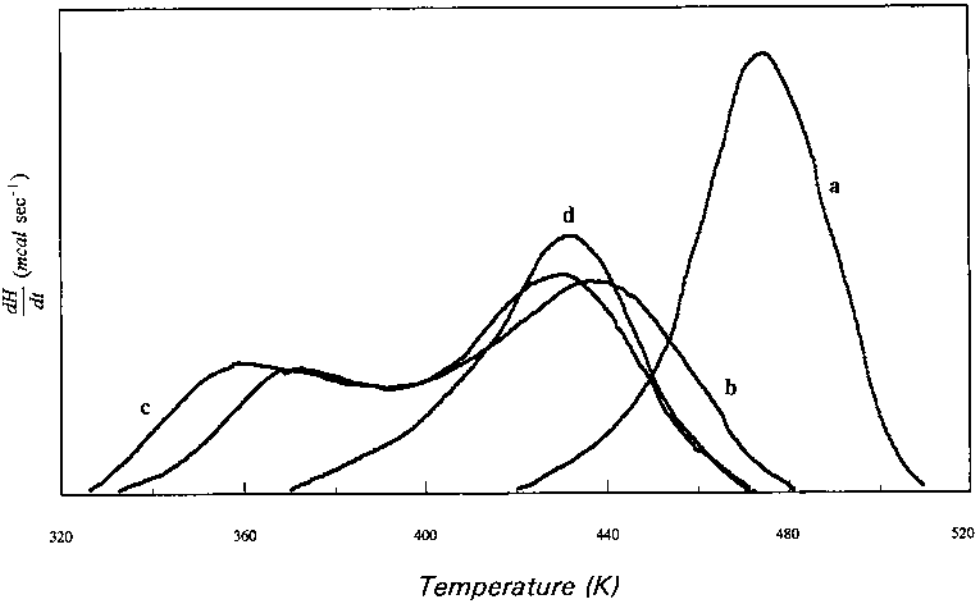


Figure 23 Thermograms for the reaction between phenol and formaldehyde: (a) no catalyst added; (b) 0.25% NaOH; (c) 0.75% NaOH; (d) 5% NaOH.

temperature scan [62–64]. The other major application of DSC is the measurement of T_g [65,66]. In the absence of endothermic or exothermic reactions, the DSC heat flow output is proportional to the sample heat capacity, and the T_g may be determined from the characteristic discontinuity in heat capacity. The T_g of a cross-linked polymer in general shows an increase with increasing degree of cross-linking, and thus provides a useful index of the degree of cure. The T_g is dependent on the chain flexibility and the free volume associated with the chemical structure as well as the overall cross-link density.

3. *Dynamic Mechanical Thermal Analysis*

As mentioned earlier, the DMTA technique measures molecular motion in adhesives, and not heat changes as with DSC. Many adhesives exhibit time-dependent, reversible viscoelastic properties in deformation. Hence a viscoelactic material can be characterized by measuring its elastic modulus as a function of temperature. The modulus depends both on the method and the time of measurement. Dynamic mechanical tests are characterized by application of a small stress in a time-varying periodic or sinusoidal fashion. For viscoelastic materials when a sinusoidal deformation is applied, the stress is not in phase with displacement. A complex tensile modulus (E*) or shear modulus (G*) can be obtained:

$$E^* = E' + iE'' \qquad (\text{or } G^* = G' + iG'') \tag{20}$$

where E' (or G') is the in-phase component (or real or storage part of dynamic modulus) and E'' (or G$''$) is the out-of-phase component (or imaginary or loss part of dynamic modulus). The mechanical loss factor corresponding to the damping of the material can be defined by tan δ. The significance of viscous dissipation in a material is described by tan δ and is often the parameter chosen to relate dynamic data to molecular or structural

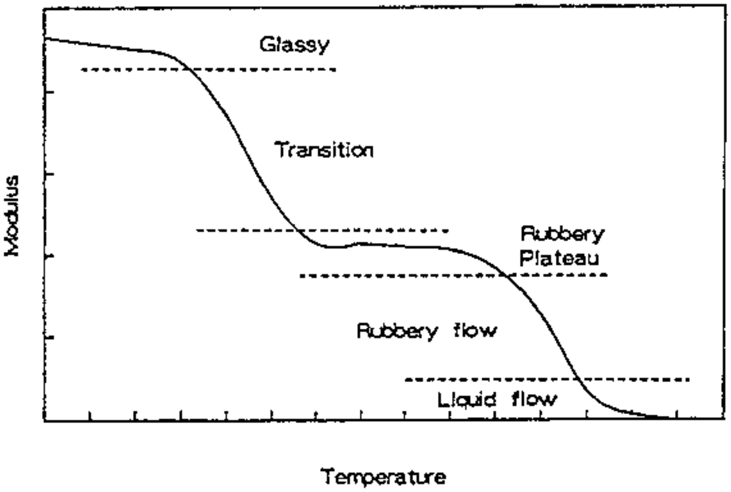


Figure 24 Typical modulus–temperature curve for an amorphous adhesive.

motion in plastics materials. The dynamic modulus for polymers is strongly dependent on temperature and frequency in the transition zones:

$$\tan\delta = E/E' \qquad (or\, G/G') \tag{21}$$

It is interesting to study E' (or G') and tan δ by changing frequency at constant temperature and changing temperature at constant frequency. Dynamic mechanical spectroscopy by studying E^* (or G^*) versus temperature and frequency can give information about relaxation processes (i.e., main chain relaxation from glass to rubber associated with the glass transition process and secondary transitions related to movements of side chains or to motions of small parts of the main chain). The elastic modulus–temperature curve for a typical amophous polymer is given in Fig. 24 and shows five different regions: (1) the glassy region where the modulus of most amorphous polymers is of the order of 10^{11} dyn/cm^2; (2) the transition region, where the modulus changes rapidly with temperature; (3) the rubbery plateau region, which is apparent only when polymers form a loose network by cross-linking or by pigment reinforcement; (4) the rubbery flow region; and (5) the liquid flow region. The modulus in these various regions of viscoelastic behavior is affected differently when the molecular weight of the polymer is changed. Figure 25 illustrates the main features observed during a DMTA scan of a semicrystalline polymer. Relaxation in the amophous phase is labeled with Greek letters (α, β, γ) with decreasing temperature. For adhesive applications, the curing of adhesives is particularly suited to DMTA-type studies, because it is the mechanical properties that are vitally important during production and in final use. During the cure process, the modulus increases with cure. The tan δ value usually rises at first, then falls rapidly as the cross-link density becomes higher and progressively inhibits conformation changes. The changes in E' and tan δ of a phenolic adhesive are shown in Fig. 26. It is apparent the uncured specimen shows a large damping peak at T_g and a smaller damping peak associated with cure. Dynamic mechanical properties of epoxy resins cured with various kinds of hardeners have been evaluated by Kamon and Furukawa [67]. The data in Fig. 27 show T_g relaxation spectra in a carbon fiber-reinforced epoxy resin; the position and area of the loss peaks in

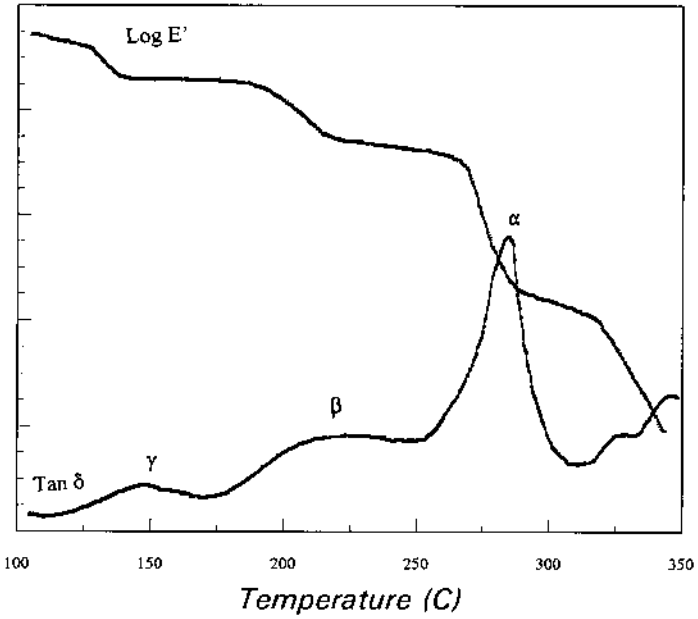


Figure 25 Typical transition behavior in mechanical storage modulus and damping for a semicrystalline polymer. Relaxations in the amorphous phase are labeled with Greek letters (α, β, γ) with decreasing temperature.

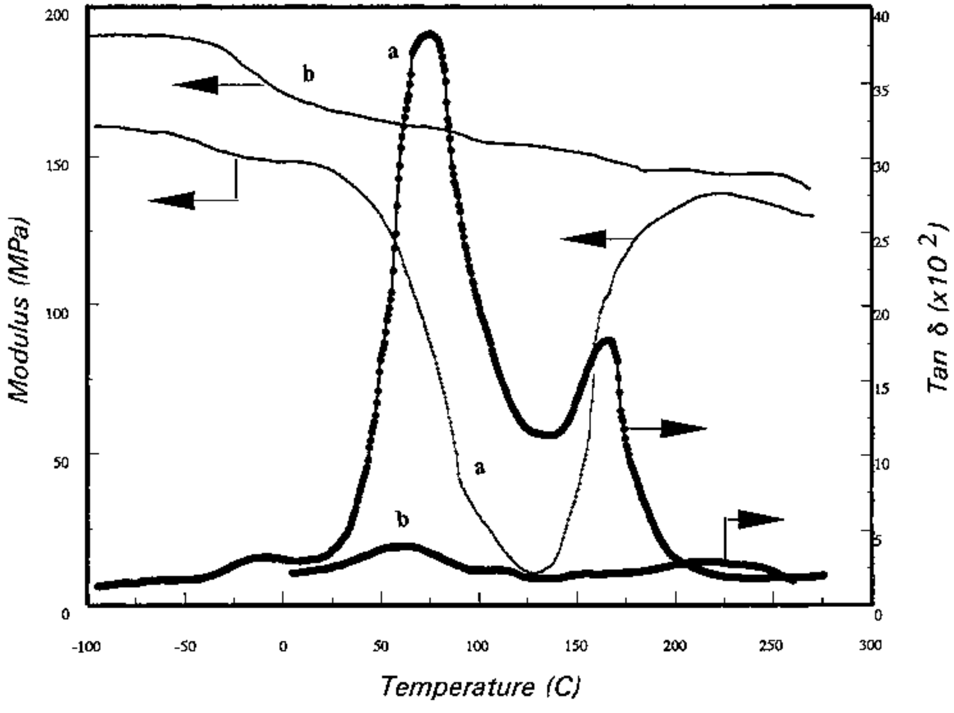


Figure 26 Shear storage modulus (thin lines) and damping (thick lines) for an uncured (a) and cured phenolic adhesive (b).

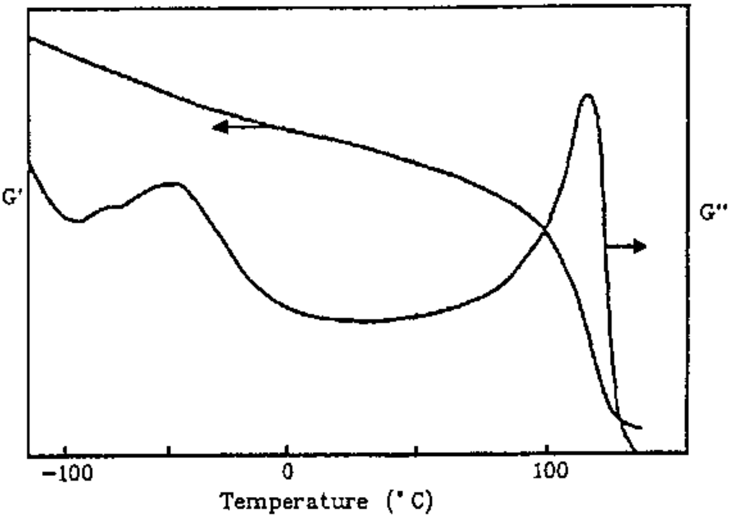


Figure 27 Shear storage modulus, G', and damping, G'', as a function of temperature for a carbon fiber-reinforced epoxy adhesive cured at 120°C.

the composites indicate the degree and direction of reinforcement, in addition to the degree of cure in the matrix of the polymer.

III. CONCLUSIONS

The example cited in this chapter clearly establish that physical analysis techniques, such as GPC, FTIR and Raman spectroscopy, NMR, DSC, thermogravimetric analysis (TGA), and DMTA, are broadly applicable in adhesive research, product development, manufacturing, and quality control or assurance programs. Unfortunately, space constraints have prevented detailed discussions of array of techniques that further enhance the utility of all the physical analysis techniques that were introduced here. Discussion of these can be found in many of the references cited in this chapter.

It has become apparent that, in most instances, no single technique will be available to give totally unambiguous information. Thus, it is frequently desirable to use several different techniques to study a specific adhesive to obtain detailed information for a particular property. The more techniques to which a problem can be exposed, the greater the chance of a solution. In some cases it may be necessary to conduct analysis or characterization with two or more techniques simultaneously.

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15

Fracture of Adhesive-Bonded Wood Joints

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I. INTRODUCTION

Adhesives are arguably the most important fastening system used with forest products. Large volumes of adhesives are used successfully in wood-, particle-, and fiber-based industries. In fact, large and important industries such as panel products would not exist without adhesives. However, the sometimes unpredictable and misunderstood behavior of wood–adhesive joints, particularly fracture, is a major constraint to improving the performance of existing products and the development of new wood–adhesive marriages. In this chapter I briefly examine current understanding of fracture mechanisms in wood–adhesive joints. The discussion is limited to joints bonded with those adhesives having sufficient strength and rigidity to cause fracture in the wood adherends. Primarily, these are the rigid, thermosetting adhesives such as phenol and urea–formaldehyde, nonrigid epoxy and thermosetting poly(vinyl acetate) adhesives, and some thermoplastic types such as poly(vinyl acetate).

The fracture of strong wood–adhesive joints (e.g., in the catastrophic rupture of a large laminated beam) may be viewed (and heard) as a macrocracking process. It may also be viewed microscopically and heard by acoustic emission technology in flakeboard as a microcracking process resulting from shrinkage. These examples are not meant to imply that beams do not fail by microprocesses or that particleboard does not fail by macro processes. Both of these examples of fracture begin with the microscopic initiation of a crack at some flaw in the material or, in this case, the bonded joint.

The initial flaw can be a discontinuity, such as a void, or an abrupt change in material properties. By nature, wood contains innumerable discontinuities, such as the cell cavity and transition zones between cell wall layers. An adhesive may contain air bubbles or fillers with properties different from the resin. A rough wood surface may not be completely wetted by the adhesive, leaving voids at the interface. The adhesive and wood also have different mechanical properties. When a joint or bonded material is subjected to some force, the resultant stress is heightened or concentrated around the discontinuities far above the average stress in the joint or material. Fracture results

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when the stress at a discontinuity reaches the ultimate stress or strength of either the adhesive, the adherend, or the interface.

The stress conditions around a cracklike discontinuity can be described by the stress intensity factor (K), which is a function of the applied load, the size of the cracklike flaw, and the material. Fracture occurs when the stress intensity factor reaches a critical level, called the critical stress intensity factor or fracture toughness (K_c). Fracture mechanics relates the applied stress at which a material fractures to the critical stress intensity factor and the critical flaw size of the material:

$$\sigma_a = \frac{K_c}{\pi a}$$

where σ_a is the applied stress at fracture, K_c the critical stress intensity factor, and a the crack length or flaw size. The stress intensity factor has been found useful for describing the fracture behavior of many materials. However, the stress intensity surrounding discontinuities in adhesive joints is extremely difficult to define because of the dissimilar materials combined in the joint. Therefore, the sensitivity of adhesive joints to stress and discontinuities is usually measured and described in terms of the energy required to initiate a crack or the energy released in forming a new crack surface (G_c) (Fig. 1). The critical stress intensity factor K_c and G_c are related through the elastic properties of the material:

$$G_c = \frac{K_c^2}{E}(1 - \nu^2)$$

where E is the tensile modulus of isotropic adherends and ν is Poisson's ratio of adherends.

The crack initiation energy can readily be determined from a mode I cleavage test using a double cantilever beam specimen [1,2]. This method has been applied to wood–adhesive joints by many researchers [3–17]. The test requires the beam compliance (C), load at crack initiation (P_c), crack length at initiation (a), specimen thickness (t), and change in beam compliance ($dC/da =$ change in displacement of load points/change in crack length) (Fig. 1b):

$$G_c = \frac{P_c^2}{2t}\frac{dC}{da}$$

Anderson and others [18] have reviewed these and other fracture test methods for evaluating adhesive bonds.

The load or force that causes stress around a discontinuity may be applied externally to a material or structure. More often, in bonded joints the force arises from differential shrinkage and swelling of the bonded members or particles. In adhesive joints and most wood products, forces tending to cleave the joint (mode I loading) are of primary importance. Sliding shear (mode II) and torsional shearing (mode III) forces are less important. However, most wood joints experience a combination of mode I with either mode II or mode III shear.

Whereas the fracture of bonded joints is due to the presence of critical discontinuity in a field of stress, the stress intensity or crack initiation energy of bonded joints and materials at which fracture occurs is also a function of the properties of the wood and the adhesive, the environment at a given time, changes in the environment, and external forces on the joint or bonded material. These relationships are explored in the following sections.

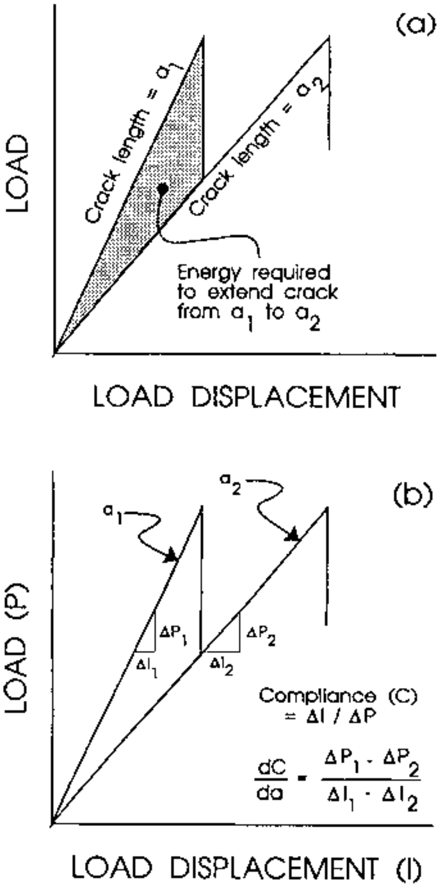

Figure 1 (a) Energy expended in forming new crack surface (shaded area), determined as the difference in the area under the load–displacement curve before crack extension (a_1) minus the area of the load–displacement curve after crack extension (a_2); (b) calibration procedure for determining the change in beam compliance with change in crack length (dC/da).

II. FRACTURE BEHAVIOR

A. Wood

Since wood fracture usually dominates the performance of well-made joints, it is worthwhile before focusing on the bonded joint and the influence of the adhesive to examine how wood itself fractures. At the molecular level, Porter [19] found that wood fractures in the amorphous, water-accessible regions of the cell wall rather than in the crystalline regions. These regions are also most susceptible to change as a result of varying temperature, moisture content, and chemicals. At the microscopic level, wood fractures in different locations depending on the type of cell, direction of load, temperature, moisture content, speed of test, grain angle, wood pH, and aging.

Anatomical features such as the S1, S2, and S3 layers of the cell wall (Fig. 2) are especially important in the fracture of wood and wood–adhesive joints. There are three general types of fracture at the microscopic level [20]: transwall, intrawall, and intercellular

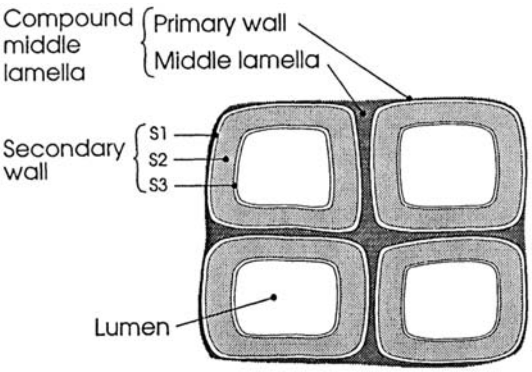

Figure 2 Transverse cross section of four wood cells showing the compound middle lamella joining them, the three layers (S1, S2, and S3) of the secondary wall, and the cell lumen.

(Fig. 3). Transwall cracks may be parallel to the longitudinal cell axis (Fig. 3a) or transverse (Fig. 3d), but in either case the cell lumen is exposed. Transwall fractures are common in thin-walled cells such as softwood earlywood tracheids, hardwood vessels, and parenchyma cells. Longitudinal transwall fracture of thick-walled latewood cells is unusual. When such fracture occurs, it is extremely fibrous and is called fine-fiber failure [21]. Transverse transwall fracture (Fig. 3d) is rare in thick-walled cells (such as hardwood fibers and softwood latewood tracheids) as a result of their great tensile strength parallel to the cell axis. Such fracture does occur in compression wood of softwoods and at the tips of splinters in tough wood. These thick-wall cells are more likely to produce a diagonal combined shear and tension transwall fracture following the helical angle of the S2 layer microfibrils (not pictured). This is the manner in which a crack grows across the grain in tough wood. Intrawall fracture (Fig. 3b) is also very common in thick-walled cells. An intrawall crack travels within the cell wall, leaving the cell lumen intact.

Intrawall fracture initiates at the discontinuities between the layers of the secondary wall (Fig. 2). The cell wall consists of microfibrils of cellulose helically wound around the longitudinal cell axis. The cell wall layers are differentiated by the angles of the microfibrils in each layer. The microfibrils in the outermost (S1) and innermost (S3) layers are wound at a large angle around the longitudinal axis of the cell. The microfibrils in the S2 layer sandwiched between the S1 and S3 layers are wound at a small angle around the longitudinal cell axis. The transition between these layers is often gradual, yet it still presents a material discontinuity. Mark [22,23] clearly pinpointed the S1–S2 interphase as the site of crack initiation in the fracture of solid wood. Intercellular cracks (Fig. 3c) travel in the compound middle lamella (CML), leaving the secondary wall and cell lumen intact.

Investigators have shown the preferential fracture of wood at various cell wall interfaces, depending on the temperature at fracture. Woodward [24] found fracture predominately in the S1 layer in the range from 20 to 77°C. At the lower end of the scale, the crack path jumped back and forth across the middle lamella from the S1 layer of one cell to the S1 layer of a contiguous cell. At the higher temperature, the crack tended to stay within the S1 of a given cell from one end to the other. Furthermore, fractures of the lignin-rich CML are rare at normal temperatures, but they are likely to occur under hot, wet conditions [20].

On a larger scale, the type of fracture varies with the density of the tissue through which a crack is growing. Fracture in the longitudinal–tangential (LT) plane is dominated

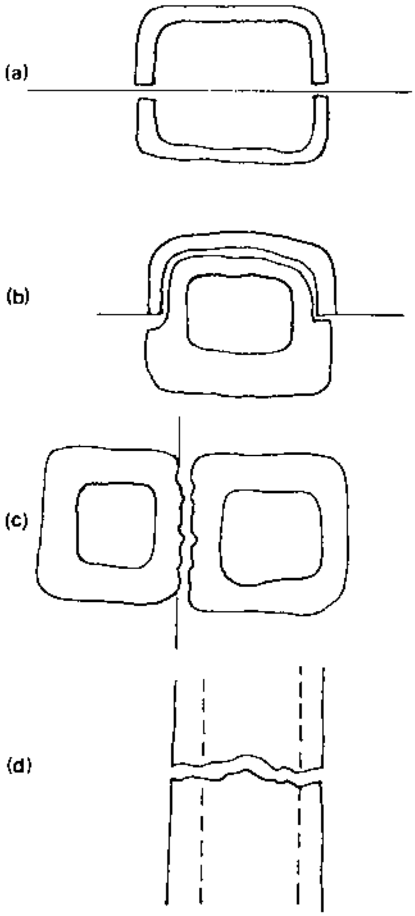

Figure 3 Schematic diagrams of fracture modes in wood: (a) longitudinal transwall; (b) intrawall; (c) intercellular; (d) transverse transwall.

by longitudinal transwall fracture of the first-formed earlywood cells. A mixture of transwall and intrawall fracture is common in the longitudinal–radial (LR) and planes intermediate to the LR and LT planes as a result of alternating high- and low-density bands of the earlywood and latewood cells. Fracture patterns similar to those described for wood have been observed in solid wood joints and in wood particles bonded with droplets of adhesive [25,26].

B. Adhesive

The fracture toughness of wood in terms of crack initiation energy ranges from 50 to 1000 J/m^2, whereas the crack initiation energies for typical thermosetting polymers are in the range 100 to 300 J/m^2 [27]. It seems interesting that wood joints bonded with conventional thermosetting adhesive also have fracture toughness values of about 100 to 300 J/m^2 (Table 1). Much higher values are possible if the adhesive is toughened by the addition of fillers or plasticizers.

Table 1 Fracture Toughness for Wood–Adhesive Joints

Mode	Adherend	Adhesive[a]	Fracture toughness K_{Ic} (kPa m$^{1/2}$)	 G_{Ic} (J/m^2)	Ref.
Cleavage	Beech	PVA	—	1206	11
		PVA/phenol	—	390	
		PF	—	170	
		RF/filler	—	390	
		EP/P	—	200	
		EP/60P[b]	—	1180	
		EP	—	200–340	13
		EP/20P	—	280–460	
		EP/40P	—	460–790	
		EP/60P[b]	—	450–1070	
	Douglas-fir	UF/filler	—	250	6
		EPI	—	900	
		ISO	—	300	
		PRF	—	800	
		PF	—	200	
		PF/PVA	—	700	
	Aspen	PRF	255	—	28
	Unknown	UF/filler	—	530	29
		UF/PVA	—	640	
		PF/PVA	—	640	
		UF/MF/filler	—	700	
		PRF	—	870	
	Yellow poplar	Casein	380	—	30
		EP	430	—	
		PRF	470	—	
		PVA	680	—	
	Spruce	PVA	310	—	
	Douglas-fir	PVA	550	—	
	Southern pine	PVA	560	—	
	Walnut	PVA	600	—	
	Ash	PVA	680	—	
	Maple	PVA	790	—	
	Western red-cedar	PRF	280	—	31
		Solid wood	180	—	
	Southern pine	PRF	520	—	
		Solid wood	430	—	
	Hard maple	PRF	690	—	
		Solid wood	490	—	
	Douglas-fir	Solid wood	410	—	32
	Southern pine				33
	Earlywood	PRF	520	—	
	Latewood	PRF	400	—	

(*continued*)

Table 1 (Continued)

Mode	Adherend	Adhesive[a]	Fracture toughness K_{Ic} (kPa $m^{1/2}$)	Fracture toughness G_{Ic} (J/m^2)	Ref.
	Southern pine	Solid wood	494	—	34
	Douglas-fir FB[c]				
	560 kg/m^2	PF	88	—	35
	800 kg/m^2	PF	350	—	
	Douglas-fir LVL[c]	PF	360	—	
	Douglas-fir	PRF	290	—	36
	Southern pine	PRF	480	—	
Sliding shear	Kaba	PVA	—	1280	37
	Southern pine	PRF	1670	—	36
	Douglas-fir	PRF	1830	—	
	Southern pine	Solid wood	1980	—	34
Torsion shear	Radiata pine	PRF	—	480	38

[a] Adhesive abbreviations are as follows: EP, amine-cured epoxy; P, polysulfide rubber flexibilizers; EP/20P, EP/40P, and EP/60P, amine-cured epoxy with 20, 40, and 60 parts polysulfide flexibilizer; EPI, emulsion polymer isocyanate; ISO, isocyanate; MF, melamine–formaldehyde; PF, phenol–formaldehyde; PF/PVA, phenol–formaldehyde flexibilized with poly(vinyl acetate); PVA, poly(vinyl acetate); PRF, phenol/resorcinol–formaldehyde; RF, resorcinol–formaldehyde; UF, urea–formaldehyde; UF/filler, UF with wheat flour; UF/MF/filler, UF/MF copolymer with wheat flour.

[b] Thick layer.

[c] FB, flakeboard; LVL, laminated veneer lumber.

Plasticizers used to reduce the modulus of thermosetting adhesives to match more closely the wood moduli perpendicular to the grain have a marked effect on the fracture toughness. The addition of 20 parts of poly(vinyl acetate) to phenol–formaldehyde (PF/PVA) adhesive increased mode I fracture toughness by 340%, from 200 J/m^2 to almost 700 J/m^2 (Table 1) [6]. Less rigid thermosetting adhesives, such as emulsion polymer isocyanate (EPI), produced joints with toughness as high as 900 to 1000 J/m^2 (Table 1) [6]. In this case the toughness varied with the amount of isocyanate cross-linking agent. Toughness first increased as the amount of isocyanate was increased from 0 to about 6 parts per 100 parts of emulsion polymer, but then decreased with further additions (not shown in Table 1). When Takatani and Sasaki [13] added polysulfide rubber flexibilizer (P) to epoxy resin (EP) adhesive, the fracture toughness of bonded joints increased from about 200 J/m^2 to 300 J/m^2 (Table 1). The toughest joints were those made with thick adhesive layers, in which case the crack initiation energies rose as high as 900 to 1200 J/m^2 (Table 1). Many other studies showed that flexible or semirigid adhesives produce joints having higher short-term strength and fracture toughness compared to rigid adhesives [13,31,39,40]. Takatani and others [11] observed that flexible adhesive improves the fracture toughness of joints made with rigid adherends such as spruce, beech, and oak; however, rigid adhesive improves the toughness of joints made with flexible adherends such as balsa.

Very high fracture toughness values for wood–adhesive joints can be attributed to a combination of adhesive plastic deformation and reduction of microcracking of the wood around the crack tip. A flexible adhesive layer, especially a thick layer, distributes the

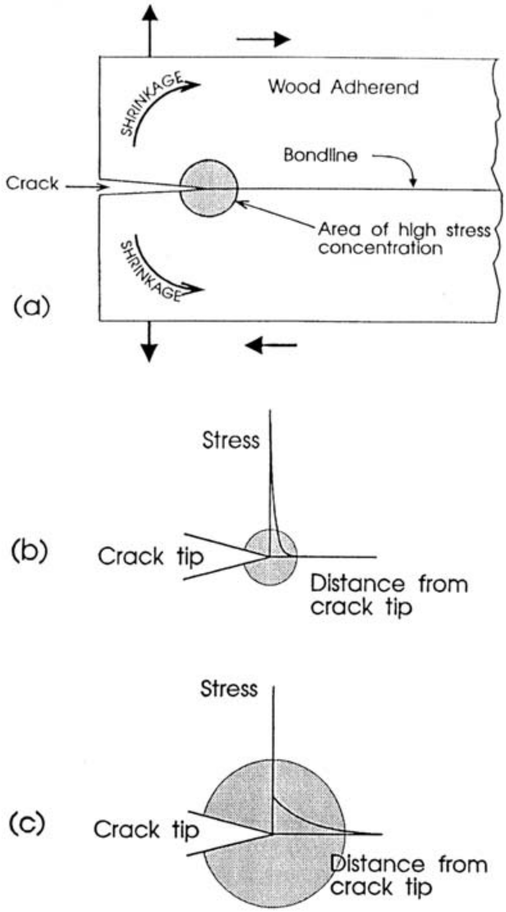

Figure 4 (a) Fracture process zone (area of stress concentration) surrounding the area or volume of the bondline immediately ahead of the crack tip when the joint is subjected to cleavage, shear, or shrinkage forces; (b) small process zone and high stress concentration with rigid adherend and adhesive; (c) large process zone and low stress concentration with flexible adhesive and adherend.

concentrated stress over a larger area (volume) and lowers the level of the peak stress (Fig. 4). This apparently inhibits microcracking in the adjacent wood. Reduction of microcracking is indicated by the lower percentages of wood failure and lower counts of acoustic emission [41] per unit of new fracture surface in joints made with nonrigid adhesives compared to rigid thermosetting adhesives.

The fracture surface of a conventional urea–formaldehyde adhesive (Fig. 5) shows distinctive smooth brittle fracture surfaces formed when the adhesive layers cracked as a result of shrinkage stress that developed during cure [42]. A moderately toughened urea–formaldehyde bonded joint (Fig. 6) shows three distinct types of fracture surface arising under differing conditions: (A) cure shrinkage, (B) vacuum-pressure soak-dry (VPSD) treatment, and external loading to fracture (C). The rough surfaces are contrasted to the smooth cure-shrinkage crack surfaces. The crack caused by cyclic VPSD treatment (B) shows signs of plastic deformation. However, the plastic deformation does not have any directional properties. It appears to have occurred when the adhesive was in a

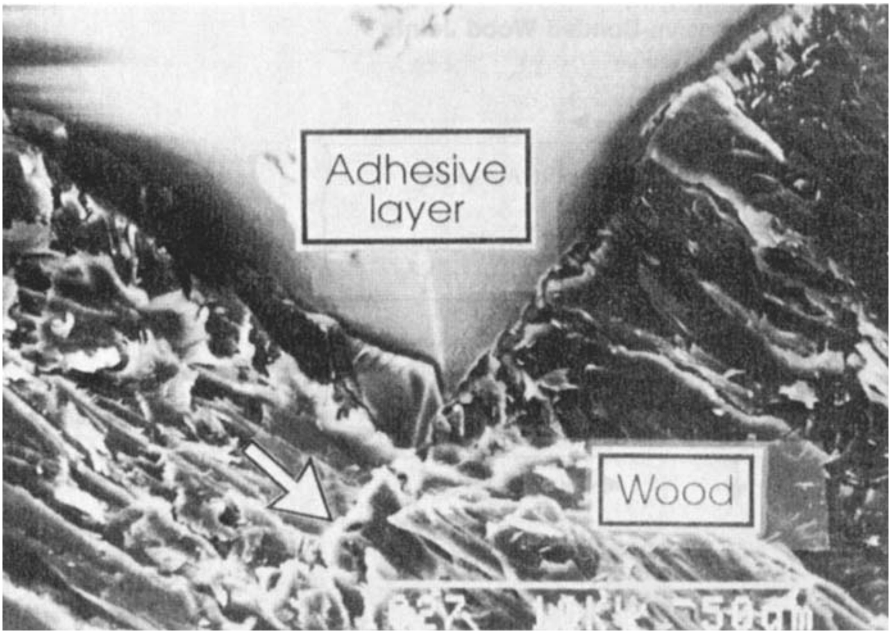

Figure 5 Smooth (glassy) fracture surface of a brittle urea–formaldehyde adhesive layer fractured by stress developed in the adhesive layer as it cured. Note the tensile rupture of the cells at the wood surface (arrow) caused by the cure-shrinkage crack in the adhesive.

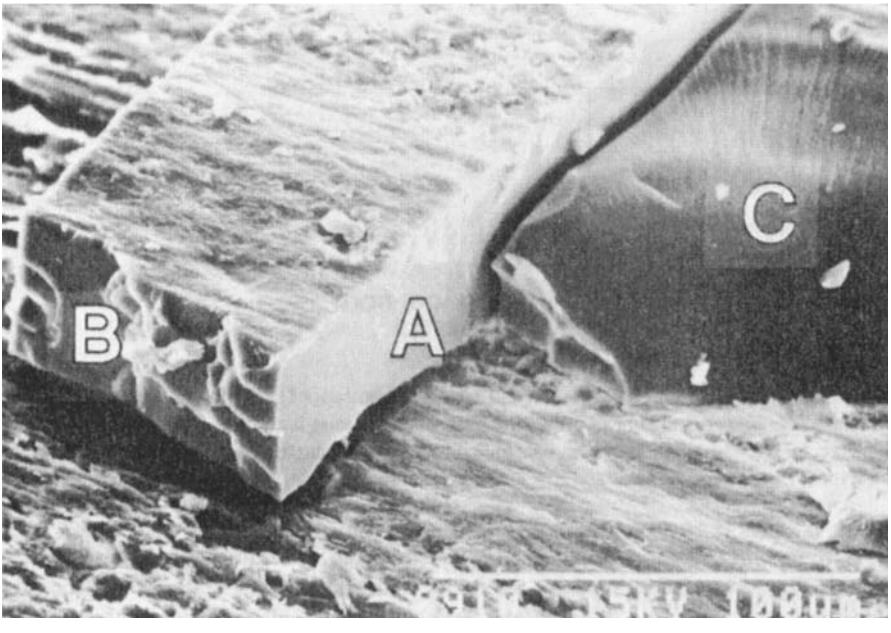

Figure 6 Fracture surfaces of an amine-modified urea–formaldehyde adhesive showing three distinct types of fracture surface: (A) cure-shrinkage crack surface; (B) vacuum-pressure soak-dry crack surface; (C) crack surface created during loading to failure.

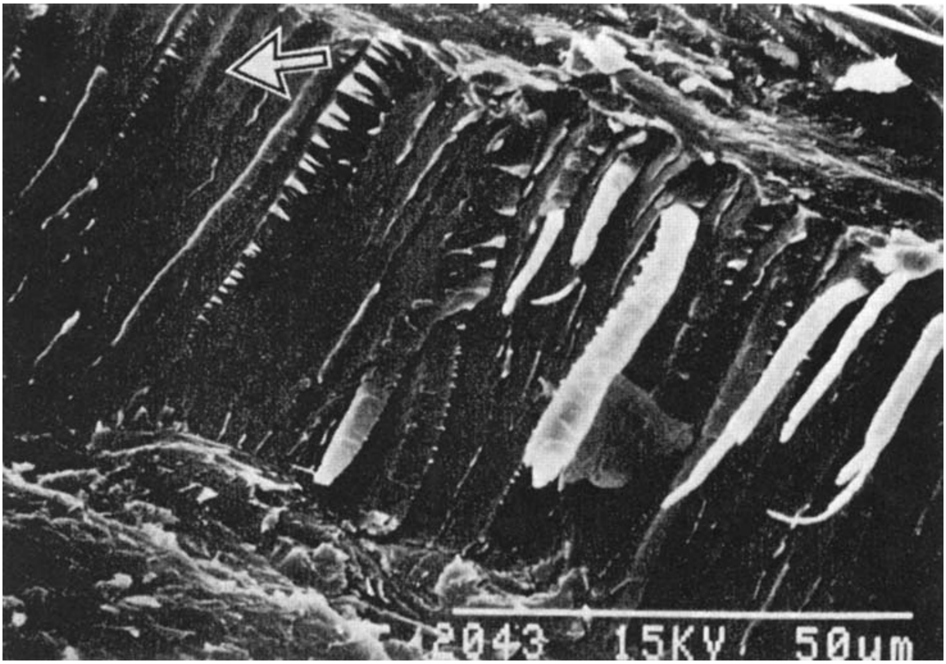

Figure 7 Fracture surface of a phenol–formaldehyde adhesive showing striations (arrow) indicative of plastic deformation, yielding, and toughness.

weakened state, such as might occur from the absorption of water. Crack surface (C) occurred during testing when the material was dry and strong. Initially, it propagated at a high rate from the adhesive's interface with the lower adherend toward the upper interface. As the crack slowed, the adhesive deformed plastically, leaving striations in the upper corner. The fracture surface (C) suggests strength and toughness. In contrast, a phenol–formaldehyde adhesive layer (Fig. 7) shows extreme plastic deformation and directionality. Both these traits suggest a tough, strong adhesive layer. In contrast to the blocky fracture surface that resulted from an adhesive layer that was precracked by cure shrinkage (Fig. 8), the phenol–formaldehyde adhesive remained uncracked until externally loaded to failure (Fig. 9). In addition to the plastic deformation seen at high magnification (Fig. 7), there are no preexisting cracks in the adhesive layer. During testing to failure, when the primary crack jumps across the adhesive layer from one interphase to the opposite, the cracked adhesive surface is most often sloped (arrow).

A rigid brittle thermosetting adhesive such as the unmodified urea–formaldehyde shown in Figs. 5 and 8 does not have the ability to arrest a growing crack, as evidenced by extensive brittle fracturing even before testing. A modified, toughened thermosetting adhesive does have this ability. Figure 10 shows an arrested crack in a fillet of amine-modified urea–formaldehyde adhesive in Southern pine particleboard subjected to 10 VPSD cycles. The rounded crack tip shows plastic deformation and blunting. A new sharp notch can be seen forming at the root of the blunt crack tip. The ability to blunt cracks in the adhesive layer or in the fillet of adhesive between particles or flakes tends to force fracture in the wood, as illustrated in Fig. 11 and discussed by River and others [42].

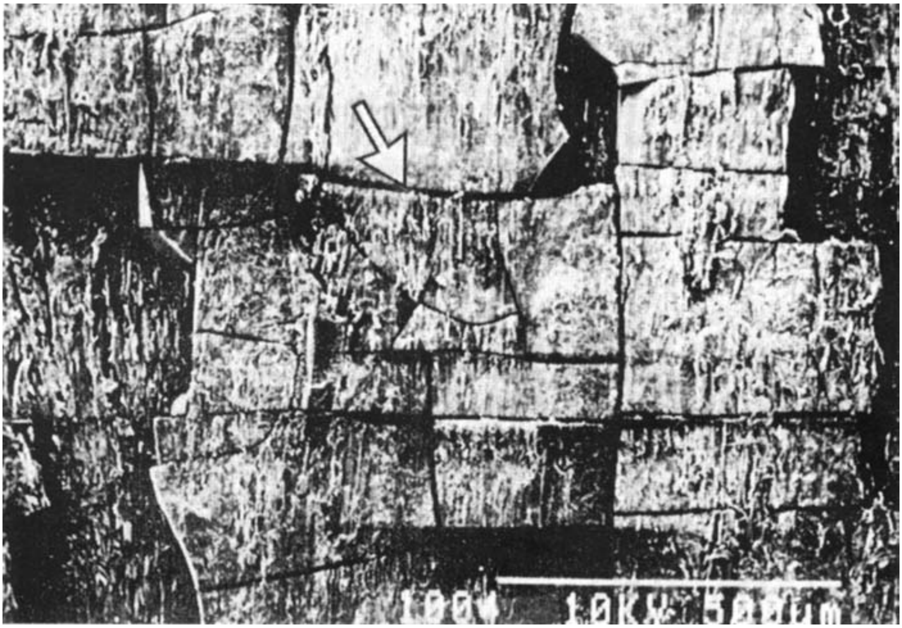

Figure 8 Fracture surface pattern produced by cleavage of a bondline weakened by precracking (arrow) of the adhesive layer as it shrinks during cure (unmodified urea–formaldehyde adhesive).

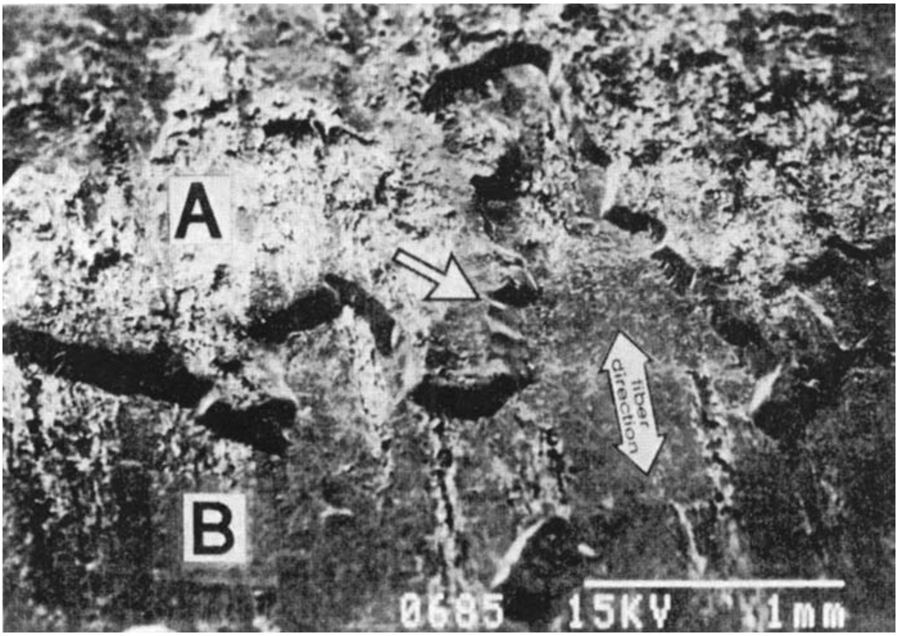

Figure 9 Overview of fracture surface of phenol–formaldehyde bonded joint showing exposed adhesive layer (A) without preexisting cure-shrinkage cracks and surface of lower adherend (B). The sloped test fracture surfaces (arrow) characteristic of phenol–formaldehyde and toughened urea–formaldehyde adhesive layers show where the crack jumped from one interphase to the opposite as the crack traveled in the fiber direction.

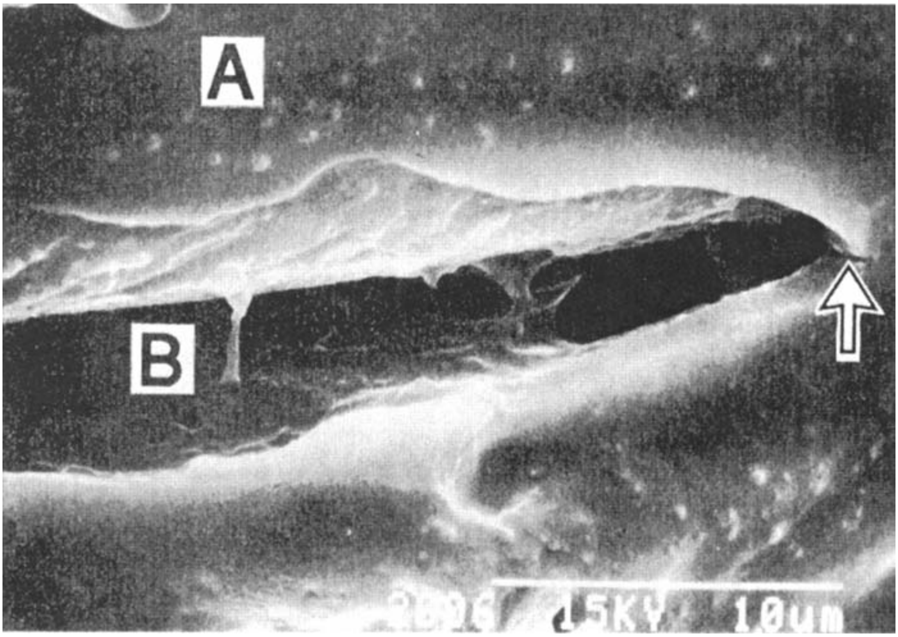

Figure 10 Fillet of adhesive (A) of amine-toughened urea–formaldehyde adhesive in Southern pine flakeboard showing an arrested crack (B) after 10 vacuum-pressure soak-dry cycles. Note the plastic deformation and blunting at the rounded crack tip and the beginning of new crack growth in the sharp notch at the end of the blunt crack tip (arrow).

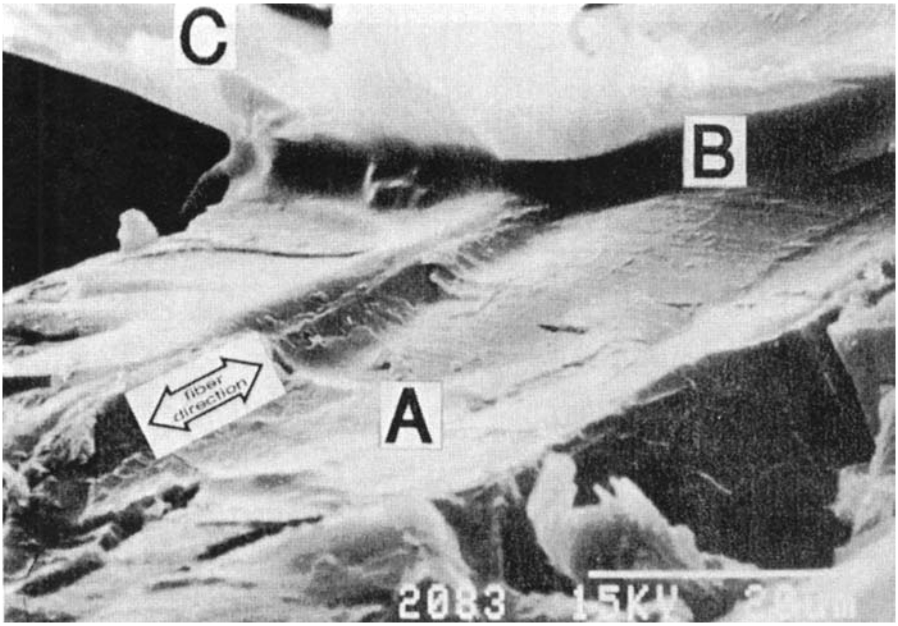

Figure 11 Fracture surface of Southern pine flakeboard showing unfractured fillet of phenol–formaldehyde adhesive: (A) original surface of wood flake; (B) adhesive fillet; (C) fragment of S1 layer of secondary wall from second wood flake.

C. Joints

1. *Crack Initiation*

Fracture of wood and bonded joints and materials begins at a geometric or material discontinuity where displacement of the adherends (due to external or internal stress) creates the greatest stress concentration and where either the adherend or the adhesive is the weakest. Examples of geometric discontinuities in adhesive-bonded wood joints are the square-cut ends of overlapped adherends, voids at the tips of fingers in finger joints, voids in reconstituted boards, voids in the adhesive layer, and even the square-cut ends of individual fibers. Examples of material discontinuities are the juncture of adherends of different density, the interface between adhesive and adherends of differing moduli, earlywood and latewood bands of widely different density, and the transition zone between the low fibril angle S1 and high fibril angle S2 layers of the cell wall. When adhesive bonds near this zone are sheared, the microfibrils in the S1 layer appear to undergo a rolling-shear failure [43]. Adhesive penetration of the cell wall was shown to affect fracture positively in the vicinity of the S2–S3 interphase [44]. An epoxy adhesive applied soon after mixing was of sufficiently low molecular weight to penetrate the cell wall from the lumen. Subsequently, when the adhesive layer was stripped from the wood surface, fracture occurred in the S2 layer. The same adhesive applied some hours after mixing was higher in viscosity (and thus molecular weight) and did not penetrate the cell wall as deeply. In this case, fracture occurred in the S3 layer and S2–S3 interphase.

The idea of an intrinsic or inherent flaw size in wood was explored by Schniewind and Lyon [32] who found the intrinsic flaw to be 3 mm. The same idea was applied to wood-based panels by Ilcewicz and Wilson [45] and to solid-wood joints by Kyokong and others [28]. Ilcewicz and Wilson used a modified fracture model based on Eringen's nonlocal theory [46] to determine the fracture toughness of flakeboard in tension perpendicular to the panel. According to their model, the critical stress intensity factor of the flakeboard is a function of the intrinsic flaw size (which they determined to be 8.6 mm), the intrinsic strength of the board (determined to be 4.5 MPa), and the "characteristic dimension." The characteristic dimension in the original model for the fracture behavior of metal is the atomic distance of the metal. Ilcewicz and Wilson [45] substituted the flake thickness for the atomic distance in their modified model for flakeboard. They found the critical stress intensity factor (K_{Ic}) of the flakeboard was indeed a function of the characteristic dimension as well as the resin content of the board. Furthermore, the effect of flake thickness decreased as the resin content in the board increased from 5% to 11%. Based on this relationship, the authors predicted that K_{Ic} would become independent of resin content at about 17% and at this point the dependency of K_{Ic} would shift from the flake thickness to some anatomical substructure, independent of resin content, such as the average lumen diameter of the cells in the flakes. Similar relationships of fracture toughness to board density, resin content, and particle size were reported by Niemz and Schadlich [47]. It seems clear that the geometric discontinuities in reconstituted materials can be minimized by using lower-modulus, more conformable woods such as aspen rather than oak, thinner flakes or strands, higher compaction ratios, and higher resin content.

Research by Kyokong and others [28] lent credibility to Ilcewicz and Wilson's hypothesis. They applied Eringen's nonlocal theory to solid poplar (*Populus tremuloides*) joints bonded with resorcinol adhesive, substituting the average vessel lumen diameter of aspen (100 μm) as the characteristic dimension. They were able to show that the nonlocal theory using this dimension correlated very closely with the fracture toughness of the joints as determined by classic (local) theory.

In solid wood members, considerable effort is devoted to minimizing geometric discontinuities through the use of scarf and finger joints instead of butt and lap joints. Scarf joints of sufficiently low slope can achieve 85 to 90% of the strength of solid wood [48]. Scarf joints effectively minimize material discontinuities between earlywood and latewood as well as geometric discontinuity. However, uniform-density wood, such as white pine, is likely to produce more efficient scarf joints than wood with growth rings of widely varying density, such as Southern pine. However, 100% efficiency is unlikely to be obtained in any case because of mismatched wood and adhesive properties. Finger joints are less efficient because the flat portion of each finger tip represents a small butt joint and geometric as well as material discontinuity. These can be effectively minimized by cutting sharp rather than blunt tips [49]. Tool wear presents a practical limitation to tip sharpness in machined finger joints, especially in higher-density woods or woods with high–density latewood bands.

Impression finger joints take tip sharpness to the extreme and would seem to approach a well-made scarf joint in freedom from geometric discontinuity. Impression joints are formed by pressing a heated die with knife-edged serrated surfaces into the end-grain surfaces to be joined. This process eliminates damage caused by cutting and has the advantage of producing essentially a side-grain surface for gluing. But because of the maximum compressibility of the wood at the finger tip by the die, impression joints are limited to woods with density less than about 0.5 [50]. Even though many structural woods are lower in density, they possess latewood bands of much higher density. However, elimination of the geometric discontinuity by the impression process densifies the finger tips but not the valleys; this results in a material discontinuity and thus stress concentration. Fracture typically occurs across the roots of the fingers as a result of these closely spaced stress concentrations.

2. *Crack Growth Stability*

Once it initiates, a crack may propagate in one of several ways. It may fracture completely and catastrophically as glass (unstable) (Fig. 12a), it may fracture in several moderate

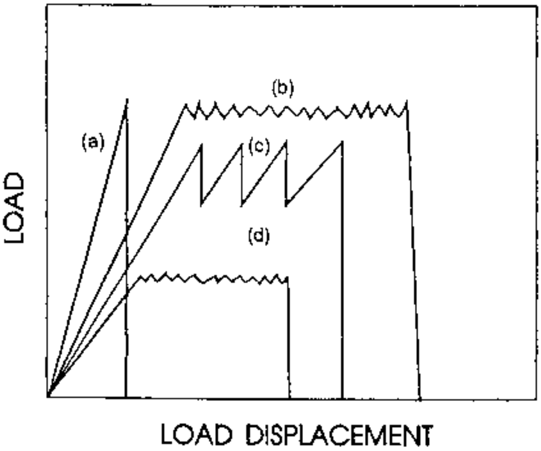

Figure 12 Characteristic crack growth behavior and fracture toughness of wood adhesive joints: (a) strong/unstable; (b) strong/stable; (c) strong/moderately unstable; (d) weak/stable.

increments of growth with intermediate arrest points (stable/unstable or stick/slip) (Fig. 12c), or it may fracture by tearing or continuous small increments (stable) (Fig.12b and d). The preferred joint is that which requires a high crack initiation energy and produces stable crack growth (Fig. 12b). Such a joint requires a great amount of energy for complete failure to occur.

Polymers, including adhesives, exhibit these behaviors. As such, an adhesive influences the fracture behavior of the joint in several ways. If the adhesive is formulated, applied, or cured improperly, its cohesive strength and toughness may be lower than that of the wood; if the adhesive does not properly wet or penetrate the wood, the adhesion strength may be lower than the cohesive strength of the wood. Under these circumstances, the crack will travel preferentially in the weaker adhesive layer or joint interface. The crack initiation energy will be low, and crack growth will be stable with little difference between the crack initiation and arrest energies. Such behavior would be expected from a starved or filtered joint or one between inactivated wood surfaces. Similar behavior would be expected from a joint made with adherends whose surfaces have been damaged by crushing during machining or by chemical degradation. In this case the crack travels in the wood or wood interphase but does not deviate far from the plane of the wood surface. The fracture surface produced by this type of crack growth behavior is often termed *shallow wood failure*. Poor adhesion also produces this type of crack growth behavior and shallow wood failure.

Stable/unstable or stick/slip crack growth occurs when the adhesive is properly formulated, applied, and cured and the grain direction is purposely directed toward the bondline. The adhesive is stronger than the wood and tough to moderately tough. The weak planes in the wood force the crack toward the bondline. Under these conditions, the crack will travel in the wood near the interphase, or in the interphase, and occasionally cross the adhesive layer [42]. The crack initiation energy will be moderately high to high, depending on the plasticity and strength of the adhesive and the species of wood. As the joint is loaded, some energy will be stored in elastic deformation of the adhesive and the adherends, and some will be consumed in plastic deformation and microcracking in the wood surrounding the crack tip. Once crack growth begins, the crack tip will advance and consume the stored energy at a high rate. The crack will arrest when the stored energy level drops below a certain level. Arrest will likely not occur in the adhesive or the interphase but in a region of lower wood density where a large amount of energy is rapidly consumed. The crack tip may remain fixed in this region or grow slowly by microcracking ahead of the primary crack tip, as additional energy is stored in the adhesive and the adherends. The later scenario seems more probable in wood joints, considering the weak interphase between the S1 and S2 layers. Rapid propagation occurs when the stored energy again reaches the critical level. This type of joint is created specifically for testing the fracture toughness of bonded wood joints. It also occurs at random in real joints as a result of the natural grain variation and variation in the plane of cut. The fracture surface resulting from this type of joint and crack growth behavior is typically interphasal or shallow-wood, although somewhat deeper wood failure may occur in low-density regions. It is also typified by occasional to frequent crossings of the adhesive layer from one interphase to the other. These crossings are due to variations of the strength and modulus of the adherends on either side of the adhesive layer. Crossings are facilitated by a precracked (cure-shrinkage cracked) adhesive layer (Fig. 8) or hindered by a continuous tough adhesive layer (Fig. 9).

Stable crack growth also occurs when the adhesive is strong and tough and has established good adhesion, the wood surface is sound, and the grain angle is parallel or away from the bondline. Under these conditions, the crack deviates into the wood according to the mechanisms described by Wang and others [51] and Knauss [52] and remains there. The fracture toughness of the joint is essentially determined by the toughness of the wood. The fracture surface does not necessarily follow the plane of the bondline. It is more likely to follow the grain angle, producing what is often termed *deep wood failure*. In this type of fracture, the crack advances by continuous transwall cracking of the thin-walled cells and intrawall or diagonal transwall cracking of the thick-walled cells. Stable crack growth will also occur when the adhesive establishes good adhesion but is weaker than the wood, as for example with elastomeric and some thermoplastic adhesives (100% adhesive failure). These adhesives are too weak to store sufficient energy in the adhesive or the adherends to support rapid crack propagation. Instead, the adhesive tears slowly when it reaches its ultimate tensile stress. In testing, this rate is controlled by the rate of crosshead movement. There is essentially no difference between the crack initiation and crack arrest energies.

The brittleness index [53] is a normalization of the energy released during a period of rapid crack growth with respect to the energy stored in the joint just at the onset of crack growth. It provides a quantitative measure of the behavior described here.

$$I = \frac{G_c - G_a}{G_c}$$

where I is the brittleness index, G_c the energy required to initiate crack growth, and G_a the energy remaining at crack arrest. According to this measurement, an ideally brittle (Fig. 12a) (unstable) material that fails suddenly and completely will have an index (I) value of 1 and an ideally plastic (stable) material that fails by continuous tearing (no difference between initiation and arrest energies) will have an I value of 0. Practically, most wood–adhesive joints fail by a combination of unstable and stable crack growth and have I values between 1 and 0. Joints tending toward stable crack growth (Fig. 12b and d) will have I values in the range 0.8 to 0.95. Joints tending toward more unstable behavior (Fig. 12c) will have I values in the range 0.4 to 0.8.

The stability of crack growth behavior was also quantified by acoustic emissions (AEs) per unit of new surface area formed by crack propagation [41]. Large bursts of AEs occurred during unstable crack growth. Fewer but continuous AEs occurred during stable crack growth. A joint producing 100% bursts of AE during fracture would correspond to a brittleness index of 1 and be perfectly brittle. A joint producing 100% continuous AE would correspond to a brittleness index of 0 and be perfectly plastic. The ratio of burst to continuous AE provides a measure of the stability or instability of the crack growth. The burst to continuous AE ratio of bonded wood joints fell in the range of 0.5 (quite stable) to about 5 (quite brittle). The maximum crack initiation energy tended to be associated with a ratio of about 1.3 times as many burst AEs as continuous AEs.

In the Suzuki and Schniewind study, the fracture toughness of joints made with a variety of conventional, modified conventional, and nonconventional wood adhesives was linearly associated with the AEs per unit area of new crack surface formed during testing. The maximum fracture energy and AEs as a function of various modifications such as filler content, fortifier, and adhesive layer thickness were clearly evident from the relationship. Two different relationships between fracture toughness and AEs were also evident. Nonrigid adhesives, including epoxy, poly(vinyl acetate) (PVA), emulsion polymer isocyanate (EPI), and PVA-modified phenol–formaldehyde (PF), were approximately 2.8 times tougher at a given AE count per unit of area as were conventional rigid thermosetting adhesives, including urea–formaldehyde (UF), PF, phenol–resorcinol formaldehyde

(PRF), and isocyanate. The less rigid adhesives absorb or dissipate more energy before cracking than do the rigid adhesives. Viewed another way, for a given level of energy expended to create a new fracture surface, a joint bonded with a rigid adhesive produced approximately 20 times as many acoustic events (microcrack formations) as did a joint bonded with a nonrigid adhesive. Obviously, some of these additional events are in the adhesive, but most are in the wood, given a high percentage of wood failure. In a sense, the less rigid adhesive protects the weak S1–S2 interface by reducing the stress concentration at the crack tip.

3. *Crack Deflection*

A natural crack initiated in the center of the adhesive layer in a symmetric joint between symmetric isotropic (metal) adherends will tend to propagate through the center of the adhesive layer. However, in wood joints, there is a strong tendency for the crack to travel in the wood near the joint. This condition should be expected in joints made with the lower-density species or in species with the low-density earlywood such as the Southern pines (*Pinus* spp.). However, wood failure is not uncommon in joints made with high-density species even when there is a starter crack in the adhesive layer before testing. There seem to be some rational explanations for this behavior.

First, a crack will deviate toward one or the other adherend if it is softer (lower in modulus) than the adhesive [51]. This is a common condition in wood joints bonded with rigid thermosetting adhesives. The tension modulus of the wood perpendicular to the grain is typically in the range 400 to 1200 MPa [54], while the tensile modulus of adhesives used with wood will be in the range 1200 to 4700 MPa at the same moisture level [55–57].

Second, shear forces that develop in the vicinity of the crack tip direct it toward one or the other adherend [52]. Shear forces arise in a cleavage specimen from unequal moduli of the two adherends and the adhesive. Unequal moduli of two wood adherends is virtually certain as a result of the variable morphology and density of any two pieces of wood. When a load is applied to the cracked joint, this inequality induces shear stress around the crack tip and thereby directs it toward one adherend or the other.

Once the crack enters the wood as a result of these mechanisms, it will travel preferentially along the weak radial–longitudinal (RL) and tangential-longitudinal (TL) planes. Unless these planes again intersect the bondline, the adhesive will not be likely to fracture beyond that point. If the fiber direction in both adherends is oriented toward the bondline (this is done purposely in some fracture toughness test methods), the crack will be forced to remain close to the adhesive layer. In this case the local density and modulus of the two adherends seems to determine on which side of the adhesive layer the fracture occurs. Since these properties vary continually, it is not unusual for the crack tip to jump repeatedly from one adherend, across the adhesive layer, to the opposite adherend according to the mechanism of Wang and others [51] and Knauss [52]. Given a locale with earlywood on one side of the adhesive layer and latewood on the other side, the crack may not travel preferentially on the earlywood side. Pervasive adhesive penetration of the earlywood may raise the density and modulus to the extent that latewood on the opposite adherend is more amenable to crack growth.

4. *Adhesive Layer Thickness*

Shear strength studies of joints bonded with rigid thermosetting adhesives over many years has resulted in the prescription that the best joints are those with an adhesive layer in the thickness range 0.05 to 0.15 mm. Ebewele and others [3],

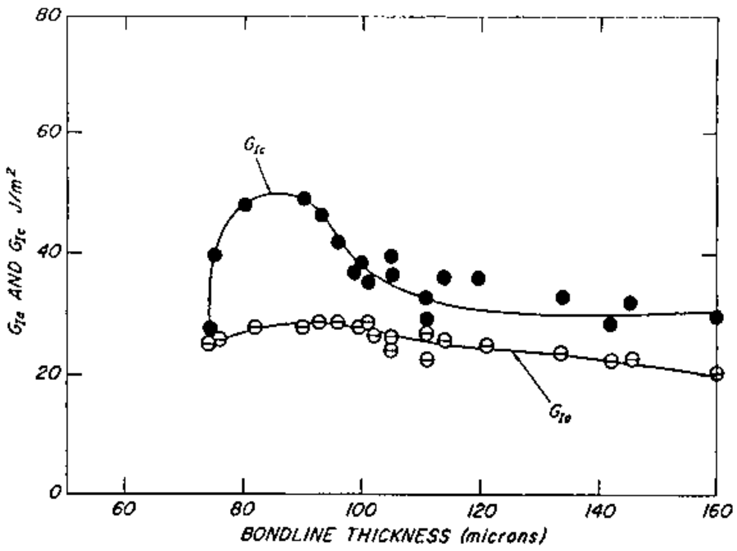

Figure 13 Effect of bondline thickness on the cleavage crack intiation energy (G_{Ic}) and cleavage crack arrest energy (G_{Ia}) of hard maple specimens bonded with rigid thermosetting PRF adhesive. (From Ref. 3.)

for example, found an optimal thickness between 0.07 and 0.08 mm (Fig. 13). Other research based on fracture mechanics [13, 28, 30] has helped to define this relationship, although not its cause. Apparently, below some minimum thickness, a joint is adhesive starved and the interphase is rife with voids. Above the optimum thickness, stress concentrations are heightened by cure-shrinkage stresses in the adhesive layer. The narrow optimal thickness range disappears if the adhesive modulus is greatly reduced. In the study by Takatani and Sasaki [13], an epoxy adhesive was flexibilized by the addition of 20, 40, and 60 parts of polysulfide. These additions decreased the adhesive modulus from 2200 MPa to 1600, 670, and 160 MPa, respectively. The last two moduli are in the range of the tensile modulus of wood perpendicular to the grain used to test fracture toughness (beech, modulus of elasticity MOE = 590 MPa). Joints of the nonflexibilized adhesive had a slight optimum at 0.3 mm thickness; however, there was actually little difference in toughness ($G_{Ic} = 220$ J/m^2) over the entire range of adhesive layer thickness from 0.1 to 1.5 mm. The addition of 20 parts of polysulfide removed the optimum at 0.3 mm thickness and increased toughness to 330 J/m^2. The big change came with the addition of 40 to 60 parts of polysulfide. Although these additions failed to increase toughness of joints with the thin adhesive layer, toughness increased dramatically with each increment of adhesive thickness. In these joints the crack initiation energy increased from about 330 J/m^2 to 1100 J/m^2 in specimens with adhesive layers 1.5 mm thick.

It is probable that very high fracture toughness values in wood joints bonded with thicker, lower-modulus adhesive layers may be due to the enhancement of an existing energy-dissipating mechanism such as microcracking of the wood as well as the adhesive.

5. *Grain Angle*

Structural joints are purposely not designed with the fibers intersecting the plane of the bondline as a result of the weakness of this design. However, this relationship can be of

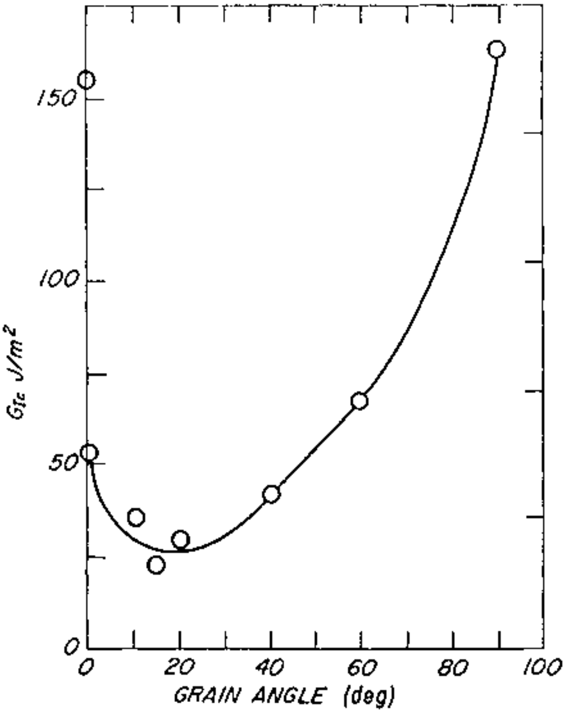

Figure 14 Effect of adherend grain angle to the bondline on the fracture toughness of bonded wood joints in cleavage. (From Ref. 3.)

great importance in the delamination of structural joints, where there are unavoidable local grain deviations, such as around knots. Furniture and picture frames often contain mitered joints in which the fibers intersect. However, the joints are often pinned or doweled for added strength.

Generally, fracture toughness increases with increasing grain angle, although there is usually a minimum toughness between about 10 and 30° (Fig. 14) [3,16,30]. The shape of the relationship varies from almost flat to very steep as a function of species and the type of adhesive. There is usually a minimum in the range 15 to 30° above the bondline and a maximum at 90°. Both the stress intensity factor (K_{Ic}) and the strain-energy release rate (G_{Ic}) follow the same trend [30]. The basis for the shape of this relationship is unclear. Ruedy and Johnson speculate that it is due to variation of adhesive penetration and stored energy at the crack tip with grain angle, while Ebewele and others [3] think the relationship is caused by variation of the Cook–Gordon "weak-interface" crack-stopping mechanism with grain angle [58]. White [33] attributed the increased toughness at large grain angle to increased penetration and reinforcement of the interphase. The depth of penetration of loblolly pine (*Pinus taeda*) by a resorcinol adhesive increased nine times and the fracture toughness doubled as the grain angle was increased from 0 to 45°.

A grain angle effect has also been reported in the shear strength of bonded joints. When the grain direction runs with the applied force (Fig. 15a), the principal stress across the grain direction is in compression (closing mode). When the grain direction runs against the applied force (Fig. 15b), the principal stress across the grain is in tension (opening mode). The shear strength of the joint is highest when the grain direction runs with the

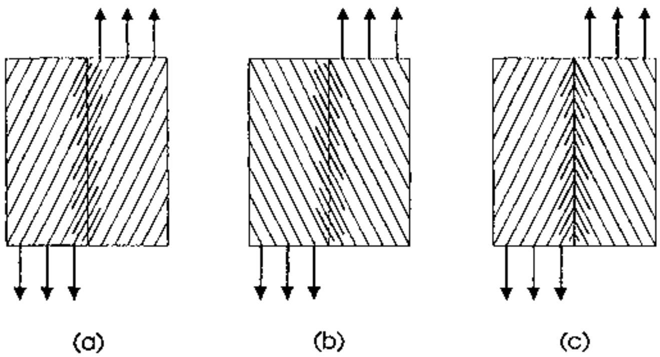

Figure 15 Schematic of joints with nonplanar grain orientations: (a) both adherends in compression (closing) mode perpendicular to the grain; (b) both adherends in tension (opening) mode perpendicular to the grain; (c) one adherend in each mode. Grain direction indicated by fine lines. Adhesive penetration indicated by heavy lines.

applied force. This effect is due to the disparity between the tensile and compression strengths of the wood and to adhesive penetration. When the grain direction is not parallel to the surface, the adhesive is very likely to penetrate the wood deeply. When such a joint is loaded in the opening mode, the strength of the cell wall, particularly the S1 layer and the S1–S2 interphase, is still the limiting factor. Adhesive penetration adds little to the tensile strength of wood perpendicular to the grain. However, in the closing mode, plugs of adhesive in the cell lumens increase the compression strength across the grain. They also distribute the shear force away from the plane of the joint. This was evident in the results of Furuno and others [43], who used tensile single lap joints for their experiments. Joints loaded in the closing mode were 25% stronger than parallel-grain joints and 45% stronger than joints loaded in the opening mode. Fracture of a joint with one adherend in the opening mode and one in the closing mode (Fig. 15c) occurred at low strength as a result of the opening mode. Swietliczny [59] conducted a similar experiment using compression block shear specimens and found the opposite results. The difference can be attributed to the method of loading, particularly the support of the specimen during loading, which inhibited opening or tensile fracture.

6. *Moisture*

The moisture content of both the wood and the adhesive affect the fracture behavior of adhesive bonded joints. Wood joints are especially sensitive to moisture effects as a result of the porosity and permeability of wood, which allows ready access by water to both the interior of the wood member and the adhesive layer. Irle and Bolton [57] showed that the superior durability of wood-based panels bonded with an alkaline PF adhesive compared to panels bonded with a UF adhesive was due to the ability of the phenolic adhesive to absorb and be plasticized by water. In the plasticized state, the phenolic adhesive is able to reduce stress concentrations that otherwise fracture the wood or the adhesive in urea-bonded panels.

Another important effect of moisture is due to a change in the moisture level, or content, of the wood member in a dynamic service environment. In thick members, changes in moisture content and the moisture-dependent dimension in the center fall behind changes that occur at the surface of the member. The difference in dimension creates stress in the member and bonded joints in the member. Adhesive bonds also restrain the swelling and shrinking of bonded members with different swell/shrink coefficients resulting from grain direction, growth-ring angle, or species. Moisture gradients and differential swelling or shrinking of the adherends are common causes of fracture of joints or materials. In this regard the size of the bonded members and the mechanical properties of the adhesive and the adherends have important roles in determining the magnitude of the stresses (and stress concentrations) that arise from moisture changes. The most severe stresses arise as both the adhesive and the wood dry because of the attendant differential increases in the adherend and adhesive moduli.

Simply changing the growth-ring orientation in adjoining laminate can alter the possibility of fracture in the vicinity of the joint caused by a change in moisture content of the laminated member. Laufenberg [60] studied the effects of growth-ring orientation in parallel Douglas-fir laminates. By finite element analysis, he showed that maximum stresses occurred at the edge of the laminate when one lamina had flat grain and the other vertical grain. He also found that a difference of growth-ring angles of only 15° was likely to produce splits or delamination as a result of moisture content cycling.

Nestic and Milner [61] also examined the effects of growth-ring orientation and found vast differences, particularly in the peak tensile stresses perpendicular to the grain, that depended on the difference between growth-ring orientation of adjoining laminae. The authors also found that the closer the pith was to a bondline, the greater the stress in the bondline induced by a moisture content change in the wood.

When the laminae are cross-laminated, the stresses are even more severe. Adherends thicker than roughly 5 mm will create sufficient stress to fracture the wood when bonded in a cross-laminated configuration. The most severe stresses arise as both the wood and the adhesive dry out, with an accompanying increase in strength and modulus. However, the stresses imposed by differential swelling of wood members are also severe in the case of an adhesive that is overly plasticized and weakened at high moisture contents. The effects of wood and adhesive properties and the environment on fracture behavior are complex. The effects of internal stress generated by wood on adhesives with varying sensitivity to moisture have been described [62]. Gillespie [62] compared the effects of medium-density, high-swelling maple (*Acer saccharum*) to low-density, low-swelling pine (*Pinus strobus*) using the same adhesives. The joints of maple bonded with moisture sensitive adhesives (PVA, catalyzed PVA, and casein) were destroyed or suffered severe and irrecoverable loss of strength from soaking. Similar joints of pine recovered all or most of their original strength upon redrying.

Internal stress may detract significantly from the apparent strength of a joint even if it is insufficient to fracture the joint. For example, if the internal tensile stress in a joint is equal to one-half the ultimate stress or strength of the weakest material, the available tensile strength of the joint is lowered by 50%.

7. *Geometry*

External loads are imposed on a bonded joint or structure by the dead weight of the structure and its contents, accumulated snow, wind, and people. The average stresses in a joint created by these loads can be calculated from structural analysis, but the maximum stress at joint edges is more difficult to determine. These stresses have been examined in some detail. Discussions by Walsh and others [63] and Glos and Horstmann [40] of the effects of external forces on the stresses in bonded wood lap joints are notable. Walsh and others applied plastic failure and fracture mechanics criteria to study the effects of the ratio of lap length (L) to primary member thickness (T) on the average failure stress of double-lap joints. The authors conclude that the plastic failure criterion (uniform stress) governs failure of the joint only at a very low L/T ratio (<1). The fracture mechanics criterion governs to an L/T ratio of 8. The authors developed the following conservative empirical design formula:

$$\frac{\sigma_{\mathrm{nom}}}{\tau_y} = (2T)^{-0.5}\left[1 + \frac{1}{8}\left(\frac{L}{T}\right)\right]$$

for $L/T = 2$ to 8 and $t/T = 0.5$ to 2, where σ_{nom} is the allowable axial stress in the adherends, τ_y the design shear stress in the joint, and t the lap adherend thickness.

Glos and Horstmann [40] systematically studied the effects of various joint design factors on the fracture of double-lap joints. These factors included (1) grain angle between two side-grain to side-grain members, (2) length of overlap, (3) shape of bonded area, (4) wood density, (5) type of adhesive, and (6) end distance. (End distance is defined as the distance to which the unloaded portion of the bonded members extends beyond the joint.) The authors found that all factors had a strong effect on joint fracture except the shape of the bonded area. Most interesting was the finding that creating a finite end distance increased the strength of joints with lap length/member thickness (L/T) ratios of 3 or less, but decreased the strength for L/T ratios above 3. The explanation given is that in short joints (those governed by the plastic failure criteria), the critical stresses perpendicular to the grain at the end of the overlap are spread over a larger area than in joints in which the adherend ends abruptly at the end of the joint. In long joints (those governed by fracture mechanics criteria), creating a finite end distance increases the sharpness of the notch from 90° compared to 0°. The increase in notch sharpness increases the stress concentration at a given load and thus reduces the average stress in the joint at which fracture occurs.

III. FRACTURE-BASED DESIGN

A. Structural Joints

There are no standard design methods for adhesive-bonded wood joints, let alone design methods based on fracture mechanics. This is obviously due in part to the complexity of the fracture behavior of wood joints and materials. The lack of adequate design methods has obviously been a hindrance in furthering the use of adhesives in structural assembly joints for wood structures. However, studies have demonstrated the power of fracture mechanics for developing generalized methods for predicting the behavior of adhesively bonded joints and materials. Conventional strength tests have not been able to predict such behavior.

Komatsu and others [64] found that the strength of double-lap joints was porportional to the bond area for relatively short overlaps. However, for long overlaps, stress concentrations and fracture mechanics controlled the strength of the joint. The authors developed the following fracture-based design equation:

$$\sigma_{\max} = \sqrt{G_c E_x S}$$

where $\sigma_{\max}$ is the shear strength of the joint, G_c the critical strain energy release rate, E_x the elastic tensile modulus of wood adherends along the grain, and S the geometrical joint parameter.

Wernersson and Gustafsson [65] developed a nonlinear fracture mechanics relationship based on pure shear for predicting the performance of lap joints of varying geometry and adherend properties based on the adhesive brittleness ratio:

$$\frac{\tau_f^2}{G_f}$$

where τ_f is the ultimate shear stress of the bondline obtained from the uniform stress test method, and G_f is the total fracture energy of the bondline. Wernersson [66] used this brittleness ratio to show how the failure of different types of joints is controlled by various criteria. Joints with a low brittleness ratio exhibit ductile behavior with uniform plastic deformation along the bondline. The joint strength is proportional to the local bond strength. Joints with a high brittleness ratio exhibit brittle behavior, with strength independent of the local bond strength. Joint strength is governed by fracture energy. The strength of joints with an intermediate brittleness ratio is affected by the local strength but also by the fracture energy and the shape of the stress–strain curve of the materials.

Based on his analysis, Wernersson proposed that the optimal adhesive properties, in terms of producing the strongest joint, are not necessarily those that produce the highest wood failure. However, Wernersson also acknowledges that this conclusion does not take into account the effects of time, temperature, or moisture. When long-term effects are considered, it is still too early to reject the long-standing requirements for high wood failure and maximum allowable cyclic delamination as indicators of the probable permanence of structural joints.

Komatsu [38] also applied fracture mechanics to the design of bonded cross-lapped knee joints that experience a torsion shear loading. Specimens were tested with the angle of the knee at 90°, 120°, and 150°. The crack initiation energies for the three angles were, respectively, 480, 600, and 1100 J/m^2. Failures at 90° and 120° were largely brittle (tension perpendicular to the grain) and had a greater correspondence to the lower torsional shear fracture toughness values than failure at 150°. The 150° joints showed a fairly uniform distribution of five different types of fracture. Some of the difference in toughness and type of fracture is no doubt due to the greater proportion of sliding shear forces in the 150° joint. Overall, Komatsu concluded that the fracture mechanics analysis gave a better prediction of strength than a method based on elastic torsional theory.

B. Wood-Based Panels

Lei and Wilson [35,67] developed a model for the fracture toughness (K'_{Ic}) of flakeboards bonded with PF resin adhesive. The model is based on the initial crack length (a) in the specimen, the average size of the inherent flaw (Ω) in the solid wood, the expected increase in crack length resulting from nonbonded interflake cracks and voids (Δa), and the K_{Ic} value of the wood used to make the flakes:

$$K'_{Ic} = K_{Ic} e^{(\Omega - 1/\mu)} \frac{a^{1/2} Y(a/W)}{(a + \delta a)^{0.5} Y[(a + \Delta a)/W]}$$

Other factors are the compliance (Y) for the specimen geometry, the board width (W), and the average length of the cracks or voids in the flakeboard ($1/\mu$). The experiment revealed that the K_{Ic} value of the flakeboard was the same as the K_{Ic} value of solid wood when the average crack length was equal to 2.5 mm, the same value as determined by Schniewind and Lyon [32] for solid Douglas-fir. Another study [35] showed that the solid wood density and the compaction ratio of the flakeboard also affect the average crack length and thus the fracture toughness of the flakeboard. The lengths of nonbonded voids and interflake crack decreased as the compaction ratio increased up to a board density of 780 kg/m^3. Mechanical damage to the flakes at a higher compaction ratio lowered fracture toughness.

IV. SUMMARY AND CONCLUSIONS

Understanding the causes and mechanisms of fracture in adhesive-bonded joints and materials is important to improving their performance, developing products based on new combinations of materials and adhesives, predicting the performance of new materials, and developing design methods for structural joints. In this chapter I have briefly discussed some aspects of wood and adhesive fracture, the influence of wood and adhesive properties upon joint fracture, the effects of environment and joint geometry on fracture, and the attempts to develop design methods for bonded joints and materials based on fracture mechanics.

Microstructure, in particular the discontinuities in the walls of thick-walled cells, is a controlling factor in the fracture of well-made joints bonded with rigid, thermosetting adhesives. The properties of the adhesive, however, play a major role in ameliorating the weaknesses of thin-walled cells and the discontinuities in thick-walled cells. Good wetting and chemical adhesion are important to bond performance, but they are not in themselves sufficient for maximum fracture toughness of bonded wood joints and materials. Hard, brittle adhesives, especially those that do not effectively penetrate the wood cell cavities and the cell wall, promote transwall cracking of thin-walled cells and microcracking and intrawall fracture of thick-walled cells. Less rigid adhesives that penetrate the cell lumens and cell wall distribute stress and inhibit microcracking in the wood.

The best adhesive for improved fracture toughness (1) does not develop shrinkage stresses during cure, (2) has a modulus close to that of wood perpendicular to the grain, (3) has a modulus that changes in parallel with the wood modulus as moisture content changes, (4) penetrates small-lumen, thick-walled cells but does not overpenetrate large-lumen thin-walled cells, and (5) can infiltrate the cell wall to reinforce the weak interphase between cell-wall layers.

The behavior of bonded joints and materials can be predicted successfully on the basis of material properties through applying the principles of fracture mechanics. However, much research is still required to achieve a method that is generally applicable to all adhesives, species, and joint geometries or material constructions. One field of particular importance and complexity revolves around the important effects of time, moisture, and temperature, and their interactions. At present, without extensive and long-term testing, there is no way to predict or evaluate the trade-offs between high short-term fracture toughness in joints or materials bonded with semirigid adhesives and reduced stress-rupture resistance of these adhesives under conditions of elevated moisture, temperature, or prolonged loading. An understanding of these relationships and the development of a model to predict the effects of trade-offs could lead to a new generation of wood-based materials and efficient adhesive-bonded wood structures.

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16

Fracture Mechanics Methods for Interface Bond Evaluations of Fiber-Reinforced Plastic/Wood Hybrid Composites

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I. INTRODUCTION

There is a worldwide need to rehabilitate and improve civil infrastructure, and to this end, new construction materials and methods are being intensely investigated to alleviate current problems and provide better and more reliable future structures. To improve performance, service life, and possibly durability of wood structures, fiber-reinforced plastic (FRP) composites are increasingly being used as reinforcement for wood. New FRP–wood hybrid materials for high volume construction applications are being developed from low-cost constituents, such as reconstituted wood composites and synthetic fibers and resins. Current applications of wood reinforcement have focused on the use of FRP strips or fabrics bonded to wood members. Two types of FRP–wood reinforcements are being employed: FRP strips (plates) bonded to wood [1] (used commercially for glulam beams, see Fig. 1) and wood cores wrapped with FRP by filament winding [2,3] [being investigated for reinforcement of railroad wood cross-ties (see Fig. 2) or wood utility poles].

Similar to wood products, the favorable attributes of FRP–wood materials are lightweight, noncorrosive, nonmagnetic, and nonconductive properties. In addition, FRP–wood materials exhibit excellent energy absorption properties, suitable for seismic response; high strength, fatigue life, and durability; competitive costs based on load capacity per unit weight; and ease of handling, transportation, and installation. The potential applications of FRP–wood materials include bridges, railroad ties, poles, long-span roof structures, buildings, highway noise barriers, fire barriers in coal mines, storage structures exposed to salts and chemicals, and many others.

Although significant increases in stiffness and strength have been achieved by this reinforcing technique, there is a concern about the reliable performance of the FRP–wood interface bond, which can be susceptible to delamination. An inadequate interface bond

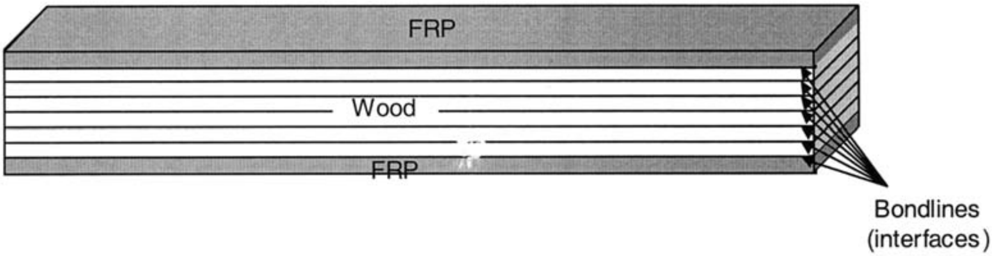

Figure 1 Composite–wood product: FRP reinforced glulam beam.

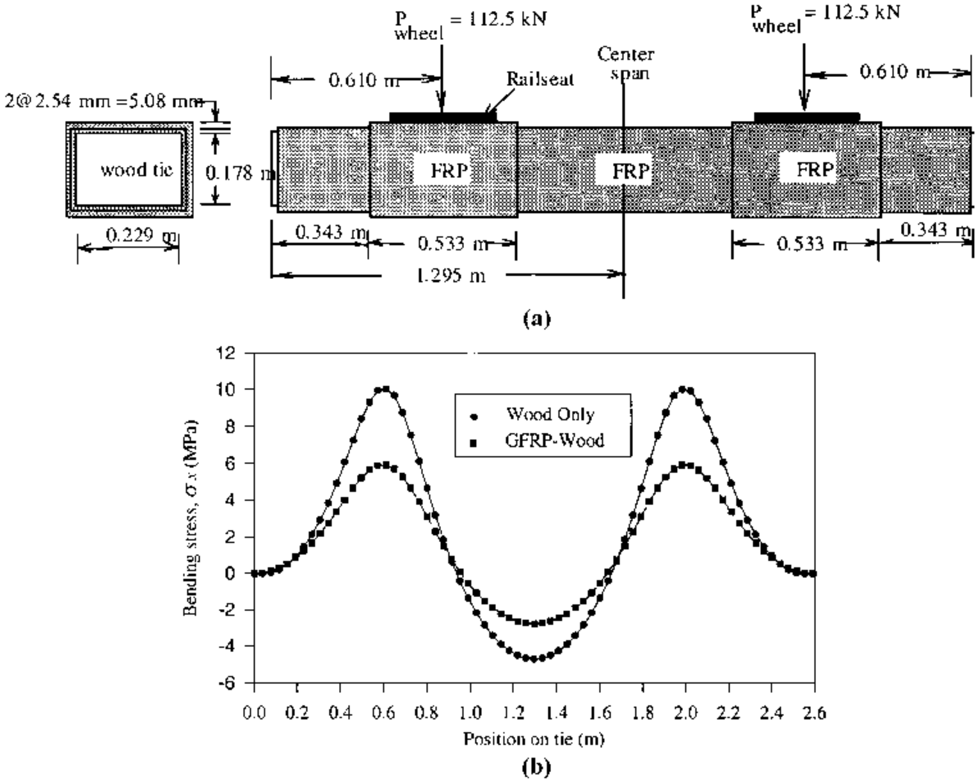

Figure 2 Composite–wood product: (a) railroad wood tie with FRP, (b) maximum bending stress (after Ref. 2).

strength and integrity can lead to delamination and premature failure of a hybrid FRP–wood composite and degrade the service performance of the product.

In this chapter, an overview of performance characterization of FRP–wood bonded interfaces by conventional and fracture mechanics tests [4–7] is presented. Modified ASTM standard tests (ASTM D2559 and D905) are first used to study the service performance and shear strength of the bond under moisture and/or mechanical loads, and then a contoured or tapered double cantilever beam specimen [8] is used to evaluate the fracture toughness of bonded interfaces under dry and wet conditions and cyclic loading.

Based on the results on performance evaluation, recommendations and guidelines are given for evaluation and qualification of wood–wood and FRP–wood bonded interfaces.

II. DESCRIPTION OF MATERIALS

Two types of FRP–wood interfaces are evaluated: FRP strips (plates) bonded to wood, and wood cores wrapped with FRP by filament winding. The wood material used is red maple, and the reinforcing material consists of either E-glass fiber rovings embedded in a phenolic resin matrix, or E-glass fiber rovings filament wound in an epoxy matrix. The phenolic fiber-reinforced plastic [phenolic FRP: 113 yield rovings (6.12/cm) and 28.35 g (1 oz) continuous strand mat surface layers; fiber volume fraction $V_f = 51\%$] composite material was produced by the pultrusion process; whereas the epoxy fiber-reinforced plastic (epoxy FRP: PPG high bond 250 yield rovings at ±45°; $V_f = 33.6\%$) composite material was produced by the filament winding process. For the phenolic FRP composite, two types of commercial wood adhesives were used to bond the wood to FRP strips: resorcinol formaldehyde (RF) (Penacolite® G-1131) and phenol-modified resorcinol formaldehyde (PRF) (Penacolite® R-400). For the epoxy FRP composite, the interface bond between the wood and FRP is directly achieved by the epoxy resin used in the filament winding process. Two distinct coupling agents, hydroxymethylated resorcinol (HMR) [9] and RF, were used as primers on the wood surface, because of the potential for improving the bond performance significantly.

III. INTERFACE DURABILITY BY DELAMINATION TESTS

The ASTM standard test D2559 was developed for specification of adhesives for structural laminated wood products for use under exterior exposure conditions. This standard test could be used to screen the best combination of parameters to achieve an adequate performance of the FRP–wood interface. Following the ASTM specifications, the specimens were subjected to the following three wet–dry cycles: (1) vacuum/pressure soaking followed by oven drying; (2) steam/pressure soaking followed by oven drying; (3) vacuum/pressure soaking followed by oven drying. The total time required to complete the test was three days, and immediately after the last cycle, the bondline delamination was measured on all end-grain surfaces with the aid of a microscope. The delamination was measured as a ratio of the delaminated (debonded) length to total bondline length for each specimen. For the materials used (red maple and FRP composites), the 8% delamination limit as specified by the ASTM standard for hardwood species was used to evaluate the bond performance for all bilayer specimens.

A. Durability of Phenolic FRP–Wood Bonded Interface

For phenolic FRP–wood bonded assemblies, the following factors relating to the performance of the bonded interface were investigated: (1) the influence of coupling agents, (2) the influence of clamping pressure, and (3) the influence of open/closed assembly time. The sizes of the specimens used were smaller than those specified in ASTM D2559. Each laminated FRP–wood assembly for the delamination test consisted of four pieces of red maple wood and two pieces of FRP strips; four wood pieces [each 19.05 mm × 76.2 mm × 609.6 mm (0.75″ × 3″ × 24″)] were placed at the center of the

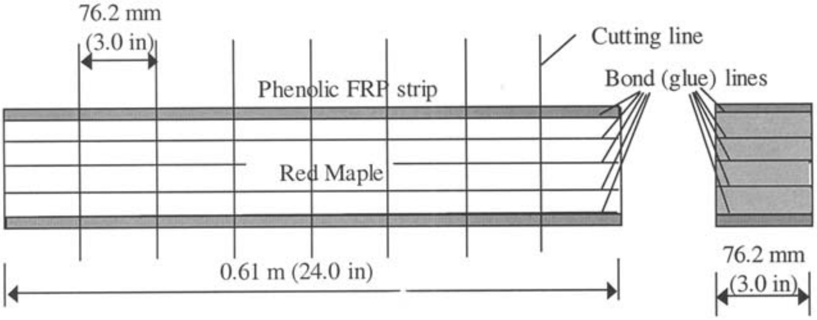

Figure 3 Manufacturing of bonded FRP–wood delamination specimens (after Ref. 4).

lamination, and FRP strips (each 4.76 mm × 76.2 mm × 609.6 mm (3/16″ × 3″ × 24″)] were located at the top and the bottom of the lamination (Fig. 3). Wood–wood assemblies for the delamination test were made by bonding six wood pieces [each 19.05 mm × 76.2 mm × 609.6 mm (0.75″ × 3″ × 24″)]. For some of the FRP–wood samples, the wood surfaces to be bonded to the FRP strips were primed with the coupling agent (HMR) following the guidelines given by Vick [9]. The HMR primer was spread with a brush at approximately 0.147 kg/m^2 (0.03 lb/ft^2) on the wood surfaces, and the primed surfaces were dried for 24 hours. All wood boards were conditioned to 12% moisture content (MC) before bonding. The adhesive, either resorcinol formaldehyde (RF) or phenol resorcinol formaldehyde (PRF), was applied with an electronic spreading roller to maintain a constant spread rate of 0.0294 to 0.0392 kg/m^2 (0.006–0.008 lb/ft^2) as recommended by industry. Each of the laminated wood–wood and FRP–wood beam-type members was cut into six 3-inch long specimens, and these specimens were tested following the ASTM D2559 guidelines. To study the influence of key parameters on the bond performance, six wood–wood and either 12 or six FRP–wood samples were tested for each combination of coupling agent, clamping pressure, and assembly time.

The effect of the HMR coupling agent on delamination performance was studied first [4]. The specimens without HMR primer showed a small percent delamination (< 3.0%) for phenolic FRP–wood interfaces, and in general, the specimens without HMR exhibited less delamination of wood–wood interfaces, particularly at layers adjacent to the phenolic FRP (see Tables 1 and 2). For face bonding of phenolic FRP–wood laminates, the fabrication parameters related to clamping pressure and open/closed assembly time could be easily controlled. The study of these parameters (Tables 3 and 4) indicated that specimens fabricated with high pressure [$p = 1.448$ MPa (210 psi)] and intermediate open/closed assembly times ($t = 5/30$ min) showed the least delamination along both the wood–wood and phenolic FRP–wood bondlines; therefore, for the RF adhesive used to bond the red maple wood and phenolic FRP composite in this study, the combination of 1.448 MPa (210 psi) for clamping pressure and 5/30 minutes open/closed assembly time is recommended.

B. Durability of Epoxy FRP–Wood Interface

Laminated red maple beams were used as the mandrel to apply the Epoxy FRP over the wood by filament winding (Fig. 4). Delamination samples both with HMR and RF coupling agents were cut from the epoxy FRP–wood beams, and the final dimensions of the

Table 1 Delamination of Bonded Interfaces with PRF Adhesive

Specimen	Coupling agent	No. of samples	Bondline	Average delamination (%)
Wood–wood	Without HMR	6	Wood–wood	3.20
FRP–wood	With HMR	12	FRP–wood	3.21
	With HMR	12	Wood–wood	8.90
	Without HMR	12	FRP–wood	2.25
	Without HMR	12	Wood–wood	0.74

Pressure $p = 1.448$ MPa (210 psi); open/closed assembly time $t = 3/50$ min.

Table 2 Delamination of Bonded Interfaces with RF Adhesive

Specimen	Coupling agent	No. of samples	Bondline	Average delamination (%)
Wood–wood	Without HMR	6	Wood–wood	4.00
FRP–wood	With HMR	12	FRP–wood	0.00
	With HMR	12	Wood–wood	6.53
	Without HMR	12	FRP–wood	2.44
	Without HMR	12	Wood–wood	1.46

Pressure: $p = 1.241$ MPa (180 psi); Open/Closed Assembly Time: $t = 5/30$ min.

Table 3 Delamination of Phenolic FRP–Wood Bondline under Different Pressure Conditions (with RF Adhesive and without HMR Primer)

Pressure p (MPa)	Open/closed assembly time t (min)	Average delamination (%)	
		FRP–wood bondline	Wood–wood bondline
1.034	5/30	0.31	8.08
1.241	5/30	2.44	1.46
1.448	5/30	0.00	1.42

Table 4 Delamination of Phenolic FRP–Wood Bondline under Different Assembly Times (with RF Adhesive and without HMR Primer)

Pressure p (MPa)	Open/closed assembly time t (min)	Average delamination	
		FRP–wood bondline	Wood–wood bondline
1.448	5/15	1.32	5.22
1.448	5/30	0.00	1.42
1.448	5/45	1.93	14.76

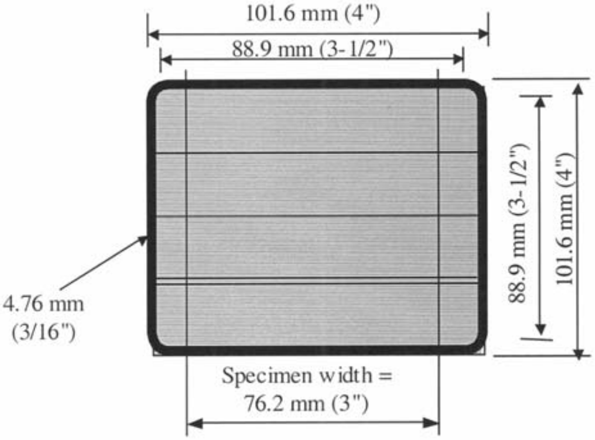

Figure 4 Fabrication of epoxy FRP–wood sample by filament winding process.

Table 5 Delamination of Epoxy FRP–Wood Laminated Samples with RF or HMR Coupling Agent

	Average delamination (%)			
	RF (6 samples)		HMR (6 samples)	
Bondline	FRP–wood	Wood–wood	FRP–wood	Wood–wood
Cycle 1	24.58	0.00	0.00	0.00
Cycle 2	43.45	1.19	0.00	0.43
Cycle 3	44.16	1.48	0.00	0.62

samples were $76.2\,\text{mm} \times 76.2\,\text{mm} \times 111.1\,\text{mm}$ ($3'' \times 3'' \times 4\frac{3}{8}''$). The epoxy FRP–wood interface bond performance under exterior or wet-use exposure conditions (three wet–dry cycles) was evaluated to study the effect of coupling agents (primers) to promote bonding. The epoxy FRP–wood interface bond was generated during the filament winding process; therefore, the open/closed assembly time and clamping pressure along the epoxy FRP–wood interface could not be controlled. The influence of two different coupling agents on bond performance [4] was investigated. The epoxy FRP–wood interface with HMR coupling agent performed well under cyclic wetting and drying delamination tests (no delamination); whereas, the interface with RF coupling agent failed to pass the delamination test (44.2% delamination after the third cycle) (see Table 5) [4]. Thus, it is recommended that the HMR coupling agent be applied to the red maple wood surface before wrapping with the epoxy FRP reinforcement, since the HMR significantly improved the bond integrity and durability of the epoxy FRP–wood interface.

IV. SHEAR STRENGTH OF FRP–WOOD BONDED INTERFACES

Tests to establish shear strengths and percent material failures for adhesively bonded wood–wood and FRP–wood interfaces were performed using a modified ASTM D905 test method [4]. Based on the best parameter combinations identified in the previous section [RF adhesive with pressure $p = 1.448$ MPa (210 psi) and open/closed assembly time $t = 5/30$ min), sets of 20 samples for both wood–wood and FRP-wood block-shear samples were fabricated and tested under dry and wet conditions. The dimensions of the samples are shown in Fig. 5. For both phenolic and epoxy FRP–wood specimens, the specified ASTM D905 block-shear samples were slightly modified, because of the limitation in thickness of the FRP composites.

To examine the bond strength degradation due to moisture effects, both dry (at 12% wood moisture content) and wet (more than 100% wood moisture content) samples were

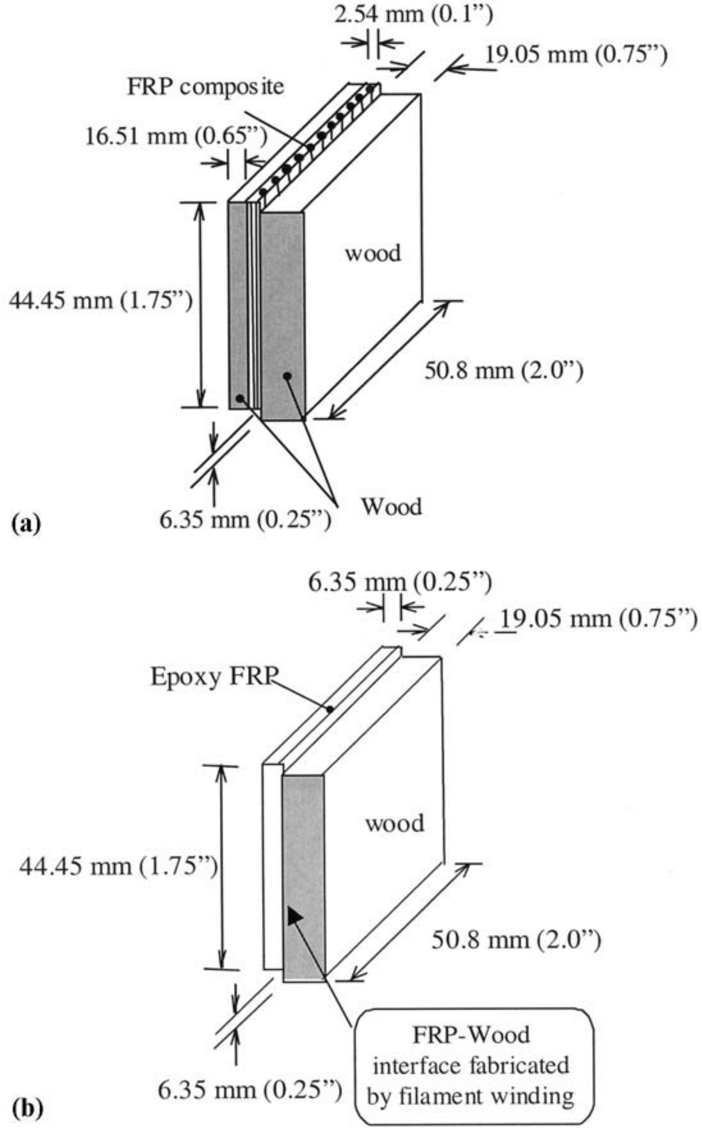

Figure 5 Modified ASTM D905 specimens for block-shear test. (a) Phenolic FRP-wood specimen; (b) epoxy FRP-wood specimen.

tested following the ASTM D905 standard. Initially, all the block-shear samples were conditioned to wood equilibrium moisture content of 12% in an environmentally controlled chamber. To obtain the wet condition, half of the block-shear wood–wood and FRP–wood samples were subjected to a vacuum-pressure soak cycle. The samples were placed in a container and submerged in water, and the container was then placed in a cylinder that was equipped to apply vacuum and pressure. A vacuum of 0.635 m (25 in) Hg was applied for 40 min, followed by a pressure of 0.690 MPa (100 psi) for another 40 min. This vacuum-pressure soak cycle was satisfactory for impregnating the wood layers with water [10]. The increase in moisture content by weight was more than 100% at the end of this cycle. The vacuum-pressure soaked wood–wood and FRP–wood block-shear specimens were immediately tested wet for shear strength according to the ASTM D905 standard. All the block-shear specimens were tested on a universal testing machine, and the loading rate (displacement controlled mode) of 0.381 mm/min (0.015 in/min) specified by the test standard was used.

A. Shear Strength of Phenolic FRP–Wood Bonded Interface

As shown in Table 6, the moisture content in the wood had a significant effect on the shear strength of wood–wood specimens (about 55%); whereas for phenolic FRP–wood specimens, there was a less significant influence of moisture content on the shear strength (about 6%). The average percent material (cohesive) failure for the wood–wood samples decreased by 29%, from about 81% for dry to 58% for wet. In contrast, the average percent material failures for the phenolic FRP–wood samples were about 81% for dry and 87% for wet, with a small increase of 7%. For the dry samples, the shear strength for wood–wood was 90% higher than for phenolic FRP–wood, while the percent material failures were nearly identical for both types of samples (about 81%). For the wet samples, the shear strength for wood–wood was 10% lower than for phenolic FRP–wood, but the percent material failure for wood–wood was 50% lower than for phenolic FRP–wood. The favorable results obtained for both dry and wet FRP–wood samples in relation to wood–wood samples is due mainly to the nature of the failure modes observed. The failure for the phenolic FRP–wood samples occurred primarily in the continuous strand mat layer of the FRP composite, and, therefore, the response of these samples was governed by the CSM in-plane or interlaminar shear strength, which is typically a relatively low value. Not only are the dry and wet shear strengths nearly identical for dry and wet phenolic FRP–wood samples, but the average value is close to the shear strength for wet wood–wood samples. This indicates that the interlaminar shear strength of the continuous strand mat is not affected much by moisture.

B. Shear Strength of Epoxy FRP–Wood Bonded Interface

As indicated in Table 7, the wood moisture content had a major effect on the shear strength of epoxy FRP–wood specimens with RF coupling agent (approximately 42.8%

Table 6 Shear Strength of Wood–Wood and Phenolic FRP–Wood Bonded Interfaces

	Dry	Wet	Difference
Wood–wood	13.50 MPa (1956 psi)	6.12 MPa (887 psi)	54.7%
FRP–wood	7.13 MPa (1033 psi)	6.73 MPa (976 psi)	5.5%

Table 7 Shear Strength of Epoxy FRP–Wood Bonded Interfaces

	Dry	Wet	Difference
HMR/FRP–wood	9.63 MPa (1396 psi)	7.10 MPa (1030 psi)	26.2%
RF/FRP–wood	8.82 MPa (1279 psi)	5.05 MPa (732 psi)	42.8%

decrease for wet samples). The epoxy FRP–wood specimens with HMR coupling agent showed a 26.2% decrease in shear strength due to moisture. The HMR/epoxy FRP–wood specimens showed higher shear strengths than the RF/epoxy FRP–wood for both dry and wet conditions (approximately 8.4% for dry and 28.9% for wet). The results indicate that the HMR coupling agent enhances the strength of interface bond. The material or cohesive failure of the epoxy FRP–wood specimens occurred entirely in wood. The average percent material failure for the HMR/epoxy FRP–wood samples increased by 15.6%, from about 77.6% for dry to 89.7% for wet. In contrast, the average percent material failure for the RF/epoxy FRP–wood samples exhibited cohesive failures of 26.6% for dry and 21.1% for wet, due to the poor performance of the RF coupling agent. The HMR/epoxy FRP–wood specimens showed a large percentage of material failure, which indicated an improved interface bond.

The favorable results obtained for both dry and wet epoxy FRP–wood samples with HMR in relation to the epoxy FRP–wood samples with RF are due mainly to the enhanced bond strength imparted by the coupling agent. The failure for the epoxy FRP–wood samples with HMR occurred primarily in the wood layer and, therefore, the response of these samples was governed by the shear strength of wood, and consistent percent material or cohesive failures for both the dry and wet samples (77.8% and 89.7%, respectively) were obtained. Moreover, these percent material failures are close to acceptable allowable values (approximately 80%) for wood failure. The failure for the epoxy FRP–wood samples with RF happened mainly at the interface between the epoxy FRP and wood, which resulted in lower shear strength and lower percent material failure, especially for wet samples.

V. MODE-I FRACTURE OF FRP–WOOD BONDED INTERFACES

Once the performance of the interface bond was established by the previous delamination (durability) tests, contoured double cantilever beam (CDCB) specimens were designed to conduct mode-I fracture tests. In this study, bilayer CDCB specimens (see Fig. 6) were designed by the Rayleigh–Ritz method [8] and used for fracture toughness tests on bonded FRP–wood interfaces under both dry and wet conditions. The critical strain energy release rate, G_{Ic}, which is a measure of the fracture toughness, is given as:

$$G_{Ic} = \frac{P_c^2}{2b}\frac{dC}{da} \tag{1}$$

where, P_c is the critical load, b the width of the specimen, and dC/da the rate of change of compliance C with respect to crack length a. The testing for fracture toughness of bonded interfaces using conventional *constant-height* double cantilever beam (DCB) specimens requires simultaneous measurements of critical load and crack length for each load step. The value of dC/da in Eq. (1) depends on the accuracy of the crack length measurement, which is generally a difficult task. The measurement of crack length can be avoided

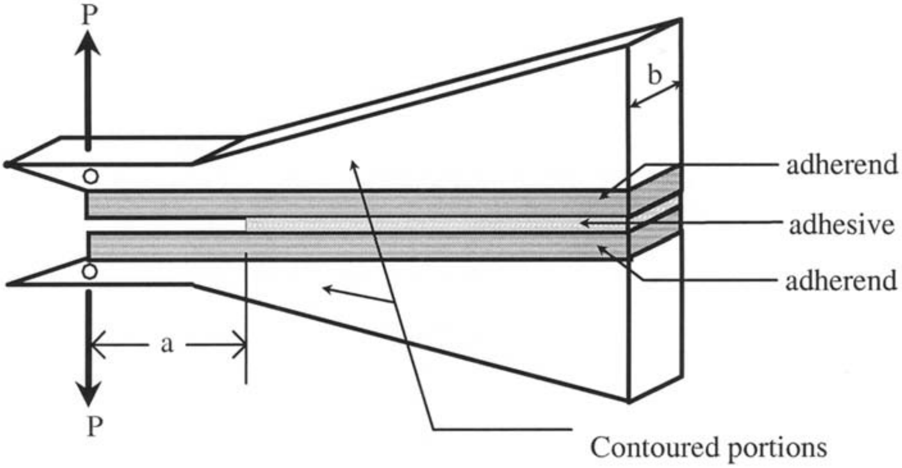

Figure 6 A schematic view of a CDCB.

by contouring the DCB specimen, such that dC/da is a constant, and in this case, the specimen is known as the CDCB.

To use the CDCB configuration for interfaces of dissimilar bonded materials, it is convenient to use constant-thickness adherends bonded to contoured portions made of a material that is easy to shape, such as wood-based materials (Fig. 6). Owing to the relative complexity of defining the shape of a CDCB specimen, a numerical method based on the Rayleigh–Ritz solution was developed [8] to design the shape of the test specimens. For a given crack length, the CDCB specimen is modeled as a cantilever beam to obtain its compliance; the expression for compliance of the specimen is derived using the Rayleigh–Ritz solution and defined as a function of the crack length and the slope of the contour. A first-order shear deformation theory [11] is used to account for shear deformation, which is important for materials such as FRP and wood. In the following sections, the design procedures for CDCB specimens based on the Rayleigh–Ritz method [8] are briefly summarized; then, the predictions and calibrations of compliance rate change (dC/da) for linear-slope CDCB specimens are discussed. The applications of CDCB specimens for fracture toughness evaluations [using Eq. (1)] of phenolic and epoxy FRP–wood interfaces under both dry and wet conditions are presented.

A. Design of CDCB Specimen for Mode-I Fracture

On the basis of the compliance derived from the Rayleigh–Ritz solution, a methodology for the design of the contour of a CDCB specimen was proposed [8]. A graphical representation of the geometric parameters used in defining the CDCB specimen is shown in Fig. 7, where the constant height of the base adherend is h_b, and the bonded contoured portion of the CDCB specimen is assumed to have an initial constant height h_1 for an initial crack length a_1. This initial constant height should provide sufficient material to accommodate loading fixtures, such as an attached hinge or a pin through the specimen. The expression for dC/da is obtained by assuming a linear shape of the contour for each

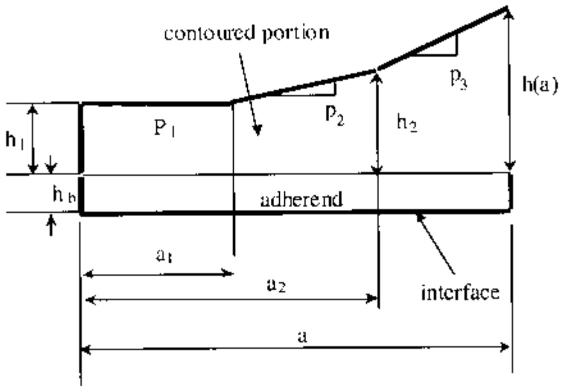

Figure 7 Geometric parameters of the contour of the CDCB specimen.

discrete crack length ($a \geq a_1$). The following step-by-step procedures are used to design the contoured specimen:

1. Compute the compliance of the CDCB specimen by the Rayleigh–Ritz method [8] as a function of crack length and specimen-slope: $C = C(a, p)$.
2. Differentiate the compliance function to obtain dC/da.
3. Evaluate dC/da for a discrete value of a, say $a = a_2$ for $a_2 > a_1$ (Fig. 7).
4. Equate dC/da, evaluated at a discrete crack-length, to a predefined constant value K to solve for the specimen-slope, say $p = p_2$. That is, let $(dC/da)(a_2, p_2) = K$ and solve for p_2.
5. Then, $h(a) = h_1 + p_2(a - a_1)$ for $a > a_1$, say $h_2 = h_1 + p_2\ (a_2 - a_1)$.
6. Repeat steps 1 through 5 to solve for p_3.

This procedure is repeated for each incremental crack length until the contour for the entire length of the CDCB specimen is obtained. When an interface of dissimilar materials is considered, the contour has to be developed for each adherend, since the stiffness of the adherends would be different and the shape of the contour would be different on the two sides of the interface bond in order to achieve the same rate of compliance for each half of the specimen.

The exact contour obtained from the above procedure has a convex shape [8], obtained by fitting a polynomial function through the discretized heights. However, the effort and cost involved in accurately manufacturing such a complex geometry can be significant, particularly since it is often necessary to test several specimens to obtain a good estimate of the fracture toughness of the interface. The exact contour can be simplified by a linear approximation function obtained through regression of the discrete heights [8]. Then, through experimental and analytical investigations of the compliance rate change [12,13], the linearity of the compliance-crack length relationship of a linear-slope CDCB specimen, or so-called tapered double cantilever beam (TDCB) specimen, can be verified for specific ranges of crack lengths, and the constant compliance rate change (dC/da) can be used in Eq. (1) for fracture toughness evaluation [14].

B. Calibration and Analytical Predication of Compliance Rate Change

As given in Eq. (1), the measurement of crack length can be avoided by tapering the specimen, such that dC/da is a constant. Extensive studies of compliance rate change of

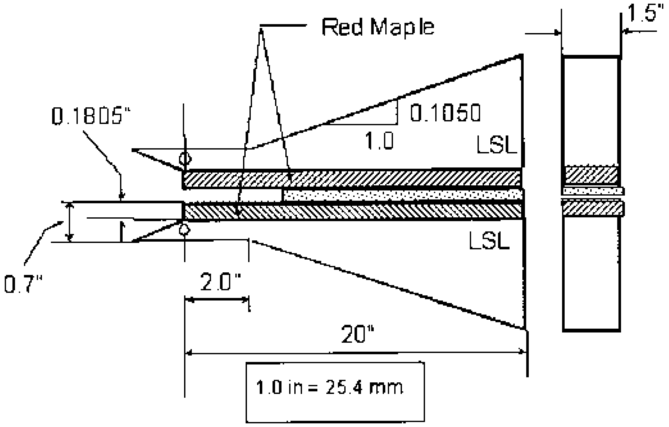

Figure 8 Geometry of the wood–wood TDCB specimen for calibration study.

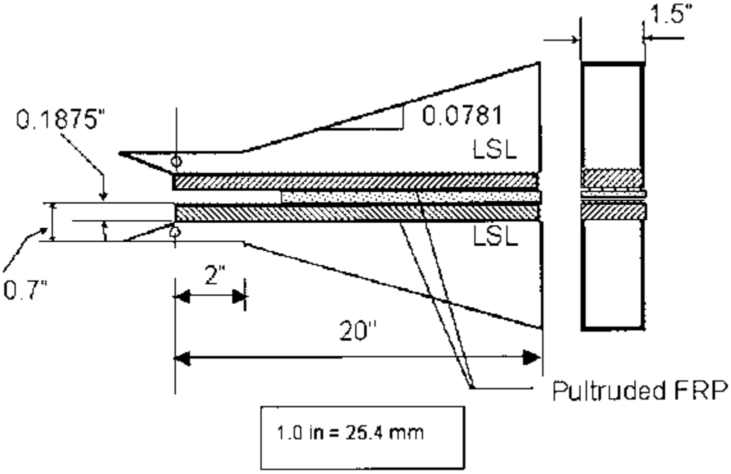

Figure 9 Geometry of the FRP–FRP TDCB specimen for calibration study.

TDCB specimens with hybrid interface bonds are given by Davalos et al. [12] and Qiao et al. [13]. The linearity of the compliance-crack length relationship of the specimen is verified by both the Rayleigh–Ritz method and finite element analysis. An experimental compliance calibration program for specimens with wood–wood (Fig. 8) and FRP–FRP (Fig. 9) bonded interfaces was carried out. In the Rayleigh–Ritz method [8], the cracked tapered portion of the specimen (Fig. 6) was modeled as a cantilever beam by assuming no displacement and rotation at the crack tip; thus, the effect of crack tip deformation was ignored. As a result, this method may significantly underestimate the compliance (C), and even compliance rate change (dC/da), values of the specimen, as shown by the large differences [12] when compared to finite element analyses and experimental data (see Figs. 10 and 11 for wood–wood and FRP–FRP bonded interfaces, respectively). Later, a modified Rayleigh-Ritz method [15] was developed, in which higher-order shape functions for deflection and rotation were introduced to

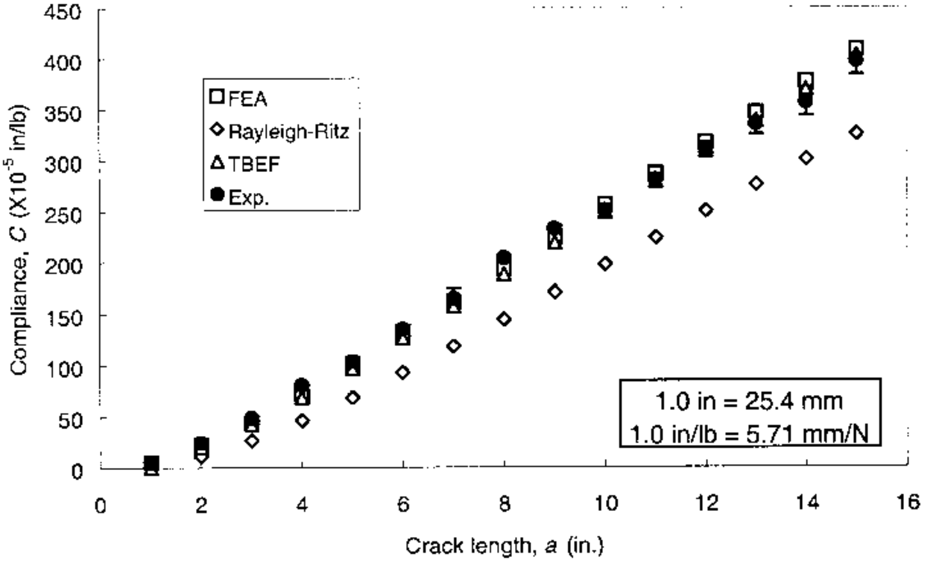

Figure 10 Compliance versus crack length for wood–wood TDCB specimen (Fig. 8). Exp., experimental data; FEA, finite element analysis; TBEF, tapered beam on elastic foundation model.

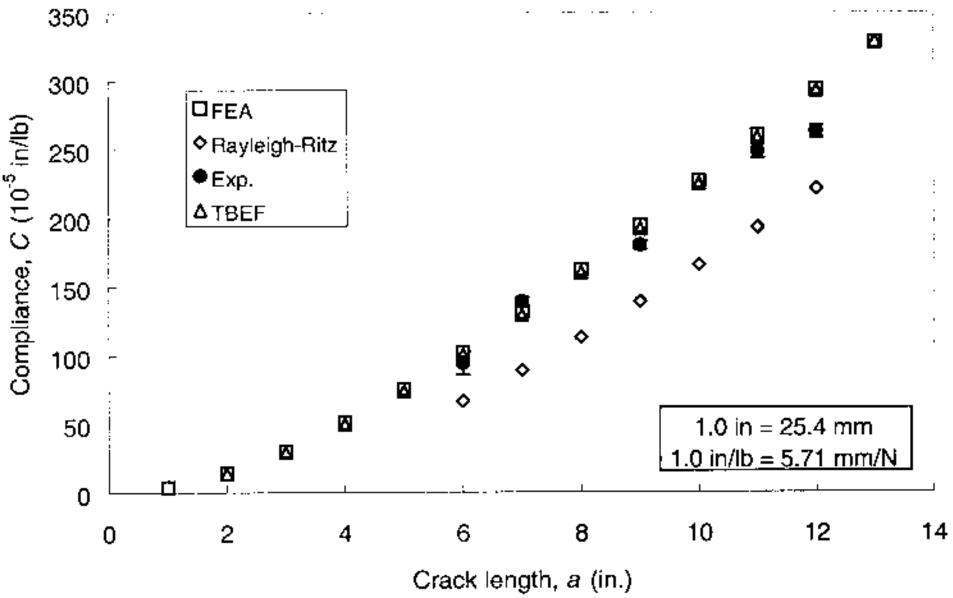

Figure 11 Compliance versus crack length for FRP–FRP specimen (Fig. 9). Abbreviations as Fig. 10.

replace the quadratic shape functions used before [8,12]; however, the accuracy of the model was only slightly improved, since cracktip deformations were not permitted. The same problem of underestimating the compliance was also observed in a study using constant cross section DCB specimens [16].

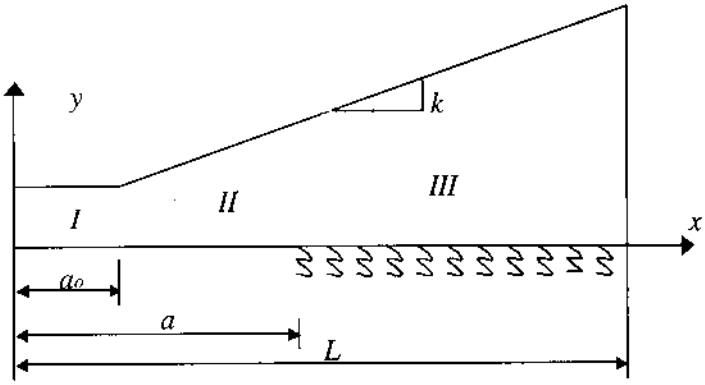

Figure 12 Modeling of TDCB specimen on an elastic foundation (after Ref. 13).

Recently, a modified beam theory [13] was developed to predict the compliance rate change of TDCB specimens for mode-I fracture of hybrid interface bonds. The analytical model treats the uncracked region of the specimen as a tapered beam on a generalized elastic foundation (Fig. 12), and the effect of crack tip deformation is incorporated in the formulation. A closed-form solution is obtained to compute the compliance and compliance versus crack length rate change. The tapered beam on elastic foundation (TBEF) model is verified with finite element analyses and experimental calibration data for wood–wood and FRP–FRP bonded interfaces (Figs. 10 and 11), and good agreements of compliance and compliance rate change are achieved for specified crack length ranges, for which a linear relation of compliance versus crack length is obtained, which can be used with experimental critical fracture loads to determine the respective critical strain energy release rate or fracture toughness of interface bonds. The analytical TBEF model, which accounts for the crack tip deformation, can be efficiently and accurately used for compliance and compliance rate change predictions of TDCB specimens and to reduce the experimental calibration effort that is often necessary in fracture studies. Moreover, the constant compliance rate change obtained for linear-slope TDCB specimens can be applied with confidence in mode-I fracture tests of hybrid material interface bonds.

C. Fracture Tests of Bonded Interfaces

On the basis of the above design procedure, the geometries of linear-slope CDCB or TDCB specimens for dry and wet FRP–wood interfaces were designed for both phenolic (Fig. 13) and epoxy (Fig. 14) FRP–wood samples. The phenolic FRP–wood bonded interface (Fig. 13) consisted of E-glass/phenolic pultruded FRP, and an integral red maple adherend–contour combination; the adhesive used for the bonded interfaces was resorcinol formaldehyde (RF), and the optimum pressure and assembly times identified above through ASTM D2559 tests [4] were used in the bonding process. The epoxy FRP–wood bonded interface (Fig. 14) consisted of E-glass/epoxy filament wound FRP, and a thin layer of red maple adherend; the material used for the contour was yellow poplar laminated veneer lumber (LVL). The adhesive used for bonding the contour LVL and red maple adherends was RF and the contour LVL and epoxy FRP composite was bonded using Magnobond 56 (a two-part epoxy resin system.

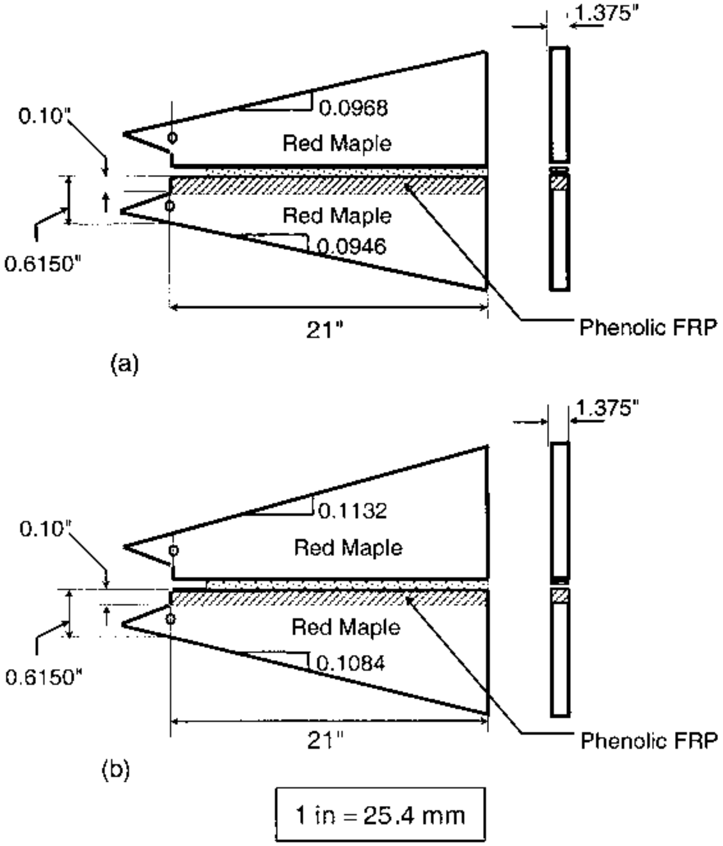

Figure 13 Shapes of CDCB phenolic FRP–wood specimens. (a) Geometry of phenolic FRP-wood/dry specimen; (b) geometry of phenolic FRP-wood/wet specimen.

For dry samples, the specimens were conditioned to 12% wood moisture content in an environmental chamber. The wet specimens were obtained by submerging the samples in a water bath under a 40-min vacuum and 40-min pressure soaking cycle, the specimens were tested immediately after the end of the cycle. The vacuum/pressure soaking cycle was used to saturate the specimens with moisture contents beyond fiber saturation point [10], and the wet samples obtained by this process exhibited more than 100% moisture contents by weight. Once the geometries of linear-slope test specimens were defined, the specimens were calibrated, experimentally and analytically by finite element analysis, to achieve a linear rate of compliance with respect to crack length [12]. In this study, only the phenolic FRP–wood samples were experimentally calibrated; hence the experimental compliance rate change, dC/da (Table 8), is used in Eq. (1) to compute the fracture toughness for the phenolic FRP–wood interface. Based on the accuracy of predicting the compliance versus crack length relationship, as verified by experimental and numerical (Rayleigh–Ritz [8,12], modified Rayleigh–Ritz [15], and finite element analysis) studies for phenolic FRP–wood samples [5], the predicted values of dC/da are used in the computation of fracture toughness for epoxy FRP–wood interfaces (Table 8).

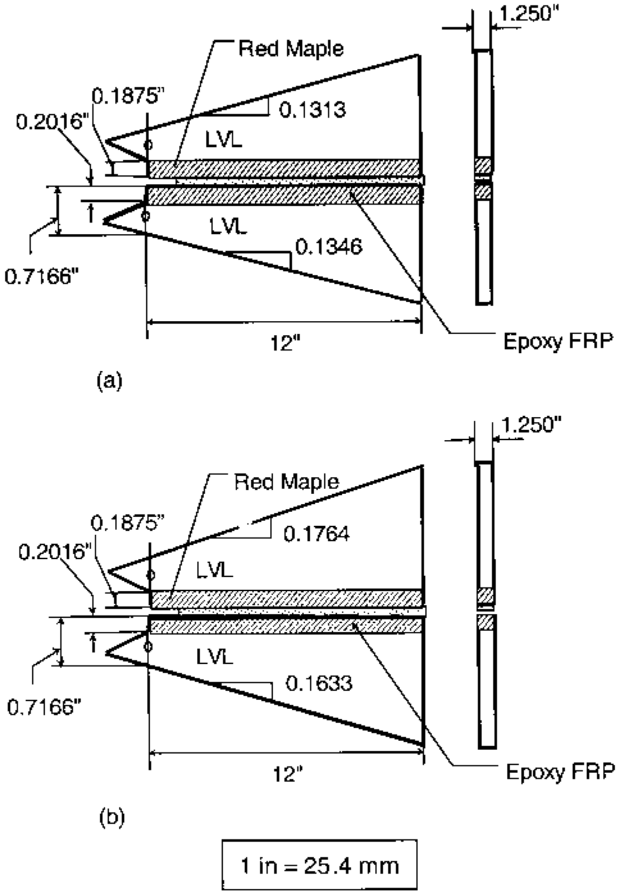

Figure 14 Shapes of CDCB epoxy FRP–wood specimens. (a) Geometry of epoxy FRP-wood/dry specimen; (b) geometry of epoxy FRP-wood/wet specimen.

Table 8 Compliance Rate Change of Linear Tapered Specimens

		dC/da ($\times$ 10^{-5} N^{-1})				
Specimen type	Slope	RR	MRR	Exp.	FEA	Difference (%) Exp. versus FEA
Phenolic FRP/dry	0.0946	5.40	6.02	6.59	6.09	7.60
Phenolic FRP/wet	0.1084	5.40	6.01	6.39	6.10	4.61
Epoxy FRP–wood/dry	0.1346	2.74	—	—	—	—
Epoxy FRP–wood/wet	0.1633	2.81	—	—	—	—

RR, Rayleigh–Ritz; MRR, modified. Rayleigh–Ritz; Exp., experimental data; FEA, finite element analysis.

The linear-slope CDCB specimens shown in Figs. 13 and 14 were used for mode-I fracture tests on FRP–wood bonded interfaces under both dry and wet conditions. A typical specimen under mode-I fracture load is shown in Fig. 15 for phenolic FRP–wood interface under dry conditions, and the corresponding critical tip load versus crack opening displacement is plotted in Fig. 16. As an illustration, the fracture surfaces of epoxy FRP–wood with HMR and RF primers on wood substrates are shown in Figs. 17 and 18,

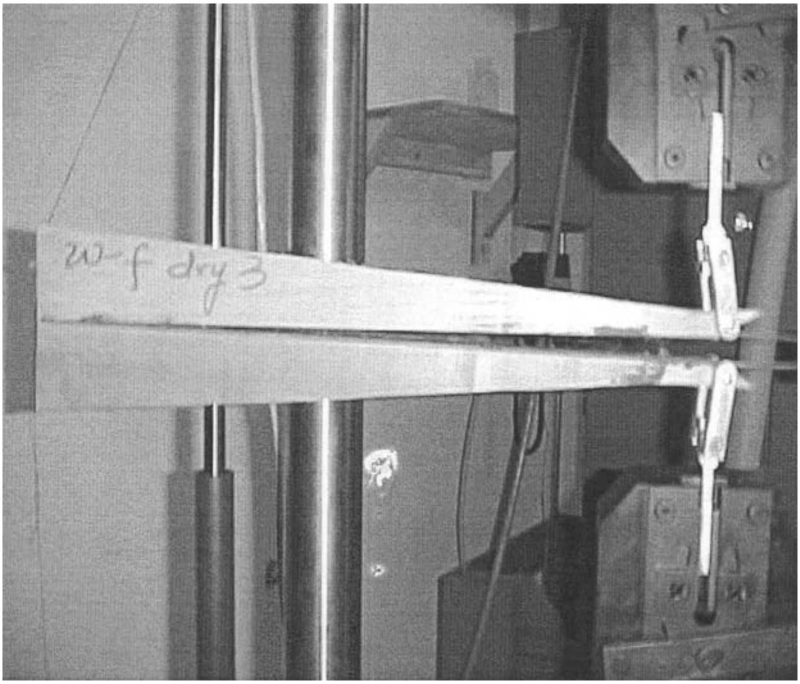

Figure 15 Fracture test on phenolic FRP–wood interface under dry conditions.

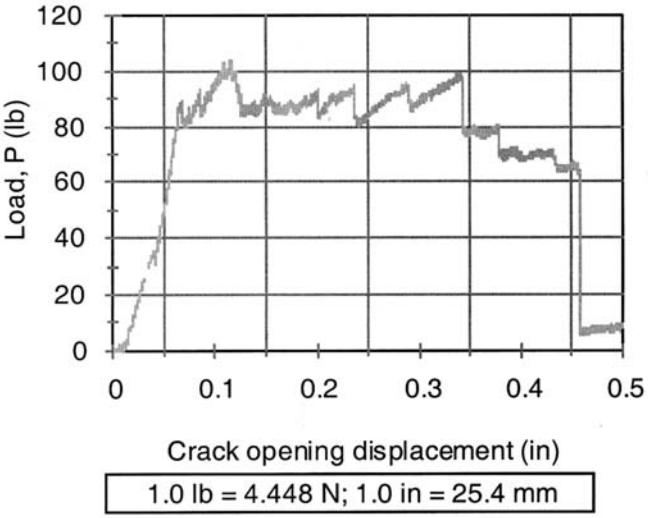

Figure 16 Crack initiation and arrest loads for phenolic FRP–wood interface.

respectively. In summary, the critical initiation and arrest loads, and fracture toughness values obtained for all of the tested samples discussed are shown in Tables 9 and 10, respectively [6]. As indicated in Table 9, an increase in interface fracture toughness due to moisture absorption was obtained for the phenolic FRP–wood and epoxy FRP–wood

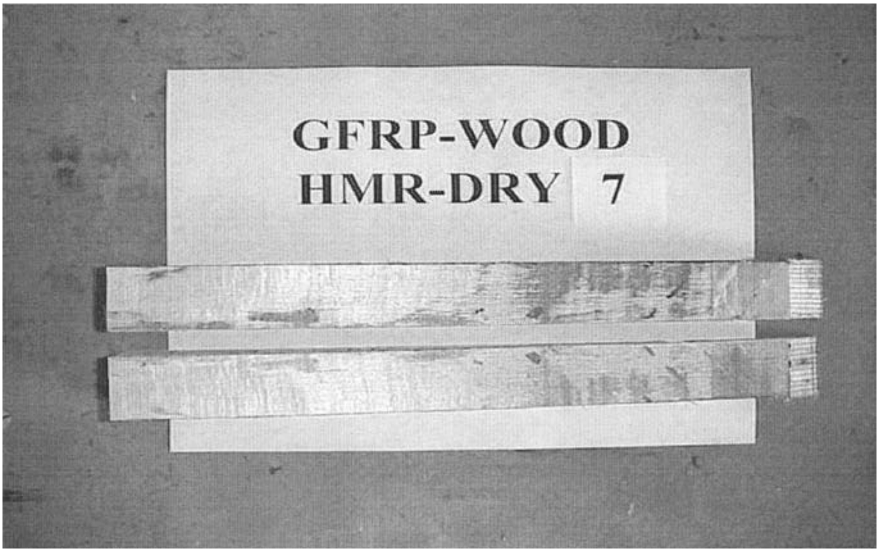

Figure 17 Fracture surfaces of epoxy FRP–wood/HMR (specimen 7) under dry conditions.

Figure 18 Fracture surfaces of epoxy FRP–wood/RF (specimen 1) under dry conditions.

samples. The toughening of the interface under exposure to moisture is due mainly to a much more plastic fracture failure mode. Also, the effects of coupling agent on fracture toughness of epoxy FRP–wood interfaces under both dry and wet conditions were investigated; the fracture toughness of interfaces with HMR coupling is much higher than of those treated with RF (Table 10). The variability of critical loads for RF-treated wet samples was significant coefficient of variance (COV) = 80.3%, with values varying from

Table 9 Comparison of Critical Initiation (P_c^i) and Arrest (P_c^a) Loads

	P_c^i (N)	P_c^a (N)
Phenolic FRP–wood/dry	487.1 (COV = 15.4%)	444.8 (COV = 17.0%)
Phenolic FRP–wood/wet	700.6 (COV = 13.1%)	653.4 (COV = 15.1%)
Epoxy FRP–wood/HMR/dry	972.4 (COV = 8.0%)	954.1 (COV = 8.8%)
Epoxy FRP–wood/HMR/wet	1263.3 (COV = 6.4%)	1249.5 (COV = 6.5%)
Epoxy FRP–wood/RF/dry	472.9 (COV = 31.8%)	433.7 (COV = 33.3%)
Epoxy FRP–wood/RF/wet	278.9 (COV = 78.0%)	270.5 (COV = 80.3%)

Table 10 Comparison of Fracture Toughness

	G_{Ic}^i (N/m)	G_{Ic}^a (N/m)
Phenolic FRP–wood/dry	224.15	185.63
Phenolic FRP–wood/wet	450.06	390.52
Epoxy FRP–wood/HMR/dry	444.81	432.55
Epoxy FRP–wood/HMR/wet	705.73	689.97
Epoxy FRP–wood/RF/dry	99.82	85.06
Epoxy FRP–wood/RF/wet	35.02	31.52

about 10 lbs–130 lbs. The RF-treated wet samples achieved only about 5% of the fracture toughness of the HMR-treated wet samples. Thus, the primer type used has a major influence on the interface performance.

VI. FATIGUE FRACTURE OF FRP-WOOD INTERFACE

Fatigue failure of materials and bonded interfaces is a complex topic and yet a quite important issue in engineering practice, since most structures are subjected to both applied and environmental cyclic loadings during their service life. The fatigue failure process has not been completely understood and there is no single accepted criterion or law to explain fatigue phenomena. However, the application of linear elastic fracture mechanics concepts has resulted in reasonable and useful explanations of fatigue failure, especially in crack propagation rate measurement and fatigue life prediction. It is generally accepted that there are three stages that characterize the fatigue process [17]: (I) near threshold region, (II) intermediate region, and (III) high growth rate region, as illustrated in Fig. 19.

The relationship between crack growth rate and fracture toughness was first established by Paris in the 1960s [18,19]. Paris introduced the well-known Power Law (or Paris Law) equation, which states that the crack growth rate da/dN, where a is the crack length and N is the number of cycles, depends mainly on the amplitude of the stress intensity factor ΔK:

$$\frac{da}{dN} = C\Delta K^m \tag{2}$$

where C and m are empirical constants dependent on materials, loading modes, environment and other factors, which need to be determined experimentally. Paris proposed an exponent $m = 4$ in agreement with his experimental data for metals. Subsequent researchers over decades showed that the exponent m in Eq. (2) was not necessarily equal to 4, and

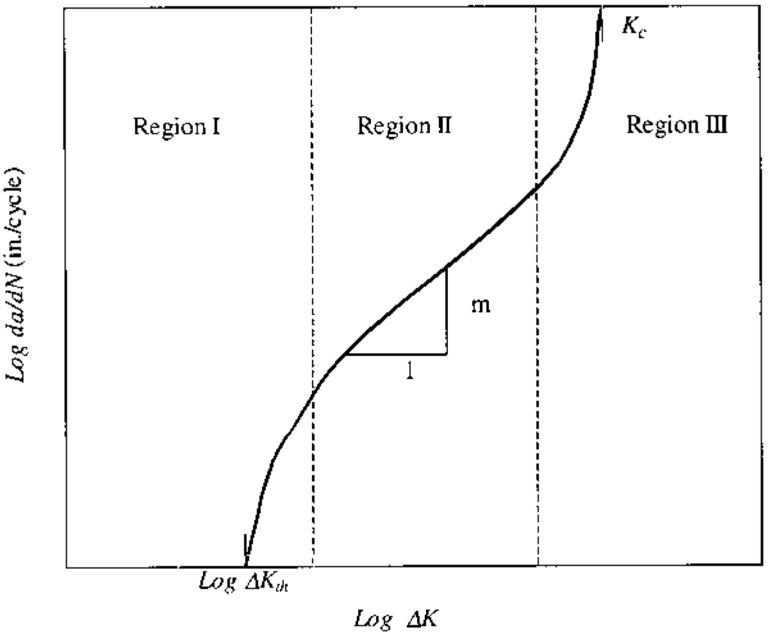

Figure 19 Schematic illustration of the three stages of the fatigue process.

the value varied depending on the type of material. It was found that the exponent *m* ranged from 2–5 for metals, was higher than 4 for many polymers and plastics and much higher for composite materials. The pertinent literature on application and development of various modified Paris Law formulations is reviewed by Jia et al. [7].

The load ratio *R* is believed to be an accepted significant parameter for fatigue crack growth rate. Many researchers have noticed that the original Power Law could not explain the load ratio effect, and therefore all kinds of modified Paris Law equations were proposed to include the load ratio effect. It is also well accepted that the threshold of the stress intensity factor range is changed with different load ratios. In this study, the load ratio effects on fatigue fracture of FRP–wood bonded interfaces using TDCB specimens [7] are summarized, and a modified Paris Law equation is proposed to characterize the crack propagation rate.

A. Fatigue Tests

A TDCB specimen designed by the Rayleigh–Ritz method [8] was used for fatigue tests on FRP–wood interfaces. The TDCB specimen was contoured to achieve a constant rate of compliance change with respect to crack length, dC/da. The details of the specimen design and applications for FRP–wood interface fracture studies [8] are given in previous sections. The geometric details of the TDCB specimen are shown in Fig. 20, and the adherends consisted of red maple and phenolic FRP with the contoured portions made of LVL. The adhesive used for bonding phenolic FRP to wood was RF.

Cyclic tension–tension fatigue tests were conducted on a computer controlled MTS servo hydraulic machine. The load ratio *R* (the ratio of minimum load to the maximum

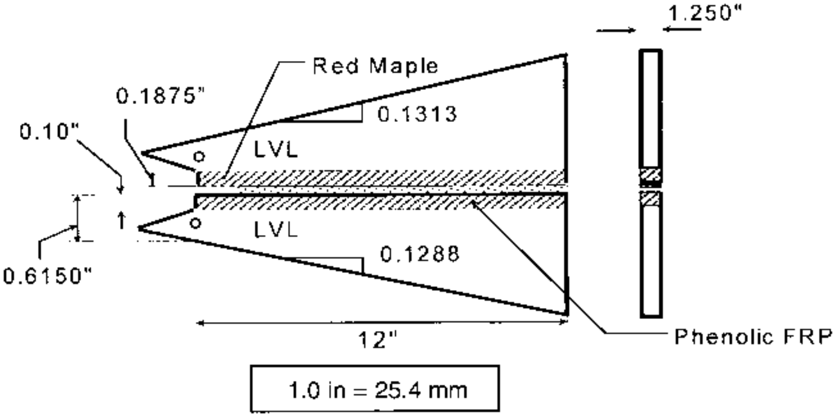

Figure 20 Geometry of phenolic FRP–wood TDCB specimen for fatigue fracture test.

load) was kept constant during the testing of each group of samples. Three groups of tests for load ratios R of 0.1, 0.3, and 0.5 were carried out under load control mode. A constant frequency of 1 Hz and a sinusoidal waveform were used for all the tests. Since only the relative value of the crack opening displacement (COD) is needed, a crosshead displacement instead of an extensometer displacement was used to measure the COD. The test environment was room temperature ($23 \pm 2°C$) and open laboratory conditions for all the samples.

The TDCB specimen (Fig. 20) was used for evaluating fracture toughness of bonded FRP–wood interfaces under mode-I loading [5], and the strain energy release rate G is given in Eq. (1). For one complete cycle, the maximum and minimum strain energy release rates are

$$G_{\max} = \frac{P_{\max}^2}{2b}\frac{dC}{da} \tag{3}$$

$$G_{\min} = \frac{P_{\min}^2}{2b}\frac{dC}{da} \tag{4}$$

The strain energy release rate range, $\Delta G = G_{\max} - G_{\min}$, is easily obtained from the difference of Eqs. (3) and (4). For the TDCB specimen, the constant compliance rate change (dC/da) with respect to crack length a is obtained, and therefore, the constant strain energy release rate range ΔG is acquired for constant cyclic loading.

The accuracy of the crack propagation rate da/dN depends on the measurement of the crack length, which is a formidable problem confronted by researchers in fracture mechanics. The COD is much easier to measure than the crack length for the TDCB specimen. The difficulty of measuring the crack propagation rate is avoided by using the COD propagation rate. The transformation from COD propagation rate $dCOD/dN$ to crack propagation rate da/dN is given as

$$\frac{da}{dN} = \frac{da}{dC}\frac{dC}{dN} = \frac{1}{kP}\frac{dCOD}{dN} \tag{5}$$

where N is the number of cycles, P is the applied load, and k is a constant equal to the reciprocal of dC/da. A typical COD propagation rate diagram from fatigue test is illustrated in Fig. 21.

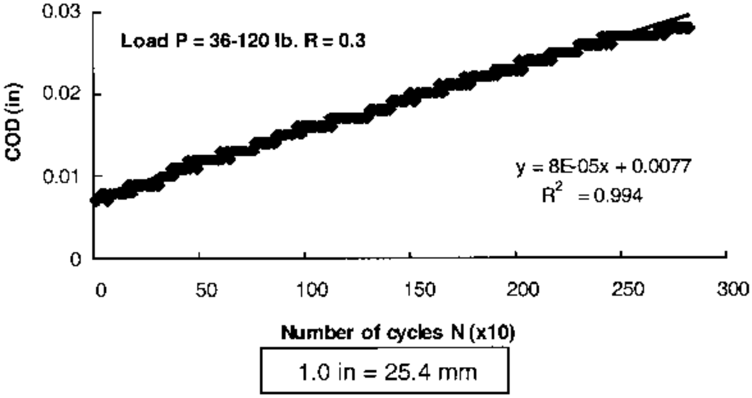

Figure 21 A typical diagram of COD propagation rate for TDCB specimen.

B. Load Ratio Effects

So far, only the load ratio effects on fatigue fracture of the FRP–wood interface have been investigated [7]. The log–log plot of the crack propagation rate da/dN versus the strain energy release rate range ΔG for load ratios R of 0.1, 0.3, and 0.5 is shown in Fig. 22. It is easily seen that there is a strong effect of load ratio R on crack propagation rate da/dN. The Crack propagation rate da/dN increases for the same strain energy release rate range, ΔG, when the load ratio increases. For each load ratio R, the following equation is used to fit the data points in Fig. 22:

$$\frac{da}{dN} = B(\Delta G)^m \tag{6}$$

where the constants B and m are obtained by regression fitting of experimental data and are listed in Table 11. As seen in Table 11, both B and m increase as the load ratio R increases. The relationship between crack propagation rate da/dN and minimum strain energy release rate $G_{\min}$ is plotted in Fig. 23. Compared with Fig. 22, the load ratio effect on crack propagation rate da/dN in Fig. 23 is reversed; as the load ratio R increases, the crack propagation rate da/dN decreases for the same minimum strain energy release rate $G_{\min}$.

As noticed by other researchers [20], the strain energy release rate range ΔG is not the only controlling parameter for the crack propagation rate da/dN. Since the minimum strain energy release rate $G_{\min}$ and strain energy release rate range ΔG have contrary effects on the crack propagation rate da/dN for different load ratios R, the minimum strain energy release rate $G_{\min}$ was included as a secondary controlling parameter to explain the load ratio effect. By following a similar approach as Hojo et al. [20], the equivalent strain energy release rate can be first defined as

$$\Delta G_{eq} = \Delta G^{(1-\lambda)} G_{\min}^{\lambda} \tag{7}$$

Then the modified Paris Law equation is expressed as

$$\frac{da}{dN} = B\left(\Delta G_{eq}\right)^m \tag{8}$$

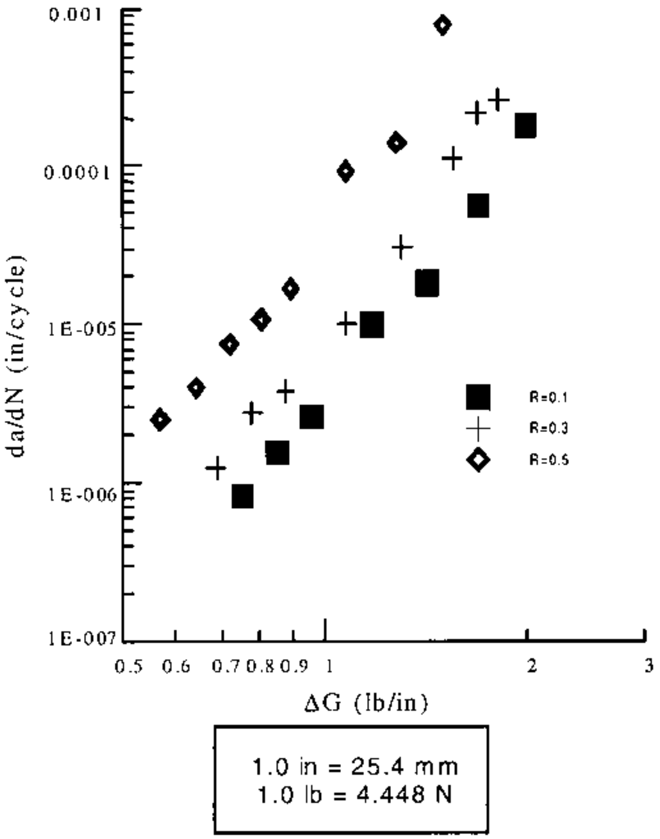

Figure 22 Relationship of da/dN versus ΔG.

Table 11 Values of Material Constants B and m in Eq. (6)

Load ratio R	B	m
0.1	4×10^{-6}	5.3717
0.3	9×10^{-6}	5.5897
0.5	5×10^{-5}	5.7734

In Eq. (7), λ is a material constant that defines the relative importance of the contribution of the minimum strain energy release rate $G_{\min}$ and strain energy release rate range ΔG to the crack growth rate. The constant λ is obtained by a trial and error method to best fit the data points. The final log–log plot is shown in Fig. 24, for $\lambda = 0.13$, $B = 7 \times 10^{-5}$, and $m = 5.34$ [7].

C. Summary of Fatigue Fracture Tests

The fatigue behavior of the phenolic FRP–wood interface bond was investigated [7], using a TDCB specimen for constant strain energy release rate range ΔG. The load ratio effect

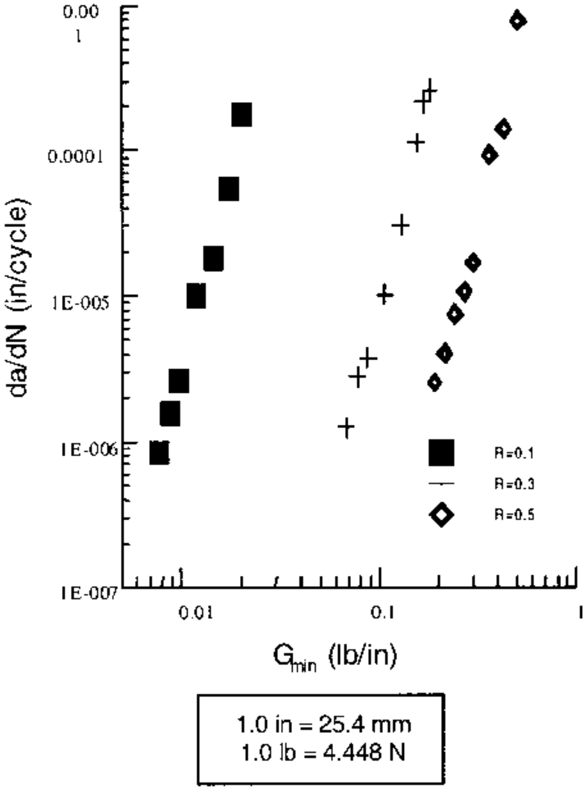

Figure 23 Relationship of da/dN versus $G_{\min}$.

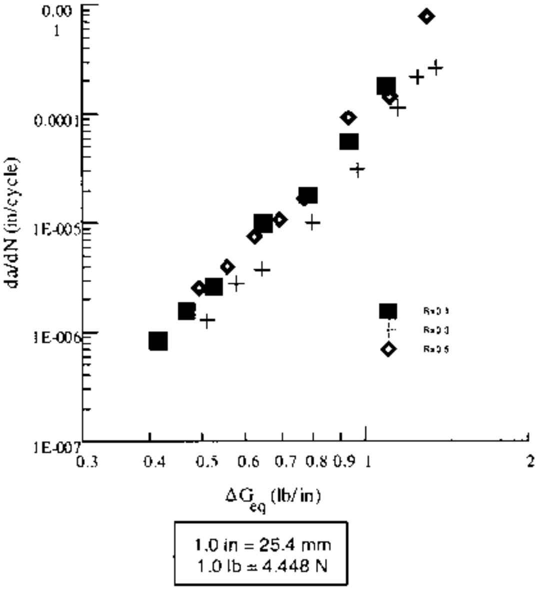

Figure 24 Relationship of da/dN versus ΔG_{eq}.

on interface crack propagation rate at room temperature and laboratory conditions was obtained. A modified Paris Law equation was proposed to explain the load ratio effect. The results of fatigue fracture of FRP–wood interface bonds are summarized as follows:

(1) The TDCB specimen is shown to be suitable for FRP–wood interface fatigue tests. The FRP–wood interface displayed the typical crack propagation behavior under constant cyclic loading as observed by others.
(2) The compliance method used for the TDCB specimen is quite simple, relatively precise, and effective for measuring the crack propagation rate of FRP–wood interfaces.
(3) The Paris Law of Eq. (6) using the strain energy release rate as a controlling parameter can be efficiently applied to a given value of load ratio *R*.
(4) Considering the minimum strain energy release rate $G_{\min}$ as a secondary controlling parameter to explain the effects of load ratio *R*, an equivalent strain energy release rate can be defined as in Eq. (7). In Eq. (7), λ is a material constant, which defines the relative importance of the minimum strain energy release rate $G_{\min}$ and strain energy release rate range ΔG to the crack growth rate. By a trial and error approach, λ is obtained equal to 0.13 for the phenolic FRP–wood interface.
(5) Finally, the modified Paris Law equation for the phenolic FRP–wood interface considered is given as

$$\frac{da}{dN} = 7 \times 10^{-5}\left(\Delta G^{0.87} G_{\min}^{0.13}\right)^{5.34} \tag{9}$$

The proposed Eq. (9) can efficiently represent the load ratio effect on any propagation rate of phenolic FRP–wood interfaces, and it can further be used for other similar studies of interface fracture of dissimilar materials.

VII. GUIDELINES FOR CHARACTERIZATION OF FRP-WOOD INTERFACES

In this study, a comprehensive program to evaluate the durability, shear strength, and fracture toughness of FRP–wood bonded interfaces was presented. The potential in-service delamination of bonded interfaces was evaluated by a 3-cycle test involving repeated wetting and drying [4]. Also, wet and dry interface strengths were evaluated through block-shear tests [4]. The fracture toughness of the interface was measured by an innovative fracture mechanics test [8]. Several key durability parameters of bonded interfaces were investigated, including use of a coupling agent (primer), open/closed assembly time, and clamping pressure; further the durability of bonded interfaces was evaluated by performing fracture tests on specimens under wet [15] and cyclic loading [7] conditions. The present interface bond characterization study can be used to qualify adhesives, establish service performance, and obtain bond shear strength and fracture toughness values for interfaces of FRP–wood composite materials.

To effectively evaluate the in-service performance of bonded FRP–wood hybrid products and to qualify adhesive systems for FRP–wood bonding, the following general guidelines for interface bond characterization are suggested:

The ASTM D2559 wetting-and-drying cyclic delamination test [4] is sensitive enough to investigate key performance parameters, such as use of a coupling agent (primer), open/closed assembly time, clamping pressure, bonding surface preparation, etc., and it can be first used as a screening test to evaluate the delamination of bonded interfaces.

Once the best combination of parameters is obtained from the ASTM D2559 tests, standard block-shear tests (ASTM D905) can then be used to evaluate average bond "shear" strength [4], which can be used in engineering design taking into account appropriate factors of safety. Also, the bond strength under various moisture contents (conditions) can be obtained.

Finally, the tapered double cantilever beam specimen [8] described in this study can be effectively used to obtain interface mode-I fracture toughness values under various environmental loadings (e.g., under dry and wet conditions [5,14,15]) and cyclic load conditions (fatigue fracture [7]); these data can be implemented in practical applications to assess the potential growth of a delamination crack at the FRP–wood interface.

VIII. CONCLUSIONS

This chapter presents a current status report on our research on FRP–wood interface bond. The qualification program is organized in two phases. First, the service performance and shear strength of adhesively bonded interfaces are evaluated by modified ASTM standard tests. The potential in-service delamination (or durability) is evaluated by a 3-cycle test involving repeated wetting and drying, and the wet and dry interface strengths are evaluated through ASTM block-shear tests. Next, the fracture toughness of the interface under dry and wet conditions and cyclic loading is measured by an innovative fracture mechanics test using the contoured or tapered double cantilever beam specimens. Several key parameters are studied, such as coupling agents (primers) to promote bonding, type of composite, open/closed assembly time, and clamping pressure. The characterization approach presented in this chapter can be efficiently used to establish the service performance and strength of FRP–wood interface bonds and to obtain fracture toughness data useful for delamination studies of bonded interfaces.

ACKNOWLEDGMENTS

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17

Spectroscopic Techniques in Adhesive Bonding

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I. INTRODUCTION

This chapter reviews the many different spectroscopic techniques that can be used to study the composition and performance of adhesively bonded materials. Such a review was deemed necessary because many new analytical techniques have been developed lately and a large number of interesting applications have been published recently. The most widely used spectroscopic techniques are x-ray photoelectron spectroscopy (XPS, also called ESCA), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), and infrared spectroscopies (FTIR). The distinction should be made here between *microscopic* and *spectroscopic* techniques for surface and interface characterization. Both types of techniques are invariably applied for the development and failure analysis of adhesives. Examples of microscopic techniques are optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission microscopy (STEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). In general, spectroscopic techniques provide qualitative analysis of the chemistry of a surface or an interface, although in certain cases quantitative analysis is possible. Microscopic techniques are primarily employed to study surface and interface morphology of adhesives and adherends. When these techniques are applied to failure surfaces, important information on failure modes can be obtained.

This review is limited to spectroscopic techniques. Excellent reviews already exist on the use of microscopic methods in adhesive bonding technology [1,2].

In general, the applications of spectroscopic techniques in the study of various aspects of adhesive bonding that have been reported are the following:

Surface characterization of materials prior to bonding; cleanliness, surface contamination, oxide thickness, and so forth

Modification of surfaces to improve bondability; examples are modification of polymer surfaces by plasma or corona treatments, anodization or other treatments of metals, plasma film depositions, deposition of functional silanes or other coupling agents to metal surfaces, and so forth

Analysis of interfaces between materials, especially for failure analysis after aging and testing of adhesively bonded systems
Study of the cure of adhesives.

The outline of this chapter is as follows. The spectroscopic techniques that can be used for surface of interface characterization of adhesively bonded materials are listed in Table 1. The most popular techniques are then discussed briefly in terms of the type of information they provide and where they can be applied. Their limitations are also described briefly. Since just a handful of techniques are used on a regular basis, notably XPS,* AES, SIMS, FTIR, and Raman spectroscopy, only these techniques will be discussed in detail. Recent and ongoing instrumental developments are described and specific applications of each of these techniques are presented and discussed. Finally, a bibliography containing many references to textbooks and important articles is given.

II. OVERVIEW OF SPECTROSCOPIC TECHNIQUES

Table 1 lists a wide range of spectroscopic techniques with details on the type of information that these techniques can provide, their sampling depth, their sensitivity, and their major limitations. Some key references are provided for each technique. The techniques are classified in five major categories: ion spectroscopies, electron spectroscopies, x-ray spectroscopies, vibrational spectroscopies, and miscellaneous techniques. This distinction is, of course, arbitrary and is based on the type of signal that is recorded in each technique. It would be equally justifiable to classify the techniques on the basis of the primary beam or excitation source or even on sampling depth [3]. However, in each group a distinction has been made between those techniques that are well known and currently widely used and techniques that are either variations of the major techniques or still in a developmental stage. The techniques that are closely related or that are variations of the same main technique are grouped together.

Another way of comparing techniques is to group them according to the combination of excitation (i.e., signal in) and response (i.e., signal out). This is frequently done in the literature [4]. This has been done here for a number of the techniques listed in Table 1. The results are shown in Table 2, which illustrates that a technique has been developed or proposed for almost all combinations of ions, electrons, and photons.

Table 1 indicates that the sampling depth for the various techniques varies from 1 monolayer to several millimeters. In general, the ion-based techniques, for instance SIMS and ISS, have the lowest sampling depths because the mean free path of ions in solids is not more than one or two monolayers. The penetration and escape depths for photons are much higher and, therefore, the techniques that are based on the detection of electromagnetic radiation, such as FTIR and XRF, give information on microns in metals and even millimeters in organics. This does not mean, however, that these techniques cannot detect monolayers. In suitable samples, both FTIR techniques and XRF can detect monolayers with high sensitivity, but it is difficult to restrict the signal acquisition to the monolayer only because of the larger sampling depths.

Methods based on electron detection have intermediate sampling depths. The sampled thickness in techniques such as AES and XPS is of the order of 50 Å. Since the escape depth of an electron is dependent on its energy, the sampling depth in XPS and

---

* See Table 1 for a definition of all acronyms used in the text.

Table 1 Spectroscopic Techniques for Use in Adhesive Bonding Studies

Technique	Acronym	Sampling depth	Information	Sensitivity	Principle	Limitation	Ref.
A. Ion spectroscopies							
Secondary ion mass spectrometry	SIMS	5 Å	Mass spectrum; mapping; SNMS also depth profile	All elements ≪ monolayer	Ion beam excitation	UHV; qualitative; matrix effects;	7–9
Static SIMS	SSIMS						6
Time-of-flight SIMS	TOFSIMS						28
Surface analysis by laser ionization	SALI						12
Fast atom bombardment SIMS	FABSIMS						6
Secondary neutrals mass spectroscopy	SNMS						8
Laser microprobe mass analysis/spectrometry	LAMMA, LAMMS	1 µm	Mass spectrum of small area	All elements	Laser excitation	Reproducibility; damage	105
Laser ionization mass analysis	LIMA						
Laser ionization mass spectrometry	LIMS						
Ion scattering spectroscopy	ISS	2 Å	Elements; heavier than primary ion	< 1 monolayer	Ion beam scattering	Spectral resolution	106
Low-energy ion scattering spectroscopy	LEIS(S)						107
Medium-energy ion scattering spectroscopy	MEIS(S)						
High-energy ion scattering spectroscopy	HEIS(S)						
Rutherford backscattering spectroscopy	RBS	> 1 µm	Depth profile; nondestr.	High	Scattering; meV ions	Equipment cost few elements	101–104
Neutral scattering spectrometry	NSS						108
Nuclear reaction analysis	NRA	1 µm					111
Electron–stimulated desorption spectroscopy	ESD	5 Å	Mass spectrum; small spot	< 1 monolayer	e^- beam excitation	Poor sensitivity; e^- damage	109
Electron-induced ion desorption	EIID						110
Electron-stimulated desorption ion angular distribution	ESDIAD						

(*continued*)

Table 1 Continued

Technique	Acronym	Sampling depth	Information	Sensitivity	Principle	Limitation	Ref.
Single photon ionization	SPI	As SIMS	Mostly as SIMS; more quantitative	Lower than SIMS	Postionization of sputtered neutrals	Lower sensitivity than SIMS	12
Surface analysis by resonance ionization of sputtered atoms	SARISA						
Resonantly enhanced multiphoton ionization	REMPI						
Non-resonant multiphoton ionization spectroscopy	NRMPI						
Hydrogen forward scattering spectroscopy	HFS	1–5 μm	H detection		H^+, $4He^+$ beams	H only	103
Forward recoil scattering spectroscopy	FRS						133
B. Electron spectroscopies							
Auger electron spectroscopy	AES	10–50 Å; to 1 μm in depth profiling; mapping	Elements; > He; depth profiles	0.1 at. -%	e^- beam excitation; e^- detection	UHV; conductors only; limited chemical info	14, 18
Scanning Auger microscopy	SAM						
X-ray induced Auger electron spectroscopy	XAES						
Ion-induced Auger electron spectroscopy	IIAES						8
Ion neutralization spectroscopy	INS						112
Appearance potential spectroscopy	APS						113, 131
X-ray photoelectron spectroscopy	XPS	As in AES; UPS lower	Elements; > H; binding states	0.1 at. -%	$h\nu$ excitation; e^- detection	UHV; mapping limited; low sensitivity	14, 114
Electron spectroscopy for chemical analysis	ESCA						
UV photoelectron spectroscopy	UPS						
Angular-resolved UV photoelectron spectroscopy	ARUPS, ARPES						115

Inverse photoemission spectroscopy	IPES						17
Bremsstrahlung isochromat spectroscopy	BIS						
Electron energy loss spectroscopy	EELS	50 Å	All elements	0.1 at. -%	e^- excitation in SEM/TEM	Low sensitivity	17
Scanning low energy electron energy loss microscopy	SLEELM						116, 117
Ionization low spectroscopy	ILS						118, 132
C. X-ray spectroscopies							
Energy-dispersive x-ray analysis	EDXA	1 µm PIXE less	Elements; > B	0.01 at. -%	e^- beam; $h\nu$ detection	No chemical info; not surface sensitive	119
Wavelength dispersive x-ray analysis	WDXA						
Electron probe microanalysis	EPMA						
Particle-induced x-ray emission	PIXE						120
Extended x-ray fine structure spectroscopy	EXAFS	varies	Chemical states	Low	Oscill. in x-ray spectra	Slow; synchrotron	121, 122
Surface extended x-ray fine structure spectroscopy	SEXAFS						
Near-edge x-ray absorption fine structure	NEXAFS						
X-ray absorption near edge structure	XANES						
X-ray fluorescence	XRF	10 µm	Elements	0.001 at. -%	$h\nu$ excitation and detection	No chemical info; no mapping	—
X-ray diffraction	XRD	10 µm	Crystal structure	Low	X-rays	Crystalline only	—
D. Vibrational spectroscopies							
Fourier transform infrared spectroscopy	FTIR	10 µm	Molecules, functional groups	Low	Excitation of bonds by $h\nu$	Mainly qualitative	38, 40, 124
Diffuse-reflectance infrared Fourier transform spectroscopy	DRIFT						

(*continued*)

Table 1 Continued

Technique	Acronym	Sampling depth	Information	Sensitivity	Principle	Limiatation	Ref.
Attenuated total reflection spectroscopy	ATR						
Reflection-absorption infrared spectroscopy	RAIR						
Multiple reflection absorption infrared spectroscopy	MRAIR						
Grazing incidence reflection (spectroscopy)	GIR(S)						
Multiple reflection infrared spectroscopy	MRS						
Multiple internal reflection (spectroscopy)	MIR						
External reflection spectroscopy	ERS						
Surface reflectance infrared spectroscopy	SRIRS						
Photoacoustic spectroscopy	PAS						
Emission spectroscopy	EMS						
Photothermal beam deflection spectroscopy	PBDS						
Internal reflection spectroscopy	IRS						
Raman spectroscopy	RS	10 μm; 50 Å in SERS	Bonds and molecules	Low	Scattered photons	Low sensitivity; qualitative	36, 62, 70
Laser Raman spectroscopy	LRS						
Fourier transform Raman spectroscopy	FTRS						
Hadamer transform Raman spectroscopy	HTRS						
Surface-enhanced Raman spectroscopy	SERS						
Resonance Raman spectroscopy	RRS						

High-resolution electron energy loss spectroscopy	HREELS	50 Å	Molecular vibrations		e$^-$ excitation	Low resolution	37
Inelastic electron tunneling spectroscopy	IETS	1 monolayer	Molecular vibrations	Low	Excitation by voltage	Sample preparation	125
Ellipsometry	—	—	Film thickness	—	Polarized light	Sample transparent	88, 91
Bombardment-induced light emission	BLE						126, 127
Glow-discharge optical spectroscopy	GDOS	> 10 μm	Depth profile of elements	High	Sputtering by Ar$^+$ ions	Quantitative	99, 100
E. Other techniques							
Low-energy electron diffraction Elastic low-energy electron diffraction Inelastic low-energy electron diffraction Reflection high-energy electron diffraction	LEED ELEED ILEED RHEED	50 Å	Crystalline surface structure			Limited applicability	128, 129, 130
Mössbauer spectroscopy	MS	High	Chemical environment of atom (e.g., Fe)	Low	Absorption of γ-rays by nucleus	Limited no. of elements	134
Nuclear magnetic resonance Electron spin resonance	NMR ESR	Bulk samples	Chemical state and free spins	High	Resonance in magnetic fields	No surface info	—
Surface composition analysis by neutral and ion impact radiation	SCANIIR						8
Electrochemical impedance spectroscopy	EIS		Impedance of coated metal			Modeling	95, 96

Table 2 Principles of Some Spectroscopic Techniques

	Signal				
Primary beam	Ions	Electrons	Photons	Neutrals	Vibrations
Ions	SIMS ISS RBS GDMS HFS	IAES INS	PIXE GDOS SCANIIR	SNMS SARISA	BLE GDOS
Electrons	ESD	AES ILS EELS LEED SLEELM	EDXA WDXA XES EPMA		HREELS
Neutrals	FAB			NSS	BLE
Photons	LAMMA SALI	XPS XAES UPS IPES	(S)EXAFS XANES XRF Ellipsometry		FTIR SERS LRS
Voltage	FIM	STM FEM			IETS

AES is not the same for all elements detected in the sample. Further, by varying the angle between the sample surface and analyzer, the sampling depth can be varied, resulting in a nondestructive quantitative concentration depth profile in the range 5–50 Å. This feature is especially useful in XPS.

The type of information provided by the techniques listed in the tables also varies greatly. Many spectroscopic techniques give qualitative and/or quantitative elemental composition. The vibrational techniques, however, generally provide information on the molecular structure. SIMS, especially in the static mode (SSIMS or TOFSIMS), can yield information on molecular structures and even orientation of monolayers [5–10]. This is particularly useful for the study of the absorption of coupling agents on metals or to determine the effects of plasma treatments on polymer surfaces [11]. TOFSIMS instruments also have capabilities for determining the two-dimensional distributions of elements or molecular species at the surface, similar to the capabilities (for elements only) offered by AES and EDXA or WDXA.

The major technique for determining a depth profile of elemental compositions is AES. A newer technique for this purpose is SNMS, which has a better interface resolution (due to a lower sampling depth) than AES and a better sensitivity for many elements than AES [10,12,13]. In SNMS the neutrals emitted in the SIMS process are ionized and then mass-analyzed. The emission of neutrals is much less matrix-dependent than the emission of positive or negative ions detected in regular SIMS. Depth profiling can also be done in regular SIMS (the so-called dynamic SIMS version), but this technique then requires extensive calibration of sputtering rates and elemental sensitivities. Depth profiling in both AES and SIMS techniques is done by sputtering, usually by means of a beam of Ar^+ ions.

The limitations of some of the more popular techniques are also given in Table 1. For many techniques, especially the more surface-sensitive ones (ion- and electron-based methods), an ultrahigh vacuum (UHV) environment is required. This requirement, of course, increases the cost of the equipment, but it also reduces the flexibility and applicability of the technique. Other limitations of certain techniques as indicated in the table are the difficult or complex sample preparation procedures, low sensitivity (long acquisition times), and poor resolution or element selectivity (e.g., ISS). Another limitation of some of the more sophisticated techniques is that they are not commercially available. To carry out certain techniques, it may be necessary to modify commercial instruments.

III. PRINCIPLES OF SELECTED SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

Despite the enormous number of spectroscopic techniques that have been described and developed, only a limited number are commercially available and are actually used in the study and development of adhesive bonding materials. These techniques will be described in more detail in this section.

The techniques highlighted here are XPS, AES, SIMS, various forms of FTIR, Raman spectroscopies, and HREELS. This selection is based on their relative ease of application and interpretation, their commercial availability, and the unique capabilities that each technique possesses for the study of an aspect of adhesive bonding. These capabilities are also highly complementary. The applications discussed are chosen to illustrate the applications in three major areas described earlier: surface characterization, modification of metal or polymer surfaces, and analysis of interfaces.

A. Electron and Ion Spectroscopies

1. *Principles*

The three important techniques in this category that are discussed are XPS (also frequently called ESCA), AES, and SIMS. The basic principles of these techniques are discussed only superficially. Recent literature on these three techniques with examples of applications to materials science problems is abundant [3–14]. The surface analysis technique ion scattering spectroscopy (ISS), frequently discussed along with XPS, AES, and SIMS, is not considered in this chapter. Excellent recent reviews of this technique are available [15,16].

(a) XPS and AES. The principles of XPS are summarized in Fig. 1. Essentially a solid surface is ionized by low-energy x-rays, e.g., AlKα of 1486.6 eV. The photoelectrons emitted by the surface are collected and their energy distribution analyzed. The characteristic peaks observed in the photoelectron spectrum represent the various electron orbitals with binding energies lower than the exciting x-ray energy and are therefore specific for the elements present in the surface layers. The electrons in the energy region of interest have a mean free path in solids in the range 5–20 Å. The sampling depth is roughly three times this length, i.e., 15–60 Å. The technique can detect all elements with the exception of hydrogen, and an important feature of XPS is that the photoelectron peaks can shift somewhat. These shifts are dependent on the chemical state of the element. The technique, therefore, can give a quantitative analysis of all elements $>$H in the outermost 60 Å of the sample and provides some information on the functional groups or oxidation states of these elements. Some molecular structure information can be derived from a detailed

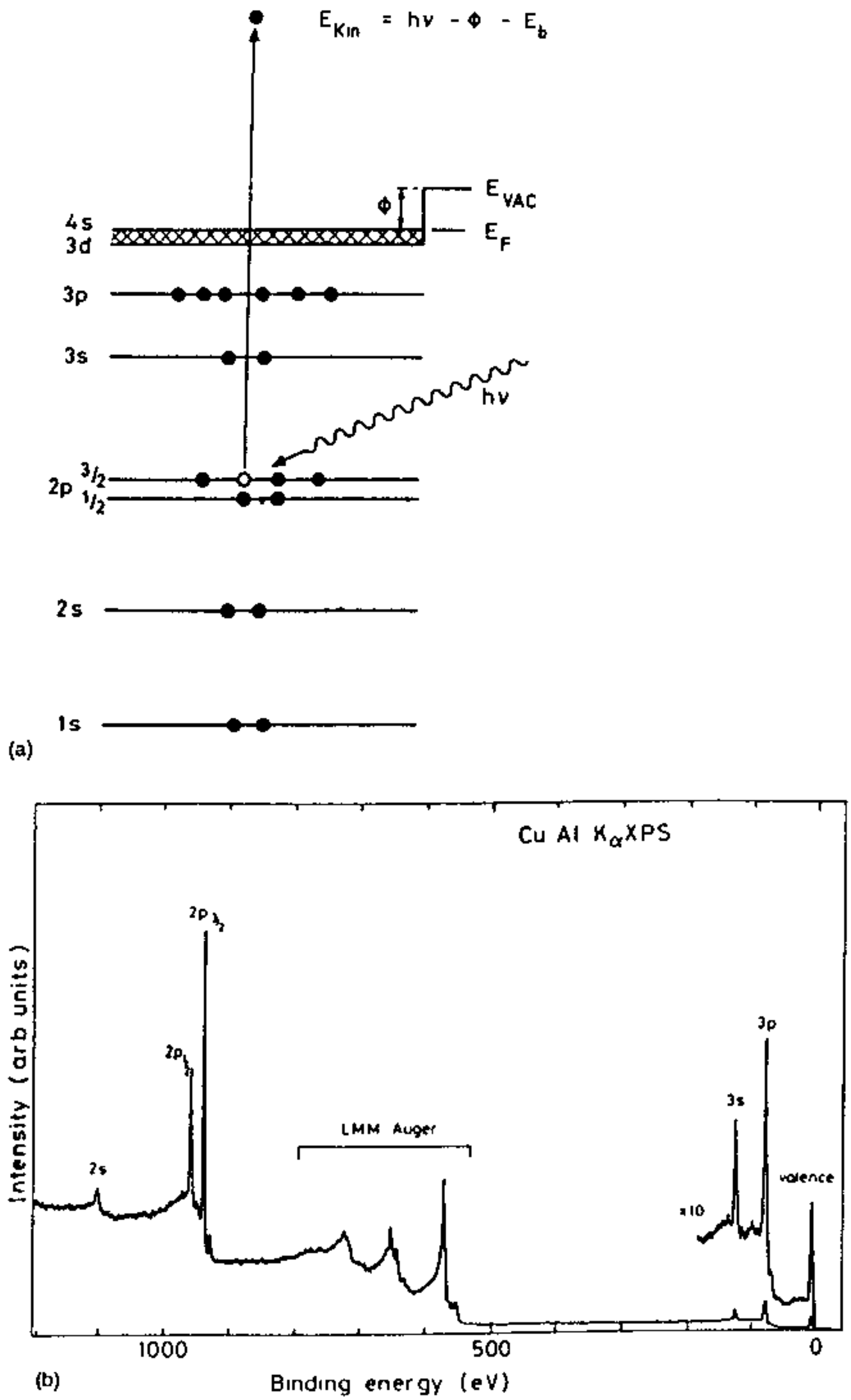


Figure 1 Principles of XPS and AES; (a) energy level diagram showing the physical basis of XPS; (b) XPS spectrum of a clean copper surface; (c) energy level diagram showing the physical basis of AES; (d) AES spectrum of a clean copper surface in the direct (top) and differentiated form (bottom). (From Ref. 17.)

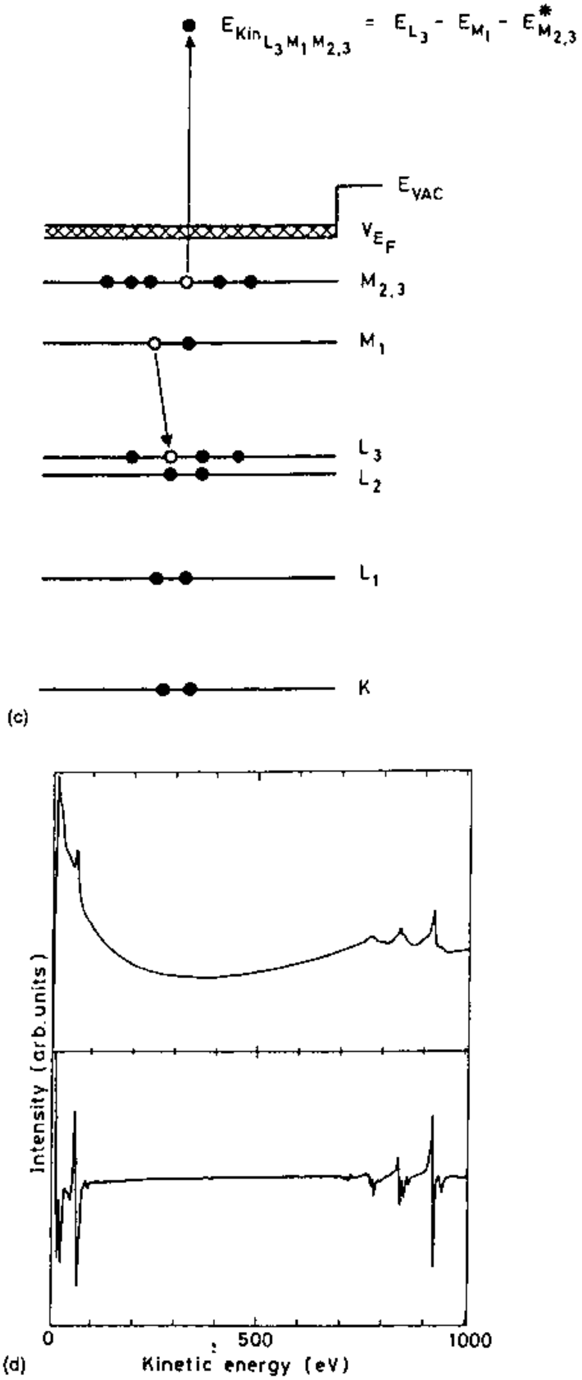


Figure 1 (Continued)

analysis of the valence band of the material, which, however, has very low intensity. A more detailed analysis of the valence band structure is possible in UPS.

XPS has been in use since the early 1970s. Currently there are five manufacturers of commercial instruments. The strengths of XPS are its ease of operation, its quantification, and its applicability to a wide range of materials and sample forms (powders, wires, foils, chunks, etc.); in addition, both conductors and insulators can be analyzed. Sample preparation is minimal. Since the sampling depth is several dozens of monolayers, the technique is not so sensitive to surface contamination as the ion-based techniques SIMS and ISS. The major limitations of the technique are its rather poor spatial resolution (although recent improvements have been made, pushing the resolution on some commercial instruments to about 10 μm), the rather low detection limits (about 0.1 at.-% for many elements, requiring many hours of data acquisition), and the rather limited chemical information obtainable on organic materials, which is nowhere near that of, for instance, NMR and FTIR.

AES differs from XPS in that the surface is ionized by a finely focused electron beam of 5–30 kV (Fig. 1). The secondary electrons have no specific information content in AES, but the Auger electrons, which are emitted shortly after the secondary electrons, and which involve transitions between different orbitals, are recorded as a function of their kinetic energy. Such Auger electrons are also emitted after ionization by x-rays in XPS and consequently the same Auger transitions lines are also observed in XPS. In XPS, this aspect of the technique is sometimes referred to as XAES (Table 1). Because of a very high background, AES spectra are conveniently represented as differentiated spectra. The peak-to-peak heights (more accurately, peak areas in the nondifferentiated spectrum) are proportional to the number of atoms in the probed sample volume.

Since the electron energy ranges are approximately the same in XPS and AES, the surface sensitivities and sampling depths in these two techniques are very similar. In both techniques, quantification is performed, in a first approximation, by dividing the areas under the peaks (or the peak heights) by the appropriate sensitivity factor for the elements, followed by normalizing to 100%. Sensitivity factors are usually provided by the equipment manufacturer and they have been determined experimentally, although they can be calculated using ionization cross-sections (in XPS) and back scattering factors (AES). The use of these standard sets of sensitivity factors enables atomic concentrations to be determined with an accuracy of about 1–5% [14,17]. Since the electrons detected for the various elements in a sample differ in energy, the depths from which their signals originate, and hence for which their concentrations are calculated, are not the same for all elements detected. This applies to both XPS and AES.

The strength of AES lies in its small spot analysis capability. Modern instruments equipped with field emission electron guns have a spot size of about 100 Å. The lateral resolution for mapping elemental distributions is therefore less than 0.1 μm, i.e., considerably better than in EDXA. The reason for this is that in AES the signal stems primarily from the surface layers; hence the broadening of the primary beam, as occurs in EDXA, does not affect the resolution in AES very much. Another capability of AES is to provide elemental concentration depth profiles using a simultaneous sputtering process by energetic ions (usually Ar^+). Depth profiling can be automated under computer control. In XPS depth profiling can also be done but only intermittently, and another problem is that electrons are collected from a much wider area than in AES and, therefore, edge effects due to non-homogeneous sputtering rates across the width of the argon beams are more likely to occur.

There are several limitations in AES. The most important one is that spectra cannot be collected (or can be collected with great difficulty) from insulating materials. Charge neutralization procedures that can be applied routinely do not exist. As opposed to surface charging in SIMS (see below), the charge in AES is of a negative sign. This limits the application of AES to metals, semiconductors, or thin films (e.g., oxides). Other limitations are the electron beam damage that easily occurs with certain materials, especially organic films, and the rather limited chemical information that can be extracted from AES spectra [18]. In principle, chemical shifts occur as in XPS, but they are more complicated because several orbitals are involved in each Auger transition and in most commercial instruments the energy resolution is not good enough to resolve such shifts. By the same token, peak overlap occurs in certain cases, especially in the energy range where many transition elements have their major AES lines, such as the range Mn–Zn (600–1000 eV). As an example, Mn in steel is very difficult to resolve and materials containing Fe, Ni, and Co would require sophisticated peak subtraction software to analyze. Other limitations are that quantification is less reliable than XPS as a result of electron backscattering phenomena, which can be estimated but not with high accuracy. Further, the ionization probability by the primary electron beam depends on the energy of these primary electrons. In the derivative mode, errors can be introduced because peak shapes change with chemical state of the elements. This problem can be resolved, however, by determining the peak areas before spectra differentiation and by using sensitivity factors derived for the nondifferentiated peaks. Similar to XPS, the detection limits in AES are not very low, i.e., for most elements of the order of 0.1 at.-% or worse.

Current developments in AES are mainly in the areas of improved electron guns with higher brightness and smaller spot sizes, and multichannel detectors with improved sensitivities. Improvements of energy resolution will enable chemical states to be studied in more detail, leading to better analysis of complex mixtures with partly overlapping peaks.

(b) SIMS. The major ion beam technique that is currently going through a period of rapid development is SIMS [4–9]. There are several variations of the technique (Table 1), but the principle common to all is that a solid surface is bombarded by energetic ions. Ions that are commonly used are Ar^+, $O_2{}^+$, O^-, Cs^+, Ga^+, and others. Their energy can be in the range 5–30 keV. The impact of these ions results in the emission of secondary ions, neutral atoms, molecular fragments, and electrons. A mass spectrometer collects the ions (positive or negative) in the form of a mass spectrum. The major variations of the SIMS technique are the following:

Static SIMS. In this form of SIMS, the total primary ion dose is so low (i.e., around 10^{12} ions/cm^2, or even less) that in the course of the experiment (1–5 min) all primary ions impinge on a fresh surface; the result is that the mass spectrum does not change with time and represents a fragmentation pattern that can be taken as a fingerprint of the material [19,20]. Both small and large ions (up to the molecular ion, or oligomers, if present) are emitted [21–23]. The sampling depth of this technique is not more than 1–2 monolayers (≈ 5 Å). SSIMS is unique in that it detects all elements (including hydrogen) and at the same time provides molecular information on the outermost surface layers of the sample. For example, it can easily distinguish polyethylene from polypropylene (as shown in Fig. 2), detects inorganic contaminants in these polymers, and also indicates surface oxidation from the presence of O-containing ions. The latter aspect is useful for studying surface modifications of polymers by plasma or corona techniques [11,24]. For elemental detection, the technique is very sensitive, especially for alkali metals (ppm level). Although the technique is primarily used in a qualitative mode, quantitative correlations between peak ratios and elemental concentrations in XPS of the same sample have been demonstrated [25,26].

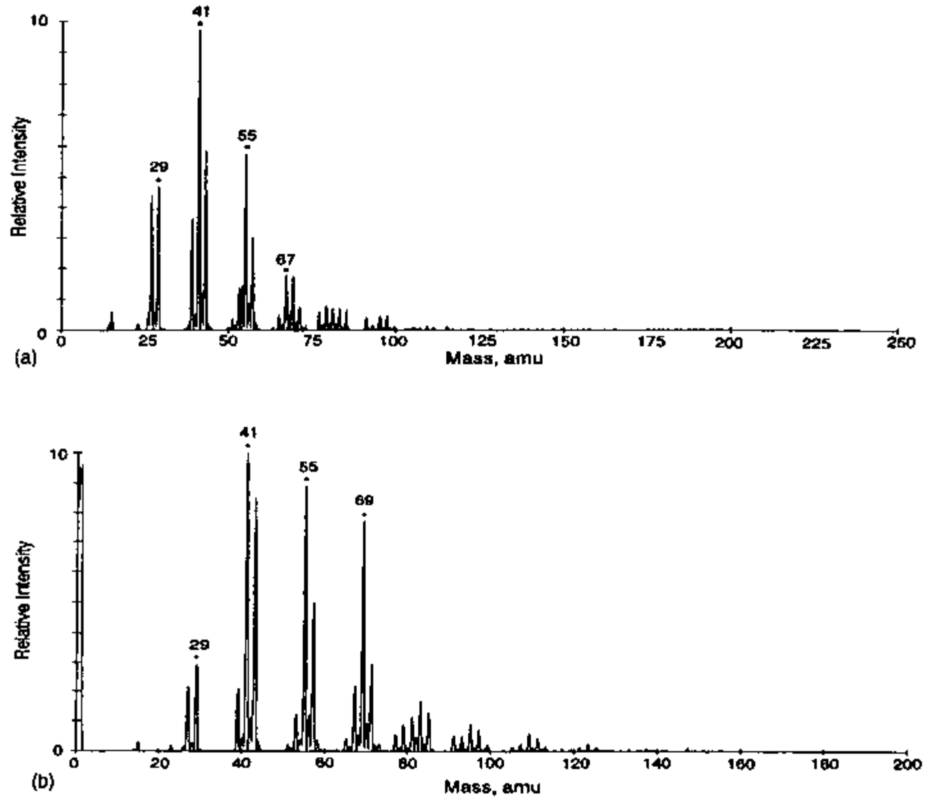


Figure 2 Positive quadrupole SIMS spectrum of surface of (a) polyethylene and (b) polypropylene. (From Ref. 20.)

Dynamic SIMS. In this version of SIMS, the total ion dose is much higher than in static SIMS, up to a factor of 10^4. Therefore, sputtering is now the dominant process and an elemental depth profile is obtained [27]. Organic structural information is no longer contained in the spectra, because organics decompose to the elements and CH_x fragments. Therefore, concentration depth profiling of organic materials, with retention of some of the molecular structure, is impossible. However, some information can be obtained if one of the constituents is specifically isotopically labeled, for instance by deuterium. As in AES, the profiling process can be automated. As a result of the lower sampling depth in SIMS, the depth resolution is better than in AES. On the other hand, the quantification of elemental concentrations is more complicated in SIMS because ion emission is strongly matrix-dependent.

Imaging SIMS. In this variation, the ion beam is rastered across a surface and a two- dimensional distribution of elements or organic materials is obtained. If this version is combined with the static SIMS mode, mapping of each peak observed in the spectrum can be performed, so even in mixtures of many organic compounds each component can be individually mapped as long as the component has at least one specific peak in the spectrum. For metals, oxides, and semiconductors, the mapping capabilities are similar to that of AES, although the sensitivity for many elements in SIMS is much higher. An example of mapping of an organic compound is shown in Fig. 3.

Figure 3 Time-of-Flight SIMS map of the distribution of the intensity of the ion –255 amu originating from stearic acid in lubricant residue at the surface of a cold-rolled steel sample; magnification approximately 500×; primary ions $^{69}Ga^{+}$ of 25 kV.

Secondary Neutrals Mass Spectrometry. This version of SIMS detects specifically the neutral molecules or atoms that are emitted in the SIMS process [12,13]. The positionization of these neutrals is performed by low-energy electrons or by lasers used in a resonant or nonresonant mode. Since in SIMS about 99% of the emitted species are neutral particles, the positionization process increases the sensitivity of certain elements. The species that had originally been emitted as ions are, of course, detected also, but they constitute only a small fraction of the total signal. The importance of SNMS is that matrix effects are largely eliminated. In general, the emission of a species (i.e., charged and uncharged) does not depend on the chemical state or the matrix, but on the sputtering coefficient only. Peak intensities can therefore be more easily converted to concentrations using sensitivity factors only. SNMS can thus be expected to become the foremost technique for quantitative depth profiling in the near future, because it is fast, very sensitive, quantitative, and has superior depth resolution.

For static SIMS of organic materials, postionization (in this case using lasers in a nonresonant mode) can also be performed. Compared with the normal SIMS spectrum, the spectrum then contains several extra peaks if postionization is applied. These are due to the monomeric repeating unit of the polymer or to entire small molecules that are emitted. These extra ions are very useful for the identification and characterization of the materials.

Time-of-Flight SIMS. The introduction of TOF analyzers, along with postionization, is one of the major developments in the SIMS techniques of the last few years.

TOFSIMS is essentially static SIMS in which the quadrupole mass spectrometer has been replaced with a time-of-flight spectrometer, which gives the technique unique capabilities [28,29]. Ions are extracted at high voltage (e.g., 3 kV) and then enter into a field-free flight tube 1–2 meters in length where they are separated according to their flight time, which depends on their mass (Fig. 4). Advantages of this type of SIMS are that both the transmission and the mass resolution of the mass analyzer are considerably higher than

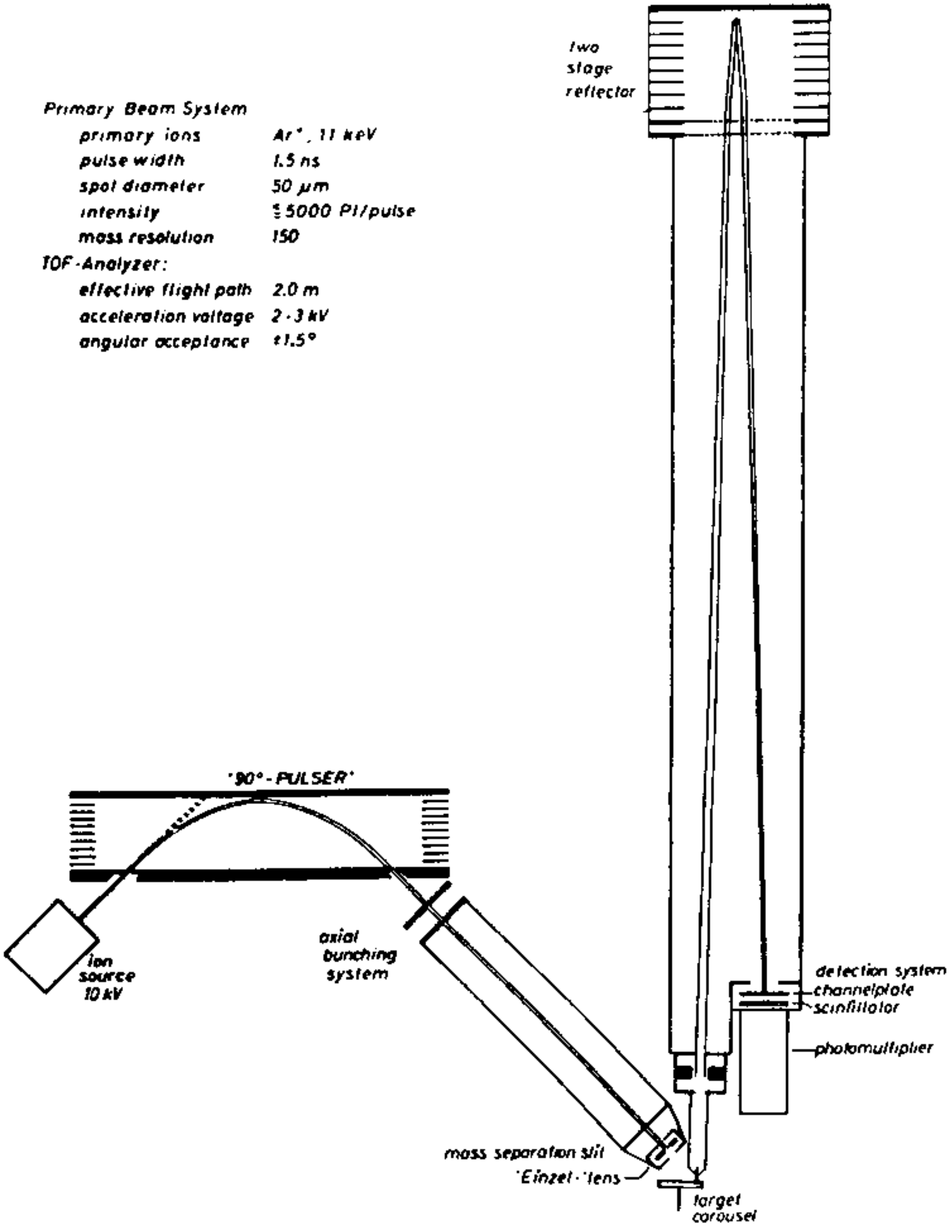


Figure 4 Principle of Time-of-Flight SIMS showing mass-separated primary beam of 10 kV Ar^+ ions and 2 meter flight tube with two-stage ion reflector system. (From Ref. 7.)

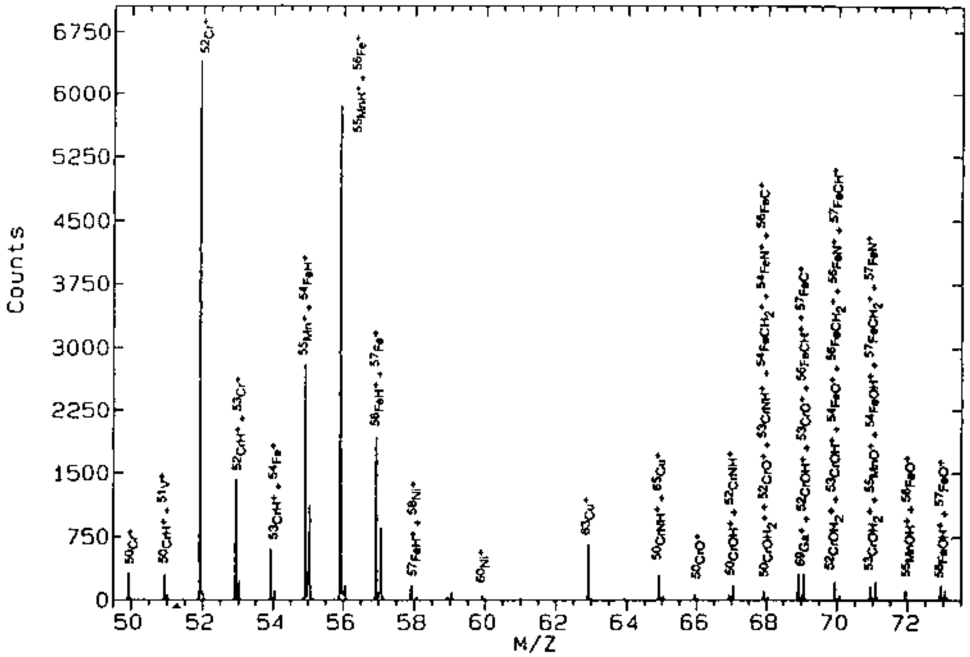


Figure 5 Part of positive, high mass-resolution Time-of-Flight SIMS spectrum of a polished 304L stainless steel surface; primary ions $^{69}Ga^+$ of 25 kV.

those of the quadrupole analyzer. As a consequence, TOFSIMS has higher sensitivity (so that spectra can be recorded with lower total ion dose) and a mass resolution that enables peaks with nominally the same mass to be separated. The actual resolution obtained depends on the quality of the ion gun, which has to deliver pulses at the nanosecond level rather than being run continuously, as in quadrupole SIMS.

Because of the high mass accuracy, peak identities can now also be identified uniquely. An example is given in Fig. 5. This capability has removed most of the guesswork from SIMS analysis and has opened up many applications in materials science that are impossible in quadrupole SIMS because of peak overlap. For instance, studies of most practical metals, e.g., Al, are very difficult in quadrupole SIMS because the metal ions of interest almost always overlap with organic ions at nominally the same mass. Another important advantage of TOFSIMS is the much higher mass range than in quadrupole SIMS, which enables very large ions to be detected. An example is illustrated in Fig. 6, which shows the distribution of oligomers present in the surface of a polymer sample [23]. However, such results cannot be obtained with bulk materials. The polymer has to be present as an extremely thin film on an active metal (usually Ag). In the SIMS process the oligomers, which are emitted as neutral molecules, then become cationized by Ag^+ ions.

The spectra in TOFSIMS are similar to those in quadrupole SIMS, but not identical. The time-of-flight analyzer can detect ions with a much greater kinetic energy spread than the quadrupole. Therefore, inorganic ions or low-mass organic fragments, such as C^+ and CH^+, which are emitted with high kinetic energies, appear in higher intensities in TOFSIMS spectra than in quadrupole spectra.

TOFSIMS is rapidly gaining popularity as a tool for studying chemistry and orientation at organic surfaces, such as polymers and polymer blends. The problem of surface

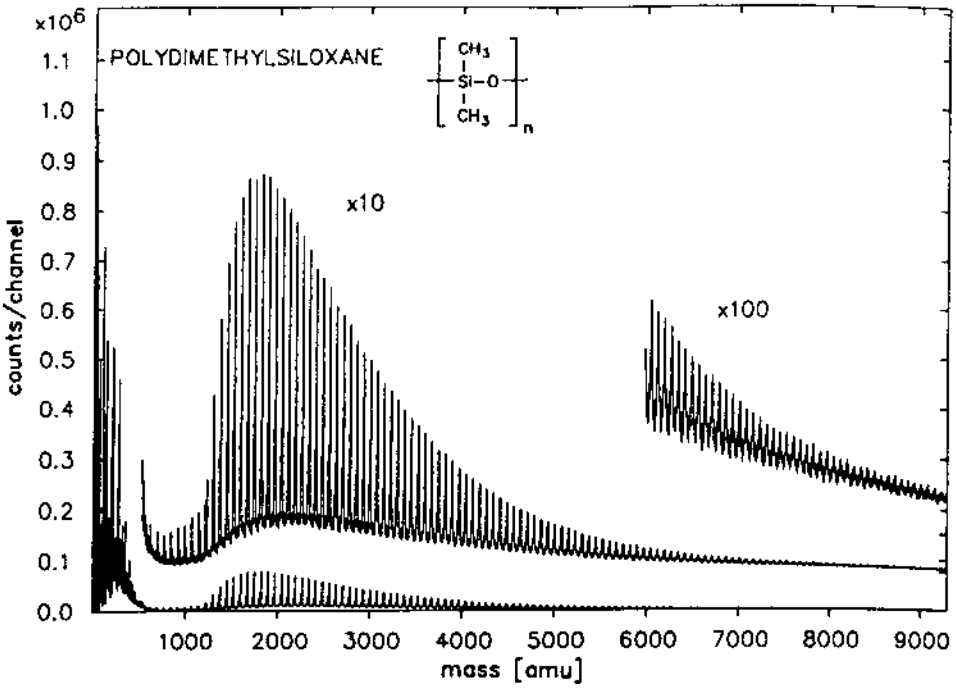


Figure 6 Positive Time-of-Flight SIMS spectrum obtained from a thin film of polydimethylsiloxane on a silver substrate showing the polymer fragmentation in the 0–500 amu range and the oligomer distribution in the higher mass ranges. (From Ref. 7.)

charging (the surface charges up positively as a result of electron emission) has been satisfactorily solved by the development of pulsed electron sources, which neutralize the charge. Imaging (as shown in Fig. 3) can be performed routinely with high sensitivity and sub-micron resolution. A limitation of the technique is, however, that standard spectra of many materials are not yet available. Although much can be derived from the chemistry of the material (if known!) and the exact mass of the ions, in many cases it is not possible to identify exactly the composition or structure of the material. Much more work needs to be done in this area before the technique can be applied routinely by unskilled analysts. Fortunately, several databases (for quadrupole SIMS) have been published [19,20] and others (for TOFSIMS) are being prepared.

2. *Some Selected Applications*

In this section some selected examples of XPS, AES, and SIMS are discussed, which may illustrate the capabilities of these techniques for adhesives-related applications.

In the example shown in Fig. 7, a thin film of plasma-polymerized trimethylsilane had been deposited on cold-rolled steel as a pretreatment for improved adhesion and corrosion [30]. The film thickness was determined by ellipsometry to be 500 Å. The composition was characterized by AES, XPS, and TOFSIMS. AES gave information on the bulk composition, surface enrichment, and interfacial oxide (Fig. 7b). Note that the C/Si ratio of the bulk of the film, after equilibrium sputtering conditions have been reached, is approximately 3, i.e., identical to that of the monomer from which the film was

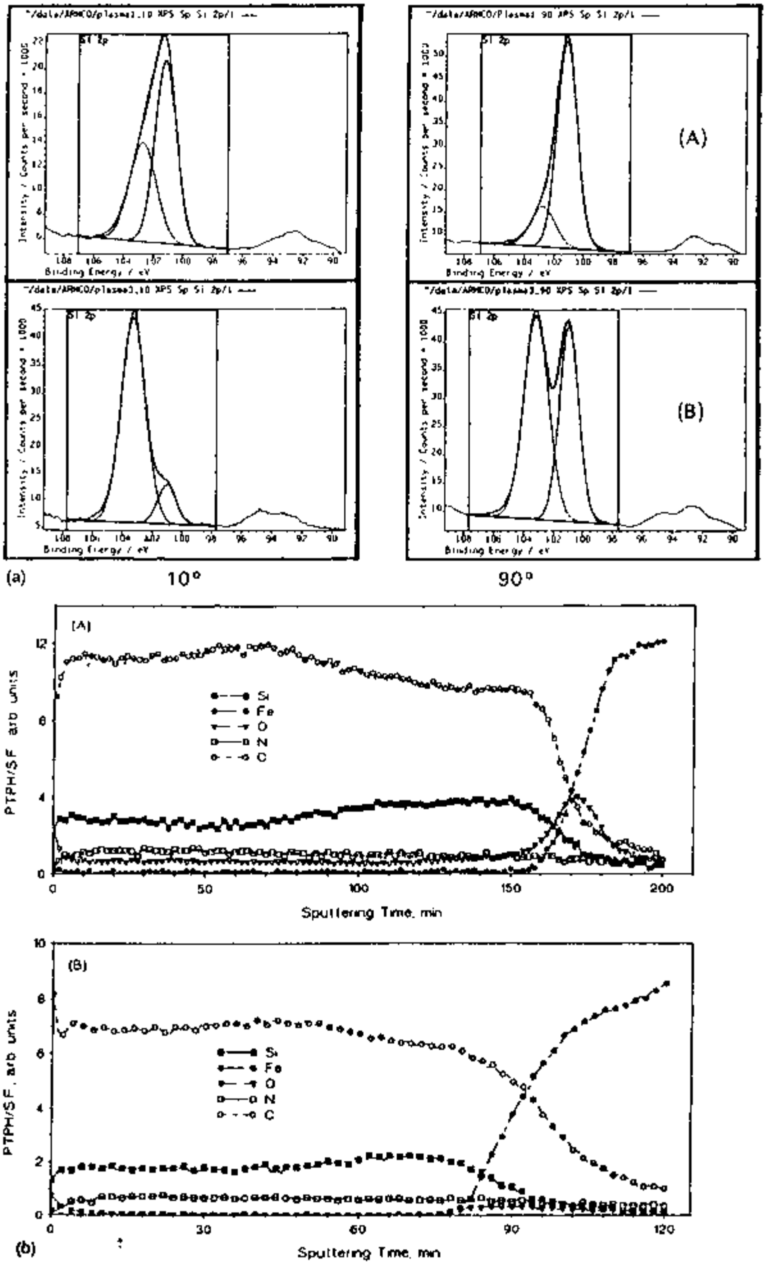


Figure 7 (a) XPS spectra at takeoff angles 10° and 90° (between sample surface and normal) of the surface of plasma-polymerized trimethylsilane films on steel substrates; film (A) was deposited in non-reducing conditions, film (B) was prepared in reducing conditions. The spectra demonstrate the presence of highly oxidized Si in the extreme surface layers; (b) depth profiles by AES of the films of Fig. 7a showing regions with different elemental composition in the films and the presence of an iron oxide in film (A); the sputtering rate was 5 Å/min; (c) positive (top) and negative (bottom) time-of-flight SIMS spectra of film (A) of Fig. 7a before and after rinsing in methanol. The changes in the spectra indicate that low molecular weight soluble components were present in the as-deposited film. (From Ref. 30.)

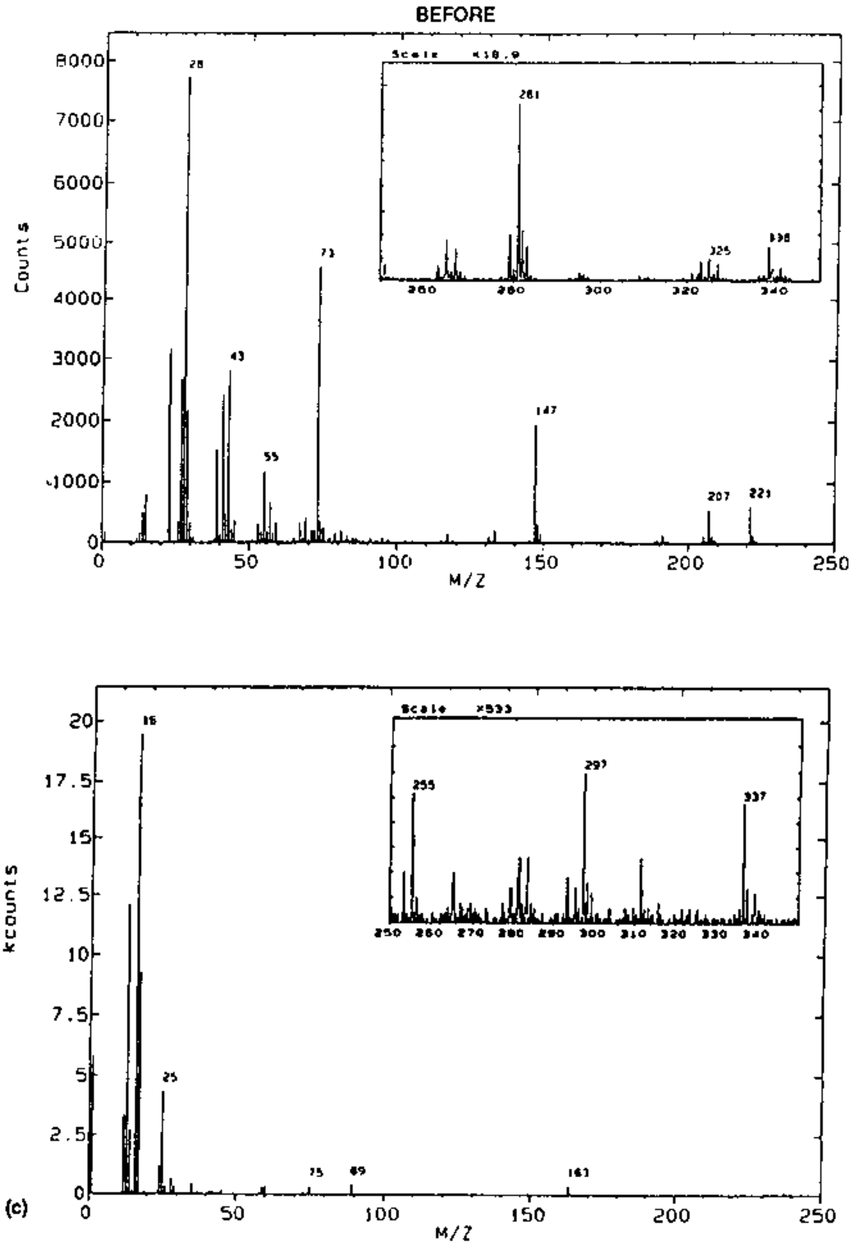


Figure 7 (Continued)

made. XPS was performed on the same samples at two different takeoff angles. Lowering the takeoff angle increases the surface sensitivity (sampling depth) of the technique. Shown in Fig. 7a are the Si2p lines from which the conclusion can be drawn that the surface of the film is enriched in Si–O bonds, whereas the bulk has a higher concentration of Si–C bonds. In Fig. 7c, parts of the TOFSIMS spectra are shown of the same film before and after solvent cleaning. This rinse was performed to check on the presence of low molecular weight materials at the film surface, which are known to form in plasma polymerization.

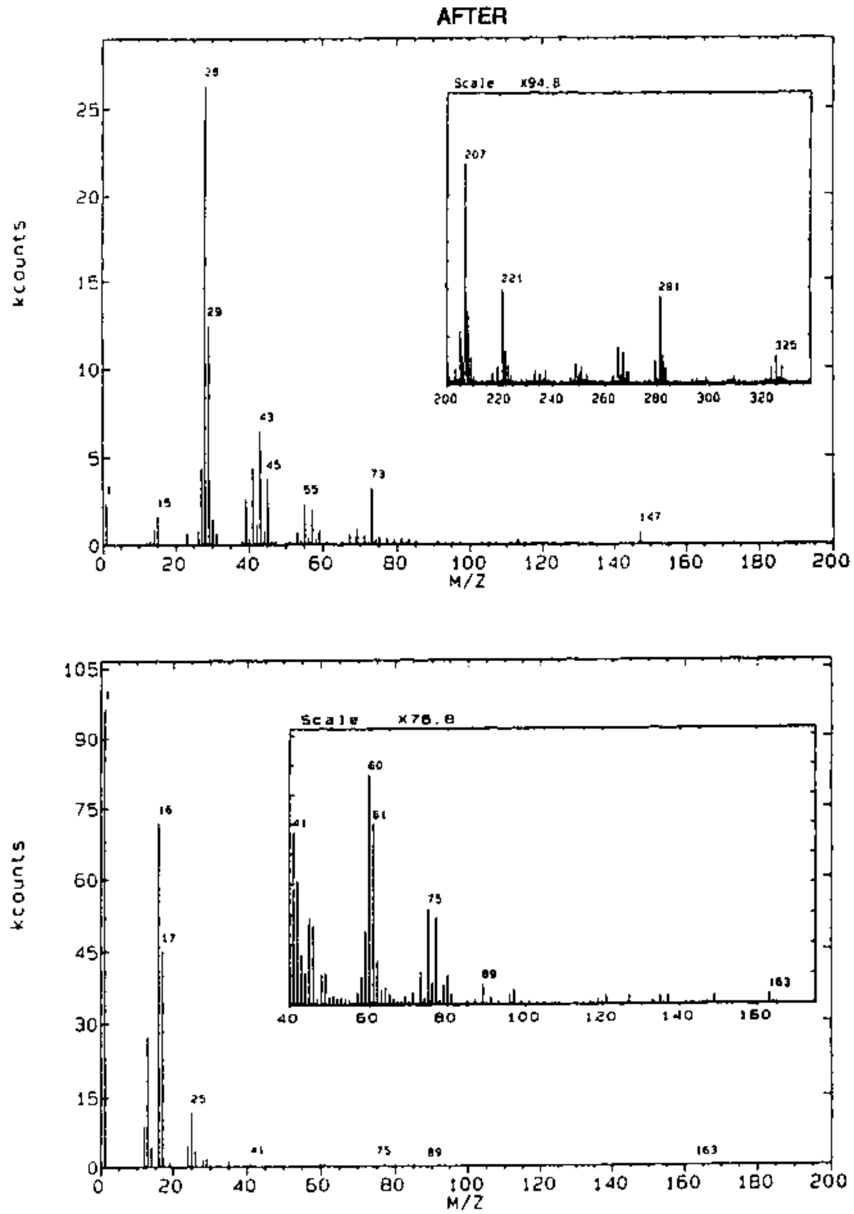


Figure 7 (Continued)

This rinsing treatment had practically no effect on the XPS and AES results, but the TOFSIMS spectra before and after rinsing are quite different. Before rinsing, the spectrum resembles that of polydimethylsiloxane [19,20]; after cleaning the surface is similar to that of SiO_2. The spectrum indicates a high concentration of silanol groups, as can be concluded from the high intensity of the peak at +45 amu ($SiOH^+$). The peak identification and the fit between observed and calculated masses are shown in Table 3 for a silane film on CRS [31]. Only those compositions were accepted that had a deviation of less than 0.01 amu from the calculated mass. It is clear from this example that application of the three

Table 3 TOFSIMS Peak Identification of Silane Film on Steel

		pH 10.5		pH 8.0	
Ion	Composition	$\triangle m$[a]	Counts/yield[b]	$\triangle m$[a]	Counts/yield[b]
−1	H^-	0	50.57	0	28.92
−16	O^-	2	16.70	3	12.60
−17	OH^-	2	10.55	1	5.56
+17	NH_3^+	1	0.41	1	1.42
+18	NH_4^+	2	0.80	2	2.65
+28	Si^+	0	23.30	0	19.29
+31	CH_5N^+	1	0.80	3	3.42
−35	Cl^-	—[c]	—	0	28.60
+39	[d]$C_2HN^+/C_3H_3^+$	1	1.85	2	4.18
−41	CHN_2^-	7	0.13	5	0.07
+41	[d]$C_3H_5/C_2H_3N^+$	3	3.30	3	5.90
+42	[d]$C_2H_4N^+/C_3H_6^+$	3	2.06	2	2.48
+43	[d]$C_3H_7^+/C_2H_5N^+$	4	2.73	1	2.60
+44	SiO^+	10	3.01	10	1.35
+45	$Si(OH)^+$	2	2.15	8	2.86
+55	$C_4H_7^+$	5	1.14	2	1.03
+56	Fe^+	0	4.76	3	0.44
−60	SiO_2^-	2	0.26	1	0.27
−61	$HSiO_2^-$	11	0.15	10	0.13
+62	$Si(OH)_2^+$				
−77	$HSiO_3^-$	6	0.07	5	0.065
+79	SiO_3^+	6	0.15	3	0.36
−89	$C_2H_7NSiO^-$	1	0.01	1	0.01
+100	$C_2H_2NSiO_2^+$	3	0.60	3	0.10
+102	$C_2H_4NSiO_2^+$	1	0.13	2	0.15
+105	$C_3H_{11}NSiO^+$				
−118	$C_3H_{10}N_2SiO^-$	4	0.03	4	0.008
+121	$C_3H_{11}NSiO_2^+$				
−121	$HSi_2O_3NH_2^-$	0	0.013	2	0.009
−127	$C_2H_3SiOFe^-$	—	—	10	0.028
−137	$HSi_2O_4NH_2^-$	5	0.008	5	0.005
+147	$(CH_3)_5Si_2O^+$	—	—	5	0.05
+149	$C_3H_{11}NFeO_2^+$	—	—	4	0.17
+163	$C_4H_{13}NSi_2O_2^+$	—	—	5	0.06
+207	$C_5H_{15}Si_3O_3^+$				
+221	$C_7H_{21}Si_3O_2^+$				
+281	$C_7H_{21}Si_4O_4^+$				

[a] Difference between listed composition and measured mass in milli-amu.
[b] Ratio of counts in peak area and total ion yield.
[c] Ions listed without $\triangle m$ and counts/yield values are for methanol-cleaned sample only.
[d] At pH 10.5/pH 8.0.
Source: Ref. 31.

techniques discussed here yields complementary information, enabling a more detailed description of the film structure than any of the three techniques alone.

An example of the characterization of a thin film of a coupling agent adsorbed on a metal surface is given in Fig. 8 [24]. The coupling agent was vinylbenzylaminoethyl

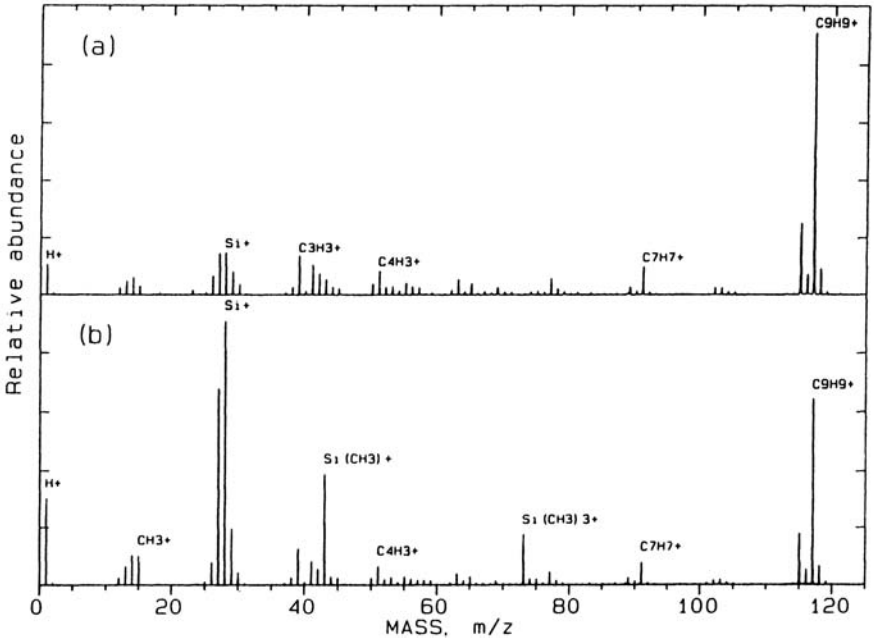


Figure 8 High mass-resolution positive Time-of-Flight SIMS spectra of films deposited on a zinc substrate of the hydrolyzed silane SAAPS (styryl aminoethyl aminopropyl trimethoxy silane); (a) immersion time 30 s; (b) immersion time 390 s. The spectra demonstrate a highly oriented film in (a) and a loss or orientation in film (b). The ion $C_9H_9^+$ is the styryl end group of the silane molecule. (From Ref. 24.)

aminopropyl trimethoxysilane (SAAPS). Following hydrolysis in a mixture of water and alcohol, the silane was applied by dipping the metal in a very dilute solution. The figure shows a very high intensity of the peak at +117 amu after short immersion times, and a high Si^+ and lower +117 amu intensity after longer immersion times. The peak at +117 amu was uniquely identified as $CH_2{=}CH–C_6H_4–CH_2^+$, i.e., the end group of the coupling agent. This example thus demonstrates that the silane is highly oriented if applied as a monolayer, but this preferred orientation is absent after deposition of several monolayers. Knowledge of this orientation is important for the optimization of surface pretreatments by means of coupling agents.

An example of the use of deuterated materials in TOFSIMS studies is given in Fig. 9. Blends of polystyrene (PS) and fully deuterated polystyrene (d^8-PS) were prepared in experiments in which segregation effects were investigated [32]. Variables were the ratios between the two polymers and the molecular weights. The most characteristic peak in polystyrene is +91 amu ($C_7H_7^+$, tropyllium) and the corresponding ion for d^8-polystyrene is at +98 amu. The spectrum in Fig. 9 illustrates that in this example of 1:1 PS/d^8-PS ratio of equal molecular weights, the deuterated material is enriched at the surface. This type of application, i.e., monolayer surface sensitivity with organic structural information capability and separation of all isotopes, is unique to SIMS. There appears to be no other technique, except perhaps SERS (to be discussed below), that could identify this phenomenon.

The final example is a combined application of TOFSIMS and XPS, which was used to characterize the interface between a metal and a polymer system [33]. The

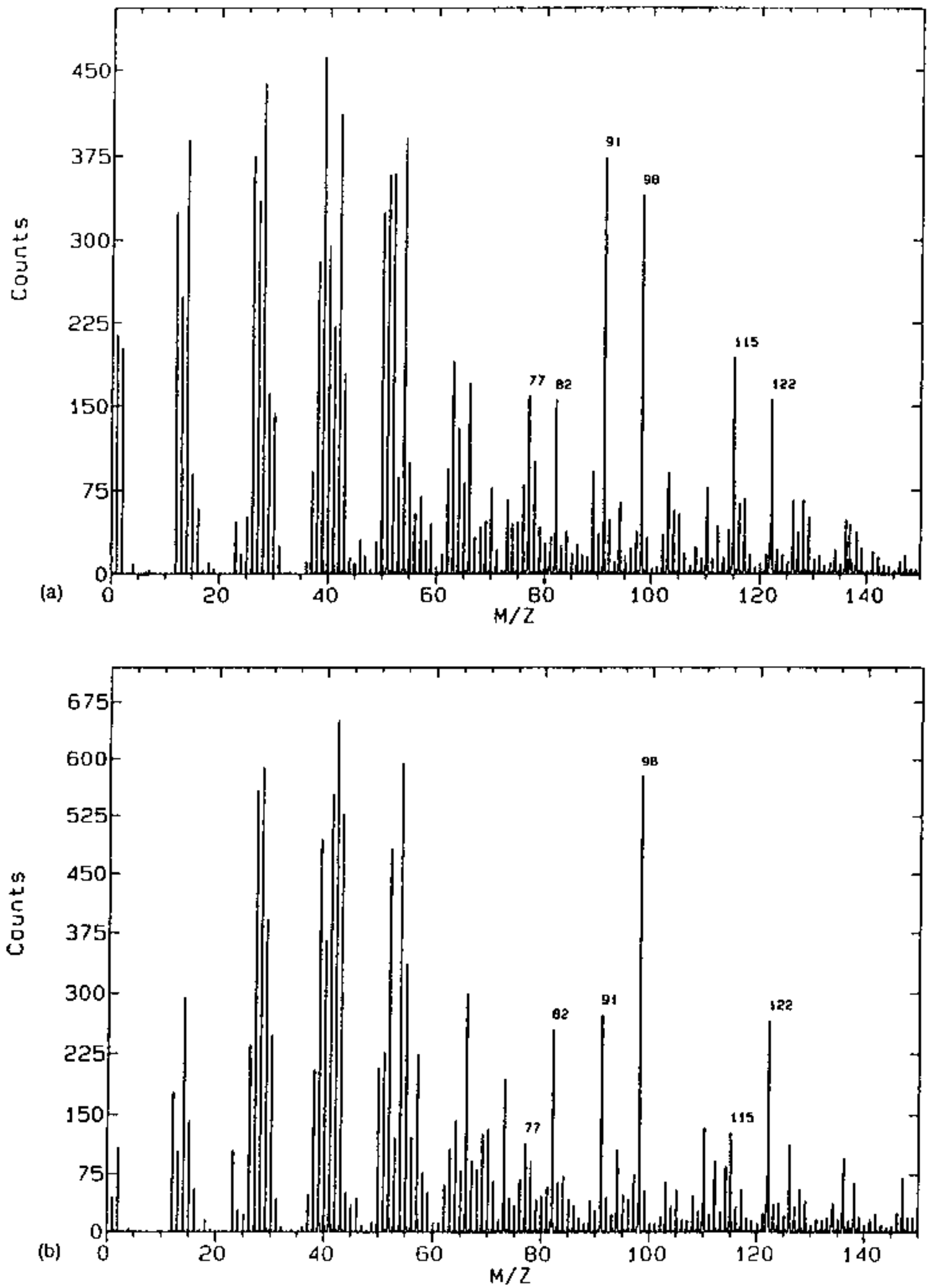


Figure 9 Positive Time-of-Flight SIMS spectra of 50/50 (by weight) blends of high molecular weight polystyrene and fully deuterated polystyrene (M_w=1,950,000 for both polymers) before (a) and after (b) annealing for 24 hours at 200°C in an inert gas. The labeled ions 82, 98 and 122 amu are the deuterated analogs formed by the deuterated polymer of the ions 77, 91 and 115 amu formed by polystyrene. The spectra demonstrate the increase of the surface concentration of the deuterated polystyrene upon annealing. Courtesy F.J. Boerio and P.P. Hong, University of Cincinnati.

polymer system was a cathodic electroprimer that is widely applied in automotive applications over the zinc phosphate conversion coating. Knowledge of the chemistry at the interface between the phosphate and the primer is important for the understanding and optimization of the adhesion and corrosion performance of the entire paint system. One aspect is, for instance, the degree of the cure of the primer, which may vary among different parts of the automobile. Therefore, an example is also given of TOFSIMS analysis of the primer surface/interface after undercure and overcure conditions.

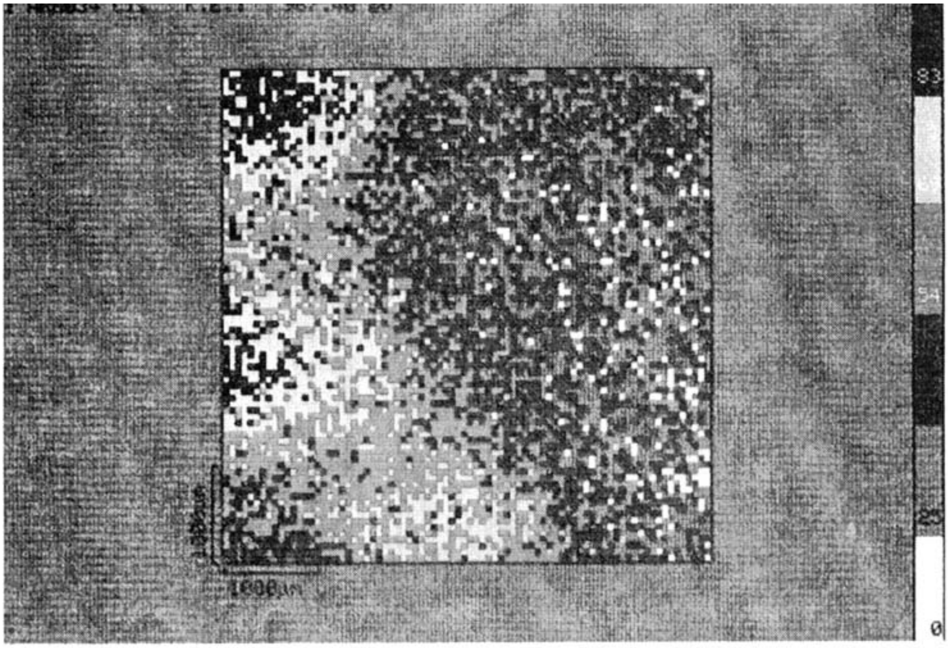
In Fig. 10, XPS maps are shown of the C1s photoelectron line and ZnLLM Auger line recorded at the metal surface of a paint-galvanized steel system following exposure in a corrosion test. The panels showed several small circular spots where corrosion had occurred. The paint had been removed after the test [33]. The distributions of the two elements in the small corrosion spots are complementary, indicating that in these local areas organic debris was covering the metal surface. SIMS analysis detected in these areas high concentrations of Na^+ ions. Areas with high sodium concentrations are normally the cathodes of the corrosion cells, the counterions being the cathodically generated OH^- ions. This experiment thus demonstrated that the local areas shown in Fig. 10 were formed at cathodic sites, probably as a result of decomposition of the polymer by alkaline attack. This is a good example of a system where the XPS mapping capability is useful. AES, despite its higher spatial resolution, is not very useful for organic surfaces and SIMS, with its much higher surface sensitivity, would also detect mainly organic material in the Zn-rich regions.

In Fig. 11, TOFSIMS spectra are presented of the two sides of the interface between a cathodic E-coat and a phosphated cold-rolled steel substrate. A variable in this experiment was the cure temperature of the paint [24]. The paint system is epoxy-based and can, after the cure, be described as an epoxy–urethane as the crosslinker is a blocked diisocyanate. The spectra indicate that in both cases the separation is very close to the metal (i.e., zinc phosphate) surface, but the difference in the spectra indicates differences in the cure conditions of the paint. Several high mass peaks, indicated on the spectra, decrease or increase with cure temperature. Other peaks that are marked demonstrate the presence of the cross-linker at the interface. Other conclusions drawn from these paint studies using TOFSIMS and imaging XPS were that the degree of cure is generally higher at the metal/coating and that the surface of the paint is always in a lower state of cure as a result of interfering oxidation reactions [33].

In similar studies in which the metal/coating interface was investigated as a function of immersion time in a dilute salt solution, it was found by TOFSIMS that paint degradation always occurred in regions with high Na^+ concentration [34]. The counterions Cl^- were not detected at the interface. These results are very important in that they prove that cation diffusion through an organic coating is a critical step in the complex series of events leading to corrosion beneath organic coatings and that alkaline paint attack plays a role in the propagation mechanism. The high sensitivity of SIMS, along with the mapping and peak identification capabilities, makes this technique very powerful for the study of metal–organic interfaces.

B. Vibrational Spectroscopies

The major spectroscopic techniques for use in adhesive bonding technology that are based on vibrational principles are several forms of infrared spectroscopy, Raman spectroscopy, and the more recent technique HREELS, the vibrational version of EELS used in electron microscopes. These techniques will be discussed in this chapter and some recent developments and applications of the techniques in adhesion studies will be given. Raman and IR



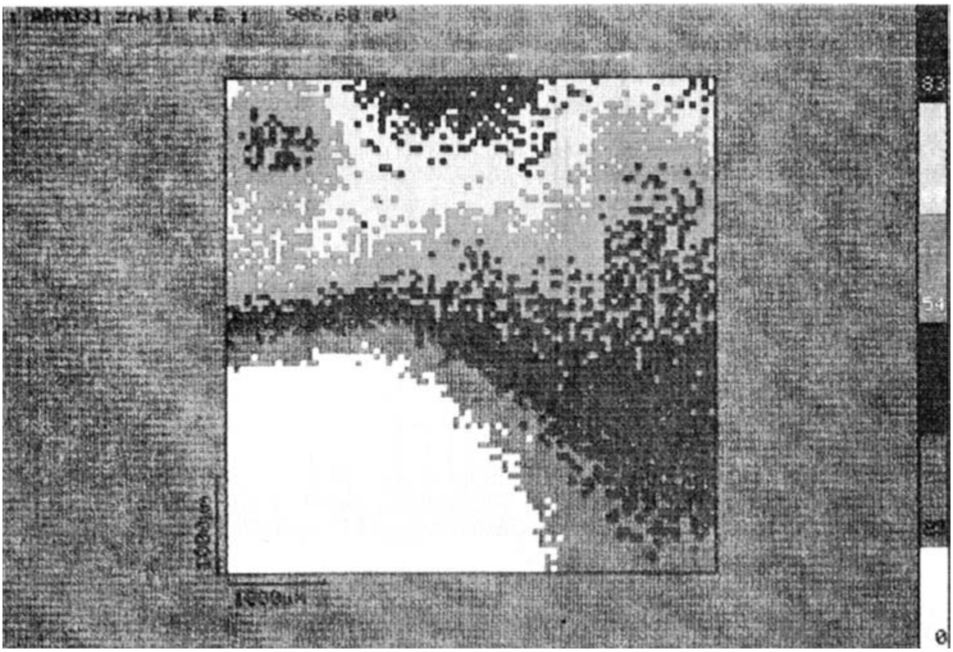


Figure 10 Element maps of carbon (C1s line, top) and zinc (ZnLLM line, bottom) recorded by imaging XPS at a corroded area on a galvanized steel surface. The area shown is 5×5 mm^2. (From Ref. 32.)

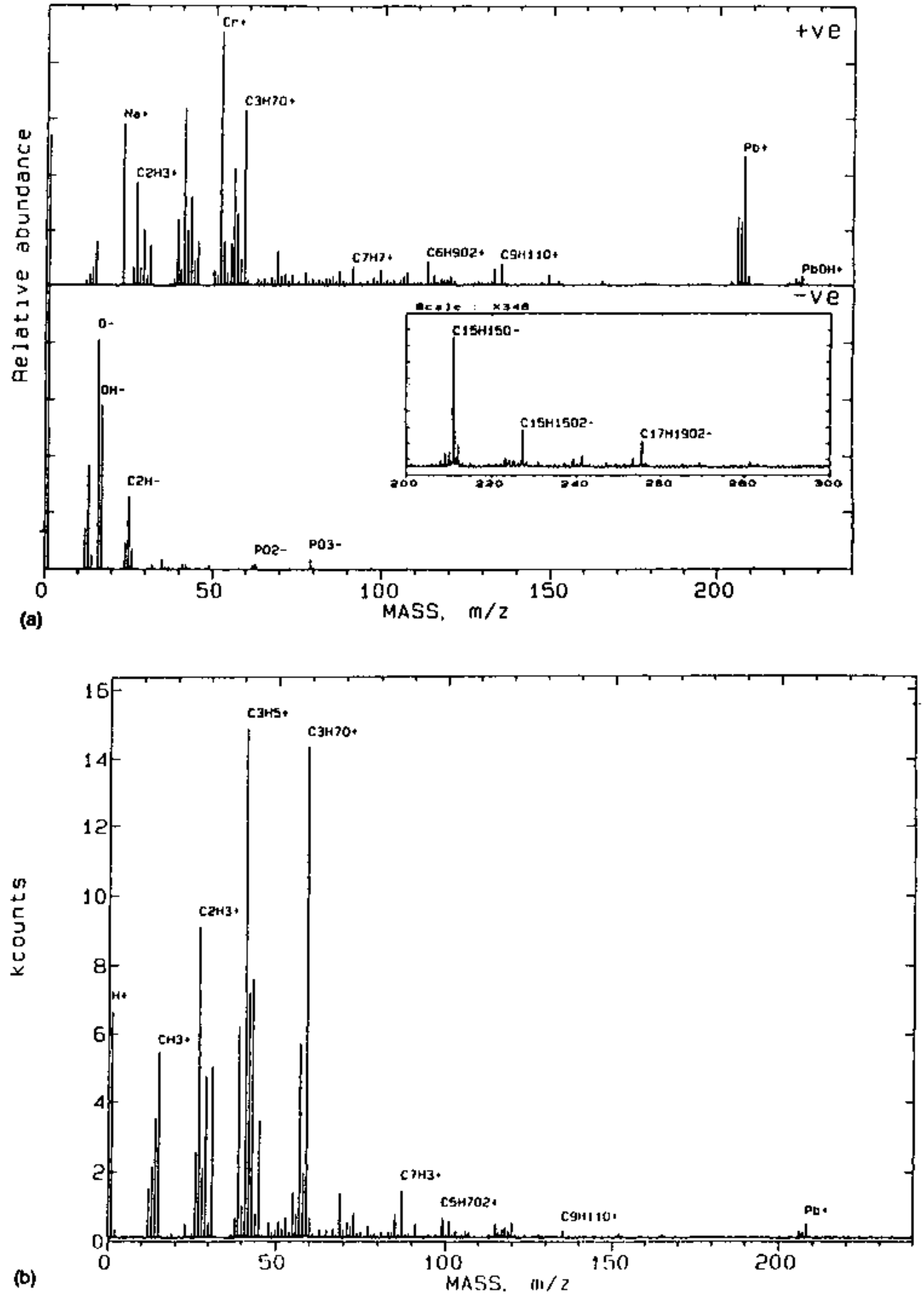


Figure 11 (a) Positive and negative time-of-flight SIMS spectra of a 100×100 μm^2 area of the metal side of the interface between an epoxy cataphoretic paint system and phosphated cold-rolled steel. The paint was slightly overcured; (b) as in (a) but positive spectrum of paint side; (c) as in (a) but paint was undercured; metal side; (d) as in (c) but positive spectrum of paint side. (From Ref. 24.)

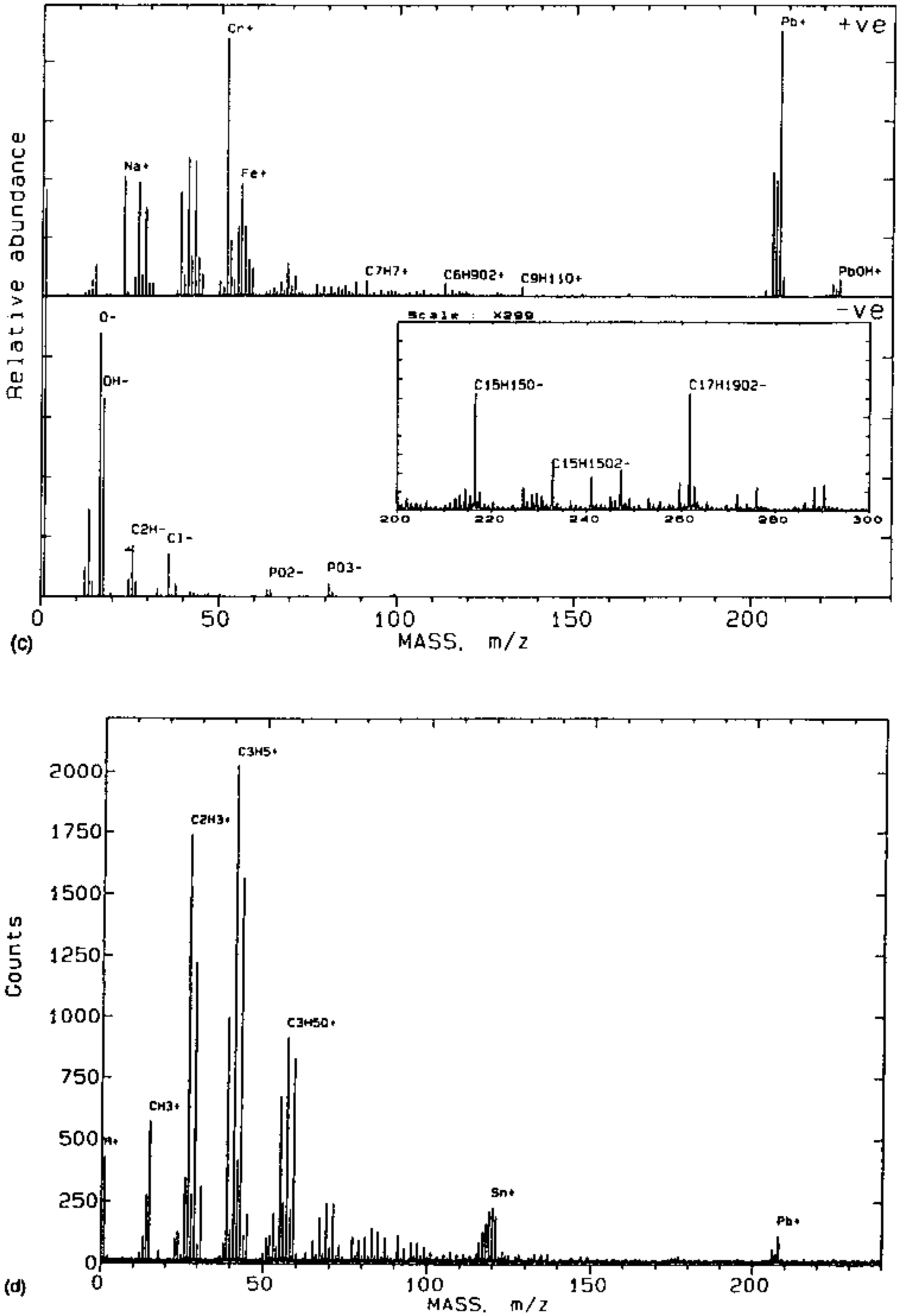


Figure 11 (Continued)

spectroscopies are optical techniques and therefore they generally do not require a UHV requirement, which is a great advantage. Molecules adsorbed at surfaces or at interfaces can be observed in situ, without the need to destroy the sample. HREELS can also be used to study interfaces in situ, but does require an UHV environment, because excitation is performed by means of a low-energy electron source.

1. *Principles and Applications*

Several recent overviews of principles and applications of Raman, FTIR, and HREELS spectroscopies are available in the literature [35–37, 124]. The use of all major surface and interface vibrational spectroscopies in adhesion studies has recently been reviewed [38]. Infrared spectroscopy is undoubtedly the most widely applied spectroscopic technique of all methods described in this chapter because so many different forms of the technique have been developed, each with its own specific applicability. Common to all vibrational techniques is the capability to detect *functional groups*, in contrast to the techniques discussed in Sec. III.A, which detect primarily elements. The techniques discussed here all are based in principle on the same mechanism, namely, when infrared radiation (or low-energy electrons as in HREELS) interacts with a sample, groups of atoms, not single elements, absorb energy at characteristic vibrations (frequencies). These absorptions are mainly used for qualitative identification of functional groups in the sample, but quantitative determinations are possible in many cases.

(a) *IR Techniques.* Infrared spectroscopy in its original dispersive form, in which the absorption of infrared (IR) light (the intensity of transmitted energy) when passing through a sample is measured by scanning through the spectrum, has been in use for a long time. The introduction of the Fourier transform principle in IR spectroscopy has prompted an interest in the use of the technique for surface analysis. The Fourier transform (FTIR) instruments use mirrors instead of slits. Each scan thus gives information over the entire spectrum resulting in higher throughput, sensitivity, and signal-to-noise ratio. The many different (and sometimes confusing!) acronyms used in IR mainly refer to different forms of sampling techniques that have been developed in recent years and all use the FT (or interferometric) principle. The most common of these acronyms are listed in Table 1. This list is not complete because some researchers use their own acronyms.

Basically, there are two categories of FTIR spectroscopies: reflection and nonreflection techniques [38]. The latter class comprises either acoustic detection or emission from the sample itself. The techniques recognized here are photoacoustic spectroscopy (PAS), emission spectroscopy (EMS), and photothermal beam deflection spectroscopy (PBDS). These techniques will not be considered further in this chapter. The reader is referred to the literature [39–42]. For adhesion studies the reflection techniques (SRIRS) are more important. The major classes of sampling techniques in SRIRS are:

Internal reflection IR (IRS); commonly known as MIR (multiple internal reflection) or ATR (attenuated total reflection).

External reflection IR (ERS); the techniques in this category can be a single reflection setup (reflection-absorption IR, RAIR, or grazing incidence reflection IR, GIR) or a multireflection setup (MRAIR). The single reflection technique is also frequently referred to as specular reflectance IR.

Diffuse reflectance IR (commonly called DRIFT).

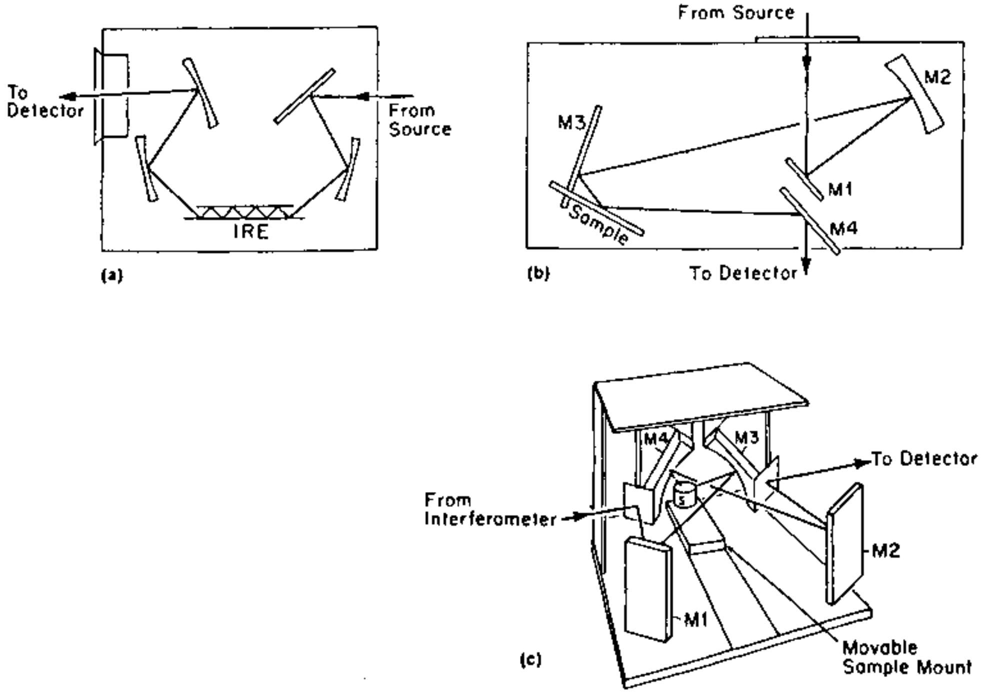


Figure 12 Attachments for IR analysis of surfaces; (a) attenuated total reflectance (ATR); (b) reflection-absorption (RAIR); (c) diffuse reflectance (DRIFT). (From Ref. 2.)

The principles of these three major categories are shown in Fig. 12. ATR is useful primarily for identification of polymer films, liquids, or other materials that can be coated onto a crystal of high refractive index, such as Ge. The sample must be in very good contact with the crystal for good spectra to be obtained. IR light is shone into the crystal at an angle of incidence that is higher than the critical angle of reflection for the crystal, so internal reflection of the radiation occurs and its intensity is attenuated as a result of absorption by the sample. Mostly rectangular crystals are used, but circular crystals have recently been developed for the study of aqueous solutions, films, and fibers [43–46]. Although the requirement of intimate contact between crystal and sample is severely limiting, the technique has the useful capability of providing a depth profile by varying the angle of incidence or by using crystals with different optical densities. As an example, the surface crystallinity or orientation of fibers with respect to their axis has been reported [46]. Further, the technique is uniquely suited for the study of solid/aqueous interfaces.

The technique of choice for studying thin films on metals (or certain other substrates) directly is single reflection RAIR [47–54]. The limitation here is that the substrate must be very smooth, but this can be easily achieved by polishing the metal before deposition of the film. Characterizations of thin organic layers on metal (oxide) surfaces, such as occur in lubricants, corrosion inhibitors, adhesives, polymers, paints, and so forth, are specific applications of this rather recent form of FTIR. It should be noted that the relative band positions and shapes may be different in this technique than in conventional transmission IR. The spectrum may also change with the thickness of the organic film, which implies that polymer/metal interactions are in principle observed [47,51]. The technique is so surface sensitive that oxidation of metals can be determined in situ [51] and the packing structure of monolayers of organic molecules or Langmuir–Blodgett films can be studied [52, 53]. In such studies the metallic substrate must have a high reflectivity. Ideal substrates are thus silver and copper. The technologically important substrates aluminum and steel have lower reflectivity or sensitivity.

In diffuse reflectance IR spectroscopy (DRIFT) light impinges on a solid powdered sample and is scattered in all directions. This light is collected and redirected to a detector. The powder must be very fine and is mixed with or dispersed in a suitable matrix, such as KCl or KBr with a particle size of less than 10 μm. It is not suitable for large powders or lumps. By using special sample preparation techniques, e.g., by placing the KBr powder over the sample, monolayers of adsorbed silanes have been studied [55], or water adsorbed on polymer surfaces has been detected [56].

In summary of this section, it can be stated that there are now numerous FTIR spectroscopy techniques, which as a result of their enhanced sensitivity and signal-to-noise ratio have contributed immensely in recent years to the understanding of molecular phenomena at surfaces and interfaces as they are related to adhesion. The development of new sampling techniques still continues, and much activity can be expected to occur in the near future in the FTIR arena, along with another promising vibrational spectroscopy tool, Raman spectroscopy, to be discussed below.

(b) Raman Techniques. This vibrational spectroscopy is related and complementary to FTIR. Although its usage is currently not so widespread as that of the various IR techniques, primarily because of its much lower sensitivity, this may well change in the future as some exciting new developments have recently been published.

Raman spectroscopy is a long-established technique for the study of bulk materials. In principle, the technique is straightforward [57–63]. A small region of a transparent sample is illuminated by a monochromatic laser beam, and light that is scattered at a 90° angle with the incident beam is collected and directed into a spectrometer. Most of the scattered light is elastically scattered and has the same frequency ν_o as the incident light. This is known as Rayleigh scattering. A small fraction of the scattered light, however, is inelastically scattered and thus contains new frequencies $\nu_o \pm \nu_k$. These frequency differences are associated with the transitions between the various vibrational levels in the sample molecules; hence the frequencies observed are in many cases similar to the wave numbers in FTIR. The lines with the lower frequencies are the Stokes lines; those with the higher frequencies are referred to as the anti-Stokes lines. The former series is usually measured in the Raman experiment. The intensities, frequencies, and polarization character of these lines can be determined. The lines are observed in a direction perpendicular to the incident beam, which is plane-polarized.

Raman spectroscopy is useful for studying aqueous solutions, e.g., of polymers, because the spectra are hardly affected by the presence of water. The two major problems of the technique are: (1) the low intensities of the Stokes lines (hence data acquisition is slow), and (2) laser-induced fluorescence effects, which may be so intense that they can completely wipe out all Raman scattering of interest.

The recent developments in the Raman technique, which are very promising and which may lead to its emergence as one of the most surface-sensitive techniques available in the near future, are the following.

Development of Fourier transform [64–66] and Hadamer transform [67] spectrometers as detectors in Raman spectroscopy, similar to FTIR; it has recently been shown that with the proper masking of the Rayleigh scattered radiation and special optical filters, fluorescence-free Raman spectra can be obtained [64].

Resonance Raman spectroscopy (RRS); if the wavelength of the incident radiation is chosen so that it coincides with an absorption band of the scattering molecules, the resonant Raman scattering cross-sections may be up to 10^6 times the cross-sections for normal Raman scattering. In such cases it is possible to detect monolayers (e.g., of dye molecules) at surfaces. This has indeed been demonstrated [68,69]. Recently RRS has found many new applications, mainly in biological studies.

Surface-enhanced Raman spectroscopy (SERS); in this resonance scattering the enhancement is caused by the substrate rather than by the adsorbed molecules.

SERS is thus a surface technique that has so far been restricted to only a few substrate metals, namely copper, silver, and gold [70–75], but it is applicable to almost any adsorbate. It is also noteworthy that the two mechanisms in RRS and SERS are additive, so that certain dyes on SERS substrates can be detected at extremely low coverage [76]. It is generally accepted now that two mechanisms contribute to the strong enhancement (up to a factor of 10^6) of Raman scattering by molecules adsorbed at the roughened surface of Cu, Ag, or Au. One factor is the generation of large oscillating dipoles and therefore oscillating electrical fields at the metal surface. The other factor is the enhancement of the polarizability of the adsorbed molecules at optical wavelengths by the substrate, i.e., a charge-transfer mechanism [35]. In addition to the substrates already mentioned, enhancement has been observed for the alkali metals, aluminum, indium, palladium, platinum, and even some oxides (NiO and TiO_2), though with lower intensities than for the metals Ag, Cu, or Au.

The range at which molecules contribute significantly to the SERS signal varies between 5 and 50 Å, i.e., comparable to the sampling depth in XPS. The SERS signal does not depend linearly on adsorbate coverage, making quantitative analysis difficult. Further, the restriction to certain substrates is a serious limitation. Recently it has been reported that the strong enhancement effects by substrates such as silver spill over for a few nanometers into an adjacent phase. Therefore, if silver is coated with a very thin film of, for instance, SiO_2, SERS can be observed for molecules adsorbed onto the silica film [77]. Other approaches include the evaporation of silver overlayers to study surfaces of thin and thick films. An example is shown in Fig. 13. In this study the surface segregation in blends of polystyrene with deuterated polystyrene was investigated. SERS was used to investigate the interface with a roughened silver substrate, but also to study the surface by means of a thin overlayer. At both interfaces the technique detected an enrichment of the deuterated form after vacuum annealing [78]. The surface segregation was confirmed by TOFSIMS. In another application the specific adsorption of one of the components of an adhesive system was studied. The results are summarized in Fig. 14 [79]. These various intricate and ingenious sample preparation methods that are currently being developed by several laboratories show great promise for an extension of the types of substrates and materials to which the SERS technique can be applied.

Extremely low-noise integrating multichannel detectors; the very recent introduction of these very special devices has made it possible for the first time to record Raman spectra from monolayers of organic materials (e.g., fatty acids) on substrates that do not give surface enhancement, for instance a water–air interface [80]. Conventional Raman spectroscopy may now have become a viable

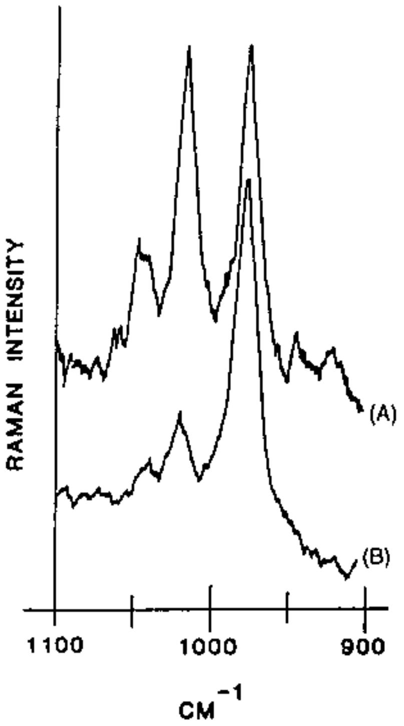


Figure 13 Surface-enhanced Raman spectra (SERS) obtained from thin films of blends of polystyrene and deuterated polystyrene before (A) and after annealing (B). Samples and conditions as in Fig. 9.

> non-UHV surface analysis tool. Advantages of conventional RS over SERS are that the scattering cross-sections are independent of the type of substrate surfaces. Further, the intensity varies more linearly with coverage and the cross-sections do not vary a great deal for different molecules. Hence the conventional Raman technique is more quantitative than SERS.

We may thus begin to see more applications of conventional Raman spectroscopy, e.g., of monolayers on well-defined substrate surfaces. On the other hand, SERS will remain a powerful technique in its own right because of its greater sensitivity and surface specificity. It remains practically the only technique available to determine nondestructively and in a non-UHV environment the orientation of molecules in situ in a dense medium, since the contribution to the observed signal by molecules farther than about 50 Å away from the interface is negligible compared with the enhanced signal from the interfacial molecules.

(c) High-Resolution Electron Energy Loss Spectroscopy (HREELS). The specific attribute of this vibrational technique, compared with the ones discussed above, is that it can provide functional group information on the surface of polymers. In addition, one can study the interactions between these functional groups and thin films of metals evaporated onto these polymers. The technique, which has gone through some recent instrumental developments, is thus important for the furthering of our understanding of metal–polymer adhesion mechanisms.

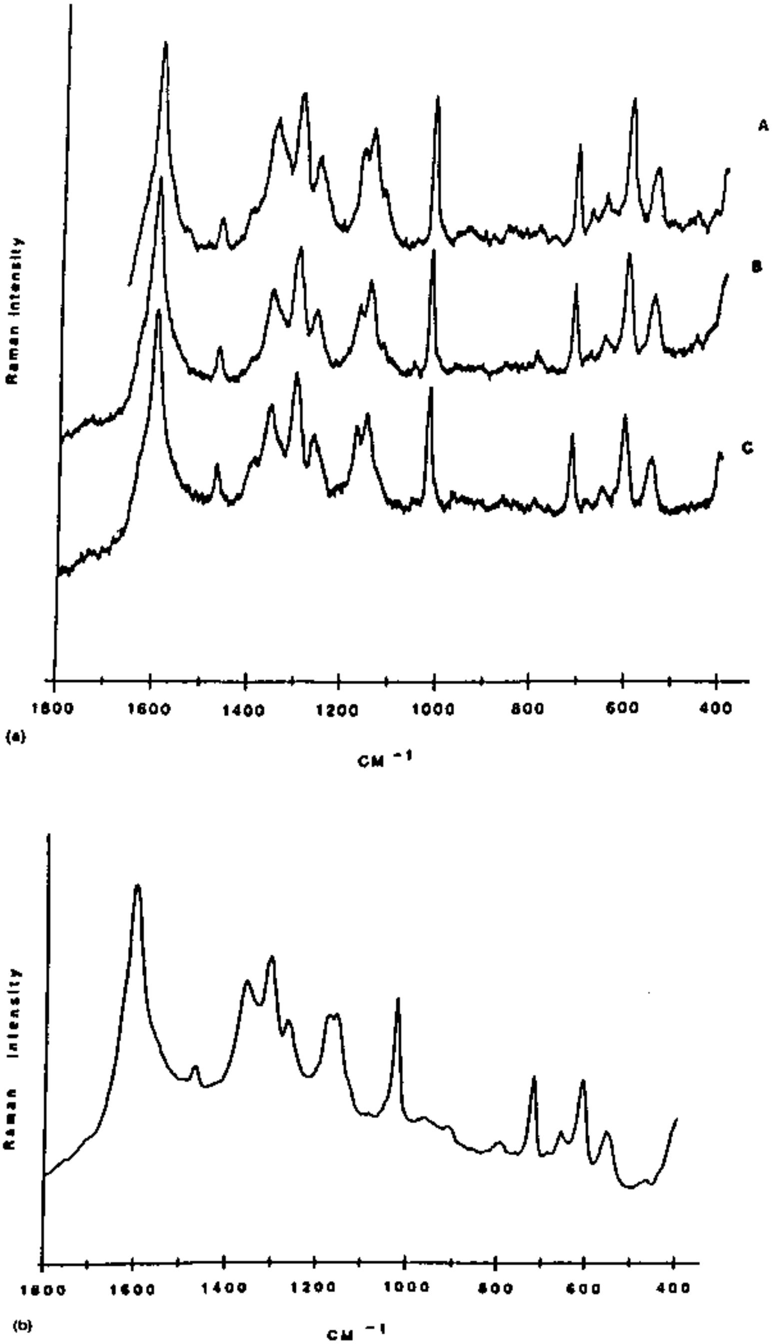
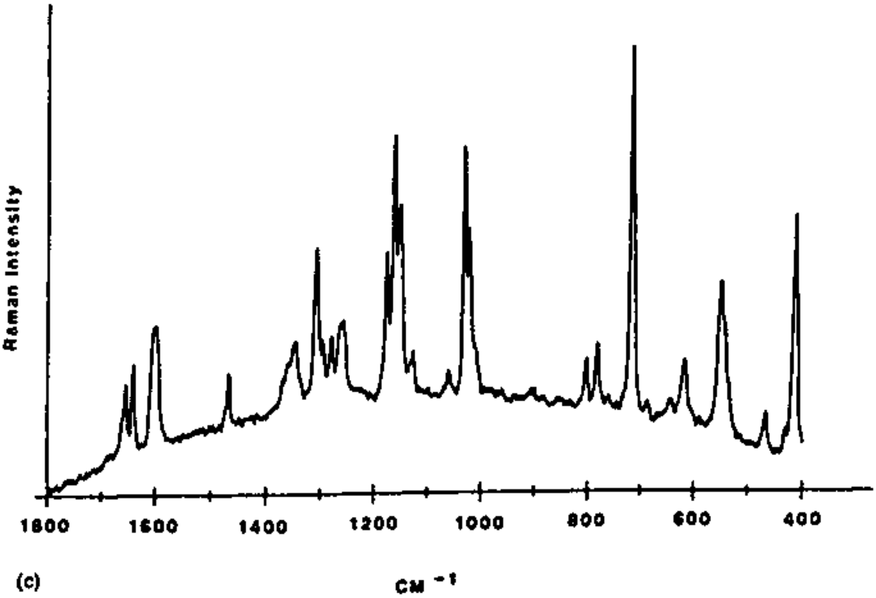


Figure 14 Surface-enhanced Raman spectra (SERS) obtained from an acrylic adhesive spin-coated onto silver island films from (A) 1% and (B) 5% solutions in acetone and (C) from the bulk adhesive; (b) SERS spectrum from saccharin spin-coated onto silver island films from a 0.1% acetone solution; (c) normal Raman spectrum of pure saccharin. The results demonstrate that saccharin, a component of the adhesive, is adsorbed on the substrate surface and this adsorption is detected non-destructively by SERS. (From Ref. 79.)



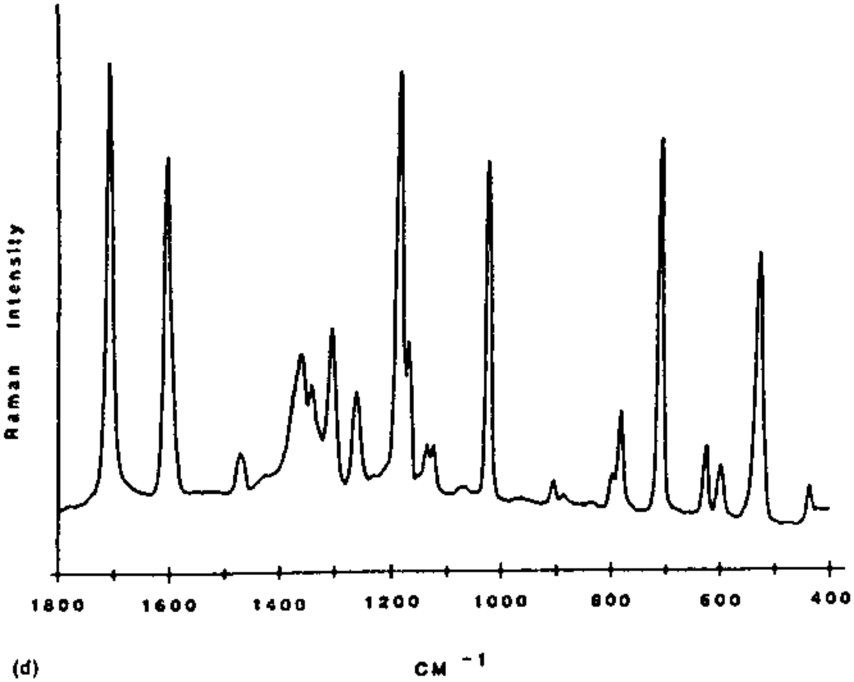


Figure 14 (Continued)

The basic experiment in HREELS in the backscattering geometry is straightforward [37]. A monochromatized electron beam of 1–10 eV is directed toward the surface and the energy distribution of the reflected electrons is measured in an electron analyzer with a resolution of up to 7 meV. The spectrum consists of the elastic peak and peaks due to energy losses to the sample surface by the excitation of molecular vibrations. If plotted as wave numbers, these vibrations are very similar to those observed in IR techniques. The resolution achievable in this technique is, however, considerably less than in IR, which becomes clear if one considers that 1 meV = 8.066 cm^{-1}, so the spectral resolution in HREELS is of the order of 100 cm^{-1} (in IR the resolution is typically around 4 cm^{-1} or better). Detection of crystallinity or other high-resolution details as is possible in IR is therefore currently not achievable in HREELS.

The most meaningful information in this technique is obtained by varying the electron impact energy and the scattering geometry (angles Θ_i and Θ_r) by rotating the sample holder or the electron analyzer.

A major problem that has hindered applications of the technique to bulk polymer surfaces until recently is the surface charging of insulators. At the low incident electron energies used in this technique, the secondary electron emission is high, so that a positive charge develops. Therefore, this problem can be overcome by using low current defocused flood guns of 1–2 keV electrons [81]. Further, although spectra can now be taken of the surface of polymers, these usually show broad peaks or bands, nowhere near the resolution obtained in IR. It is remarkable that heating (or annealing) polymers in vacuum for a few minutes at temperatures in the range 200–250°C sometimes results in a pronounced sharpening of the peaks. No satisfactory mechanism for this effect has been put forward yet.

The major strength of the technique lies in the fact that vibrational information of organic surfaces can be obtained with absorption bands that are identical to those observed in IR. In this respect the technique bridges a gap between XPS and IR. Information can be obtained on the polymer surface itself or on molecules segregated to or adsorbed on the polymer surface. Aliphatic and aromatic groups can be distinguished and hydrogen is also detected via functional groups. The adsorption of water on polymer surfaces is also detected easily. On the other hand, because of the high surface sensitivity, it is difficult to prepare clean model surfaces for HREELS studies. The similarity between HREELS and IR bands facilitates spectral interpretation immensely. There is no systematic difference between peak positions in the two techniques. The intensities of the bands in the two techniques are vastly different, however, because electron and photon excitation of molecular vibrations seem to follow different selection rules. At present, the excitation mechanism in HREELS is not completely understood, making quantification impossible. No practical theory is available to quantify electron-induced vibrational spectra of polymers.

Some polymer surface studies that have been reported recently are the detection of the molecular orientation at polymer film surfaces. For instance, the spectrum of iostactic polystyrene is different from that of the atactic material [82]. The spectra of thin films of poly(methylmethacrylate) (PMMA) cast on Au, Al, or Cu were also different; especially the intensity of the $C=O$ stretching band at 1710 cm^{-1} varied considerably [83]. Thus HREELS seems to be capable of identifying molecular long-range order in polymeric surfaces.

Other recent and very interesting studies are those in which monolayers of metals have been evaporated onto polymeric substrates. This allowed a conclusion as to the nature of the interaction and the molecular sites that are preferably attacked by the metal atoms. Systems that have been studied recently are Cu–polyimide, Cr–polyimide,

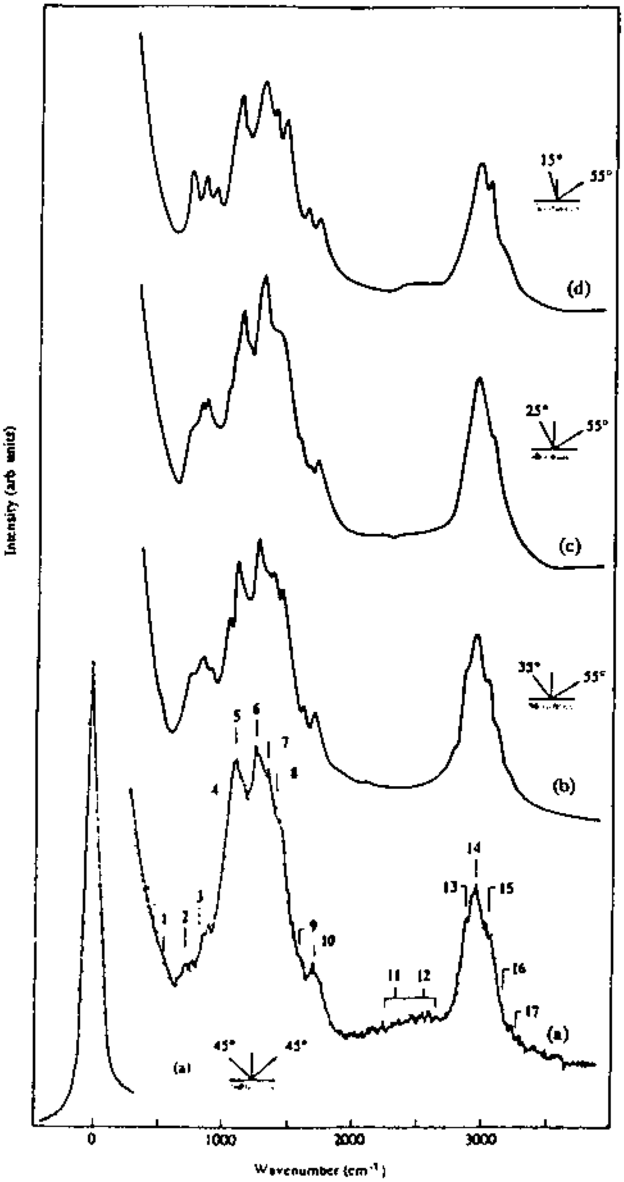


Figure 15 HREEL (three-point smoothed) spectra of a PET sample in different geometrical configurations: (*i*=incidence angle; *r*=reflection angle) (a) $i=45°$, $r=45°$; (b) $i=35°$, $r=55°$; (c) $i=25°$, $r=55°$; (d) $i=15°$, $r=55°$. (From Ref. 87.)

and Al–polyimide [84–86]. Very recently the interfaces formed between vacuum-evaporated Al and polyvinyl alcohol, polyacrylic acid, and polyethylene terephthalate (PET) were investigated [87]. Figure 15 shows the HREELS spectrum of PET. The vibrational assignments and their comparison with IR intensities are shown in Table 4. The HREELS spectra observed during PET metallization are shown in Fig. 16. The bands that disappear are those of O–CH_2 and C=O, and the new band that forms has been ascribed to the formation of a C–O–Al group and eventually a carboxylate.

Table 4 Comparison of IR and HREELS Vibrational Bands of PET

	Infrared bands[a]		HREELS loss energy		
Band	cm^{-1}	Intensity	meV	cm^{-1}	Assignment
1	502	m	63	510	$\gamma_w(C{=}O)$
2	730	s	89	720	$\nu_{11}(B_{1u})$ benzene
3	875	m	107	860	$\nu_{17B}(B_{1u})$ benzene
4	1020	m	128	1030	$\nu_{18A}(B_{2u})$ benzene
5	1120	s	138	1110	$\nu(O\text{–}CH_2)$
6	1263	s	157	1270	$\nu(O\text{–}C{=})$
7	1343	m	169	1360	$\gamma_w(CH_2)$
	1370	w			
8	1455	m	181	1460	$\delta(CH_2)$
	1470	w			
9	1580	w	198	1600	$\nu_{8A}(A_1)$, $\nu_{8B}(B_1)$
	1617	w			
10	1725	s	213	1720	$\nu(C{=}O)$
11			Unlocalized		ν–(O–H), hydrogen-bonded water
12			Unlocalized		ν(O–H), hydrogen-bonded water
13	2890	w	360	2900	$\nu_s(CH_2)$ amorphous or $\nu_a(CH_2)$ crystalline
14	2970	m	367	2960	$\nu_a(CH_2)$ amorphous
15	3068	w	381	3070	$\nu_{20A}(B_{2u})$ and $\nu_{20B}(B_{3u})$ benzene
16			393	3170	ν(O–H)?
17	3440	w	409	3500	ν(O–H)

[a] Spectrum measured in this work; s = strong; m = medium; w = weak.
Source: Ref. 87.

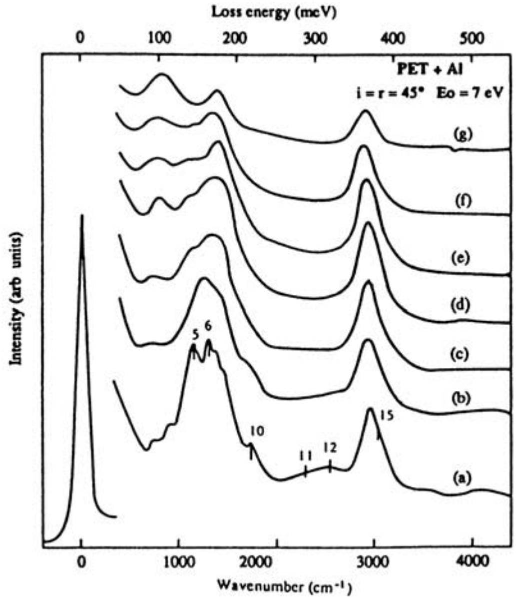


Figure 16 High-resolution electron energy loss (HREEL) spectrum of a metallized PET sample; (a) clean PET; (b)–(g) increasing coverage of the PET by Al atoms. (From Ref. 78.)

In summary, the HREELS vibrational spectroscopy technique appears to be a new and promising highly surface-sensitive tool for the study of interactions between metals and polymers related to adhesion phenomena. Current limitations are the lack of quantification, the lack of knowledge on the sampling depth, the difficulty to prepare clean polymer surfaces, the need for a clean vacuum (as opposed to the optical vibrational techniques), and the lack of suitable fingerprint spectra of clean surfaces of technological interest. However, as mentioned for Raman spectroscopies, we can expect much activity in the near future and the technique may be capable of carving its own niche in the gamut of available surface spectroscopies.

C. Miscellaneous Spectroscopies

The ion/electron and vibrational spectroscopies are the most widely used techniques in adhesive bonding technology. However, several lesser known spectroscopies are worth mentioning here briefly also, because they can provide unique information on metal–polymer interfaces in certain cases. A more complete list with suitable references is given in Table 1. The techniques that are discussed in this section are ellipsometry, electrochemical impedance spectroscopy (EIS), glow discharge optical spectroscopy (GDOS), and Rutherford backscattering spectroscopy (RBS).

1. *Ellipsometry*

This is a widely used optical technique for measuring film thicknesses. The technique uses polarized light at oblique incidence and yields information on the optical constants of materials and the thickness of overlayers. The signal is generated by interference of the components of the primary beam, which are reflected at phase boundaries between the substrate and the film. Best results are obtained when the films are no thicker than only a few multiples of the wavelength of the light. Discontinuous or island film structures can also be studied. An ellipsometric analysis gives two numbers delta and psi (Δ and Ψ), which together define the so-called complex reflection ratio ρ of the reflection coefficient in the directions parallel and perpendicular to the plane of incidence. More information on the principles can be found in the literature. There is a wealth of literature on the subject [88–91], both concise introductions and more comprehensive discussions or conference proceedings.

For applications in adhesive bonding research or technology, ellipsometry is useful for the quantitative determination of film thicknesses. Especially aluminum is a metal that has been studied extensively. It lends itself well to oxide thickness measurements because Al_2O_3 is transparent, which is a requirement. The thickness of the oxide formed in certain media can be determined [92]. Other studies reported on the use of ellipsometry to investigate the corrosion or rate of oxide film dissolution in certain environments in situ. As the film dissolves, the formation of pores and differences between the densities of different layers in the oxide film can be distinguished and related to the conditions of the anodizing process [93].

2. *Electrochemical Impedance Spectroscopy (EIS)*

This technique has rarely been used in adhesive bonding studies, but is well suited to determine the environmental degradation of adhesively bonded systems. Currently it is frequently used to study the degradation processes of painted metals immersed in an electrolyte, such as 5% Nacl [94]. Essentially the technique measures the total impedance of a sheet metal coated with a film of high resistivity. The metal is immersed in the electrolyte, held at its corrosion potential, and a small AC voltage perturbation is applied. The current response is measured and plotted as impedance $|Z|$ versus the frequency. The usual spectrum is a plot of this impedance versus frequency over the range 0.1–10^5 Hz (Bode plot), although there are other formats as well. The spectrum is recorded at several intervals, for instance once a week or month.

From the Bode plot the total capacitance of the coating system and the total resistivity of the system can be determined directly from the graph by extrapolation to zero frequency. With the use of a so-called equivalent circuit, a hypothetical electrical circuit that would give the same response over the frequency range, the capacitance and resistivity can be broken down into the individual components for the metal, the interface, and the coating [95,96]. Parameters such as coating capacitance, double-layer capacitance, pore resistance, and polarization resistance can all be derived from the appropriately chosen model. These can then be converted to physical properties such as percentage of water uptake, diffusion rates of ions and liquid water through the coatings, numbers of pores, corrosion reactions (anodic and/or cathodic) that take place at the interface, blister resistance (related to adhesion of the coating), and so forth. These parameters are normally determined as a function of immersion time so that the best system of metal pretreatment and type of coating can be determined and further optimized quickly and in the laboratory without having to rely on lengthy exposure in outdoor tests.

Excellent correlations between EIS analyses and field exposure of painted metals have been reported [97]. The coatings can be very thick (such as paint systems or adhesives), but very thin films, such as oxide, plasma coatings, conversion coatings, or other pretreatments, can also be investigated. As an example, Fig. 17 shows EIS curves as a

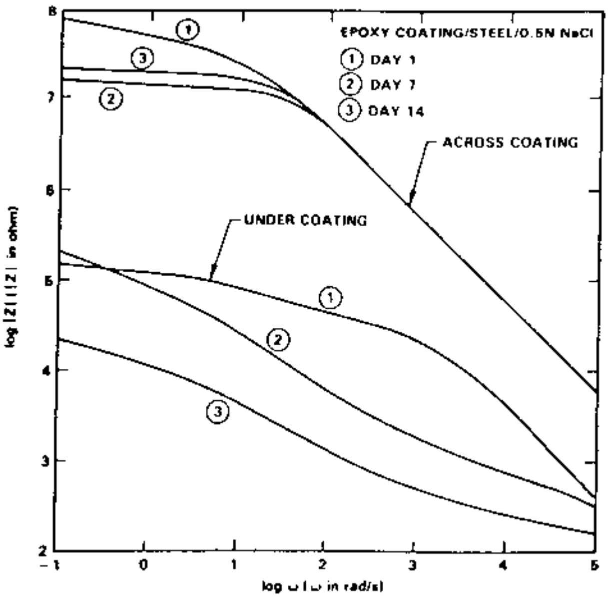


Figure 17 Electrochemical impedance data (Bode plots) for epoxy-coated steel as a function of immersion time in 0.5 N NaCl solution. (From Ref. 98.)

Table 5 EIS Parameters Versus Corrosion Performance of Cold-rolled Steel Coated with a Thin Film of Plasma-Polymerized Trimethylsilane

Sample	C_p (F)	R_{po} (Ω)	C_{dl} (F)	R_p (Ω)	R_1	% Rust
A	4.3×10^{-6}	196	3.0×10^{-5}	1.0×10^{3}	0.49	60
B	1.5×10^{-6}	618	1.2×10^{-6}	9.8×10^{4}	1.22	0
C	1.7×10^{-6}	182	1.6×10^{-6}	6.5×10^{3}	1.02	20
D	6.0×10^{-6}	69	8.6×10^{-5}	9.2×10^{2}	0.33	80
Control (15 min)	—	—	5.9×10^{-4}	3.6×10^{2}	—	100
Control (1 h)	—	—	1.6×10^{-3}	1.8×10^{3}	—	100

C_p = capacitance of coating; R_{po} = pore resistance of coating; C_{dl} = double-layer capacitance (interface); R_p = polarization resistance (interface); R_1 = slope of impedance curve in range 10^2–10^4 Hz.
Source: Ref. 98.

function of immersion time in 3% NaCl of a cold-rolled steel sample coated with a film of plasma-polymerized trimethylsilane [98]. The variable in this study was the plasma cleaning procedure applied to the metal prior to film deposition. Table 5 shows a comparison of the parameters that can be derived from the impedance data as a function of pretreatment using an equivalent circuit consisting of two resistances and two capacitors plus the resistivity of the electrolyte. It is seen that all parameters show the same ranking order and that order is identical to that observed in actual corrosion exposure. This example thus exemplifies that EIS data are quick and reliable and can be obtained in a fraction of the time required for actual exposure in a corrosion test. Further, the results of this study indicate that the pretreatment of the metal is by far the most important step in the plasma polymerization process. The actual composition of the deposited coating or its thickness is of secondary importance [98].

EIS and other electrochemical methods appear to be useful for the study of the performance of metal pretreatments (cleaning processes, anodization, phosphating, chromating, etc.) prior to adhesive bonding. A quick comparison of methods can be achieved, and because the method is fast and straightforward, it can be used as a quality control method. On adhesively bonded system EIS could be performed in more fundamental studies that would provide information on the nature and locus of degradation processes, when immersed in aggressive solutions.

3. *Glow Discharge Optical Spectroscopy (GDOS)*

This technique and a variation, GDMS (glow discharge mass spectrometry), are essentially depth-profiling techniques [99]. However, there is a major difference between GDOS and depth profiling in typical surface analysis techniques such as AES and SIMS. The rate of profiling in GDOS is of the order of 1–5 μm/min. A high-intensity argon lamp (DC gas discharge) is used for sputtering the material. The sputtered elements are detected in the plasma by a spectrochemical analysis of the glow light via an optically transparent window. Because of the requirement of fast, simultaneous detection, a grating spectrometer is used, so each element requires its own photomultiplier.

Sputtering in GDOS occurs by the positive ions generated in the gas discharge glow from where they are accelerated toward the sample. The electrically conductive sample is pressed against the cathode of which it forms a part. The high sputtering rate allows depth profiling through metallic coatings of industrial interest, e.g., zinc coatings on

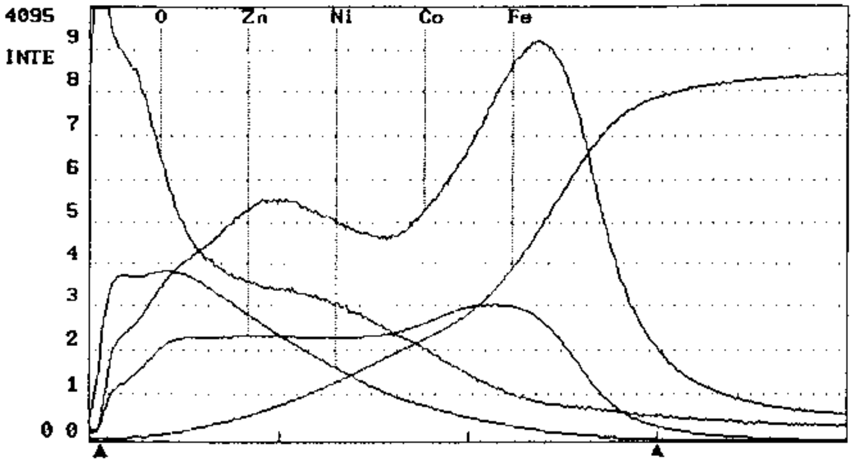


Figure 18 Glow discharge optical spectroscopy (GDOS) depth profile of an electrodeposited metallic coating system consisting of 1 μm Zn-1%Co base layer and 3 μm Ni–20%Zn top layer on cold-rolled steel substrate. Sputtering time is in seconds.

galvanized steel [100]. Residual elements such as carbon can be detected below the coating. Also, entire conversion coatings can be profiled rapidly, such as phosphates and chromates or anodization layers, which are beyond the scope of AES or SIMS depth profiling. The technique could thus be used in quality control, for instance for determining the homogeneity of electrodeposits across the width of the strip, or for control of the oxide thickness in metal pretreatment operations.

The technique requires only a moderate vacuum and has a spatial resolution of a few millimeters. Currently, two commercial instruments are available. Most elements can be detected, including hydrogen. Limitations are the quantification, which requires suitable standards, and the sample has to be electrically conductive. Nonconductive samples can be analyzed only by grinding them and mixing them with a metallic or graphite powder.

As a typical example, Fig. 18 shows the depth profile of a several microns thick metallic coating on steel [100].

4. *Rutherford Backscattering Spectroscopy (RBS)*

This is another widely used technique that provides concentration depth profiles of materials. Detailed recent reviews of this technique are available [101–103]. Essentially, in RBS a sample is bombarded with a collimated beam of high-energy light ions, (typically $^4He^+$ of 1–2 meV, although proton beams are also used). The scattered ions are energy-analyzed and counted using solid-state detectors. The scattering angle is very high, usually $>90^\circ$ (typically 170°). The technique provides a depth profile and compositional analysis and is quantitative and nondestructive. A major drawback is, however, the need for a large particle accelerator.

Basically, what is measured in RBS is the distribution of the energy of the backscattered ions. The energy scale can, however, be converted to a mass scale because for a given projectile/target combination and scattering geometry it can exactly be calculated how much energy the primary particle loses in collisions with an atom of a particular mass. Energy loss to heavy atoms is less than to light atoms. The positions on the energy scale are thus related to collisions with surface atoms. However, surface atoms scatter only a

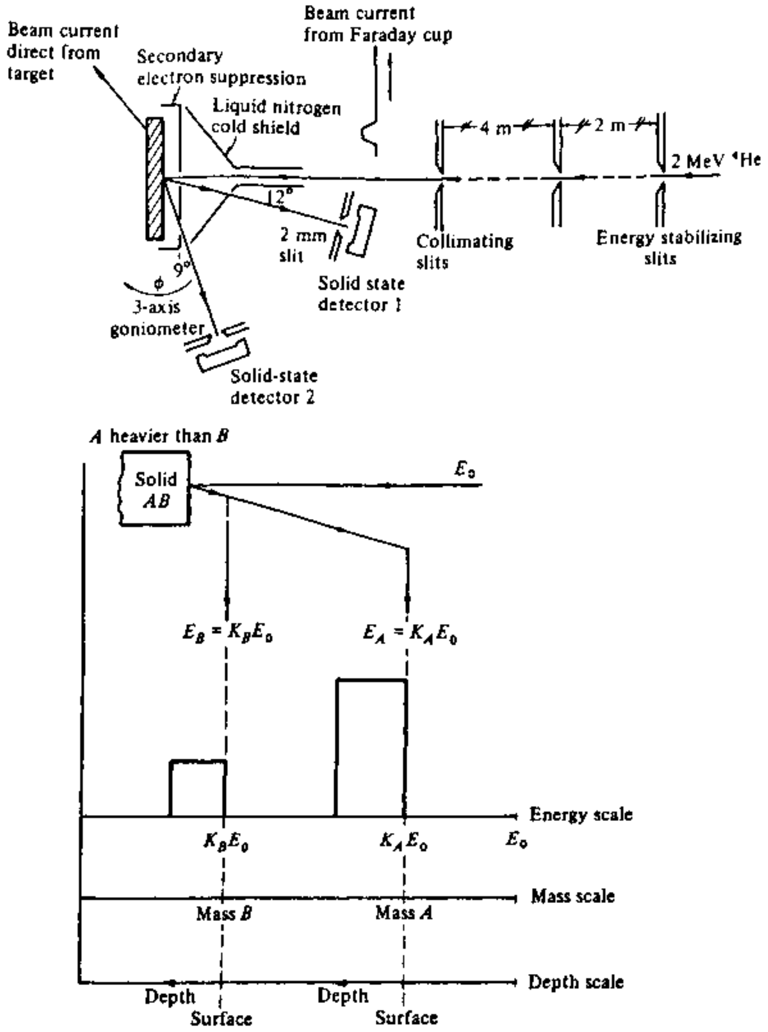


Figure 19 Experimental arrangement for Rutherford backscattering spectroscopy (RBS) (top) and schematic of Rutherford backscattering from a solid composed of elements of mass A and B (bottom). (From Ref. 101.)

small fraction of the primary particles. Below the surface, inelastic energy losses occur also. Therefore, the mass scale can also be converted to an energy scale. These principles are schematically shown in Fig. 19.

In addition to providing a depth profile, RBS can also give crystallographic information if the instrument is equipped with a precision goniometer. In certain directions of single crystals the phenomenon of channeling occurs. The backscatter yield is reduced when the beam is aligned with the major low index axes [104]. By aligning both incident and reflected beams along such directions, the relative positions of surface atoms can be determined with high precision. Also, the sites of impurity atoms can be determined, because for interstitial positions the backscatter yield is the same as for the random direction value.

Table 6 Parameters in Rutherford Backscattering Spectrometry

Probe beam	H^+, $^4He^+$, other light ions
Probe energy	1–3 meV
Beam diameter	~0.5–1.0 mm (~2 μm with microbeam)
Beam current	~2–20 nA
Analysis time	~5–30 min
Integrated charge	~1–40 μC (6×10^{12}–2.5×10^{14} ions)
Scattering angle	170°
Energy analyzer	Surface barrier detector 15–25 keV energy resolution
Probing depth	~1–2 μm
Depth resolution	20–30 nm (3–4 nm with tilted targets)
Mass resolution	Isotope resolution up to ~40 amu
Sensitivity	10^{-2}–10^{-4} monolayers for heavy surface impurities 10^{-1}–10^{-2} monolayers for light surface impurities
Accuracy	3–5% (typical)

Source: Ref. 101.

RBS can be considered an almost ideal tool for the analysis of thin films of a few microns thickness if stoichiometric information is required. All elements > H are detected. Quantitative measurements of film thickness and composition and concentrations of impurities can be performed. A single RBS spectrum can show the amount of an impurity and its distribution throughout a thin film.

In general, however, only rather simple structures and compositions can be investigated successfully. The depth range that can be accessed varies but is of the order of 1–2 μm for proton and alpha particle beams. This depth depends on the primary particle energy, which has an upper limit of a few meV above which nuclear reactions may occur. The depth resolution is very high, e.g., 10–300 Å, and can be improved for very low depths by tilting the sample.

Table 6 summarizes some of the parameters of RBS and Fig. 20 shows an example of the quantitative measurement of the epitaxial growth of an oxide film [101].

IV. CONCLUDING REMARKS

This chapter summarizes the principles of some of the many spectroscopic techniques that are available for the analysis or study of aspects of adhesive bonding science and technology. As indicated in Table 1, there are dozens of techniques and new acronyms appear almost on a daily basis. The number of instrumental spectroscopies available today to the scientist is bewildering, especially the many techniques for surface characterization. Therefore, it is likely that some techniques have been missed, although it was attempted to cover them all, at least in Table 1. The choice of techniques from that listing that were actually discussed in this chapter had to be limited and was in some cases somewhat arbitrary and subjective. However, some emphasis was put on techniques that can be used in the study of the science of adhesive bonding technology. Techniques for routine analysis, e.g., NMR or the various mass spectrometries, were not discussed in depth.

It is clear that tremendous developments have been made in recent years with certain techniques. A large number of spectroscopic techniques are now available that can be adapted, with little or no adaptation, to the study of various aspects of adhesive bonding.

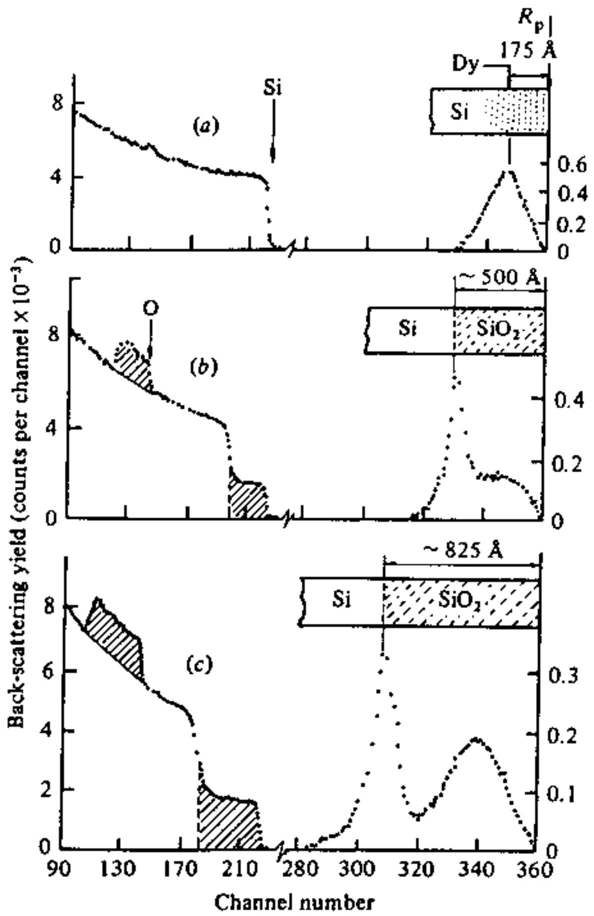


Figure 20 RBS spectra obtained from Si implanted with Dy^+ ions; (a) after implantation; (b) after growth of 500 Å of SiO_2; (c) after growth of 825 Å of SiO_2. (From Ref. 101.)

Important questions, such as adhesion mechanisms, failure mechanisms, locus of failure, and so forth, can now be addressed successfully by several experimental methods. The application of such spectroscopies has evidently led to a better understanding of the performance of materials used in adhesive bonding and such knowledge has triggered the development of new or improved materials.

In the choice of a particular spectroscopic technique, one should be well aware that no single technique, no matter how sophisticated, can solve all problems or answer all questions. Therefore, some insight in to the principles and capabilities of the many techniques that one could choose is required for anyone who wishes to tackle problems in materials science. Providing this insight, and referring the interested reader to the appropriate literature for further studies, was the main objective of this chapter.

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18

Ultraviolet Stabilization of Adhesives

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I. INTRODUCTION

Antioxidants (including hindered phenols, phosphites, and thioethers) are commonly used in hot-melt adhesive (HMA) and sealant formulations [1–4]. Relatively high levels of antioxidants are used (typically, 0.5 to 1.0%) in some adhesives (e.g., hot melts) to protect the polymers from oxidation when they are subjected to high temperatures during compounding and processing. The presence of these additives further protects the adhesive during the final end-use application. Antioxidants are also used in adhesive subjected to less severe processing (e.g., solvent- and water-based adhesives) to protect the adhesives during storage and end use. The thermal stabilization of adhesives is addressed in Chapter 19.

Some applications require exposure of sealants and adhesives to ultraviolet (UV) radiation. While the conventional antioxidants mentioned above will provide some protection against UV-initiated oxidation, many applications necessitate the incorporation of "light stabilizers" to reduce photoinduced polymer degradation. Two general classes of light stabilizers are used, ultraviolet absorbers (UVAs) and hindered amine light stabilizers (HALSs). In this chapter we discuss the stabilization mechanism of each of these classes and the relative importance of each of these stabilizers in preventing degradation of a thin-film adhesive versus a "thick" sealant. Although we focus on the fundamental aspects of the UV stability of adhesives, several examples are given to illustrate how these principles can be put into practice.

II. PHOTODEGRADATION OF ADHESIVES AND SEALANTS

The general autooxidation scheme for hydrocarbons shown in Fig. 1 represents the core reaction for hydrocarbon degradation [5]. As adhesives are mixtures of polymers and oligomers, this scheme can be used to understand the oxidative degradation of adhesives. Several aspects of the scheme are worth emphasizing before we examine the effect of UV light on polymer degradation. First, the formation of a peroxyradical ($ROO^\bullet$) from a polymer free radical ($R^\bullet$) is an extremely fast (diffusion-controlled) reaction in the presence of oxygen. Second, the hydroperoxides (ROOH) formed from the peroxyradicals can further decompose to generate two new free radicals ($RO^\bullet$, $HO^\bullet$), which can initiate

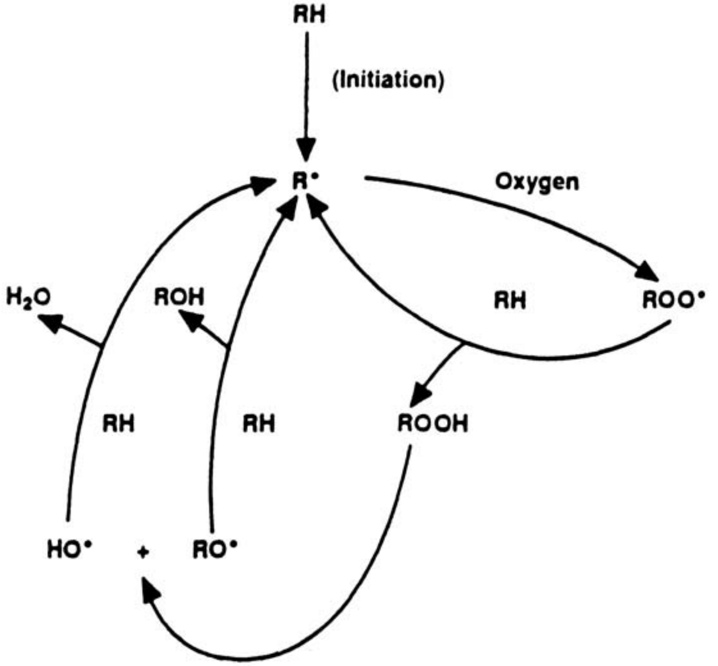


Figure 1 Autooxidation scheme for polymer degradation showing the cyclic nature of the process.

further reactions. This autocatalytic mechanism results not only in the cyclic nature of autooxidation but also in an *exponential* increase in the number of free radicals available to initiate new degradation reactions. Although the same scheme is the basis for photooxidation of polymers, the presence of UV light exacerbates the situation, especially with regard to the initiation reactions.

Thermolysis of hydroperoxides (ROOH) becomes significant only above 100°C. Although this high-temperature reaction is a major cause of degradation in hot-melt adhesives, it is less important at ambient temperatures. However, *photolysis* of ROOH does occur to a significant extent at ambient temperatures and is a major cause of photoinduced polymer degradation [6]. Other photoinduced reactions can occur due to light absorption by trace levels of carbonyl impurities resulting from thermal oxidation of the polymer during manufacture, storage, and processing.

Although we focus here on these photooxidative pathways, it is important to mention the purely photolytic degradation of adhesives. Polymers that are chromophores in the UV range can directly absorb UV light without first undergoing oxidation. These polymers may undergo photolytic rearrangements, providing another nonoxidative pathway for loss of physical or chemical properties. Examples of these polymers are aromatic polyurethanes or polyesters.

III. ULTRAVIOLET ABSORBERS

The simplest and most direct method to reduce photooxidation is to block the UV radiation from reaching the polymer, much as a sunscreen is used to prevent sunburn.

Fillers (carbon black, pigment, talc, TiO_2, etc.) can potentially provide an improvement in UV stability by this mechanism, but may cause other complications (e.g., additive adsorption or deactivation, metal impurities, etc.). Chemical UVAs are used routinely to prevent the photooxidation of polymers. There are several major requirements for chemicals to function as UVAs: (1) they must absorb strongly in the UV region (290 to 400 nm) but must have a sharp cutoff in the visible region (>400 nm) so as not to contribute color to the polymer, (2) they must be photostable, and (3) they must dissipate the photoexcitation energy in a harmless way. Representative structures of two common classes of UVA that fulfill these requirements, the 2-hydroxybenzophenones and the 2-hydroxyphenylbenzotriazoles, are shown in Fig. 2.

The absorption of light follows Beer's law, which says that the absorption of light equals a constant (extinction coefficient) multiplied by the UVA concentration multiplied by the path length:

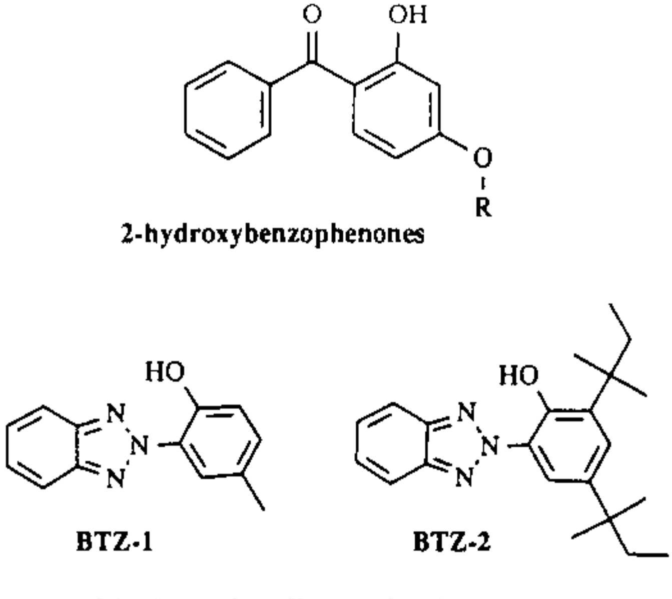
$$\text{absorption} = \text{const.} \times \text{concentration} \times \text{path length}$$

in which

$$\text{absorption} = \log\frac{I_0}{I}$$

where I_0 is the intensity of incident light and I is the intensity of light having passed through the sample. This relationship implies that both the type and concentration of the absorbing species are important as well as the sample thickness.

To illustrate the function and limitations of these UVAs, we will look at the optical properties of a typical 2-hydroxyphenylbenzotriazole (BTZ). The UV absorption properties are shown in Fig. 3 for several concentrations of a solution of BTZ-2. Although the



2-hydroxybenzophenones

BTZ-1

BTZ-2

2-hydroxyphenylbenzotriazoles

Figure 2 Representative structures of ultraviolet absorbers.

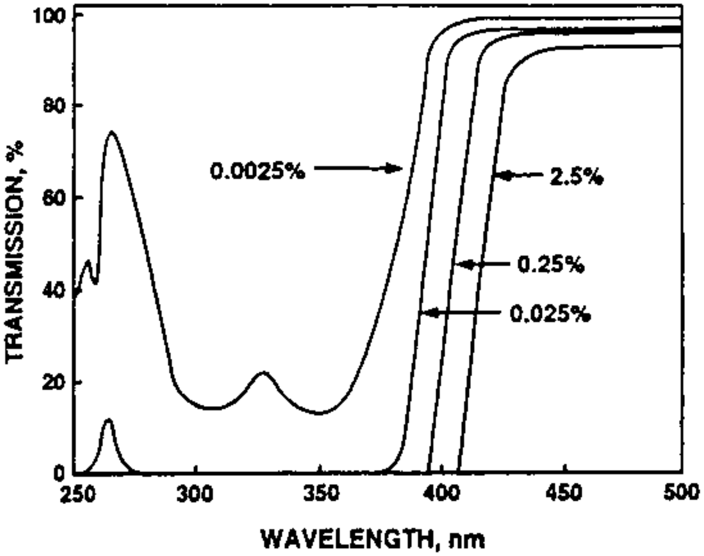


Figure 3 Ultraviolet absorption spectra for various concentration of a solution of BTZ-2 (1.0-cm cell in cyclohexane).

actual amount of light absorbed is a function of wavelength, for this discussion we can use an approximate value of 90% UV light absorption at a BTZ concentration of 0.0025% and a path length (sample thickness) of 1.00 cm. Beer's law tells us that if 90% of the light is absorbed by a 0.0025% BTZ solution in 10 mm (0.4 in.), 90% of the light is also absorbed by a 0.025% BTZ solution in 1.0 mm (0.04 in.), and 90% of the light will be absorbed by a 0.25% BTZ solution in 0.10 mm (0.004 in., 4 mils). A BTZ concentration of 0.25 to 1.0% is typical for protection of a polymer.

Carrying this further, if at this concentration of 0.25% BTZ, 90% of the light is absorbed in the first 0.10 mm, then 99% of the light is absorbed in the first 0.20 mm and 99.9% is absorbed in the first 0.30 mm of the sample. This explains why UV absorbers are very effective at protecting all polymers of sufficient thickness but are not effective at protecting sample surfaces or very thin films. This is demonstrated clearly in Fig. 4, where a sample of polypropylene exposed to UV radiation from sunlight is microtomed and analyzed for degradation (loss of molecular weight and hence viscosity) [8]. With no light stabilizer, UV radiation is at a high intensity throughout the transparent sample. As oxygen diffuses in from both sample surfaces, the UV light accelerates oxidation. In the presence of a UVA, the bulk of the sample is protected except for the surface exposed to the UV light. (The effect of the HALS is explained below.) This dependence on sample thickness also explains why UV absorbers are widely used in sealant application but have limited efficacy in adhesive films, where typical thickness may be about 0.025 mm (1 mil).

IV. HINDERED AMINE LIGHT STABILIZERS

As alluded to above, a second class of light stabilizers, the hindered amine light stabilizers (HALSs), provide additional stability to polymers and can function even in thin film or in sample surfaces. The chemistry of HALSs is based on the 2,2,6,6-tetramethylpiperidine derivatives (Fig. 5). Unlike UVAs, HALSs have no significant UV absorption and

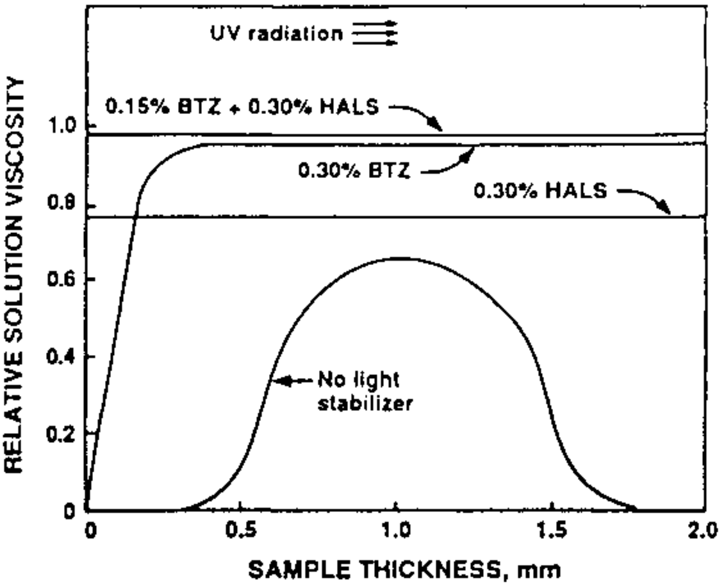
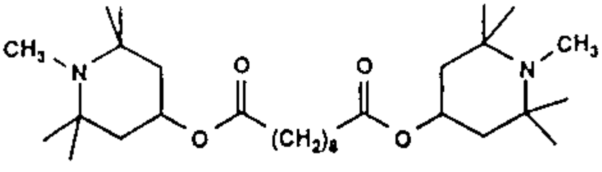
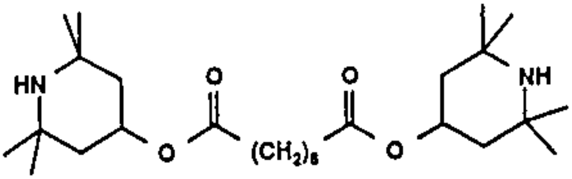


Figure 4 Effect of UV exposure on 2-mm-thick polypropylene at various depths.



HALS - 2



HALS - 1

Figure 5 Representative structures for hindered amine light stabilizers.

therefore have no effect on the incident radiation. The mechanism of protection by HALSs is still being investigated [6,7,9], but the primary mechanism involves the HALS acting as an extremely efficient hydroperoxide decomposer and free-radical scavenger, involving a cyclic mechanism that regenerates the active HALS species (Fig. 6).

Referring back to Fig. 1, the HALS functions not by blocking the offending UV radiation but by destroying the unstable and radical-initiating hydroperoxides and by scavenging free radicals before they can be involved in the propagation reactions. Thus,

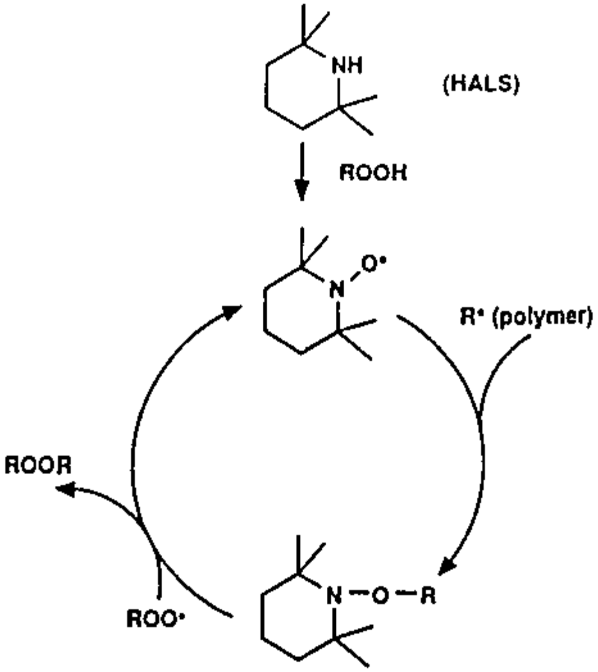


Figure 6 Regenerative mechanism for hindered amine light stabilizers.

by attacking a second pathway, the addition of a HALS to a polymer can provide additional stability beyond what can be achieved with a UVA alone. More important, since HALS efficacy is not dependent on competitive absorption of light, HALSs protect the surface layer of a polymer and can protect thin films. Again this is demonstrated in Fig. 4, where even the exposed surface of the polymer is protected from degradation. The term *hindered amine light stabilizer* is a somewhat limiting misnomer, as this class of additive is also finding wide use as a thermal stabilizer. Unfortunately, HALSs, functioning as antioxidants, cannot protect aromatic polymers from the nonoxidative photolytic processes described above.

V. ACCELERATED AGING OF POLYMERS

While the most meaningful exposure testing of polymers is done under actual exposure to sunlight, accelerated aging devices are used routinely to provide predictive and reproducible data in a reasonable amount of time [10,11]. The UV output of several commercial weathering devices is shown in Fig. 7. While many of these instruments are equipped to regulate temperature, humidity, and water spray, the most important environmental parameter to duplicate is the spectral distribution of sunlight. For instance, a carbon-arc lamp emits a high intensity of low-wavelength, high-energy radiation, which may initiate photoreactions not seen in actual use. The xenon-arc lamp more closely matches the spectral distribution of sunlight and has been found to correlate well with outdoor weathering. Other exposure devices, including the Q-U-V weathering tester [11], have shown good correlation with outdoor exposure when used with a UV-340 bulb.

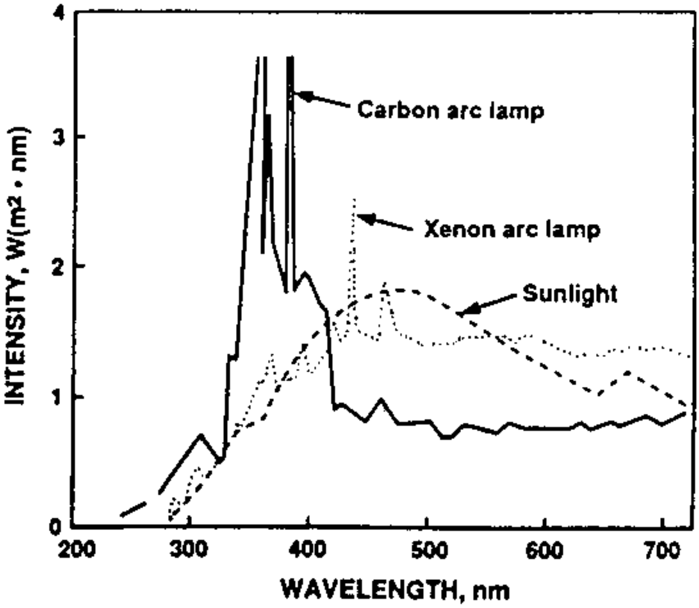


Figure 7 Comparison of sunlight versus artificial weathering device's spectral distribution.

VI. UV ABSORPTION BY HYDROCARBON POLYMERS

The photostability of most hydrocarbon polymers is generally not a function of their tendency to absorb light but rather of their propensity toward oxidation (free-radical formation). Although it is well known that the inherent UV stability of an unsaturated polymer is inferior to that of a saturated analog, this effect cannot be attributed to an increase in light absorption by the unsaturated system. For example, the UV spectra of a styrene–butadiene–styrene (SBS) block copolymer compared to the saturated styrene–ethylenebutylene–styrene (SEBS) analog shows no significant absorption in the important 300 to 400 nm UV range for sunlight. Thus for many polymers the relative UV stability correlates well with the thermal stability. Obviously, this may not hold where polymer photolysis becomes important.

VII. UV STABILITY OF ADHESIVE FILMS

With the considerations noted above, we can now look at the performance of UV stabilizers in several illustrative examples. Table 1 shows the effectiveness of BTZ-2 and HALS-1 at preventing the degradation of a natural rubber/hydrocarbon tackifier water-based adhesive when exposed to UV light. Natural rubber undergoes chain scission upon oxidation, resulting in a loss of molecular weight and hence a loss of cohesive strength. Samples were coated on polyester film, adhered to a glass plate, and exposed in a carbon-arc weatherometer (CAW). The extent of degradation was monitored by following discoloration, and by peeling the tape from the glass and observing cohesive failure. As shown by the data and as would be predicted from the arguments above, a HALS is more effective than the BTZ at protecting the adhesive. The BTZ/HALS combination

Table 1 UV stability of Natural Rubber Adhesive After Accelerated Aging in a Carbon-Arc Weatherometer (1.0 Mil Thick)

	Exposure in carbon-arc weatherometer		
	Unaged	8 h	16 h
Yellowness index[a]			
Unstabilized	6	9	10
BTZ-2, 2.0%	4	7	8
HALS-1, 2.0%	4	4	4
BTZ-2/HALS-1, 1%/1%	4	4	4
Cohesive failure[b]			
Unstabilized	Okay	Fail	Fail
BTZ-2, 2.0%	Okay	Okay	Fail
HALS-1, 2.0%	Okay	Okay	Okay
BTZ-2/HALS-1, 1%/1%	Okay	Okay	Okay

[a] Higher numbers indicate more color development.

[b] Visual evaluation after peeling polyester film from glass slides.

Table 2 UV Stability of Tackified Acrylic Adhesive Film After Accelerated Aging in a Xenon-Arc Weatherometer (1.0 Mil Thick)[a]

	Yellowness index:[b] exposure in xenon-arc weatherometer			
Stabilizer	0 h	50 h	100 h	250 h
Hydrogenated tackifier[c]				
Unstabilized	7	9	10	10
Nonhydrogenated tackifier[d]				
Unstabilized	9	17	18	20
BTZ-2, 0.5%	9	10	12	13
HALS-1, 0.5%	8	8	9	10
BTZ-2/HALS-1, 0.25%/0.25%	9	10	11	12

[a] Formulation contains 70% acrylic polymer and 30% tackifier.

[b] Higher numbers indicate more discoloration.

[c] Hydrogenated rosin ester tackifier.

[d] Nonhydrogenated rosin ester tackifier.

was as effective as the HALS alone, which may indicate that a lower concentration of HALS would be sufficient under these exposure conditions.

In the second example (Table 2), two acrylic adhesive formulations are compared. The first contains a hydrogenated rosin ester tackifier, which shows relatively good UV stability. This tackifier can be replaced by one of lower stability (and lower cost), such as the nonhydrogenated rosin ester, by the incorporation of the appropriate light stabilizers. As these data show, some improvement in stability is seen when a BTZ is used at 0.5% (or a combination of BTZ/HALS at 0.25%/0.25%), but the best stability is achieved when the adhesive is stabilized with a HALS at the same level (0.5%). It should be pointed out that BTZs are commonly used in films and coatings (e.g., automotive clear coats) when the objective is to protect the material below the film. Similar applications can be imagined where UVA-containing adhesive films are used to screen and protect other substrates.

Conversely, in cases where the adhesive is very difficult to stabilize, the UVA can be incorporated into the substrate exposed to UV light to protect the adhesive.

To illustrate the effect of sample thickness, we can compare adhesives to sealants, which in many cases can be viewed as thick adhesives. As the sample thickness is increased, the benefit of the BTZ is clearly demonstrated. In Table 3 a SEBS/hydrogenated hydrocarbon tackifier sealant formulation was prepared as a hot melt and poured into shallow petri dishes. Although both of these polymers have good inherent stability, sealant applications may require extended exposure to UV radiation. The discoloration data show that the BTZ prevents yellowing of the sealant. However, examination of the sealant surface shows surface crazing and cracking when not protected by incorporation of the HALS. The combination of the two classes of light stabilizers provides the best overall performance.

As shown above regarding acrylic adhesive formulation, the use of light stabilizers may allow the incorporation of a less stable (and less expensive) tackifier in sealant formulations. The data in Table 4 compare two SEBS sealants, one containing a

Table 3 UV Stability of SEBS Sealant Film After Accelerated Aging in a Xenon-Arc Weatherometer (2.0 Mils Thick)[a]

	Apparent gardner color: hours XAW exposure			
Stabilizer	0	500	1000	2000
Unstabilized	1	5	6	6
BTZ-1, 0.5%	1	2	3	3
HALS-1, 0.5%	1	4	4	5
BTZ-2/HALS-1, 0.25%/0.25%	1	3	3	3

[a]Formulation contains 70% SEBS and 30% hydrogenated rosin tackifier. Compounded as hot melt.
XAW, xenon-arc weatherometer.

Table 4 UV Stability of SEBS Sealant Film After Accelerated Aging in a Xenon-Arc Weatherometer (2.0 Mils Thick)[a]

	Yellowness index:[b] hours XAW exposure				
	0	100	500	750	1000
Hydrogenated HC tackifier[c]					
BTZ-2/HALS-1, 0.2%/0.2%	9	9	11	12	17
Hydrogenated HC/rosin ester[d]					
BTZ-2/HALS-1, 0.0%/0.0%	6	55	110	120	125
BTZ-2/HALS-1, 0.2%/0.2%	6	25	80	90	100
BTZ-2/HALS-1, 0.4%/0.4%	7	9	60	80	80
BTZ-2/HALS-1, 0.8%/0.8%	7	8	16	28	30
BTZ-2/HALS-1, 1.5%/1.5%	7	7	9	10	11

[a]Formulation contains 70% SEBS and 30% tackifier. Solvent-based solutions coated onto glass slides.
[b]Higher numbers indicate more discoloration.
[c]Hydrogenated hydrocarbon tackifier.
[d]Containing a mixture of 50% hydrogenated hydrocarbon and 50% pentaerythritol rosin ester tackifier.
XAW, xenon-arc weatherometer.

hydrogenated hydrocarbon tackifier and the second containing a mixture of the same hydrocarbon tackifier with a rosin ester. Comparable stability to the "stable tackifier" can be achieved in a mixed formulation with a combination of BTZ and HALS.

VIII. SELECTION OF LIGHT STABILIZERS

In the preceding discussion we dealt with BTZs and HALSs as classes of light stabilizer without much attention to structure variations within each class. As demonstrated by the numerous chapters of this book, many polymers are used for adhesive applications. Each of these materials may have unique photostability concerns. It is beyond the scope of this chapter to address the stabilization of specific adhesives. Similarly, it is beyond our scope to discuss the many structural variations of UVA and HALS chemistry. Many derivatives of these compounds are commercially available, and some adhesive and sealant formulations and/or applications may dictate the use of one stabilizer over another.

In the case of BTZs, the UV absorption properties of the compounds are relatively similar, with some variations in absorptivity and absorption maxima (λ_{max}). Since sufficient BTZ is typically used to remove essentially all the light in the surface layer of the polymer, the performance characteristics of BTZs are usually comparable. Selection of the BTZ is therefore based on physical properties, not photochemical properties. Properties such as volatility (molecular weight) and physical form are usually considered, as well as economic concerns.

In the case of HALSs, the activity is dependent on the amine functionality concentration. Therefore, the highest-activity HALSs are generally those with a high portion of the molecular weight contributed by an amine such as HALS-1 and HALS-2. Additional structure built into the molecules may dilute and decrease the activity, but in some applications may increase polymer compatibility or decrease volatility. Oligomeric HALS have found extensive utility in high-surface-area applications such as films and fibers, due to their reduced volatility. Almost by definition, adhesives have high surface areas, but they also are between two substrates, which will limit volatility. As in the case of BTZs, physical properties are also important. Additionally, due to the basicity of the amine functionality, the use of conventional HALSs is intolerable in some applications, and structural modifications of the HALS functionality are used to reduce interactions.

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Thermal Stabilization of Adhesives

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I. INTRODUCTION

Adhesives are, in general, produced by the compounding of several different components: polymers, tackifier resins, and waxes or oils. The hydrocarbon-based components are susceptible to thermal oxidation and degradation [1]. Many adhesives are exposed to elevated temperatures as a result of compounding, storage, and end use. Hot-melt adhesives (HMAs), for example are extremely prone to oxidation due to their high compounding and application temperatures. Each hydrocarbon-based component in an adhesive formulation follows a similar oxidation mechanism. The result of degradation, however, can be very different and can greatly influence the overall thermal stability of the adhesive formulation.

II. MECHANISM OF THERMAL OXIDATION AND DEGRADATION

The basic scheme for the autooxidation of polymers is detailed in Table 1 [2]. The scheme can be broken down into several distinct reactions: initiation, propagation, and termination. The first step in the oxidation mechanism, initiation, occurs when a polymeric free radical (R•) is formed by exposure to heat, light, shear, or impurities. The propagation reactions involve the very rapid reaction of the polymer free radicals with oxygen-forming peroxy radicals (ROO•). The peroxy radicals can then react with the polymer to produce hydroperoxides (ROOH), which can decompose further to form two new free-radical species (RO• and HO•), which, in turn, can participate in other propagation reactions. The mechanism of autooxidation is cyclic in nature and leads to an exponential growth of free radicals. The termination mechanisms of these free-radical reactions are cross-linking and chain scission. The ramifications of degradation via cross-linking include hardening, skinning, gel formation, a decrease in tack, and an increase in viscosity. Degradation via chain scission results in softening, a viscosity decrease, an increase in tack, and a loss of cohesive strength. In addition to the change in physical properties as a result of degradation, discoloration is also possible. Although sample discoloration, in itself, may have a

Table 1 Major reactions : Polymer Oxidation, Chain Scission, and Cross-Linking

---

Initiation

$\mathrm{ROOH} \xrightarrow{\text{heat}} \mathrm{RO^{\bullet}+HO^{\bullet}}$

$\mathrm{2ROOH} \longrightarrow \mathrm{RO^{\bullet}+ROO + H_2O}$

$\mathrm{RH} \xrightarrow{\text{heat/light}} \mathrm{R'^{\bullet}+H}$

$\mathrm{R'^{\bullet} + O_2} \longrightarrow \mathrm{R'OO^{\bullet}}$

$\mathrm{RO^{\bullet}+R'H} \longrightarrow \mathrm{ROH + R'^{\bullet}}$

Propagation

$\mathrm{ROO^{\bullet}+R'H} \longrightarrow \mathrm{ROOH + R'^{\bullet}}$

$\mathrm{RO^{\bullet}+R'H} \longrightarrow \mathrm{ROH + R'^{\bullet}}$

$\mathrm{HO^{\bullet}+R'H} \longrightarrow \mathrm{H_2O + R'^{\bullet}}$

$\mathrm{R'^{\bullet}+O_2} \longrightarrow \mathrm{R'OO^{\bullet}}$

$\mathrm{2R'OO^{\bullet}+R'H} \longrightarrow \mathrm{R'^{\bullet}+2R'OH + O_2}$

Termination and cross-linking

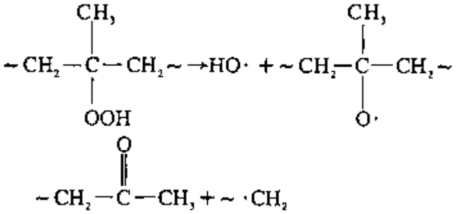
$\mathrm{R'^{\bullet}+R'^{\bullet}} \longrightarrow \mathrm{R' - R'}$

$\mathrm{R'O^{\bullet}+R'^{\bullet}} \longrightarrow \mathrm{R'OR'}$

$\mathrm{R'OO^{\bullet}+R'^{\bullet}} \longrightarrow \mathrm{R'OOR'}$

$$\left.\begin{array}{l}\mathrm{R'OO^{\bullet}+R'O^{\bullet}} \longrightarrow \\ \mathrm{R'OO^{\bullet}+R'OO^{\bullet}} \longrightarrow\end{array}\right\}\textit{nonradical products}$$

Chain scission



$$\sim\mathrm{CH_2}-\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{OOH}}{\mathrm{C}}}-\mathrm{CH_2}\sim \rightarrow \mathrm{HO\cdot} + \sim\mathrm{CH_2}-\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{O\cdot}}{\mathrm{C}}}-\mathrm{CH_2}\sim$$

$$\sim\mathrm{CH_2}-\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3} + \sim\cdot\mathrm{CH_2}$$

ROOH=peroxide (impurities)

R′H=polymer

---

minimal effect on the physical properties of an adhesive, the color formation results in an undesirable appearance which may be interpreted as being that of an inferior product.

The tactics used to inhibit the autooxidation process involve the obstruction of one or more of the degradation pathways. To inhibit or prevent the undesirable effects of degradation as a result of thermal oxidation, antioxidants are used in adhesive formulations [3,4]. Antioxidants are generally added to each component of an adhesive formulation and, in most cases, are also added to the final formulation.

III. ANTIOXIDANTS

There are two major classes of antioxidants and they are differentiated based on their mechanism of inhibition of polymer oxidation: chain-terminating or primary antioxidants and hydroperoxide-decomposing secondary antioxidants [5]. Primary or free-radical scavenging antioxidants inhibit oxidation via very rapid chain-terminating reactions. The majority of primary antioxidants are hindered phenols or secondary aryl amines. Generally, hindered phenols are nonstaining, nondiscoloring, and are available in a wide

Table 2 Key to antioxidants

AO-1	2,6-di-*t*-butyl-*p*-cresol
AO-2	Tetrakis[methylene(3,5-di-*t*-butyl-4-hydroxylhydrocinnamate)]methane
AO-3	2,4-bis(*n*-octylthio)-6-(4′-hydroxyl-3′,5′-di-*t*-butylanilino)-1,3,5-triazine
AO-4	2,4-bis[(octylthio)methyl]-*o*-cresol
AO-5	Triethyleneglycol-bis-3-(3′-*t*-butyl-4′-hydroxy-5′-methylphenyl)propionate
AO-6	Butylated reaction product of *p*-cresol and dicyclopentadiene
AO-7	Hindered phenol

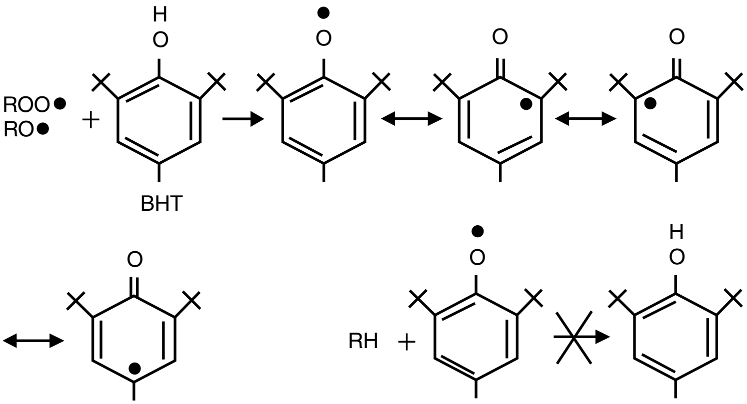
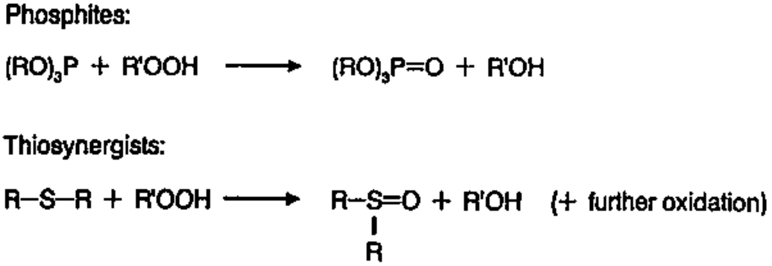


Figure 1 Radical stabilization using hindered phenols.

range of molecular weights and efficiencies. Amine-based primary antioxidants are very effective. However, they tend to interfere with peroxide cross-linking, and they discolor and stain. They are used primarily in situations where their color addition is unimportant or can be hidden.

A typical hindered phenol primary antioxidant is AO-1 (2,6-di-*tert*-butyl-*para*-cresol) (Table 2). Stablilization is achieved through proton donation from the -OH of AO-1 to a peroxy or alkoxy radical (Fig. 1). This reaction is in favorable competition with proton donation from a polymer carbon atom. Important to note, however, is that the resulting phenoxy radical is stable and does not abstract a proton from the polymer chain. This would be an undesirable effect, because the antioxidant would then be acting as a chain transfer agent. Due to its low cost, AO-1 is widely used as an antioxidant. In adhesive formulations, where exposure to high temperatures is possible (e.g., HMAs), the high volatility level of AO-1 renders it virtually useless. To solve this problem, state-of-the-art lower-volatility antioxidants are used to achieve the necessary level of stabilization (Table 2). In addition to their lower volatility, these antioxidants show higher activity, compatibility, and a resistance toward the formation of colored byproducts during compounding and application temperatures of HMAs.

The performance of a primary antioxidant can be improved by the use of a secondary antioxidant. Secondary antioxidants or peroxide decomposers do not act as radical scavengers but undergo redox reactions with hydroperoxides to form nonradical stable products (Fig. 2). This class of antioxidants (Table 3) includes phosphites such as tris(nonylphenyl)phosphite (PS-1) and thiosynergists or thioesters such as dilauryl



$$(RO)_3P + R'OOH \longrightarrow (RO)_3P{=}O + R'OH$$

$$R{-}S{-}R + R'OOH \longrightarrow \underset{\displaystyle R}{\overset{}{R{-}\underset{|}{S}{=}O}} + R'OH$$

Figure 2 Radical stabilization with secondary antioxidants.

Table 3 Key to Secondary Antioxidants

PS-1	Tris(nonylphenyl)phosphite
TS-1	Dilauryl thiodipropionate

thiodipropionate (TS-1). Phosphites reduce hydroperoxides to alcohols as they are oxidized to phosphate. Phosphites are generally highly effective process stabilizers and are nondiscoloring. Thiosynergists or thioesters are also nondiscoloring and are used with primary antioxidants to achieve long-term heat stability. Secondary antioxidants are generally used exclusively in combination with primary antioxidants. Thus secondary antioxidants are referred to as "synergists" because the overall level of stability achieved when a primary and a secondary antioxidant are used in combination is much greater than if either were used alone.

A variety of factors, including compounding or processing conditions, end use, and expected performance, should influence the selection of an appropriate antioxidant system. These factors include compatibility with the polymer and other additives or components, antioxidant mobility and volatility, discoloration, resistance to hydrolysis, extraction resistance, radical trapping efficiency, toxicity, and cost-effectiveness.

As mentioned previously, hot-melt adhesives are primarily a blend of several hydrocarbon based components, each of which is susceptible to thermooxidative degration. The stabilization of adhesive compounds against thermooxidative degradation is complex. Typically used to inhibit or prevent degradation, antioxidants are added to each hydrocarbon component [6] as well as to the final adhesive formulation. To gain a better understanding of the stabilization of an adhesive formulation, it is beneficial to examine the degradation mechanisms of the individual components.

IV. STABILIZATION OF ADHESIVE COMPONENTS (RAW MATERIALS)

A. Stabilization of Polymers (Elastomers)

Typically, the polymers used in adhesive formulations have only a minimal level of stabilization to endure isolation/coagulation, drying/finishing, and warehouse storage. As an adhesive producer, it is most desirable to understand the level of performance of a stabilized polymer and determine whether additional stabilization is needed to provide the necessary level of performance.

1. *Stablilization of Ethylene–Vinyl Acetate Copolymers*

Ethylene–vinyl acetate (EVA) copolymers are used in HMAs. The EVA acts as the binder, contributing cohesive strength to the adhesive formulation. Typically, an EVA used in a HMA is approximately 18–28 mol% vinyl acetate (VA). In an EVA copolymer, the crystalline polyethylene (PE) region provides strength, compatibility with the wax, and the desired high-temperature properties. The amorphous region containing both VA and PE provides compatibility with the tackifier.

Figure 3 shows the performance during static oven aging at 170°C (338°F) of a stabilized EVA polymer. The base stabilization of the EVA polymer by the producer using AO-1 provided an unsatisfactory level of stability. The presence of skinning and a more pronounced level of discoloration in the base AO-1–stabilized EVA requires additional antioxidant to meet the performance needs of a HMA. Upon the addition of AO-2 to the base polymer, it is clear that the stability of the EVA is improved significantly, skin formation is not observed, and color development is reduced substantially. The formation of insoluble gel as a result of cross-linking is also reduced dramatically with the addition of AO-2, as shown in Fig. 4.

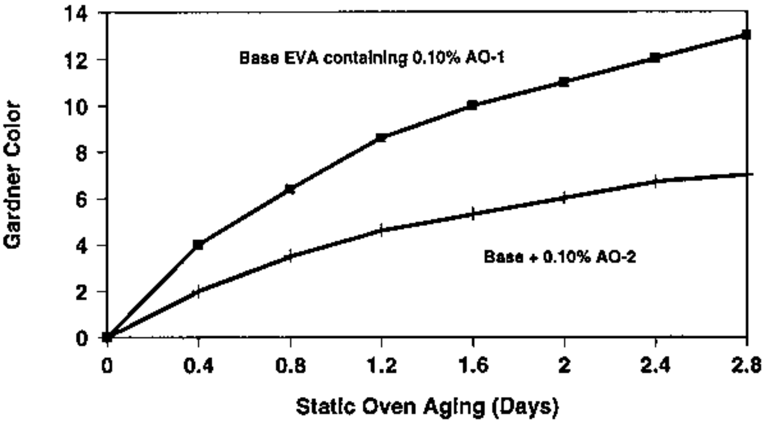


Figure 3 Discoloration of EVA polymer: Gardner color, days at 170°C (338°F).

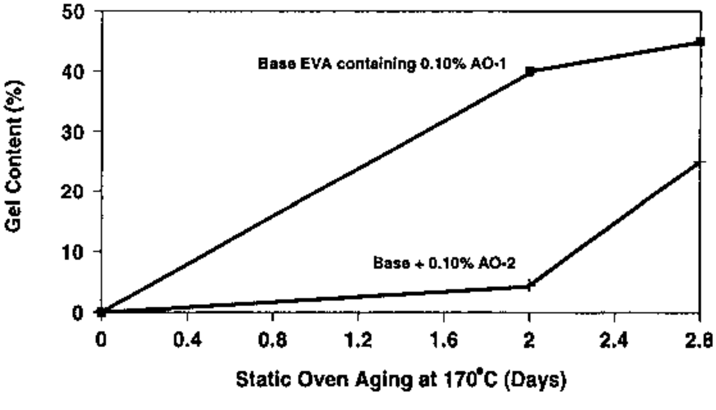


Figure 4 Gel formation in EVA polymer: gel content, percent insoluble in toluene at 25°C (77°F).

2. *Stabilization of SIS Thermoplastic Elastomers (Styrene–Isoprene–Styrene Block Copolymer)*

Thermoplastic elastomers (TPEs) with blocks of polydiene rubber are subject to degradation at the carbon–carbon double-bond sites and require proper stabilization. In SIS block copolymers, chain scission is the predominant degradation mechanism. In an SIS block copolymer, the addition of a more effective stabilizer, AO-3, alone or blended with a secondary antioxidant, PS-1, can provide a significantly superior performance over AO-1 alone or with PS-1. Resistance to discoloration after static oven aging at 80°C (176°F) is improved dramatically (Fig. 5). Viscosity stabilization (melt flow index stability) (Fig. 6) is also improved drastically using AO-3/PS-1.

3. *Stabilization of Styrene–Butadiene–Styrene (SBS) Thermoplastic Elastomers (Styrene–Butadiene–Styrene Block Copolymer)*

SBS block copolymers degrade primarily via cross-linking. The thermal stability of SBS copolymers can be improved with the addition of a more effective stabilizer system. Figures 7 and 8 show gel formation and discoloration of a SBS copolymer stabilized

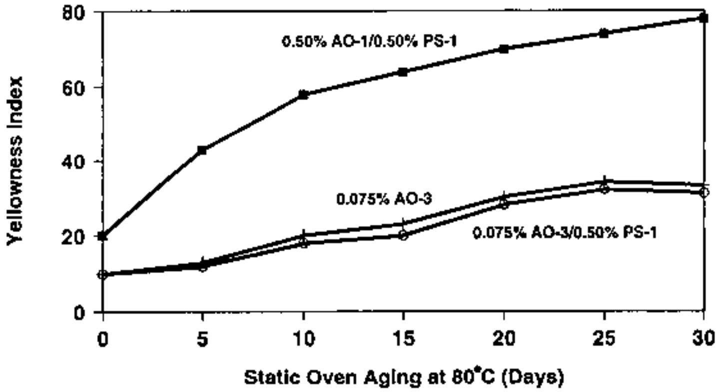


Figure 5 Discoloration of SIS polymer: yellowness index, days at 80°C (176°F).

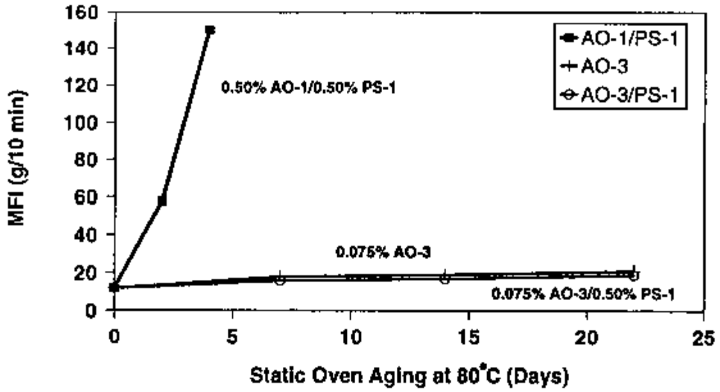


Figure 6 Viscosity stabilization of SIS polymer. Melt flow index (MFI), days at 80°C (176°F) MFI (g/10 min)-200°C/5 kg.

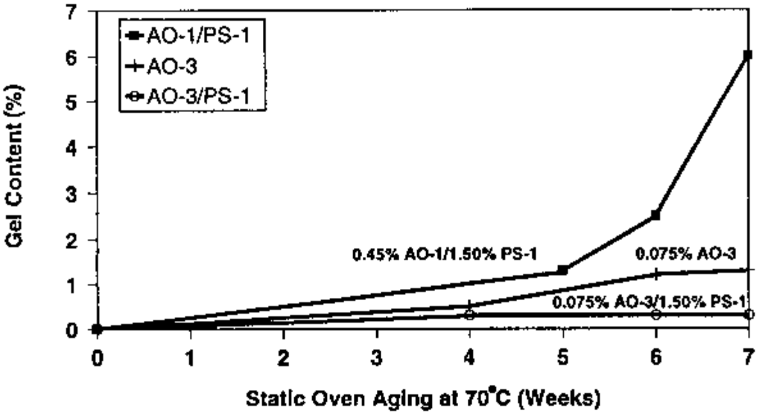


Figure 7 Gel formation in SBS polymer: gel content, percent insoluble in toluene at 20°C (68°F).

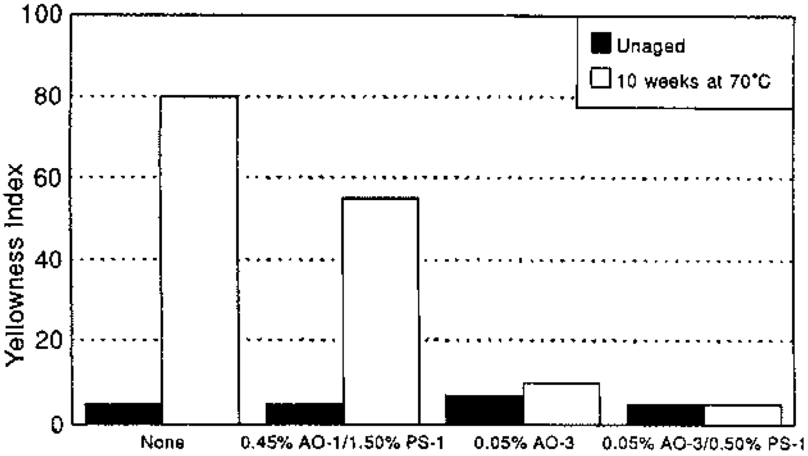


Figure 8 SBS polymer oven aging at 70°C (158°F): color formation, yellowness index.

with different stabilizer systems after static oven aging at 70°C (158°C). As seen previously in SIS copolymers, a higher-molecular-weight, more effective stabilizer such as AO-3, alone or in combination with a secondary antioxidant, PS-1, provides superior color stability and resistance to gel formation than does the AO-1/PS-1 stabilizer system.

4. *Stabilization of Carboxylated Styrene–Butadiene (X-SBR) Latices*

Carboxylated SBR latices are used as adhesives in applications where durability and flexibility are desired. Some of the major uses for X-SBR latex are in tufted carpet backing, paper coatings, wall and vinyl floor tile adhesives, and pressure-sensitive adhesives. Typically, discoloration is the first measure of the degradation of an X-SBR latex. Discoloration of a dried latex film can often be related to a loss of the physical properties and subsequently, to inferior performance in an adhesive formulation. Figure 9 illustrates the effects of adding an effective antioxidant system to an X-SBR latex on the level of discoloration as a result of static oven aging at 150°C (300°F). The addition of AO-4 alone

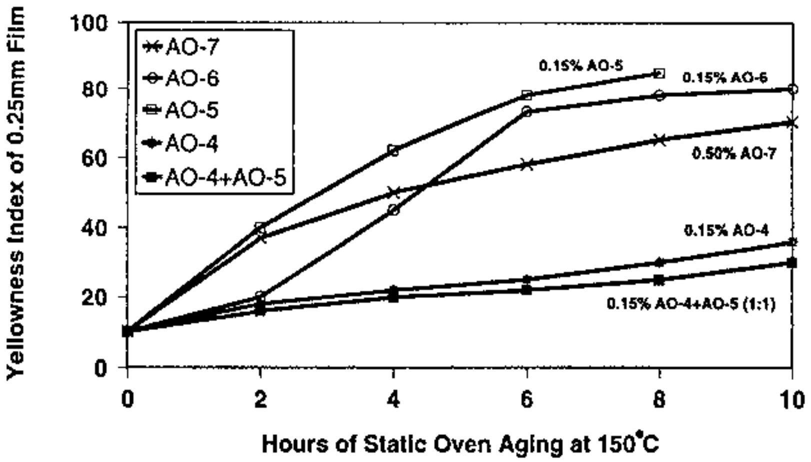


Figure 9 Discoloration of X-SBR latex: yellowness index, hours at 150°C (300°F).

and a combination of AO-4 and AO-5 in a 1:1 ratio dramatically increases the resistance to discoloration compared to that of a traditional stabilization system such as AO-6 or AO-7.

B. Stabilization of Tackifier Resins

The adhesion or performance of nonpolar elastomers to various substrates can be increased by the addition of a tackifier resin. The tackifier modifies the elastomer by improving wettability, modifying the viscoelastic properties, and increasing polarity.

Tackifier resins are susceptible to thermooxidative degradation. It is not uncommon for tackifier resins to degrade rapidly at room temperature. The integrity of the tackifier resin is very important to the final properties of an adhesive formulation. Tackifier resins must be effectively stabilized to prevent degradation during storage in order to maintain their properties until production of the adhesive formulation. Degradation leads to changes in both the chemical and physical properties of the tackifier, such as compatibility, melt viscosity, and discoloration. The mechanism of tackifier oxidation follows the autooxidation as outlined in Table 1. The degradation of tackifiers can be followed by determining the hydroperoxide formation, color development, and viscosity changes during static oven aging at warehouse storage temperatures.

1. *Stabilization of Rosin Ester Tackifier Resins*

In static oven aging at 40°C (104°F) of a rosin ester tackifier (Fig. 10) the rate of hydroperoxide formation was reduced significantly using AO-2, with even better results using AO-3. The hydroperoxides are fairly stable at room temperature. At temperatures associated with hot-melt compounding or drying of solvent- and water-based formulations, hydroperoxides decompose spontaneously. The decomposition products initiate further reactions, which can result in the formation of color species. The addition of AO-2 and AO-3 which reduces the level of hydroperoxides formed, subsequently reduces the level of tackifier discoloration after oven aging (Fig. 11).

Melt viscosity relates to stability during processing and to end-use performance. A stable melt viscosity is a very important property of a rosin ester tackifier. The melt

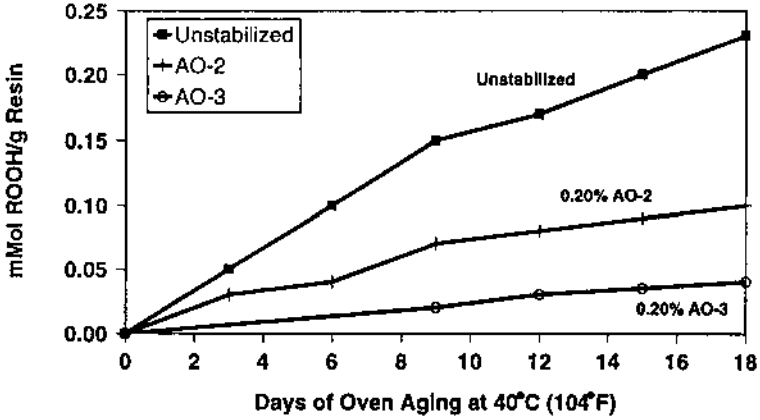


Figure 10 Stabilization of rosin ester tackifier. Hydroperoxide formation during oven aging at 40°C (104°F).

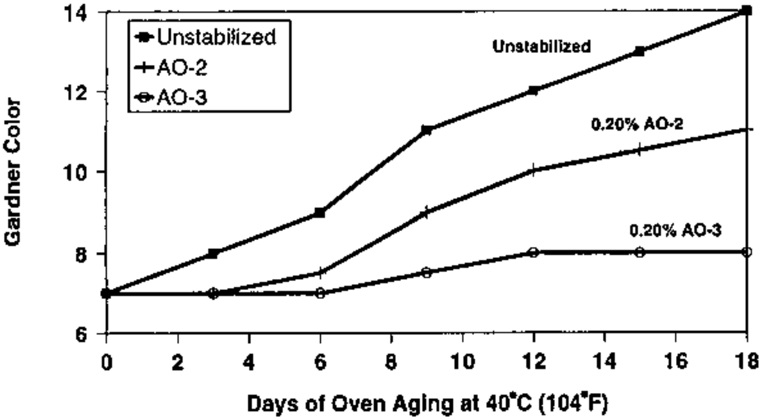


Figure 11 Stabilization of rosin ester tackifier: Gardner color after oven aging at 40°C (104°F).

viscosity can also be related to the hydroperoxide content of the tackifier after aging. Figure 12 shows that the addition of AO- 2 and AO-3 can significantly reduce the increase in the melt viscosity of the rosin ester during static oven aging at 40°C (104°F).

2. *Stabilization of C_5-Hydrocarbon Tackifier*

As shown in rosin ester-based tackifiers, the addition of AO-2 can greatly reduce the hydroperoxide formation of aC_5-hydrocarbon based tackifier during static oven aging at 40°C (104°F) (Fig. 13).

3. *Effects of Tackifier Stability on the Physical Properties of a HMA*

The prolonged effects due to thermal oxidation of a tackifier during storage correlate directly with the level of discoloration and viscosity changes in the HMA formulation. An effectively stabilized tackifier will produce a HMA with good color and controlled viscosity. When used in a HMA formulation, an unstabilized tackifier will result in a

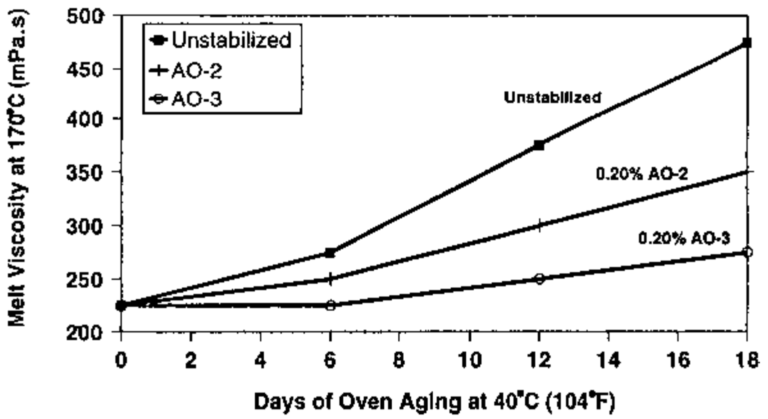


Figure 12 Stabilization of rosin ester tackifier: melt viscosity at 170°C (338°F) after oven aging at 40°C (104°F).

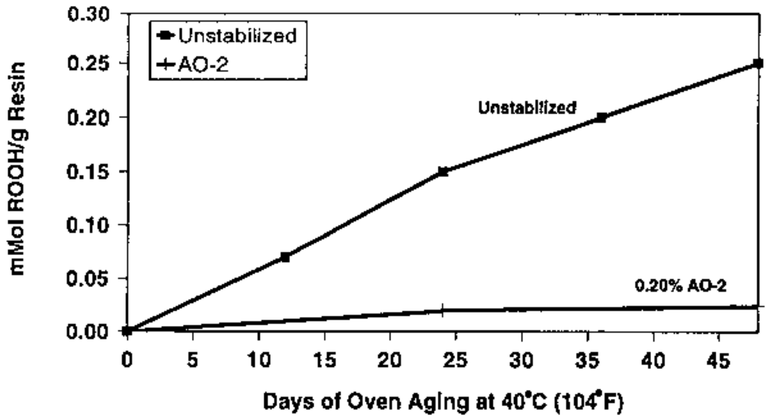


Figure 13 Stabiliztion of C_5-hydrocarbon tackifier: hydroperoxide formation during oven aging at 40°C (104°F).

HMA with high degree of discoloration and an unstable viscosity. Stabilizing a HMA formulation, however, will not correct for the addition of an unstabilized or preoxidized tackifier. The best performance can be achieved with the addition of an effective stabilizer to both the tackifier and the HMA.

C. Stabilization of Waxes

Waxes are used primarily in HMA formulations. Waxes are generally highly crystalline hydrocarbons. Waxes are added to HMA formulations to lower cost and decrease viscosity. Some of the HMA properties that are affected by wax content are the softening point and open time. Typically, waxes are thermally stable. During high-temperature storage and compounding, however, waxes can discolor very rapidly. Degradation of a wax can result in a reduction in the thermooxidative stability of the overall HMA formulation. As shown in Fig. 14, the addition of an antioxidant during static oven aging at

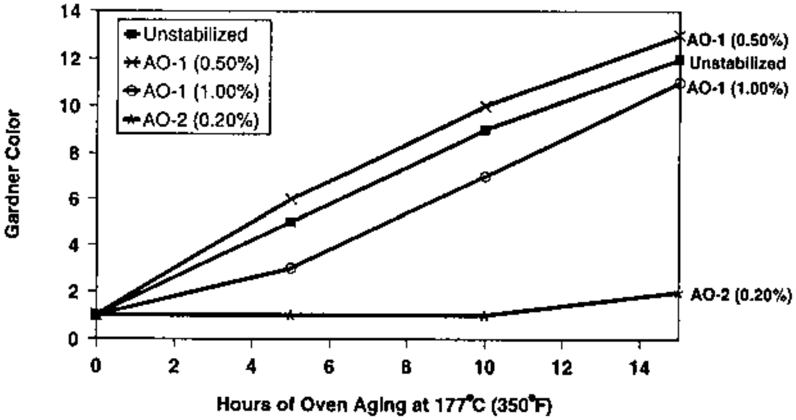


Figure 14 Stabilization of a microcrystalline wax: color formation during oven aging at 177°C (350°F).

177°C (350°F) of a microcrystalline wax can greatly reduce the degree of discoloration. The less volatile AO-2, at lower concentrations, significantly outperforms the more volatile AO-1. This reinforces the importance of volatility when an antioxidant is selected for a high-temperature application.

D. Influence of Stabilized Raw Materials on Adhesive Properties During Production and Storage

It has been demonstrated that the hydrocarbon-based raw materials of an adhesive formulation do undergo thermooxidative degradation and that the addition of antioxidants is necessary to maintain the integrity of these components during storage and compounding. In this section we illustrate the effects of using unstabilized raw materials in adhesive formulations in comparison with stabilized raw materials.

1. *EVA Hot-Melt Adhesives*

The effects of storage time of an unstabilized and a stabilized rosin ester tackifier on the properties of an EVA HMA are illustrated in Figs. 15–17. Significant effects on the initial color of the EVA HMA (Fig. 15) are observed when using an unstabilized tackifier. An increased level of hydroperoxides is also noted. In this situation, the addition of an antioxidant to the HMA will not correct the problem. However, the addition of an antioxidant to the HMA may reduce further discoloration during compounding or end-use applications.

Figure 16 illustrates the effects of an unstabilized tackifier on color formation as a result of high-temperature aging of the EVA HMA formulation. In this scenario the tackifier was aged for 18 days at 50°C and then combined with the other components at 177°C (350°F). The final HMA formulation was then aged at 170°C (338°F). Use of the unstabilized tackifier results in a darker initial color and a more rapid rate of discoloration than that of HMA using the stabilized tackifier.

A consistent viscosity of the EVA HMA during high-temperature aging can be achieved using a stabilized tackifier (Fig. 17). The EVA HMA usig the unstabilized

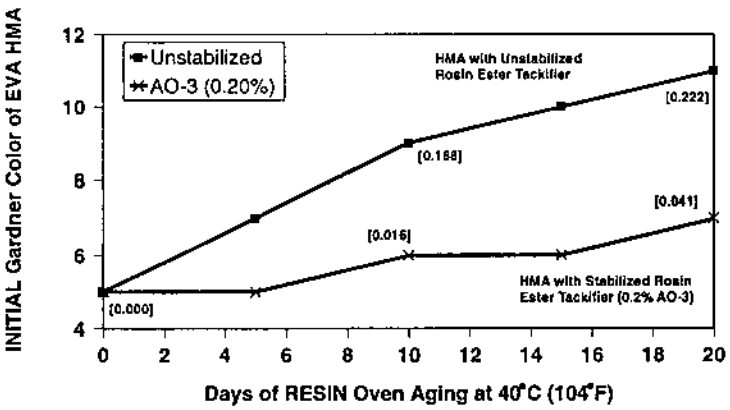


Figure 15 Influence of tackifier resin quality on EVA: hot-melt adhesive properties. Numbers in brackets represent ROOH content of the resin before compounding.

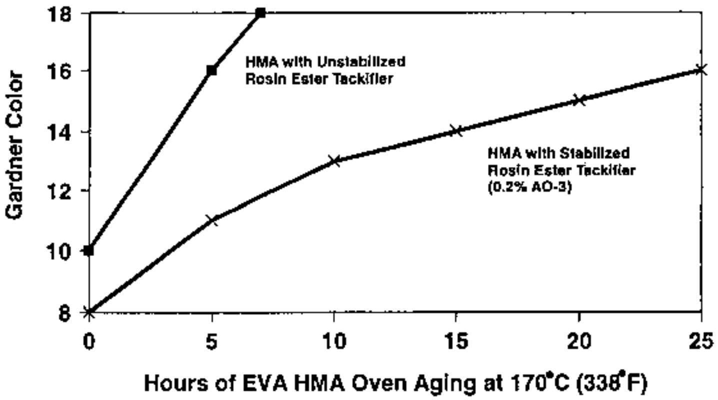


Figure 16 Influence of tackifier resin quality on EVA: hot-melt adhesive properties discoloration. Resin aged for 18 days at 50°C before compounding.

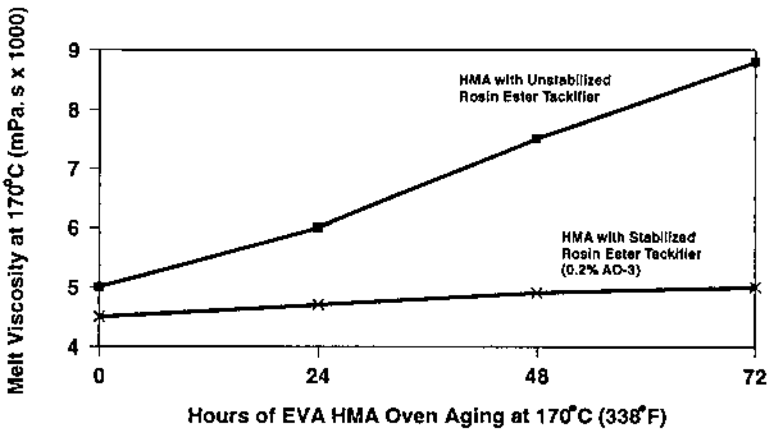


Figure 17 Influence of tackifier resin quality on EVA: hot-melt adhesive properties—melt viscosity. Resin aged for 18 days at 50°C before compounding.

tackifier has a higher initial viscosity and a more severe increase in viscosity during aging than those of the EVA HMA prepared with the stabilized tackifier.

E. Stabilization of Adhesive Formulations

In addition to stabilization of the raw materials, increased performance of an adhesive can also be achieved by the addition of antioxidants to the completed formulation. Typically the antioxidant is added during the compounding stages of an adhesive.

1. *Stabilization of SIS Hot-Melt Adhesives*

SIS-based HMAs degrade under high-temperature compounding and application conditions. Degradation of the bulk SIS HMA results in skin formation, viscosity changes, and discoloration. In a pressure-sensitive adhesive (PSA) film application, the film can degrade under moderate storage conditions, resulting in loss of tack and peel strength. Improved performance of both the bulk adhesive and the PSA film can be achieved with the addition of AO-2 (Figs. 18 and 19).

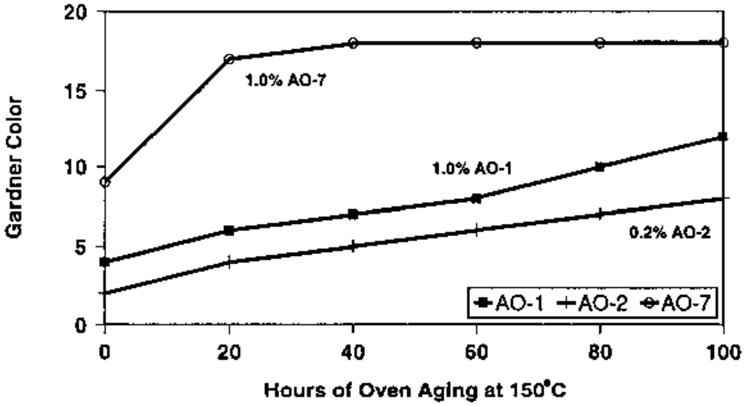


Figure 18 Stabilization of an SIS HMA: color development during oven aging at 150°C (300°F).

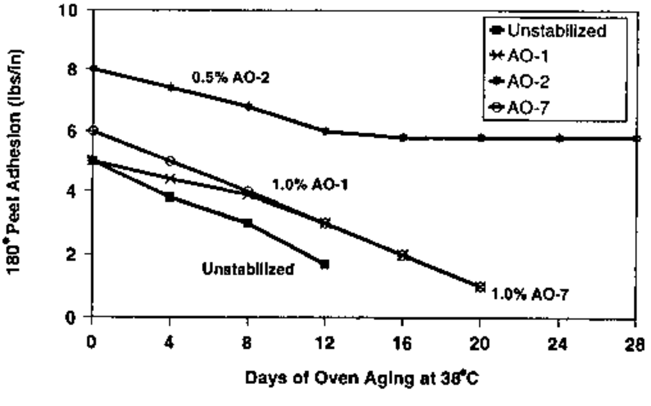


Figure 19 Stabilization of an SIS HMA: peel adhesion after oven aging at 38°C (100°F).

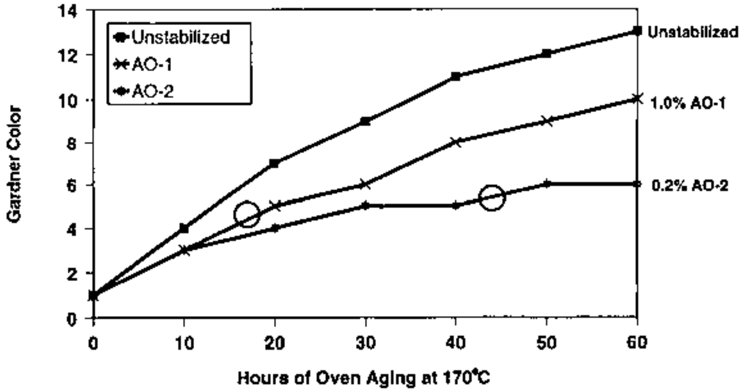


Figure 20 Stabilization of an EVA HMA: color development during oven aging at 170°C (338°F). (O) onset of skinning.

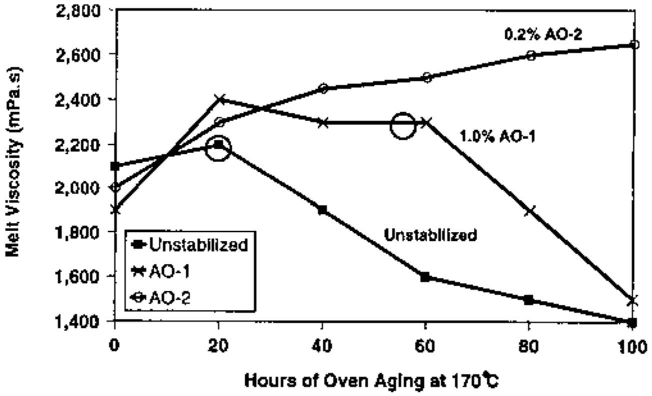


Figure 21 Stabilization of an EVA HMA: melt viscosity during oven aging at 170°C (338°F). (O) onset of skinning

2. *Stabilization of EVA Hot-Melt Adhesives*

EVA HMAs are widely used in the packaging and bookbinding marketplace due to their superior adhesion to most substrates, their versatility, and their ease of formulation. EVA-based HMAs degrade under high-temperature processing and application conditions. Degradation usually results in discoloration, viscosity changes, and skin formation. EVA HMAs can be effectively stabilized against discoloration and viscosity changes using AO-2 (Figs. 20 and 21).

V. CONCLUSIONS

The hydrocarbon-based raw materials used by the adhesives industry are prone to thermooxidative degradation. This degradation can occur during isolation, storage, compounding, and end use. Raw material degradation can affect the performance of the final adhesive formulation detrimentally. Raw materials that have been stabilized with effective stabilizers in the early stages of their production will have increased storage life while maintaining consistent quality. Effective stabilization of the raw materials will result in an adhesive formulation with improved physical properties. The use of antioxidants only in the final formulations cannot “reverse” the effect of using predamaged unstabilized raw materials. The performance of the final adhesive formulation can be improved significantly by the further addition of effective antioxidants. Selection of the most effective antioxidant system to meet the performance demands will produce an adhesive that will maintain its physical properties during storage, compounding, and end use.

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Protein Adhesives for Wood

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I. INTRODUCTION

Human beings have apparently had a propensity for gluing things together since the dawn of recorded history and probably before. By experimentation, we learned over time that certain natural products or extractives could develop bonds in wood of sufficient strength to break in the material being glued rather than in the glue film itself. These observations ultimately led to papyrus laminating, decorative wood veneering, and furniture and musical instrument assembly, practiced by the early Chinese and Egyptians and virtually every other civilization since that time using nature's own glues [l–3].

By today's standards, the ancient adhesive raw material choices were limited. Starch, blood, and collagen extracts from animal bones or hides were the principal early sources. Somewhat later, milk protein and fish skin extracts were discovered and included. Interestingly, vegetable proteins appear *not* to have been utilized as adhesives until recent times [4]. Tree pitch and petroleum bitumen were known and exploited as weatherproof coatings and caulks but not as adhesives, due to their plastic-flow behavior [5]; that is, the joints would creep and thus could not be used for structural support.

Adhesive durability has always been a problem. Although starch and protein glues were able to maintain long-term adhesive strength when kept completely dry, none were to any significant degree resistant to water or mold. Heat-cured blood glues and casein glues eventually provided some moisture resistance, but that was as durable as the technology of the times permitted. This fact limited the uses of adhesives strictly to interior or at least covered exterior applications from early historical times down through the Industrial Revolution and nearly to the present. From the middle of the nineteenth century onward, knowledge regarding more efficient means of dispersing and denaturing protein adhesives began to accumulate [6,7]. The results were significant improvements in protein glue working properties, bond strength, and water resistance, but still well short of true exterior durability. The urgencies of World War I brought protein-based adhesives to their nearest attainment of this goal in the form of chemically denatured, heat-set blood glues. These were used to assemble, among other things, laminated wooden airplane propellers and structural components in support of the war effort [8].

In the early 1920s the first of the phenol–formaldehyde and urea–formaldehyde resin adhesives were developed [9,10]. These early resins were slow to cure and somewhat difficult

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[†] *Deceased.*

to use, but they ushered in the era of "thermoset" polymeric adhesives and true exterior durability. The urgencies of World War II forced the rapid development of these and other synthetic resin glues for their water and weather resistance but left protein adhesive technology to evolve and flourish in applications for which "interior" durability was still adequate [11]. In the years following the war, the greatly expanded and partly idle petrochemical industry went looking for appropriate new markets. Among the opportunities identified were synthetic resin adhesive applications. Within a decade, these were converted from costly wartime adhesive specialties to bulk commodity glues. Throughout this synthetic resin expansion, however, protein adhesives held onto their "interior durable" product applications, due in large part to their unique combination of low cost and cold-curing capability or, alternatively, very fast hot press curing (about twice as fast as phenolics) [12,13]. This situation continued into the 1960s, at which time the price of petrochemically based adhesives had become so low that they literally displaced protein adhesives from their traditional interior markets. Specifically, phenolic and urea–formaldehyde resins replaced blood, soybean, and starch glues in all plywood and composite wood panels; resorcinol–formaldehyde resins replaced casein glues in lumber laminating and millwork applications; and poly(vinyl acetate) and acrylic emulsion glues replaced virtually all collagen adhesives (animal and fish bone/skin derived) from furniture, musical instruments, and general interior wood assembly [14]. Limited and specialized applications for protein glues, mainly in combination with synthetic resin polymers, continue to the present, however. These are discussed in the following sections. It is worth noting that protein glue technology in each of the application areas described above remains fully useful and industry approved in a backup sense and could be reintroduced rapidly if world petroleum resources were to be threatened again through events beyond national control, as in 1973.

In this chapter we address three of the most widely used families of protein-based adhesives for wood: soybean, blood, and casein. The technology presented is drawn primarily from the years 1930 through about 1960, when the consumption and technical refinements of these adhesives were at their peak. Soybean glues are discussed first because they were often utilized in combination with blood or casein to yield adhesives of intermediate performance properties as well as being used alone.

II. SOYBEAN ADHESIVES

A. Raw Material Source and Preparation

Soybeans are legumes, the seeds of a low-growing field vine. These vines are ancient in culture; the written record of their domestication in China dates back almost 5000 years [15]. From that time until now, soybeans have remained a very important agricultural crop for almost every temperate-climate civilization because of their unusually high content of both triglyceride oil and edible protein.

To process soybeans into these useful products, the beans are dehulled and the oil is removed by crushing at very high pressure or by solvent extraction. If the resulting dry soybean meal is intended for food, it is heated to 70°C or higher to coagulate the proteins and caramelize the carbohydrates, thus improving their nutritional qualities. If the soybean meal is intended for adhesive use, it is processed at temperatures below 70°C to preserve the alkaline solubility of the proteins [16].

The protein content of oil-free soybean meal ranges from about 35 to 55% on a worldwide basis. However, the industrial grades are generally blended to yield a uniform protein content of 44–52%, depending on the source. The other principal constituents of soybean meal are carbohydrates, totaling about 30%, and ash at 5 or 6% [17]. The moisture content after processing is quite low, usually less than 10%.

Production experience has shown that to perform well as a protein glue, adhesive-grade "untoasted" soybean meal must be ground to an extremely fine flour [18]. Typically, the dry extracted meal is ground or milled until at least 40%, and preferably 60–80%, will pass through a 46-μm (325-mesh) screen. For easier quality control with flours of this fineness, an alternative specific surface test method is available that determines average particle size in terms of surface area per gram [19]. For the range of mesh sizes recommended above, the corresponding specific surface values are about 3000–6000 cm^2/g.

B. Formulation

Soybean flour will wet and swell in plain water but will not disperse to yield useful adhesive properties. For this purpose, treatment with a soluble alkaline material is necessary. Almost any organic or inorganic alkali will disperse wetted soybean flour to some degree. However, soybean wood glues of maximum bonding efficiency require dispersion with several percent of a strong alkali such as sodium hydroxide or trisodium phosphate [20]. The effect of this strongly alkaline treatment is to break the internal hydrogen bonds of the coiled protein molecules, literally unfolding them and making all their complex polar structure available for adhesion to wood. Although essential for adhesion, this alkaline dispersion process exposes the protein structure to gradual destruction by alkaline hydrolysis. Thus a dispersed soybean glue has a definite useful life, slowly losing viscosity and adhesive functionality over a storage period of 6–12 h.

Although these strongly alkaline soybean glues are nearly colorless in an applied film, they cause a reddish-brown stain on wood surfaces as they cure, due to alkali burn of the cellulose itself [5]. If a colorless glue line on wood is desired, the wetted soybean flour must be dispersed with a less strongly alkaline material, such as hydrated lime or ammonia [21]. However, the adhesive bond strength of these low-color, mildly dispersed soybean glues is considerably less than that obtained with fully dispersed, highly alkaline formulations. Typical high- and low-alkali soybean glue formulations are listed in Tables 1 and 2.

Table 1 High-Alkali Soybean Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	87.5
Adhesive-grade soybean flour[a]	48.5[b]
Pine oil or diesel oil defoamer: mix 3 min or until smooth in a counterrotating mixer	1.5[b]
Water at 16–20°C: mix 2 min or until smooth	72.5
Fresh hydrated lime (as a slurry in)	6.0
Water at 16–21°C: mix 1 min	12.0
50% Sodium hydroxide solution: mix 1 min	7.0
Sodium silicate solution: mix 1 min	12.5[c]
Orthophenyl phenol or other preservative: mix 10 min	2.5

[a] 44% protein, specific surface 3000–6000 cm^2/g.

[b] Normally dry-blended for easier handling and dust control.

[c] 8.90% Na_2O, 28.70% SiO_2, 41° Baumé.

Table 2 Low-Alkali Soybean Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	112.5
Adhesive-grade soybean flour[a]	48.5[b]
Pine oil or diesel oil defoamer: mix 3 min or until smooth in a counterrotating mixer	1.5[b]
Water at 16–21°C: mix 2 min or until smooth	75.0
Fresh hydrated lime (as a slurry in)	15.0
Water at 16–21°C: mix 5 min	25.0

[a] 44% protein, specific surface 3000–6000 cm^2/g.
[b] Normally dry-blended for easier handling and dust control.

The additions of hydrated lime and sodium silicate solution in the high-alkali mix (Table 1) accomplish two purposes: (1) they help maintain a level glue viscosity for a longer adhesive working life, and (2) they improve the water resistance of the cured glue film by forming some insoluble proteinates [22].

The starchy constituents of soybean flour also disperse in the presence of strong alkali to become useful adhesive molecules contributing to dry bond strength. However, this starchy fraction also retains its well-known sensitivity to water and is considered primarily responsible for limiting the performance of soybean glues with respect to water resistance [23].

The final addition of preservative shown in this formulation is essential in virtually all protein glues to provide mold resistance in high-humidity service. Without this protection, even heat-cured soybean adhesives *will* mold as the moisture content of the bonded wood approaches 20% [24]. Copper-8-quinolinolate, and copper naphthenate are among the few remaining preservatives permitted to be used in the United States at this time for wood products. Where the use of chlorinated phenols or orthophenyl phenol is still permitted, they are also very effective preservatives for protein glues at the addition level shown. In this case, the sodium hydroxide content of the glue formulation converts the water-insoluble chlorinated fungicides to their soluble sodium salts.

Large quantities of this high-alkali soybean glue formulation were used to bond interior grades of softwood plywood between about 1940 and 1960 [13]. It was also used to some extent for assembling prefabricated wooden building components [11]. Its primary advantages were very low cost and the capability to bond almost any dry wood surface. It also offered real versatility in a bonding process because it could be hot pressed or cold pressed to promote cure. Appropriate pressing schedules for each curing mode are provided in tables that appear later in this chapter.

The low-alkali formulation (Table 2) has been used widely as a briquetting binder for wood, charcoal, and other absorbent particles. It is particularly suitable for paper and softboard laminating, where a colorless glue line and minimum swelling of the glue film on high-humidity exposure are desired [25]. It is not recommended for structural uses such as sheathing plywood because of its lower degree of protein dispersion and thus lower bonding strength. Substituting borax or monosodium phosphate for the hydrated lime dispersing agent will yield similar nonstaining glues.

Over the years a number of denaturants or cross-linkers have been added to soybean glues to improve their water resistance, working life, and consistency. These may be roughly categorized as formaldehyde donors, sulfur compounds, and inorganic complexing salts.

Table 3 Soybean Glue: Hot-Pressing for Interior Douglas Fir Plywood

(a) Pressing schedule

Rough panel thickness (mm)	Number of plies	Panels per press opening	Platen temperature (°C)	Pressing time at full pressure (min)
4.8	3	2	110	3
6.4	3	2	116	3
7.9	3	2	121	3½
7.9	3	3	127	5
9.5	3	2	127	4
11.1	3	1	116	3
11.1	3	2	132	4¾
12.7	5	1	110	3½
12.7	5	2	121	6
14.3	5	1	110	3¾
14.3	5	2	121	6
15.9	5	1	116	4
17.5	5	1	121	4
19.0	5	1	127	4¼
20.6	5	1	132	4½
20.6	7	1	127	5
23.8	7 and 9	1	132	5½
27.0	7 and 9	1	132	6
30.2	7 and 9	1	132	7
33.4	9	1	132	7½
36.5	9	1	132	8
39.7	9 and 11	1	132	9

(b) Glue application rates

Core thickness (mm)	Mixed glue per single glue line (g/m^2)
1.59	195
1.54, 2.82	208
3.18	220
3.63, 4.23, 4.76, 6.35	232
All constructions 5 or more plies, 20.6 mm and thicker	245
On rough or warm veneer, add at least 12 g extra glue spread.	

(c) Other conditions

1. Total assembly time per press load, 15 min.
2. Veneer temperature not to exceed 43°C.
3. Veneer moisture content not to exceed 8%.
4. Not less than 14 kg/cm^2 uniform hydraulic pressure.

Each of these groups of compounds appears to react with the starchy constituents of whole soybean flour as well as the dispersed protein molecules. Formaldehyde itself acts too rapidly and thus is difficult to control. Instead, such compounds as dialdehyde starch, dimethylol urea, sodium formaldehyde bisulfite, and hexamethylenetetramine have been used successfully to toughen the cured glue film and improve its water resistance [26,27]. Similarly, carbon disulfide, thiourea, and ethylene trithiocarbonate, among the sulfur compounds [28,29], and the soluble salts of cobalt, chromium, and copper have been used to improve soybean glue working properties and adhesive performance [30,31]. These modifiers are generally added last when preparing the glue. The range of addition of all such denaturants is 0.1–1.0% based on the weight of soybean flour. Also, 5–20% of an aliphatic epoxy resin has been added to soybean glues, yielding significantly improved durability, but the cost is high [32]. Similarly, alkaline phenol–formaldehyde (PF) resins have been incorporated for both durability and mold resistance. Proportions have ranged from a straight soybean glue with a minor resin addition to a primarily PF resin glue containing a moderate quantity of soybean flour [33,34]. Soybean protein is presently being evaluated as a cost-reducing adhesive constituent in phenolic and urea–formaldehyde resin binders for wood particle and cellulosic waste reconstituted products.

C. Mixing, Application, and Pressing

Soybean glues are very easy to mix, provided that they are wetted with plain water as a first step. (If any form of alkali is present in the first mixing water, the dry soybean flour will form permanent lumps.) As with all protein glues, the first mix is kept thick to break down any lumps of dry powder that may be present. The division of water additions in both formulations listed earlier demonstrates this mixing procedure. Once the soybean flour particles have been uniformly wetted, further dilution and dispersion steps can follow without difficulty. Water additions are adjusted to yield a mixed glue viscosity in the broad range of 500–25,000 cP at 25°C, depending on purpose. Briquetting and paper laminating glues would typically be 500–1000 cP, while cold-press plywood glues should be 10,000–20,000 cp for best performance [35]. Hot-press formulations would be midrange. Particularly because of the heavy first mixing stage and the high final viscosities, an appropriate soybean glue mixer should have relatively strong, slow-turning blades plus a counterrotating scraper for continuous removal of glue buildup from the mixer walls.

Low-viscosity soybean briquetting adhesives are generally applied by spray. Paper and softboard laminating glues are usually applied by curtain coater, knife, or indirect roller. High-viscosity plywood and lumber assembly formulations are fairly well limited to application by spreader roll or extrusion. For very small assembly jobs, soybean glue can easily be applied by brush.

One of the real advantages of protein glues generally is their ability to be cured (under pressure) either hot or cold. Typical commercial schedules for each mode of cure are given in Tables 3 and 4. The cold-pressing schedule in Table 4 is the result of an interesting laboratory observation and subsequent industry-wide patent [35]. Alkaline protein glues, particularly soybean glues, lose water quite rapidly into adjacent dry wood surfaces. As a result, they gain sufficient gel strength in 15–20 min to permit removal of a glued wood assembly from its clamping device without loss of intimate contact between the glued surfaces. Cure is then completed over the next 6–12 h simply by placing the bonded products in storage at ambient temperatures with minimum handling. This method of cold pressing, called the no-clamp process, was used throughout the softwood plywood industry for many years. Prior to its introduction, all protein-bonded cold-press plywood was clamped for 6–8 h with bulky steel beams and turnbuckles.

Because protein glues develop bond strength primarily by water loss over time, roll pressing has proved unsuccessful as a clamping method for wood products. The short, intense period of pressure simply squeezes the still-fluid mix off the glue line without

Table 4 Soybean Glue: Cold-Pressing (No-Clamp) for interior Douglas Fir Plywood

(a) Glue application rates

Core thickness (mm)	Mixed glue per single glue line (g/m^2)
2.54	305–318
2.82	313–323
3.18	318–330
3.63	325–337
4.23	330–342
4.76	330–342
All constructions 5 or more piles, 20.6 mm and thicker	367
For rough or warm veneer, and an extra 20 g over these spreads.	

(b) Other conditions

1. Hold press load 5 min after assembling last panel before applying pressure.
2. Total assembly time limit per press load, 25 min.
3. Veneer temperature not to exceed 43°C
4. Veneer moisture content not to exceed 8%
5. Use 12–14 kg/cm^2 uniform hydraulic pressure.
6. Pressing time to be measured after gauge reaches full pressure.
7. Pressure to be retained for 15 min.

affording sufficient time for water loss and gelation. An exception is the soft rubber roll or brush roll lamination of paper to paper or paper to wood [36]. This can be accomplished at production speeds because of the extreme rapidity with which dry paper removes water from a protein glue film.

D. Blended Formulations

As mentioned earlier, the single largest commercial use of soybean flour in wood glues during the recent past has been as a blend with other adhesive proteins, mainly blood and casein, for bonding interior-grade plywood, doors, and millwork. These blended formulations exploit several unique properties of the soybean glues themselves and incorporate useful adhesive characteristics from the other protein materials.

1. *Soybean–Blood Glues*

For example, a blend of soybean flour with spray-dried soluble animal blood, a fairly expensive but very efficient adhesive protein, yields a glue with the best properties of each material [37]: namely, the cost becomes moderate and the consistency ideal for wood product assembly (slightly granular) because of the soybean flour. The hot-press curing time is very short and the cured glue bonds are considerably more water resistant because of the blood's thermosetting properties. Fortunately, both proteins require the same neutral wetting procedure and strongly alkaline dispersion steps. They are otherwise compatible in all proportions, yielding a series of cost/performance-related adhesives. Soybean–blood blend glues were by far the most widely used protein hot-press adhesives for interior structural plywood from the early 1940s until about 1960 [13]. Also, when the oil embargo

Table 5 Low-Blood-Content Soybean Blend Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	100.0
Adhesive-grade soybean flour[a]	36.0[b]
Dried soluble animal blood	7.5[b]
75-μm Wood flour[c]	5.0[b]
Pine oil or diesel oil defoamer: mix 3 min or until smooth in a counterrotating mixer	1.5[b]
Water at 16–21°C: mix 2 min or until smooth	110.0
Fresh hydrated lime (as a slurry in)	4.0
Water at 16–21°C: mix 1 min	8.0
Sodium silicate solution: mix 1 min	20.0[d]
50% Sodium hydroxide solution: mix 5 min	5.0
Orthophenyl phenol or other preservative: mix 5 min	2.5

[a] 44% protein, specific surface 3000–6000 cm^2/g.
[b] Normally dry-blended for easier handling and dust control.
[c] 0.074 mm (200 mesh) and finer.
[d] 8.90% Na_2O, 28.70% SiO_2, 41° Baumé.

Table 6 High-Blood-Content Soybean Blend Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	80.0
Dried soluble animal blood	35.0[a]
Adhesive-grade soybean flour[b]	8.5[a]
74-μm Wood flour[c]	5.0[a]
Pine oil or diesel oil defoamer: mix 4 min or until smooth in a counterrotating mixer	1.5[a]
Water at 16–21°C: mix 2 min or until smooth	195
Fresh hydrated lime (as a slurry in)	4.0
Water at 16–21°C: mix 1 min	8.0
Sodium silicate solution: mix 1 min	22.5[d]
50% Sodium hydroxide solution: mix 5 min	8.0
Powdered hexamethylenetetramine: mix 3 min	1.0

[a] Normally dry-blended for easier handling and dust control.
[b] 44% protein, specific surface 3000–6000 cm^2/g.
[c] 0.074 mm (200 mesh) and finer.
[d] 8.90% Na_2O, 28.70% SiO_2, 41° Baumé.

of 1973 quickly placed phenolic resin adhesives on allocation through petrochemical restrictions, the plywood industry immediately returned to the use of soybean–blood hot-press glues for interior structural grades. Typical examples of low and high-blood-content soybean-blend glues are described in Tables 5 and 6.

Both glues are ready to use when mixed and have a working life of 6–8 h at inside temperatures. Several points of difference between these glues should be noted:

1. The water content of the high-blood-glue formulation is much larger, which offsets most of the material cost increase. This is possible because the "water

requirement" of alkaline-dispersed blood is much higher than that of soybean flour.

2. The order of addition of alkaline dispersing agents in the high-blood mix is partially reversed. Experience has shown that this helps impart a more granular consistency to the dispersed blood, which is otherwise very slick and smooth.
3. The final addition of hexamethylenetetramine illustrates the use of a formaldehyde donor to partially denature or cross-link the dispersed proteins. This adds further granular character to the mixed glue, lengthens its working life, and improves the water and mold resistance of the cured adhesive film.
4. As with straight soybean glues, the low-blood-content formulation requires a mold-inhibiting ingredient to meet plywood performance standards, whereas the high-blood-content glue does not [24].

2. *Soybean–Casein Glues*

Blends of soybean flour with ground and screened casein also yield a very useful series of protein adhesives, in this case, mostly cured cold [38]. While alkaline-dispersed casein yields strong, water-resistant cold-cured bonds in wood, its sticky dispersed consistency does not permit the rapid water loss needed for quick-clamping procedures. By combining it with an appropriate amount of soybean flour, the cold-press no-clamp process can be used. Formulations of this type have proved so successful for bonding plywood faces onto wooden flush-door cores and frames in a short cold-pressing cycle that the entire industry has employed these protein adhesives from about 1950 to the present [39]. As a special performance property, the bonds of soybean–casein door glues maintain strong adhesion in a fire until the glue lines are literally charred away. Thus glues of this type are widely used to bond flush-design fire doors. They are also excellent adhesives for millwork in general [40]. Some current formulations also contain minor amounts of blood.

The formulation of the typical soybean–casein blend glue listed in Table 7 is quite different from any protein adhesive described thus far in that all ingredients, dispersing

Table 7 Soybean–Casein Dry Glue: Ingredients and Mixing Procedure

	Amount (kg)
Adhesive-grade soybean flour[a]	29.0
250-μm Lactic acid casein[b]	9.5
Fresh hydrated lime	3.5
74-μm Wood flour[c]	2.5
Granular sodium carbonate	2.5
Granular sodium fluoride	1.0
Granular trisodium phosphate	0.5
Pine oil or diesel oil defoamer	1.5
Water at 16–21°C	100
Dry glue: mix 2 min, until smooth and thick; let stand 15 min or until thinning has occurred; mix until smooth	50
Water at 16–21°C: mix 2 min or until smooth	25

[a] 44% protein, specific surface 3000–6000 cm^2/g.

[b] 0.250 mm (60 mesh).

[c] 0.074 mm (200 mesh) and finer.

agents included, are dry-blended into a single packaged composition that requires only the addition of water to prepare. The uniform oiling of all ingredients during the blending operation is a key, since it slows down the solution of the alkaline ingredients long enough for the soybean flour and casein to wet out under reasonably neutral conditions. Then the alkaline agents dissolve. Highly alkaline dispersing conditions are provided by reaction of the sodium salts with lime to yield sodium hydroxide in situ plus insoluble calcium salts [6]. (The sodium hydroxide needed for this strongly alkaline dispersion step could not be included in a one-package composition because of its hygroscopic behavior). These sequential solution and dispersion reactions require some time for completion, which is the reason for the 15-min pause in glue preparation.

The dry ingredients are blended intensively in an appropriate dry powder mixer while the defoamer is sprayed in to provide uniform distribution. Mixing directions are given in Table 7. The second water addition may be increased or decreased to obtain the final viscosity desired. (A normal range is 4000–8000 cP.) Working life is 4–6 h at inside temperatures. Application rates must be determined by experience but will generally range from 245 to 345 g of mixed glue per square meter of a single glue line.

While the soybean–casein blend glue can be used according to the short-cycle no-clamp process on dry softwood, it will require 4–6 h of clamp time to cure to machining strength when used on dense hardwoods. Water removal from the glue film is simply too slow on hardwoods to develop adequate early gelation. However, the ultimate bond strength is excellent. Note that this formulation represents about the maximum casein content at which short-cycle clamping is possible for softwood flush-door or millwork assembly. Above this level water loss is too slow, interfering with normal production rates through the press.

III. BLOOD GLUES

Since soybean–blood blend glues were covered in the preceding section, in this portion of the chapter we deal only with all-blood adhesive compositions.

A. Raw Material Source and Preparation

Historically, animal blood could be used for adhesives only in reasonably fresh liquid form. These glues performed well on wood. However, the very rapid spoilage rate of liquid blood imposed real limitations on the general availability and use of this adhesive raw material. It was not until about 1910 that techniques were developed for drying whole blood in commercial quantities without denaturing its protein content, thus maintaining its water solubility [41]. As a result, blood could be collected, processed, and stored indefinitely for later use. The effect of this development was to stimulate rapid growth in the technology of blood-based adhesives, especially for wood, about the time of World War I.

Virtually all the proteins in animal blood can be dispersed into useful adhesive form. These include the serum albumin and globulin and even the red cell hemoglobin [42]. The fibrin clotting substance is sometimes removed before drying (by agitation or acidification) because of its instability in solution. Thus, except for residual moisture content, dried blood is essentially 100% active adhesive protein.

The principal North American bloods sold in quantity for adhesive uses are beef and hog, with lesser amounts from sheep and horses. Because of its high lysine content, poultry blood is utilized almost exclusively as a feed additive or binder and is seldom available otherwise. For adhesive purposes, there are significant viscosity differences relating to species among these dried bloods, beef being highest and poultry lowest [43]. Viscosity and water-holding properties are also influenced by animal age, diet, activity, and other factors. As a result, industrial-grade dried soluble blood is generally blended in large quantities to provide average and reproducible properties for adhesive formulating.

The method employed for drying blood is now entirely spray drying. (Formerly, a certain amount of vacuum pan-dehydrated blood was also available.) Spray-drying conditions relating to temperature, dwell time, and humidity can be adjusted to produce a wide range of blood solubilities [44]. Also, chemical denaturants such as glyoxal can be added to the blood solution prior to drying to further modify its adhesive characteristics [45]. Solubilities from about 20 to 95% can be prepared with ± 5% control. (Dried bloods below 20% solubility can only be redissolved in strongly alkaline solutions, which destroy a significant portion of the adhesive proteins.) This controllable range of solubilities permits the formulation of blood glues with a variety of handling and performance properties.

Generally speaking, the lower the solubility of a dried blood product, the more granular and water holding is its alkaline-dispersed form [46]. For instance, blood glues of 20–40% solubility make excellent cold-press formulations (which *must* have a granular consistency) [42]. They also yield the most water- and mold-resistant (near-exterior) glue bonds when cured hot. By comparison, highly soluble bloods in the range 85–93% yield very slick and livery alkaline dispersions of somewhat lower water-holding capacity. Soybean flour is normally blended with these highly soluble bloods to produce appropriately granular glues. If soybean flour is not used, they must be combined with a particulate cellulosic filler such as wood flour or nutshell flour to develop this functional consistency. Examples of these glue types are provided in the following section.

B. Formulation

As with the soybean glues discussed previously, dried blood adhesives must initially be wetted or redissolved in plain water and then be subjected to one or more alkaline dispersing steps. Unlike vegetable proteins, however, high-solubility blood proteins can be dispersed and rendered strongly adhesive by more moderate alkaline agents such as hydrated lime or ammonia [47]. Especially with a denaturing compound added, these glues represented the most water-resistant adhesives available until the advent of phenol–formaldehyde resins [5]. An example is shown in Table 8. This mix is unique in the quantity of denaturant it employs. The aldehyde reaction actually causes the blood protein to gel for a short period before thinning out again to a working viscosity level.

Table 8 Blood Glue: Ingredients and Mixing Procedure

	Amount (kg)
90% Soluble spray-dried animal blood	50.0
Water at 16–21°C: mix 3 min or until smooth	40.0
Water at 16–21°C: mix until smooth	30–60
Ammonium hydroxide, sp. gr. 0.90: mix 3 min	3.0
Powdered paraformaldehyde (sift in slowly while mixing)	7.5
Allow mix to stand 30 min; mix briefly until glue is fluid and smooth.	

Table 9 Dry Heat-Treated Blood Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	150
20% Soluble spray-dried animal blood	37.5[a]
74-μm Wood flour[b]	10.5[a]
Pine oil or diesel oil defoamer: mix 3 min or until smooth	2.0[a]
Water at 16–21°C: mix 2 min or until smooth	165.0
Fresh hydrated lime (as a slurry in)	5.0
Water at 16–21°C: mix 1 min	10.0
50% Sodium hydroxide solution: mix 10 min	8.0
Sodium silicate solution: mix 5 min	17.5[c]

[a] Normally dry-blended for easier handling and dust control.
[b] 0.074 mm (200 mesh) and finer.
[c] 8.90% Na_2O, 28.70% SiO_2, 41° Baumé.

Table 10 Hot Water-Coagulated Blood Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 63°C	100.0
90% Soluble spray-dried animal blood	40.0[a]
74-μm Wood flour[b]	9.0[a]
Pine oil or diesel oil defoamer: mix 10 min	1.0[a]
Water at 10–16°C	175.0
Pine oil or diesel oil defoamer: mix 2 min or until smooth	1.0
Fresh hydrated lime (as a slurry in)	3.5
Water at 10–16°C: mix 2 min	7.0
50% Sodium hydroxide solution: mix 2 min	7.5
Sodium silicate solution: mix 5 min	17.5[c]

[a] Normally dry-blended for easier handling and dust control.
[b] 0.074 mm (200 mesh) and finer.
[c] 8.90% Na_2O, 28.70% SiO_2, 41° Baumé.

The useful life is 6–8 h. This formulation can be cured hot or cold, but hot pressing yields the most durable bonds.

The next resurgence of blood glue technology came during and after World War II. By that time, the highly alkaline multistep dispersing systems of soybean glues had become well established and were employed successfully with blood glues. Two examples utilizing low-solubility blood in typical plywood glue formulations are shown in Tables 9 and 10. The second mix (Table 10) demonstrates the use of hot water to coagulate the blood and lower its solubility *during* the mixing procedure [48]. Both these glues are excellent adhesives for interior-grade plywood when cured either hot or cold. Preservative or denaturant additions are not normally required to meet plywood performance standards.

As a point of interest, blood glues are not affected by many of the protein denaturants used to improve the performance of soybean glues: specifically, sulfur compounds and complexing salts [49]. However, they are very sensitive to aldehyde-acting compounds, and these have been employed at levels of 0.1–1.0% to yield improved consistency and water resistance. Typical of these are glyoxal, paraformaldehyde, methylol ureas, and formaldehyde addition compounds such as dialdehyde starch and sodium formaldehyde bisulfite.

A special class of blood protein denaturants, used primarily with higher levels of blood solubility, are the alkaline phenol–formaldehyde (PF) resins. Low-molecular-weight, low-alkali PF resins cause granulation of dispersed blood protein without much effect on viscosity, usually a reduction [50]. Highly advanced, high-alkali PF resins such as those used as plywood adhesives generally cause rapid thickening and gelation of dispersed blood glues if not employed with care [33,51]. Resins of intermediate advancement and alkalinity are almost passive to dispersed blood. These interactions have been exploited to formulate blood–resin glues for different hot-press applications at almost every level of combination. Two examples at the extremes of the range will suffice (Tables 11 and 12). In the case of the low-resin-content formulation (Table 11), PF resin addition also functions as a preservative agent and was used widely for the purpose. This formulation is for hot pressing only. The bond-durability level can be characterized as “mid-exterior”.

For the high-resin-content formulation (Table 12), a partial addition of the PF resin can be made just after the initial mix and before sodium hydroxide addition if more fluidity is needed for propeller-type stirring. This formulation is more properly termed a blood-fortified exterior PF resin adhesive for hot-pressing plywood or laminated veneer lumber [52]. Even in quantities this small, the effect of the animal blood is to reduce the hot-press curing time by 20–30% over that of phenolic resins used alone. For purposes of adhesive solid, calculation, the blood content can legitimately be included with the phenolic resin solids.

A special application for which 80% soluble blood is particularly suited is its use in phenolic resin glues as a foaming agent to produce “air-extended” PF adhesives [53]. These are currently used to manufacture plywood on automated production lines. For this purpose, the mixed adhesive containing blood is put through a special high-speed stirring and air-injection system that lowers the specific gravity of the adhesive from about

Table 11 Low-Resin Blood Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	87.5
20% Soluble spray-dried animal blood	25.0[a]
90% Soluble spray-dried animal blood	12.5[a]
74-μm Wood flour[b]	11.0[a]
Pine oil or diesel oil defoamer: mix 3 min or until smooth	1.5[a]
Water at 16–21°C: mix 2 min or until smooth	200.0
Fresh hydrated lime (as a slurry in)	3.0
Water at 16–21°C: mix 1 min	6.0
Sodium silicate solution: mix 1 min	22.5[c]
45–50% Solids low to intermediate advancement PF resin: mix 3 min	13.5[d]

[a] Normally dry-blended for easier handling and dust control.

[b] 0.074 mm (200 mesh) and finer.

[c] 8.90% Na_2O, 28.70% SiO_2, 41° Baumé.

[d] Georgia-Pacific 3195, Borden Cascophen 335-1, Neste CB 118.

Table 12 High-Resin Blood Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	250.0
74-μm Nutshell flour[a]	75.0
Winter wheat flour	25.0
90% Soluble spray-dried animal blood	17.5
Diesel oil defoamer: mix 5 min or until smooth	2.5
50% Sodium hydroxide solution: mix 2 min	28.0
Granular sodium carbonate: mix 15 min	10.5
43% Solids highly advanced PF resin: mix 5 min while cooling the glue at 21–27°C	610.0[b]

[a] 0.074 mm (200 mesh) and finer.
[b] Georgia-Pacific 5763, Borden Cascophen 318-G, Dynea CB 303.

Table 13 Foamable Glue: Ingredients and Mixing Procedure

	Amount (kg)
Water at 16–21°C	170
Industrial wheat flour	50
80% Soluble spray-dried animal blood: mix 7 min	20
PF plywood resin	110[a]
50% Sodium hydroxide solution: mix 15 min	12
PF plywood resin	275[a]
50% Sodium hydroxide solution: mix 2 min	5
Surfactant: mix 2 min or until smooth	1[b]

[a] 43% solids phenolic resin; Borden Cascophen 3136, Dynea CB 305, Georgia-Pacific 4922.
[b] Emersol or equivalent.

1.0 to 0.2 with very fine air bubbles. The low-density adhesive foam is then extruded onto passing veneer surfaces, which are assembled and hot pressed to produce exterior grades of plywood. (Recycled glue is deformed and recirculated.) The primary advantage of this kind of adhesive is lowered cost: for example, savings up to 25% over that of conventionally applied phenolic adhesives. A typical foamable glue mix is described in Table 13.

C. Mixing, Application, and Pressing

As the formulations show, straight blood and soybean–blood blend glues are prepared in generally the same sequence and manner as outlined for soybean glues. Finished glue viscosity ranges are somewhat lower, typically 5000–8000 cP for hot-press formulations and 8000–20,000 cP for the thicker and grainier cold-press glues. Glue life at room temperature is 4–8 h: the cooler, the longer.

With respect to application methods, blood glues can be spread on wood surfaces by most conventional means. These include roller, knife, and extrusion but do not include curtain coating or spray, for which the glues must be thinned below practical film retention levels. The major advantage of alkaline-dispersed blood glues over all other wood glues except resorcinol-based synthetic resin adhesives is their sensitivity to heat, resulting in extremely fast hot-press curing times [54]. This property is of sufficient importance to warrant reproducing an entire plywood hot-pressing schedule for purposes of comparison. The commercial blood glue pressing times shown in Table 14 are literally half those of current phenolic plywood resin adhesives. They are also significantly faster than those listed earlier

Table 14 Blood Glue Hot-Pressing Schedule for Interior Douglas Fir Plywood

Rough panel thickness (mm)	Number of piles	Panels per press opening	Glue spread per single glue line (g/m^2)	Minimum stand time[a] (min)	Pressing time (min at full pressure)			
					110°C	116°C	127°C	138°C
6.4	3	2	171	3	3	2¾	—	—
7.9	3	1	183	3	1¾	1½	1¼	1
7.9	3	2	183	3	3½	3	2¾	2¼
7.9	3	3	195	3	—	7	6	5¼
9.5	3	1	195	3	1¾	1¾	1½	1¼
9.5	3	2	195	3	—	4¼	3¾	3
11.1	3	1	208	3	2	1¾	1¾	1½
11.1	3	2	208	3	—	4½	4¼	4
11.1	5	1	171	3	3	—	—	—
11.1	5	2	171	3	—	6	—	—
12.7	5	1	183	3	2¾	2¼	2	1¾
12.7	5	2	195	3	—	6	5½	5
14.3	5	1	195	3	2¾	2½	2¼	2
14.3	5	2	208	3	—	7	6	5¼
15.9	5	1	195	3	3½	3	2½	1¼
15.9	5	2	208	3	—	7½	6½	5½
17.5	5	1	208	3	4	3½	3	2½
17.5	7	1	208	3	4¼	4	3¾	3¼
19.0	5	1	208	3	—	4¼	3¾	3
19.0	7	1	208	3	—	5	4¼	3¾
20.6	5	1	208	3	—	4½	3¾	3¼
20.6	7	1	208	3	—	6	4¼	4
22.2	7	1	208	3	—	—	4¼	4
23.8	7 and 9	1	220	4	—	—	6	5
25.4	7 and 9	1	220	4	—	—	7	5½
27.0	7 and 9	1	232	4	—	—	7	6
28.6	7 and 9	1	232	4	—	—	7½	6¼
30.2	7 and 9	1	232	4	—	—	8	6½
33.4	9	1	244	5	—	—	9	7
36.5	9	1	244	5	—	—	10	8
39.7	9 and 11	1	244	5	—	—	12	9

Other conditions:

1. Total assembly time limit per press load, 16 min.
2. Veneer temperature not to exceed 43°C.
3. Veneer moisture content not to exceed 8%.
4. On rough or warm veneer, add at least 12 g of extra glue spread.
5. Not less than 12 kg/cm^2 uniform hydraulic pressure.

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[a] Stand time after assembling last panel before loading press.

for soybean glues. This hot-pressing schedule is suitable for all straight blood adhesive formulations and also for soybean–blood blend glues containing at least half blood as the active protein ingredient.

Blood and soybean–blood blend glues of appropriate high viscosity and granular consistency can be pressed cold according to the schedule shown for soybean glues. For this purpose they must contain a terminal addition of about 5% preservative based on dry glue weight in order to meet product standards for mold resistance [24].

IV. CASEIN GLUES

A. Raw Material Source and Preparation

As with blood, the adhesive qualities of casein curd from milk were recognized in relatively ancient times. Mixed with a simple alkali such as lime, casein protein became an important adhesive for furniture and paint pigments and the preferred sizing agent for the canvas of Renaissance paintings [6,55].

Medieval furniture assembly was divided between casein glues and animal gelatin adhesives made from boiled extracts of bone and hide. The gelatin glues were applied to joints as a hot solution and gained bond strength almost immediately on cooling. The casein glues required much longer clamping times to develop adhesion by water loss and insoluble caseinate formation. However, the casein glues had true water resistance, whereas the animal gelatin glues remained forever sensitive to even slight moisture and heat exposure [5]. Thus casein tended to be used where durability was required. This association with water resistance has remained a favorable performance factor for casein glues down to the present.

Casein protein is recovered from skim milk by acid precipitation to pH 4.5. Mineral acids may be used or the milk can be cultured with bacteria that convert lactose (milk sugar) to lactic acid, which in turn precipitates the casein. The precipitated protein curd is washed free of acid with hot or cold water and is then dried and ground. The commercial designation for casein often includes its method of acid precipitation (e.g., "lactic acid or sulfuric acid casein").

Since industrial casein competes directly with the worldwide food uses of milk and its proteins, the price of casein tends to vary widely as the supply/demand economics of milk products rise and fall. In recent years, the cost has remained well over $2 (U.S.) a pound. Even at this price, however, certain casein blend and specialty glues continue to hold a significant place in current markets.

B. Formulation

For adhesive uses, the particle size of ground casein is normally controlled within the range of about 250–500 μm [56]. Particles coarser than 500 μm (30 mesh) may not dissolve and disperse completely during glue preparation. Those much finer than 250 11 μm (60 mesh) tend to form immediate lumps on wetting, even if oiled. For single-package casein glues (by far the most widely used type), preliminary oiling of the dry ingredients is a very important manufacturing step. It helps prevent the pickup of atmospheric moisture by alkaline salts in the dry composition followed by premature attack on the casein during storage. Oiling also slows down the solution of these salts in water at the time of glue mixing, thus allowing the casein particles to become wetted and lump-free in reasonably neutral water.

The lime content of casein glues is similarly important. A high percentage of lime (above 30% of dry casein weight) ensures maximum water resistance of the cured glue film but sharply reduces mixed adhesive working life. A lime content below 10% provides a long working life and adequately strong dry bonds on wood but significantly reduces moisture resistance. Most commercial adhesive formulations balance these properties by utilizing lime additions in the range 15–25% [57].

As with blood and soybean flour, the maximum adhesive capability of casein is attained only by complete aqueous dispersion of the folded protein molecules with a strongly alkaline inorganic salt such as sodium hydroxide [56]. Since sodium hydroxide cannot be incorporated successfully into a dry adhesive composition, it is quickly produced on mixing through a double decomposition reaction between calcium hydroxide and strongly ionized but less alkaline salts such as sodium fluoride, sodium carbonate, and trisodium phosphate. (The residues from this reaction are insoluble calcium compounds.)

The viscosity and consistency of casein glues can be altered substantially by reaction with most of the classic protein denaturants such as sulfur compounds, formaldehyde donors, and complexing metal salts [6,56]. One or more of these are frequently used as manufacturing control to offset the natural variability of casein and produce glues of uniform properties. The water resistance of cured casein glues is also improved by moderate denaturing.

Finally, to provide mold resistance adequate for interior and covered exterior structural requirements, a fungicide must be added to casein glues [40,58]. In this case there is no excess of sodium hydroxide in the glue composition to convert a water-insoluble fungicide to its soluble sodium salt. Therefore, it is added as a prepared soluble salt in order not to upset the fairly precise alkaline balance in the dry glue composition needed to fully disperse the casein. Sodium orthophenylphenate and sodium pentachlorophenate are examples.

The casein adhesive formulation described in Table 15 embodies all the foregoing technology. The dry ingredients are intensively blended in an appropriate dry powder

Table 15 Casein Dry Glue: Ingredients and Mixing Procedure

	Amount (kg)
500–250 μm Lactic acid casein	15.0
500–250 μm Sulfuric acid casein	15.0
74-μm Wood flour[a]	5.0
Fresh hydrated line	6.5
Granular trisodium phosphate	4.0
Granular sodium fluoride	2.0
Powdered dimethylol urea	0.05
Diesel oil defoamer	1.45
Sodium orthophenylphenate or other preservative[b]	1.0
Water at 16–21°C	100
Dry glue: mix 2 min, until smooth and thick	50
Let stand 15 min or until thinning has occured; then mix 2 min or until smooth.	

[a] 0.074 mm (200 mesh) or finer.

[b] Dowicide A, Dow Chemical Co.

mixer while the defoamer is sprayed in to provide uniform distribution. The dimethylol urea addition, a protein denaturant, is variable for glue viscosity control. The small adjustment is made in the defoamer. Mixing directions are provided in Table 15. The finished glue viscosity should be in the range 4000 to 8000 cP at room temperature, thickening gradually over several hours and attaining a firm gel overnight.

In a totally different area of application, casein adhesives for paper sizing, chipboard laminating, and label gluing are more nearly “casein solutions” [59,60]. They are simple dispersions with ammonia or borax at moderate pH and low viscosity. They are frequently combined with latexes or soluble rosin derivatives for special performance improvements [59].

C. Mixing, Application, and Pressing

Casein glues for wood pass through an early thick-consistency stage that requires fairly strong agitation to reduce them to a uniform and lump-free state. The mixer should be equipped for sidewall scraping to work thickened glue continuously back into the stirred composition. Counterrotating paddle mixers and bread dough mixers have proved ideal for this purpose.

Because of their thick, sticky consistency, casein glues are generally applied to only one of a mating pair of wood surfaces by roller, knife, or extrusion. Adequate adhesive wetting and transfer occur when the wood surfaces are brought together.

The stickiness of alkaline-dispersed casein glue provides two of its best performance attributes: long assembly-time tolerance and wipe resistance (difficulty of removal). A film of casein glue on dry lumber, for example, may allow an open/closed assembly time of 1–2 h before clamping is required. This property is especially useful in the timber laminating industry, where it permits many pieces of lumber to be stacked over each other, adjusted for position, and assembled into large, complex laminated beams [61]. This long assembly tolerance plus the gap-filling and wipe-resistant capabilities of casein glues made them the outstanding choice for laminated structural wood products from the mid-1930s onward. Today’s phenol–resorcinol–formaldehyde laminating adhesives, which ultimately displaced casein glues on the basis of exterior durability, could still use a large measure of these working properties of casein glues.

While casein glues can be heat cured and were employed in the past to make hot-press plywood, most of the high-volume bonding applications have involved cold pressing. Casein glue films are adequately cured by water loss and insolubilizing of the proteins through various chemical reactions at room temperature [62]. Heating does not yield significantly improved water resistance. Except for soybean–casein blend glues, which take on the granular consistency of the soybean constituent, the inherent stickiness of straight casein glues dictates a fairly long clamping time to bring about water loss and adhesive hardening. Progressive shear tests have shown that these glues develop about half their dry strength in 3 h and substantially all of it in 6–8 h at room temperature. However, moisture resistance continues to improve for several days [63].

As mentioned previously, another performance attribute of casein glues that recommends their use in structural wood laminates is fire resistance [64]. While all three of the proteins discussed in this chapter burn to a char before losing bond strength, casein adhesives appear particularly durable in this respect. Thus casein glues remain the adhesives of choice for the economical assembly of wood-based fire doors of flush and panel designs. In yet another attribute, the combined adhesive strength and toughness (as opposed to brittleness) of casein glue films has made them an ideal bonding agent for wooden sporting equipment and other applications required to withstand flexing, vibration, and shock, such as racquets, hockey sticks, and fishing rods [6,65].

V. OTHER PROTEINS

Reference was made to the historical use of collagen glues derived from the gelatin extracts of animal bones and hides. This does not properly indicate the true importance to the wood industry of these materials. From ancient times to the present, animal glues have in fact remained one of the primary assembly adhesives for wooden furniture, cabinets, and musical instruments [66]. Applied as a hot, viscous solution to furniture joints, they rapidly develop gel strength on cooling that permits the prompt removal of clamping pressure. On subsequent drying, these glues cure to resilient, high-strength bonds between wood surfaces, especially those involving end grain. Animal glue bonds are strong and permanent as long as they are kept dry and reasonably cool but are subject to softening and fungicidal attack when moistened or heated. Water and temperature resistance can be improved through the incorporation of most of the protein denaturants listed earlier [67,68].

Animal glues are used widely in a variety of ways with paper. For example, they have been the dominant adhesive for rewettable gummed paper tapes, labels, and envelope seals [69]. They are an important coadditive with synthetic wet-strength resins and rosin sizes for coated paper products [70]. They have been a primary binder for the grit that forms sandpaper [71].

In contrast to their widespread use in furniture and paper products, animal glues have not proved useful as structural adhesives for wood. When used as the principal protein constituent, their water sensitivity is excessive compared with other available proteins. When combined with soybean, blood, or casein, animal gelatin glues are completely hydrolyzed and destroyed by the strong alkalies required to disperse these proteins. In addition, they soften when severely heated, which, by law, prohibits their use in structural wood products [5].

Although in recent years animal glues have been replaced substantially by the newer synthetic adhesives, particularly the vinyl and acrylic emulsions, large quantities are still sold in dry and stable liquid forms for furniture assembly or repair and paper bonding applications.

Generally similar comments can be made with respect to fish skin adhesive extracts regarding these and other wood gluing applications. Fish skin glues are normally prepared in stable liquid form through mild acid hydrolysis and are frequently combined with animal glues for improved rewettability, tack, and adhesion of paper to glass or metal surfaces [72]. They differ from animal glues in one important respect: namely, they will not soften at elevated temperatures, especially when treated with aldehydic or polyvalent metal ion cross-linkers. Thus, in addition to the more conventional paper bonding applications, this property has created a major field of use for fish gelatin extracts as durable but temporary protective coatings and light-convertible photoresist films [73].

Other vegetable protein sources are occasionally mentioned as substitutes for soybeans. These have included cottonseed meal, peanut flour, Alaska pea, and rapeseed meal, to name just a few. Although they do contain 25–35% useful protein substance, they have never made significant inroads on soybean flour for wood-gluing applications on the basis of comparable performance. However, they can be used and are prepared for adhesive purposes in the same manner as soybean flour itself.

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21

Animal Glues and Adhesives

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I. INTRODUCTION

Animal glues have been used for thousands of years in traditional adhesive and sizing applications. In later times, they also found uses as protective colloids, flocculants, coatings, in composition, and as a component of compounded adhesives. The earliest known use of animal glue, for veneering, dates to the period 1500–2000 B.C. in ancient Egypt and has been referred to in literature from biblical times. Commercial manufacture dates back to about A.D. 1690 in England and Holland. Numerous patents relating to the manufacture of animal glues were issued during the period 1754–1844. The first manufacture of animal glue in the United States was early in the nineteenth century [1].

Until 1940, natural materials, including animal glues, were the only adhesive materials available. Animal glues were the adhesives of choice for such uses as woodworking, paper manufacture and converting, bookbinding, textile sizing, abrasives, gummed tape, matches, and a variety of other applications. The acceptance of animal glues as adhesives is based on their unique ability to deposit a viscous, tacky film from a hot aqueous solution, which forms a firm gel while cooling, and provides an immediate, strong, initial bond. Subsequent drying provides the final bond of high strength and resiliency. Ease of preparation, high tack, fast set, ready application, and good machining properties, even in high-speed operations, are characteristics of importance.

After introduction of emulsion-based adhesives, and later hot melts, animal glues were displaced in part or completely from their traditional uses, but they have retained a relatively small but significant share of the adhesive market due to their unique properties. It is estimated that U.S. consumption of animal glues is in the range 30 to 35 million pounds, and production worldwide is about 90 million pounds annually (W.E. Blair, Swift Adhesives, private survey, 1992).

II. CHEMICAL COMPOSITION

Animal glues are derived by the hydrolysis of the protein constituent collagen of animal hides and bones. Collagen in its natural state is water insoluble and must be conditioned to solubilize the protein. Collagen molecules are triple helices of amino acid sequences and contain both nonpolar and charged acidic and basic side chains. The conversion of collagen to the soluble protein of animal glue (gelatin) involves breaking the intra- and intermolecular polypeptide bonds through the use of acid or alkali and heat. The collagen–glue (gelatin) transition has been described as a stepwise process involving the melting of the trihelical network to an amorphous form, followed by the sequential hydrolysis of various types of covalent bonds [2,3].

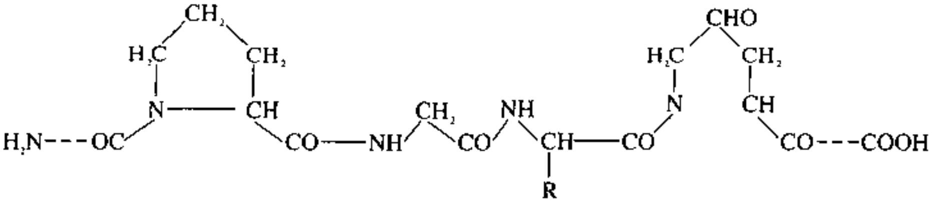
Glues and gelatins are described as hydrolyzed collagen with the following formula [4,5].

$$C_{102}H_{149}O_{38}N_{31} + H_2O \rightarrow C_{102}H_{151}O_{39}N_{31}$$

The approximate chemical composition of glue (gelatin) protein is

Carbon	50.3%
Hydrogen	6.2%
Oxygen	25.6%
Nitrogen	17.8%

Animal glues are composed of α-amino acids joined in polypeptide linkages to form long-chain polymers [5–8]. A typical chain fraction with three amino acids:



In aqueous solutions of animal glues, the polypeptide chains take up random configurations of essentially linear form. Studies have indicated that most glue molecules consist of single chains terminated at one end by an amino group and at the other end by a carboxyl group [7]. The molecules may also have side chains and contain cyclic structures. They may in part conform to the oriented chain in the original collagen. The polypeptide chains are of varying lengths and consequently, widely different molecular weights. A wide range of average molecular weights has been reported, ranging from approximately 10,000 to over 250,000. Molecular weight distribution is of equal importance in studying animal glue (gelatin) protein systems [3].

Amino acid studies corroborated by various analyses indicate that there are 18 different amino acids present in collagen and animal glue (gelatin) in varying amounts (see Table 1). The acidic and basic functional groups of the amino acid side and terminal groups confer polyelectrolyte characteristics to the protein chains. The chains contain both amine and carboxylic groups which are reactive and ionizable. These electrically charged sites affect the interactions among protein molecules and between protein molecules and water. These polar and ionizable groups are believed to be largely responsible for the gelation and characteristic rheological properties of animal glues. Cross-linkage between protein molecules is possible through hydrogen, ionic, and covalent bonds.

Animal glues are amphoteric because the amine and carboxyl groups contained in the polypeptide protein chain are reactive and ionizable. In strongly acid solutions, the protein is positively charged and acts as a cation. In strongly alkaline solutions it is negatively charged and acts as an anion. The intermediate point, where the net charge on the protein is zero, is known as the *isoelectric point* (IEP) and is designated in pH units.

Table 1 Amino Acids Present in Collagen and Animal Glue

Amino acid	Average residues per 1000 total of all residues [9]	Character of R-radical [10]	
		Polarization	Ionic character
Alanine	103.2	Nonpolar	Neutral
Arginine	46.2	Polar	Basic
Aspartic acid	47.7	Polar	Acid
Glutamic acid	73.3	Polar	Acid
Glycine	339.8	Nonpolar	Neutral
Histidine	4.4	Polar	Basic
Hydroxyproline	97.8	Polar	Neutral
Hydroxylysine	6.2	Polar	Basic
Isoleucine	12.8	Nonpolar	Neutral
Leucine	24.4	Nonpolar	Neutral
Lysine	29.8	Polar	Basic
Methionine	5.4	Polar	Neutral
Phenylalanine	13.4	Nonpolar	Neutral
Proline	122.8	Nonpolar	Neutral
Serine	31.5	Polar	Neutral
Threonine	17.9	Polar	Neutral
Tyrosine	3.6	Weakly polar	Very weakly acid
Valine	20.7	Nonpolar	Neutral

The isoelectric point varies, depending on pretreatment of the collagen, whether acidic or alkaline. During processing, the acidic or alkaline treatments used hydrolyze the amide groups in the collagen to a greater or lesser extent, liberating the acid functions. Acid-processed glues (little amide group modification) have an isoelectric point near 9.0, and alkaline-processed glues (low residual amide groups) have an isoelectric point close to 4.8.

Gelation of aqueous solutions of animal glues upon cooling is an important characteristic. Gelation involves both intra- and intermolecular reorientation upon cooling of the solution. It is caused by the formation of random primary and secondary bonds. Intermolecular network formation is primarily the result of a cross-linking mechanism between molecular chains by hydrogen bonds [11].

III. TYPES OF ANIMAL GLUE

There are two major types of animal glue, hide glue and bone glue, differing in the type of raw materials used. Although process conditions may differ, both are obtained by hydrolysis of the collagen in the hide and of connective tissue or bone structure of the raw material. Both types are principally of cattle origin with tanning and meat-packing industries as the principal sources of raw materials.

IV. MANUFACTURE OF ANIMAL GLUE

Basic manufacturing procedures for animal glues generally involve alkaline pretreatment (for hide glues) or acidic pretreatment (for bone glues). The raw materials for hide glues include salted, limed, or pickled hide trimmings or splits, and chrome-tanned leather scrap. Tanned leather scrap requires special processing because of the chrome tannage.

Hide glues from hide trim and splits are prepared by initial washing with water. The stock is then soaked in lime (calcium hydroxide) and water for a period of weeks, which dissolves and removes extraneous protein-related materials, as well as conditioning the collagen for subsequent glue extraction by hydrolysis. The conditioned collagen is then washed with water, followed by acidulation with dilute acid such as sulfuric, hydrochloric, or sulfurous, for pH adjustment, followed by a final water rinse.

Chrome-tanned leather scrap for hide glues may be treated initially with lime or caustic, followed by a strong acid bath to remove the tannage. The stock is then soaked in magnesium hydroxide and rinsed prior to extraction. Alternatively, the chrome stock may be treated with a magnesium hydroxide soak only, prior to extraction, in which case the chromium tanning salts remain in the residue after extraction. The treated collagen is transferred to extraction kettles or tanks, where it is heated with water to convert the collagen and extract the glue. Several hot water extractions at progressively higher temperatures are made under carefully controlled conditions. Separate, successive dilute glue solutions are removed from the stock until the glue is completely extracted, usually in four extractions.

The dilute glue extractions, ranging from 2 to 9% glue solids, are filtered and concentrated by vacuum evaporation to 20 to 50% concentration prior to drying. In some plants the glue is chilled until it will gel, then dried in tunnel dryers which circulate heated air over gelled sheets stacked on wire nets with air space between, taking up to 48 h to dry. In newer installations, the concentrated glue solutions are cooled to the gelling point and are extruded in noodle form into a continuous dryer which completes the drying in 2 to $2\frac{1}{2}$ h by circulating conditioned, filtered, heated air. The dried product, at 10 to 15% moisture content, is then ground to the desired particle size.

Bone glues fall into two categories, green bone or extracted bone. Green bone glues are prepared from fresh or "green" bones, which come primarily from the meat-packing industry. The bones are crushed, washed, and normally treated with dilute acid, either sulfuric or sulfurous, prior to extraction. Extracted bone glues are prepared from dry bones that have had a preliminary degreasing treatment with solvent prior to conditioning for extraction.

The glue is extracted from the conditioned bones by hydrolysis in pressure tanks by the successive application of steam pressure and hot water. Separate successive dilute glue solutions are removed from the tanks, followed by filtering or centrifuging to remove free grease and suspended particles. The dilute solutions are vacuum evaporated to high concentration, followed by drying and grinding, as described for hide glues. Modern animal glues, whether of hide or bone origin, contain adequate preservatives for protection against bacteria or mold growth under normal conditions of use, and may contain defoaming agents where foam control is desired in the end application.

V. PROPERTIES OF ANIMAL GLUES

Commercially available animal glues are sold in granular or pulverized form, and are dry, hard, odorless materials that vary in color from light amber to brown. Animal glues may be stored indefinitely in the dry form. The density of animal glues is approximately 1.27. A moisture content of 8 to 15% is considered commercially dry. An inorganic ash content of

2.0 to 5.0%, and a grease content of 0.2 to 3.0%, are in the normal range for commercial animal glues. The pH range of commercial glues is 5.5 to 8.0.

Animal glues are hydrophilic colloids and are soluble only in water. In cold water, the glue particles absorb water and swell, resulting in a jellylike sponge. Upon application of heat, the particles dissolve, forming a solution. Upon cooling, the solutions set to an elastic gel. The gelation is a thermally reversible reaction, and on application of heat the gel reverts to liquid form. The melting or gelling point will vary from below room temperature to over 120°F, depending on glue concentration, grade, and possible presence of modifiers.

An important characteristic of animal glues is their film forming and bonding properties. Dried films are continuous, noncrystallizing, permanent, and possess great strength and resilience. Tensile strengths in excess of 10,000 psi have been reported [12]. Animal glues are insoluble in oils, greases, waxes, alcohols, and other solvents. Being soluble only in water, the continuous films are ideally suited as barriers against these materials. With suitable practical methods, the films may be made moisture resistant.

Sensitivity to the effects of moisture may be reduced by the use of various insolubilizing agents (sometimes referred to as "tanning" or "hardening") which cross-link the protein molecules, rendering them less susceptible to hydration and solution. These agents include formaldehyde, paraformaldehyde, hexamethylene–tetramine, glyoxal, and dialdehyde starch. Metal salts will thicken, coagulate, and sometimes precipitate animal glue solutions. A degree of moisture resistance and raising of solution melting point may be obtained with these salts. Salts of aluminum, chromium, and iron have this effect on animal glue solutions.

Animal glues are readily compatible with and are frequently modified by water-soluble plasticizers such as glycerine, sorbitol, glycols, and sulfonated oils to increase film flexibility. They are also compounded with many other materials, such as dextrins, starches, sugars, various salts, pigments, poly(vinyl alcohols), and acetates, as well as some water-soluble solvents such as butyl cellosolve acetate for specific properties. Viscosities can be modified by compounding with thickeners, including compatible natural gums, alginates, and synthetic thickeners such as carboxymethyl cellulose.

Because of their amphoteric properties, animal glues possess electrical charges which unmodified or with suitable modification by simple chemical additives are highly effective as colloidal flocculents and as protective colloids in such applications as paper manufacturer, rubber compounding, ore and metal refining, and for water and industrial wastewater treatment.

A wide range of viscosities is possible, from almost water thin to in excess of 70,000 cP by variation of the dry glue concentration and test grade. Animal glues are available in a number of grades from low to high, varying in inherent viscosity and gelling properties. The gel property determines the grade and is the controlling factor in speed of set of a glue film for adhesive applications.

VI. GRADES AND TESTING

Animal glues are graded on the basis of gel strength (an arbitrary measure of the gelling property) and viscosity, which increases with an increase in gel strength. These properties have a marked bearing on glue application and end use. One of the earliest grading systems was introduced by Peter Cooper about 1844, establishing a basis for comparative values and market stability. The National Association of Glue Manufacturers adopted

Table 2 Glue Test Grades

Peter Cooper Standard Grade	National Association of Glue Manufacturers Grade	Bloom (g) Range	Bloom (g) Midpoint	Millipoise Value (minimum)
5A Extra	18	495–529	512	191
4A Extra	17	461–494	477	175
3A Extra	16	428–460	444	157
2A Extra	15	395–427	411	145
A Extra	14	363–394	379	131
#1 Extra	13	331–362	347	121
#1 Extra special	12	299–330	315	111
#1	11	267–298	283	101
1XM	10	237–266	251	92
1X	9	207–236	222	82
$1\frac{1}{4}$	8	178–206	192	72
$1\frac{3}{8}$	7	150–177	164	62
$1\frac{1}{2}$	6	122–149	135	57
$1\frac{5}{8}$	5	95–121	108	52
	4	70–94	82	42
	3	47–69	58	
	2	27–46	36	
	1	10–26	18	

Table 3 Comparative Properties of Hide and Bone Glues

Property	Hide Glue	Bone Glue
Gel strength (g)	50–512	50–220
Viscosity (mP)	30–200	25–90
pH	6.0–7.5	5.0–6.5
Moisture	10.0–14.0	8.0–11.0
Ash	2.0–5.0	2.0–4.0
Grease	0.3–1.0	0.4–4.0

standard methods for testing animal glues in 1928. Table 2 shows animal glue test grades. Bone glues differ from hide glues, having a lower range of viscosities and gel strengths, due primarily to greater hydrolysis of the protein by the higher heat used during extraction. Table 3 shows the comparative properties of hide and bone glues.

The standard method for animal glues determines the viscosity by measuring the flow time in seconds of a 12.5% solution at 60.0°C through a standard pipette, and converting the results to millipoises. The method for gel strength (measured in grams) calls for cooling the 12.5% solution to 10.0°C and holding for 16 to 18 h, followed by determination of the weight in grams required to depress a 0.5 in.-diameter plunger a distance of 4 mm into the surface of the gelled sample using a bloom gelometer or comparable instrument. The pH is determined electrometrically on a 12.5% solution at 40°C. The moisture content of dry glue is measured by drying a 10-g sample for 17 h at 105°C [13]. Compounded animal glue products made from known grades of animal glues are normally checked for viscosity using a Brookfield viscometer, and for solids by the oven-drying method or refractometer.

VII. PREPARATION OF ANIMAL GLUES

Since dry and compounded animal glues are used over a wide range of dilutions from 1% or lower to over 50%, no general ratio can be given. Dry glues are generally available in coarse (10 to 30 mesh) or fine (30 mesh and finer) granulation. Powdered glues (100 mesh and finer) are also available for special applications. Compounded glues are available as dry blends, in gelled cake form, or as liquid products.

Dry glues are readily prepared for use. The direct addition of dry glue to hot water in a jacketed, mechanically agitated mixer is recommended for fastest preparation. Thermostatic controls are recommended to hold the glue temperature at 140 to 145°F for use. Alternatively, the dry glue can be soaked in cold water until swollen, then transferred to a jacketed melting tank with agitator, melting, and stirring the glue into solution.

For best results, the dry glue should always be weighed. Water may be measured or weighed. Stainless steel mixing tanks are preferred. Water-jacketed mixers with low-pressure steam injection are recommended for large batches. Electrically heated mixers are usually preferred for small batches. Good agitation is important. Compounded dry blends are prepared in the same manner as dry glues. Cake glues (usually in 5 to 10-lb slabs) are placed in a suitable mixer, diluted as required with water, melted, and held at 140 to 145°F for use. Liquid glues are ready to use as is at room temperature. Cake glues contain modifiers such as corn syrup, sugars, magnesium sulfate (epsom salt), glycerine, sorbitol and other glycols, dextrins, clays and pigments, water-soluble organic solvents, and surfactants, depending on desired properties, as well as water, preservatives, and odorants.

VIII. FLEXIBLE AND NONWARP GLUES

Flexible and nonwarp glues are compounded animal glue-based products available in cake or dry blend form. Flexible cake glues are formulated to provide a permanent, flexible, resilient film. Glycerine is normally the primary plasticizer and may be modified with sorbitol and other glycols. Higher grades of animal glue are normally used to provide film strength and resiliency. The ratio of plasticizer to dry glue controls the film flexibility, and can be varied from a moderate degree of flexibility to a fully flexible film. These products are used in such applications as bookbinding, including hardcover books, directories, and catalogs, notebook binders, and soft-sided luggage.

Nonwarp cake glues are designed to provide a "lay flat" or nonwarp film with little or no curling upon drying. The nonwarp property is obtained through the use of various sugars and corn syrup. Tack and speed of set can be varied by choice of glue grade and ratio of dry glue to the sugars and other modifiers. Glues supplied in cake form have the advantage of ease of melting and minimal water dilution by the user (normally up to 20%). Dry blends are basically simple, nonwarp formulations supplied by the manufacturer in dry, fine mesh form, which the customer dissolves in hot water prior to use. These products have indefinite shelf life and lower shipping cost because of the absence of water.

Major areas of use for nonwarp glues are for set up boxes, casemaking for book covers, hard notebook binders, slipcases, looseleaf computer manuals, record covers, hard luggage, caskets, and laminating. Because of differences in equipment, application, and end-use requirements, compounded glues are formulated for each use and/or customer, and may be further modified to compensate for seasonal changes in humidity and temperature. Speed of set, for example, can vary from almost instantaneous to over 5 min. Properties of importance include viscosity at the recommended operating temperature, degree of tack and speed of set, and final bond characteristics.

IX. LIQUID ANIMAL GLUES

Liquid animal glues are modified dry glue solutions containing a gel depressant, usually urea, thiourea, ammonium thiocyanate, or dicyandiamide, so that they remain fluid at and somewhat below room temperature. Liquid animal glues can be modified with clays or calcium carbonate as fillers, and wetting and dispersing agents, plasticizers, and other modifiers as required. Solids are usually in the range 35 to 65%, with a viscosity range of 3000 to 5000 cP at room temperature.

X. GLUE APPLICATION

Recommended use temperature for dry animal glues and compounded products (except liquid glues) in most applications is 140 to 145°F (60 to 63°C). A range of 135 to 155°F (57 to 68°C) is acceptable but not preferred. Use at lower temperatures results in undesirable properties such as high viscosity, poor machinability, excessive glue use, and premature gelation, resulting in bond failure. Use at temperatures that are too high causes excessive water loss and degradation of the glue by heat hydrolysis. Excessive dilution of a glue solution to retard gelation is a bad practice that can result in a "starved" bond with insufficient glue to adhere. Use of a lower grade of glue or a gel depressant is indicated. Dry glues and compounded dry blends for adhesive use are usually prepared at 25 to 55% solids. Compounded cake glues are used as is, or diluted up to 20% with water. The amount of water used depends on glue grade, speed of operation, and type of material to be bonded.

Four basic steps for adhesive applications are as follows:

1. Deposit a thin, continuous glue film on one of the surfaces to be bonded.
2. Allow the glue film to become tacky (transition point from liquid to gel) before applying pressure.
3. Apply uniform pressure to ensure complete contact between surfaces to be bonded.
4. Continue pressure long enough to ensure a strong initial bond.

Grade selection for many uses involves consideration of the desired viscosity and gel properties for the specific end use. High test grades have the greatest water-taking properties, high viscosity, rapid gel formation and strength, fast speed of set, and greatest reactivity with insolubilizing materials. Low test grades have long tack life and open time, slow rate of gel formation and set, and best film-forming properties at high solids. Medium test grades provide intermediate properties. Grade selection for adhesive use generally involves matching the gelation rate of the animal glue solution with the time from the application of the glue film to the bonding of the substrates (open time). The gelation rate and viscosity of animal glue solutions are usually closely related.

Table 4 Viscosity (cP) at 140°F for Dry Glues of Given Grade Test and Millipoise Value

Glue Concentration (%)	High Test (155 mP)	Medium-High Test (102 mP)	Medium Test (63 mP)	Low Test (32 mP)
5	3.0	2.4	2.0	1.6
10	8.8	5.6	3.6	2.6
12.5	15.5	10.2	6.3	3.2
15	28.0	17.2	8.4	5.0
20	79.0	46.0	22.4	10.0
25	196	112	49.6	19.6
30	524	264	108	37.6
35	1,360	612	224	72.0
40	3,216	1,320	476	133
50	16,320	7,240	2,400	566

Source: Ref. 10, p. 146.

Table 4 illustrates the viscosity in centipoise at 140°F for solutions of dry glues of given test and millipoise value [10].

XI. END USES

Current end uses for animal glues and compounded products include (see Fig. 1) bookbinding and directory/catalog binding, paper manufacture and converting, abrasives, ore and metal refining, paper box manufacture, matches, gummed tape, woodworking, luggage, case covering and lining, rubber compounding, textiles, glass chipping, picture frame and decorative molding composition, and leather manufacturing.

A. Bookbinding

There are two areas where animal glue adhesives are used extensively: for hardcover books in casemaking and backlining operations, and for perfect binding of directories and catalogs. Animal glues, primarily compounded products, are used because of their good film flexibility, excellent tack and speed-of-set properties, and ease of cleanup. For hardcover books, the largest application is in casemaking for covers, where good tack when turn-ins are made, and a wide range of open times, which can be adjusted to meet the speed requirements of various types of casemaking equipment (from 20 to 120 cases per minute), are important properties. Reduction of scrap is also an important factor. The casemakers can be run at low speed, or can be stopped briefly for adjustment, without loss of covers. Film flexibility can be adjusted so that warpage of the cover is minimized. Machine cleanup is easy with hot water. Emulsion adhesives and hot melts have proved unsuitable, due to tack and open-time limitation, as well as difficult cleanup.

In addition to machine casemaking there are various related applications, including manual and semiautomated casemaking operations for such applications as looseleaf binders and sample books, where animal glue products are used because of good tack and open-time properties under a wide range of conditions. Animal glue products are also used for backlining and headbanding, a process that applies adhesive to the spine of the book to provide round and dimensional stability to the spine, and to adhere reinforcing

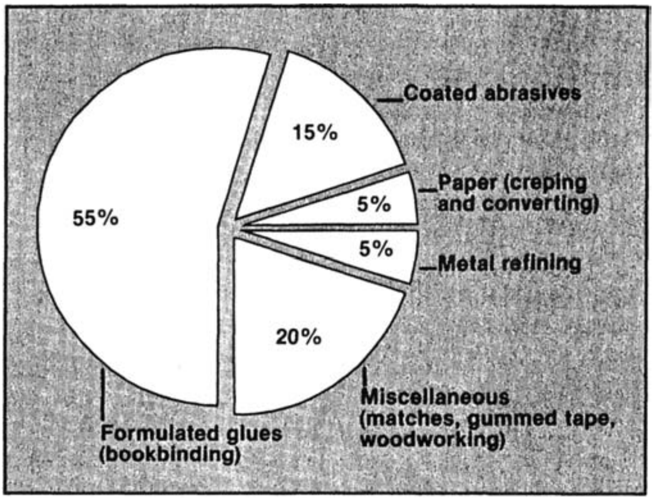


Figure 1 Use of animal glue product by end-use markets. (From Ref. 14.)

cloth, decorative headbands, and paper liner. The modern backlining operation is usually in line, with the backliner preceded by a rounder and backer that shapes the book, followed by a casing-in unit that applies the covers. These units operate in the range of 40 books per minute. Animal glue adhesives compete with hot melts for this application but are used widely because of their good film flexibility, tack and speed-of-set properties, and adhesion to gluing of adhesives, cloth, and paper. Wide latitude during short machine stops and ease of cleanup are also factors.

Books bound with animal glues range from inexpensive children's books to textbooks, which must withstand rough handling and continuous usage during their lifetime, to encyclopedias and reference books, which must retain their functionality for an extended period of time. Directories and catalogs are perfect bound with animal glue adhesives. In perfect binding, the book signatures (sections) are assembled and the spine is cut and leveled with saws and knives to separate the signatures into individual pages. Books range from less than $\frac{1}{4}$ in. to over 3 in. in thickness. The binder first applies an animal glue-based primer to the spine of the book. This adhesive penetrates to bind the cut edges of the pages tightly into the book, as well as to provide flexibility when the book is opened. The primer application is followed in line by the cover adhesive, which adheres the cover to the book and also provides a flexible film that will not crack when the book is opened. The perfect-bound book relies solely on the adhesive to bind the pages and cover strongly into one unit, in contrast to stapled books. Perfect-bound books are trimmed to final size after binding and cover application.

With binder speeds up to 200 to 250 books per minute, important factors are fast tack and speed of set. High bond strength of pages to cover is a requirement. When used properly, animal glue adhesives provide high "page pull" values, with paper failure in many cases. Flexibility of the adhesive film under a wide range of temperature and humidity conditions is also of great importance. A major factor in the use of animal glue adhesives in this application is their repulpability (the film is water soluble and biodegradable), which permits an economic return on the scrap trimmed from the book. Current competing hot melts are not repulpable, resulting in loss of trim for recycling.

B. Paper

Animal glues, in both dry and liquid forms, have been used extensively in the manufacture of paper and paper products. Attributes of importance include film forming, colloidal, amphoteric, and adhesive properties. Animal glues have application in the creping of various types of tissue, such as facial, toilet, and toweling. Creping typically involves machine speeds up to 5000 ft/min and dryer temperatures in the range of 600°C. Creping glues can be added at the paper machine head box, or by spray application to the surface of the dryer, typically a large single steam-heated cylinder known as a Yankee dryer. The creping glue adheres the paper tissue to the face of the cylinder, where a doctor blade peels it off, thereby forming the familiar crinkled pattern as the paper leaves the dryer. Solutions of 1 to 3% glue concentration, alone or in combination with poly(vinyl alcohols), release oils, and plasticizers, are typical. The amount of animal glue applied is generally not over 0.1% on the dry paper furnish.

Animal glues provide good adhesion to the dryer face, without which the paper sheet lifts or blows from the dryer surface with little or no crepe effect. Animal glue provides the final tissue with a fine, evenly textured crepe with a soft feel or hand. Longer doctor blade life has been reported when using animal glue. Repulpability of animal glues when recycling the tissue trim is an added benefit. Maintaining the required glue film on the face of the dryer is easy, as is removal during cleanup.

Animal glues have been used for both internal and surface paper sizing. Glue is a protective colloid for rosin used in beater sizing of fine, rag-content papers, particularly in hard-water conditions. In practice, the glue is added near the end of the beater operation after the pH of the furnish has been adjusted. The paper fiber is positively charged, so the rosin–glue particle is attracted to and binds with the paper fiber. The addition of small quantities of animal glue (typically 0.3 to 0.6% on the paper furnish) enhances the internal sizing strength, density, formation, and resistance to scuffing and erasure, particularly on bond papers. Animal glue can also be used as a wet-strength additive in conjunction with resins that are aldehyde donors, which renders the animal glue insoluble.

Animal glues are used for the surface sizing of fine papers such as bond, currency bank note, blueprint and reproduction, and chart and map papers. When animal glues are used alone or in combination with starch sizing, higher grades of glue are generally used. Application is either by immersion in tub sizing, or by surface application through a size press. The function of the sizing is to provide a protective film on the surface of the sheet, laying down the fibers and closing the pores to improve ink holdout, increase surface strength, and resist picking of paper fibers. By proper use of hardening agents such as aldehyde donors or metal salts such as aluminum, a good degree of moisture resistance can be imparted to the sheet. The good film-forming properties of animal glues, as well as resistance to oil, grease, and fats, are beneficial factors. Animal glues were used extensively for the retention and recovery of paper fiber, both on machine and in save-alls, because of their amphoteric, flocculating ability, but have largely been supplanted by synthetic resins.

C. Paper Converting

An example of the use of animal glue adhesives in the paper converting field is for the covering of rigid boxes and containers with paper, typically lithographed decorative labels in setup box manufacturing. Animal glue adhesives are preferred because of their controlled tack, nonwarp properties, and permanence of adhesion. In this operation, a thin paper cover is fed through a roller applicator and coated with adhesive. The paper is delivered to a belt and then to a spotting station, where the box is placed on the cover mechanically or by hand. The machine then wraps the cover material around the box and ejects the finished box. Animal glue adhesives are also used for record albums, paper laminating, convolute and spiral cans such as oil and juice cans, and other specialty box operations, such as cosmetics and cigarettes.

D. Abrasives

The coated-abrasive industry consumes a large volume of animal glue in such applications as sandpaper and cloth in rolls, sheets, and various specialties. Animal glue is also used for "set up" abrasive wheels, belts, disks, cones, and bobs, as well as in greaseless abrasive composition, which is basically a mixture of animal glue, water, and abrasive in stick form for application to polishing wheels. Abrasives are involved in the production and finishing of wood products and for fine metal finishing, which is of importance in the production of machinery, automobiles, household equipment, appliances, and similar products.

In the production of coated abrasives, the backing material, especially in the case of cloth, is sized as required with low- to medium-grade animal glue or glue and starch, and is applied in the concentration range 30 to 40% to impart body and strength. The base or "make" coat is applied to the paper or the presized cloth by a roller applicator which deposits the glue film in a thickness determined by the grit size: the larger the grit, the thicker the film. The base coat takes advantage of the gelling property of the animal glue. Glue concentration is in the range of 25 to 40% and may contain extenders such as calcium carbonate. Higher-grade glues are used for silicon carbide and aluminum oxide, medium grades for emery and garnet, and the lower grades for flint.

The adhesive grain is applied uniformly to the tacky glue film on the moving backing sheet from a gravity-fed hopper. The grain is held in place as the glue gels and can be electrostatically oriented into a vertical position as the sheet passes through the initial drying stage. The partially dried sheet is passed through a second coating machine, which applies a thin film of animal glue (or in some cases a resin), usually in the concentration range 10 to 15%, to lock the grit firmly in position. The abrasive cloth or paper is then dried in a controlled hot-air dryer and wound into jumbo rolls for storage and subsequent slitting and cutting to the desired shape and form.

Closely allied with coated abrasives is the use of animal glues by the end user for set up, polishing wheels, belts, disks, and bobs. The user prepares these by applying an animal glue base coat and an appropriate abrasive grain, and sometimes a top coat, followed by drying. The principles, grade selection, and handling are similar to those for coated abrasives. Applications include metal finishing, glass grinding, granite finishing, and leather finishing.

A major advantage of animal glues over phenolic resins used for the same purpose is film resilience. Phenolic films tend to be brittle, which can result in scratching and other undesirable finishing problems, especially with the finer grades of abrasives. A common practice is to use an animal glue make coat and a phenolic resin size coat, to take advantage of the adhesive and film properties of animal glue while imparting moisture resistance.

E. Woodworking

Animal glues were the traditional adhesives for woodworking, finding acceptance for edge gluing, assembly, veneering, inlays, and finishing. They have been largely supplanted by ready-to-use, synthetic, water-based emulsion adhesives, and to a smaller degree by hot melts for some applications. Animal glues are still used in high-quality furniture and for critical applications such as pianos.

Edge gluing includes the joining of wood pieces for table and desk tops, chair bottoms, core stock construction, and posts and blocks for turning. Assembly gluing is the putting together of panels and parts in cases, cabinets, chairs, and drawer construction. For high-speed edge gluing, assembly gluing, post lamination, and operations with short assembly times, medium to higher testing grades are used. Low to medium grades are usually preferred for slower-speed assemblies, veneering, and edge banding operations. For medium to high test grades, water/glue ratios vary from $1\frac{1}{2}$ to $1\frac{3}{4}$:1 for rapid assembly times in the range 0 to 15 s closed time, to 2 to $2\frac{1}{2}$:1 for slow assembly times in the range of 1 min closed time until pressure is applied. For low to medium grades, water/glue ratios vary from $1\frac{1}{8}$ to $1\frac{3}{8}$:1 for rapid times to $1\frac{1}{4}$ to$1\frac{3}{4}$:1 for slow times.

In edge and assembly gluing, a thin uniform coat of glue is applied to the surface to be bonded. The surfaces are lined up, joined, and then clamped under adequate pressure (in the range 100 to 150 psi). The pieces are then removed for final air drying until the full strength of the bond is developed. Animal glues possess high tensile strength—greater than that of the wood—in addition to their tack and set properties. Also, the film does not creep. Liquid animal glues, usually 50 to 60% solids, find application in panel or frame assembly of hard board to wood for cabinets, drawer assembly, corner blocking, trailer assemblies, and other applications where a ready-to-use adhesive with a relatively long open time is desired.

As less commonly known use of animal glues is as a size for the finishing of high-quality furniture surfaces. In this procedure, a dilute, warm glue solution is applied to the surface of the wood and is allowed to dry. The compression grain of the wood is raised and the glue fills the exposed, porous wood surface. On sanding, a glasslike surface is obtained which takes a uniform, lasting stain at reduced levels of finish.

F. Matches

Animal glues continue to be used for the production of book and wooden stick matches. Efforts to replace it have been without success. The production of matches is dependent on the presence of the animal glue in the head. It not only serves as the binder for the ignition chemicals, combustible fillers, and inert materials, but also because of its air-entraining properties ensures a match head of proper density and burning characteristics.

The animal glue content of the match head is normally 10 to 12% of the dry ingredients. High-grade glues are used for book matches, and medium- to high-grade glues are used for safety and “strike anywhere” wood stick matches. Glues for matches require a low grease content, usually 0.3% or below, and controlled foam properties. The foam creates a uniform, porous head containing oxygen to promote ignition and combustion.

G. Ore and Metal Refining

In ore refining, the flocculating or suspending properties of animal glues, which depend on the relative electrical charges, are used to separate valuable metal-containing ores, including uranium, zinc, lead, and others, from base materials such as clay. The glue acts as a protective colloid (floc stabilizer) to inhibit precipitation or “sanding out” of fines during leaching, and as a flocculent to aid settling of fines and subsequent filtration.

Animal glues are used in the electrolytic refining and winning of such metals as copper, zinc, lead, tin, gold, and silver. Electrorefining is a process where metal is dissolved from an anode containing impurities, and replated on a cathode. In electrowinning, the metal is recovered from solution by deposition on a cathode. Glue is added at a level of 0.03 to 0.15% to the acid electrolyte solution and produces a uniform high current density, resulting in the production of a smooth, dense cathode deposit in which nodular growths, spines, and needle growths, which can ultimately short circuit the electrolytic cell, are avoided.

H. Gummed Tape

Low-test animal glues, both bone and hide, were used extensively in gummed tape manufacture. Animal glues have been displaced to a considerable extent by dextrins and starches. They are still used as an additive to dextrins and starches to improve adhesive properties, and also alone or with dextrins for specialty paper or cloth tapes. Animal glues possess a high, aggressive tack, good open time and set properties, permanent bond, and excellent machinability. Properties are frequently modified as to tack, open time, set, and wettability by the addition of modifiers such as wetting agents, plasticizers, and gel depressants, in addition to dextrins.

The gumming adhesive is generally prepared at 50% concentration and applied at a dry adhesive deposit of about 25% on the basis weight of the paper or cloth backing. The adhesive is applied to the backing by roller applicator at 140 to 145°F and either passed over drying rolls or through a tunnel dryer. It is stored in rolls for subsequent slitting, printing, and cutting into standard rolls for use.

I. Miscellaneous Application

1. *Textiles*

Animal glues have been used for many years as a warp size to protect yarn from breaking and chafing during weaving. These glues have particular applications on rayon, acetate, and viscose, and cotton, nylon, Orlon, and Dynel have also been sized successfully. Sizing solutions commonly contain 2.5 to 8% glue solids using various grades of glue, depending on the operation. The glue is usually modified with plasticizers and softening agents such as sulfonated oils, glycerin, and wax emulsions as well as wetting agents. The modifiers are generally used at a level of 20 to 45% of the glue solids. These agents act to lubricate and provide flexibility to the size film on the yarn.

In the process of weaving crepe fabrics, the yarn is held in a tight twist by a glue film during weaving. The fabric is washed after weaving to remove the glue, which releases the twist and forms the characteristic crepe effect. Animal glues are also used in textile finishing as dye leveling agents, and in silk screen printing.

2. *Rubber Compounding*

Animal glues are used in rubber compounding to modify the physical properties of the rubber. In particular applications such as textile rollers, cots, and aprons used in weaving cloth, the glue prevents static buildup during weaving, which causes fiber lapping or winding of fibers around rollers. The static electricity is discharged through the rollers, due to the electrolytic properties of the glue and the humidity in the air. Because of their amphoteric electrolytic properties, animal glues are also used as suspending or coagulating agents in rubber–water emulsions.

3. *Luggage and Case Covering*

Large volumes of compounded animal glue adhesives are used for soft- and hard-sided luggage, case, casket, and table pad covering and lining. These are basically hand operations where the glue is applied by roller applicator to the covering or lining material, usually uncoated or coated cloth or leather, and the material is positioned on the piece and glued into place. This is generally followed by riveting or sewing to finish the unit. These products are characterized by good tack to hold the material in place, and long open time to allow movement of the material into final position. For soft-sided luggage, dry film flexibility is also important, to prevent glue cracking. The adhesive should also have a low reducible sulfur content, to minimize tarnishing of metal fittings.

4. *Gaskets*

Animal glue-impregnated gasket materials are used as seals between two joined surfaces. They are water, oil, and solvent resistant, flexible, compressible, economical, and do not bond to the sealed surface. In the production of fiber or paper gaskets, the saturating procedure is carried out by drawing the fiber or paper stock through a shallow tank containing a glue–plasticizer solution. The saturated sheet then passes through squeeze rolls to remove excess liquid. It next passes through a second bath of hardening or curing agent (an aldehyde donor) and plasticizer. The sheet is then slowly dried under controlled conditions and cut into widely varied shapes.

5. *Glass Chipping*

An unusual application for animal glues is in glass chipping, recently the subject of revived interest. Chipped glass is used for decorative panels in such items as doors, windows, and lampshades. The frost or fernlike design is produced by pouring an animal glue solution of about 30 to 35% solids on a clean, sandblasted glass surface, and allowing the glue to dry under controlled conditions. The glue adheres to the glass, and as the film dries, it contracts, pulling particles of glass from the surface and creating the design. The pattern is controllable, within limits, by choice of glue grade. Use of higher grades makes larger designs, while lower grades produce a finer, more even texture.

6. *Other Applications*

Animal glues are used in leather manufacturing as a component of fat liquoring compounds which are used to impart softness to the leather, and as a filling agent to give added body to the leather. They are also used in finishing.

Low-grade animal glues are employed as a component with whiting, linseed oil, and rosin in composition for picture frames and decorative moldings on wood. High-grade glues are used to make molds for plaster casting. Medium- to low-grade animal glues with good foaming properties and adhesive qualities are utilized to produce strong, lightweight, cellular concrete.

Selected animal glues, also known as technical gelatins, are used in the production of protein hydrolysates for use as a source of protein in such products as cosmetics, shampoos, and skin care lotions and creams. Generally, the glue protein is hydrolyzed to a molecular weight below 2000 by use of enzyme, acid, or alkaline treatment.

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Carbohydrate Polymers as Adhesives

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I. INTRODUCTION

Carbohydrates in the form of polysaccharides are readily available from all plants, the exoskeletons of various marine animals, and some microorganisms. Because up to three-fourth of the dry weight of plants consists of polysaccharides, it is not surprising that many polysaccharides are readily available at low cost. Polysaccharides, especially from plant sources, have served a variety of uses in human history, ranging from basic necessities, such as food, clothing, and fuel, to paper and adhesives.

Three major carbohydrate polymers are readily obtained from biomass and are commercially available. These polysaccharides are cellulose, starch, and gums. The use of each of these types of carbohydrate polymers in and for adhesives is discussed in this chapter.

II. ADHESIVES FROM CELLULOSE

Cellulose is the principal structural material in the cell wall of all plants and is also found in algae, bacteria, and animals (tunicates). Approximately 10^{11} tons of cellulose is formed each year; this puts cellulose among the most important renewable resources in the world [1].

A. Cellulose Structure

Cellulose is a homopolymer of β-D-anhydroglucopyranose monomeric units that are linked via ether linkages between C-1 of one monomeric unit and C-4 of the adjacent monomeric unit (Fig. 1). As illustrated, every other monomeric unit is rotated approximately 180° about the long axis of the cellulose chain when compared to its two neighboring monomeric units. Because of this rotation, cellobiose is usually considered to be the

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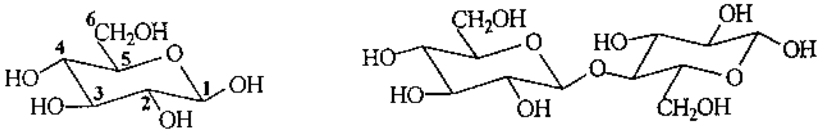
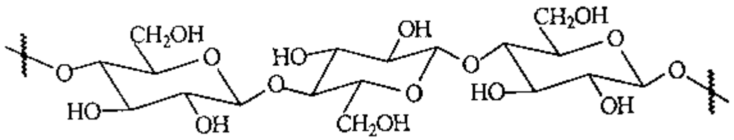


β-D-glucose

Cellobiose



Cellulose

Figure 1 Molecular structures of β-D-glucose, cellobiose, and cellulose. β-D-Glucose is the main building block of cellulose, while cellobiose is the actual repeating unit.

repeat unit of the cellulose polymer. Chain lengths in cellulose can range from 700 to 25,000 glucose units, depending on the source [2]. The two most common sources for cellulose are cotton linters and wood pulp, with approximate chain lengths of 1000–5000 and 500–2100 glucose units, respectively.

As a result of the large number of hydroxyl groups, cellulose molecules readily form hydrogen bonds with other cellulose molecules to give highly crystalline structures. Because the hydrogen bonding between cellulose molecules is not easily disrupted, cellulose does not dissolve in most common solvents. As a consequence, cellulose itself is not useful as an adhesive. Instead, cellulose is converted to various derivatives that can be used in the formulation of adhesives. Both esterification and etherification reactions can be carried out at the hydroxyl groups of cellulose. These cellulose esters and ethers can readily be dissolved into aqueous or organic solvents. Certain derivatives are thermoplastic and thus have been used in plastics and as hot-melt adhesives.

B. Modification of Cellulose

Each glucose unit in a molecule of cellulose has three hydroxyl groups that can be used to derivatize the cellulose by reactions common to all alcohols. It is uncommon, and for some derivatives impossible, to achieve a degree of substitution (DS) of three. Most important derivatives of cellulose have a DS that is somewhat below that value. For a given derivative, the DS must be specified since the properties of the derivative depend almost as much on DS as they do on the substituting agent.

1. *Esters*

Esterification of cellulose to give cellulose trinitrate was discovered by Schönbein in 1846 using a mixture of sulfuric and nitric acids. The resultant compound was so flammable that its first use was as smokeless gunpowder. By the end of the ninteenth century, cellulose nitrates had been prepared with a lower DS, and they could safely be used for other purposes. All cellulose nitrates are prepared by Schönbein's method, in which an aqueous slurry of cellulose is reacted with nitric acid in the presence of sulfuric acid (Fig. 2a). The reaction is in equilibrium and thus the removal of water during the reaction forces the reaction to completion [3]. The relative concentrations of the reacting species determine the ultimate DS that can be obtained. Boiling the nitrated product in water removes sulfate groups that can make the cellulose nitrate unstable, and digestion may be the final preparation step if a lower-viscosity material is desired.

The discovery that cellulose esters could be prepared with organic substituents led to the development of cellulose derivatives that had decreased flammability compared to that of cellulose nitrate. The most important organic ester is cellulose acetate. It is prepared by the reaction of acetic anhydride on cellulose in the presence of sulfuric acid. Acetic acid is

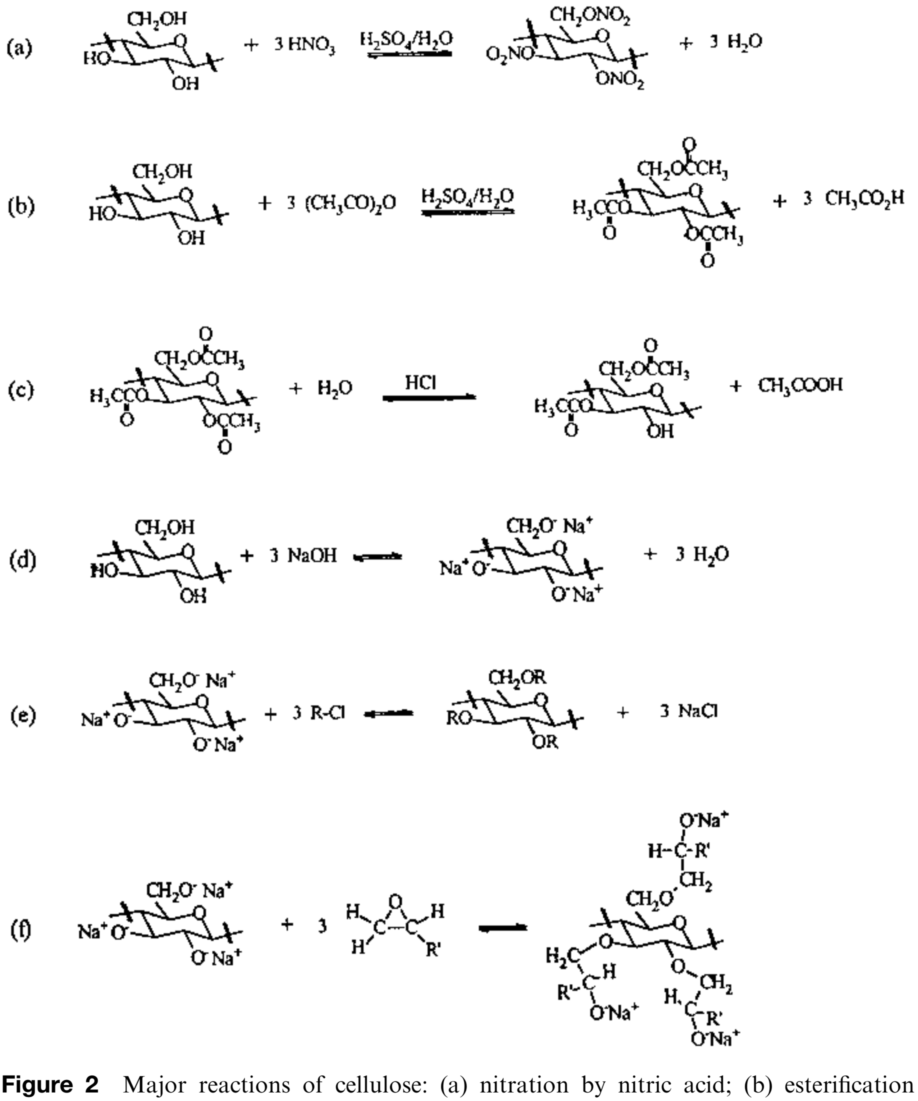


Figure 2 Major reactions of cellulose: (a) nitration by nitric acid; (b) esterification by acetic anhydride; (c) hydrolysis of tertiary cellulose acetate by hydrochloric acid; (d) deprotonation of cellulose, the first step in etherification; (e) etherification of sodium cellulose by an alkyl halide; (f) etherification of sodium cellulose by an epoxide.

used as the solvent and the reaction is carried out for about 8 h to yield the triester (defined as having a DS greater than 2.75) (Fig. 2b). The derivatives with lower DS values are obtained by the hydrolysis of the triester by hydrochloric acid to yield the desired substitution (Fig. 2c).

Esters of other aliphatic acids are prepared in a similar manner using the appropriate anhydride. Industrially important esters include cellulose propionate, cellulose butyrate, cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB). The mixed esters, CAP and CAB, are prepared by using a mixture of anhydrides in the desired ratios, or by reacting cellulose with propionic or butyric acid and acetic anhydride. Both reactions require sulfuric acid as a catalyst.

2. *Ethers*

Cellulose ethers are prepared by replacing the hydrogen on the cellulose hydroxyl groups with an alkyl group. The substitution reaction first involves the removal of the hydrogen by sodium hydroxide to make sodium cellulose (Fig. 2d). The sodium cellulose is then reacted with the appropriate alkyl halide or epoxide. Reaction with an alkyl halide yields the cellulose ether plus sodium halide (Fig. 2e). The epoxide reaction involves opening the epoxide ring (Fig. 2f), yielding a hydroxyl group on the substituent, which is deprotonated in the strongly basic reaction medium. Cellulose ethers that have been used as adhesives include methyl, ethyl, carboxymethyl, hydroxyethyl, and benzyl cellulose.

Methyl cellulose and ethyl cellulose are prepared using methyl chloride and ethyl chloride, respectively, as the alkyl source. Carboxymethyl cellulose (CMC) is the most important ether prepared from cellulose. It is commonly available as its sodium salt, which is prepared in an alcoholic solvent using either chloroacetic acid or sodium chloroacetic acid as the substituting agent. Hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose (HPC) are both prepared using epoxides: ethylene oxide for HEC and propylene oxide for HPC. The reaction is carried out in a water-miscible solvent, such as the lower alcohols. Because the hydroxyethyl and hydroxypropyl substituents have alcohol groups, further reaction can occur at these groups. Therefore, it is possible to get more than three substituents per anhydroglucose unit. For this reason, a quantity called molar substitution (MS) is defined to be the average number of hydroxyethyl or hydroxypropyl groups per ring, including both those attached directly to the ring and those attached to the ether substituent.

C. Properties and Uses

Adhesives derived from cellulose are used in a wide variety of applications that require an economical means for bonding porous substrates. Specific uses and formulations of various cellulose ester and ether adhesives are discussed in the following sections.

1. *Cellulose Nitrate*

Cellulose nitrates with DS values of 1.8–2.3 are used in plastics, lacquers, coatings, and adhesives. The most common use as an adhesive is as general-purpose household cement, in which the nitrate and a plasticizer are dissolved in a mixed ketone–ester organic solvent. Upon application to the substrate, the solution rapidly loses solvent to form tough, moisture-resistant, clear films. These thermoplastic films are prone to discoloration upon exposure to sunlight, and, as might be expected, are very flammable.

2. *Cellulose Acetate*

Cellulose acetate is the most important ester produced from cellulose; however, its use in adhesives is limited. Both the triacetate (DS greater than 2.75) and secondary acetate (DS of 2.4–2.6) are used industrially in plastics and textiles. The triacetate is soluble in mixtures of organic solvents, and the secondary acetate is soluble in acetone. Cellulose acetate is more heat resistant than cellulose nitrate but is less water resistant and tends to become brittle with age.

3. *Cellulose Acetate Butyrate*

Use of the mixed ether cellulose acetate butyrate helps to overcome some difficulties associated with using cellulose acetate as an adhesive. CAB is soluble in a greater range of organic solvents than is the pure acetate, and it is more compatible with common plasticizers. It can be applied either as a hot-melt adhesive or in a solvent solution. Because CAB is grease resistant, it has been used in paper sizing and coating to make the paper more resistant to staining.

4. *Methyl Cellulose*

Methyl cellulose with a low DS (0.4–0.6) is soluble in dilute aqueous sodium hydroxide. As substitution is increased, the methyl cellulose becomes soluble in water (DS 1.3–2.6), then in organic solvents (DS 2.4–2.6). The most commonly used derivatives have a DS of 1.2–2.0. which results in cold-water solubility and solution stability for pH 2–12. Upon drying, solutions of methyl cellulose give clear, odorless, tasteless films that are resistant to oils and organic solvents. Methyl cellulose is used for paper coating and sizing to impart grease resistance, in ceramics as a binder, as a nonstaining paste for wallpaper, and in adhesives for leather drying. The last application takes advantage of the fact that upon heating, methyl cellulose thickens reversibly. Thus hides that are attached to the platen during the drying process are easily removed when dry. Table 1 shows a formulation for a leather adhesive [4].

5. *Ethyl Cellulose*

In contrast to methyl cellulose, ethyl cellulose is commonly prepared in its organic soluble state with a DS of 2.3–2.6. Films of ethyl cellulose are thermoplastic, and they resist alkali and salts. Because of their organic solubility, the films tend to swell very little in the presence of water. The resistance of ethyl cellulose to chemical degradation has led to its use in films, lacquers, and adhesives. In adhesives, ethyl cellulose may either be applied in a solvent or as a hot-melt.

Table 1 Formulation of Leather Adhesive with Methyl Cellulose

Component	Amount (part)
Methyl cellulose (4 Pa s)	2.0
Plasticizer	0.2
Casein	0.3
Water	97.5

6. *Carboxymethyl Cellulose*

Carboxymethyl cellulose, generally as its sodium salt, is the most widely used cellulose ether. CMC is water soluble with a DS of 0.4–1.2 in common applications. It was originally used as a replacement for natural gums in adhesives, but it has since developed many uses of its own. Sodium carboxymethyl cellulose is readily water soluble because of its ionic nature; its largest use is in laundry detergents, where it helps to suspend soil particles during washing. This resistance to greases and soil has made CMC useful in fabric sizing as a soil repellant. Because CMC is completely nontoxic, it is used in many food applications, where its affinity for water prevents drying of the product. Although it is generally no longer used as an adhesive, per se, it is still used in adhesives as a thickener.

7. *Hydroxyethyl Cellulose*

Hydroxyethyl cellulose with an MS value greater than 1.6 is soluble in hot or cold water; with an MS value of 2.3–2.6, it is soluble in organic solvents. HEC forms oil- and grease-resistant films that retain clarity over time. It is used as an adhesive in billboards, corrugated board, plywood, and wallpaper, and as a sizing and binding agent in paper products. Although not approved for direct use in food, HEC is used as an adhesive in packaging materials for foodstuffs.

III. ADHESIVES FROM STARCH

Starch is produced by plants as a way to store the chemical energy that they produce during photosynthesis. Starch is found primarily in the seeds, fruits, tubers, and stem pith of plants, most notably corn, wheat, rice, sago, and potatoes. In 1985 alone, more than 1.6 billion kilograms of starch was used in applications involving bonding of materials [5]. Clearly, this makes starch a very important adhesive material.

A. Starch Structure

Like cellulose, starch is a naturally occurring polymer of glucose. It differs from cellulose in two significant aspects: the glucose rings are in the α-D configuration rather than the β-D configuration, and starch can be differentiated into two types of polymers. One polymer, amylose consists of α-D-anhydroglucopyranose monomeric units combined linearly through 1–4 linkages with little or no branching. The other polymer, amylopectin, is linked through 1–4 linkages but also has branches that form at the primary alcohol group on C-6 (Fig. 3). Careful analyses of various starches have shown that there is also an intermediate fraction that is thought to be an infrequently branched amylopectin [6].

The amount of amylose and amylopectin in a starch depends on the source of the starch. Most starches contain 20 to 30% by weight of amylose, although certain hybrids can contain more than 80% amylose. The most commonly available industrial starches are waxy cornstarch, regular cornstarch, high-amylose cornstarch type V, and high-amylose cornstarch type VII, with amylose concentrations of 0, 28, 55, and 70%, respectively [7].

Starch alone suspended in cold water is essentially unable to act as an adhesive because the starch is so tightly bound in granules. The granules consist of crystalline regions where straight-chain molecules and straight sections of branched molecules are aligned. The crystallite regions are linked together by more amorphous areas where the molecules are not aligned. Within the starch granule, the molecules and crystallites are

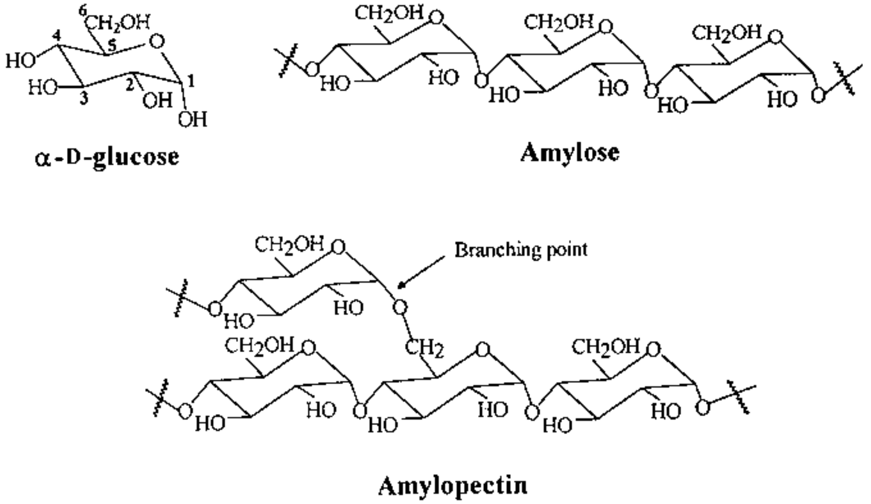


Figure 3 Molecular structures of α-D-glucose and the two major molecules that make up starch, amylose, and amylopectin.

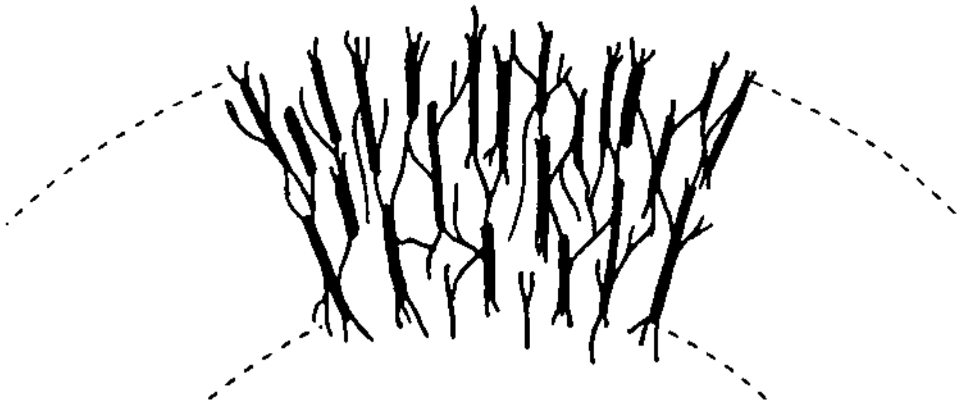


Figure 4 Outer surface of starch granule showing radial arrangement of crystallites. Crystallites are shown as thicker lines. [Adapted from K. H. Meyer, *Adv. Colloid Sci. 1*: 168–169 (1942).]

arranged radially in concentric layers (Fig. 4). It is these granules that must be opened to obtain adhesive bonding.

B. Modification of Starch

Starch must be modified before it can be used as an adhesive. Methods for opening the starch granules include heating, alkali treatment, acid treatment, and oxidation.

1. *Heat Treatment*

The simplest method of breaking up starch granules is well known to the cook. To thicken a sauce, cornstarch must be heated. During the heating process, the starch granules first swell and then burst with a coincident thickening of the suspension. The temperature at which this thickening occurs is called the gelation temperature. For starches in pure water, gelation occurs between 57 and 72°C [8]. Observation of gelled starch under a polarizing microscope indicates that the crystallinity of the starch granule is lost during the gelling process. However, the starch is not truly in solution but rather in a colloidal suspension. Suspensions of amylose and high-amylose starches have a tendency to harden and become solid upon cooling. This process is called retrogradation or setback and is a result of the tendency of linear molecules to align with one another. This aligning effect also means that at the same solids content, suspensions with a higher ratio of amylose to amylopectin have a higher viscosity.

2. *Alkali Treatment*

The gelation temperature can be lowered by the addition of sodium hydroxide to a starch suspension. If sufficient alkali is added, the starch can be induced to gel at room temperature.

3. *Acid Treatment (Thin-Boiling Starches)*

Acid modification of starch is achieved by heating the starch to 49–54°C with small amounts of aqueous mineral acid, followed by neutralization with base. The acid acts mainly on the amorphous regions of the starch granules, leaving the x-ray and birefringence patterns of the crystalline regions essentially unchanged. Dried acid-modified starch appears very similar to its unmodified counterpart; however, upon heating a suspension to the gelation temperature, the differences become obvious. The acid modified starch tends to give a much thinner solution at the same solids content when compared to unmodified starch. This makes the modified starch useful in applications that require a higher solids content.

4. *Oxidation*

Oxidized starch is commonly obtained by aqueous alkaline hypochlorite treatment. A starch suspension at pH 8–10 is treated with hypochlorite (5–10% Cl based on starch) for long enough to produce the desired viscosity. Acid is liberated during the reaction, so base must be added to maintain the pH for optimum reactivity. The resultant starch contains a mixture of carboxyl and carbonyl oxygens. Some shortening of chain length is observed during the reaction, but as in acid modification, there appears to be little change in the crystalline region of the starch. Dried oxidized starch is generally whiter than unmodified starch, since the oxidation and subsequent rinsing tend to remove impurities that may be present in native starch. Oxidized starches behave similarly to the acid-modified starches upon gelling. However, the oxidized starches have greater tack and adhesive character, and thus they are used more frequently in adhesive preparations.

C. Dextrins

Dextrins are the product of dry-roasting starch in the presence of an acid catalyst. Although potato, tapioca, and sago starches are the easiest to convert to dextrins, the low cost and ready availability of cornstarch, make it the most commonly used starch. Dextrins are generally divided into three categories: white dextrins, canary or yellow dextrins, and British gums. Their differences are determined by the roasting time and temperature and the amount of catalyst used.

1. *White Dextrins*

White dextrins are produced at low temperatures (120–130°C) and roasting times (3–7 h) in the presence of a high concentration of catalyst. The primary reaction that occurs during the formation of white dextrin is hydrolysis of the starch molecules [9]. This reaction initially acts at the 1–6 linkages, and continues with the 1–4 linkages as the concentration of 1–6 linkages decreases. Eventually, repolymerization occurs, which yields small, highly branched dextrins. Very little repolymerization occurs in white dextrins, resulting in a white or buff powder with a degree of polymerization of approximately 20. The solubility of the white dextrins can range from 1 to 95% in water, with the lower-solubility grades resembling starch in their characteristics. The higher-solubility grades are more similar to the lower-conversion yellow dextrins. The small amount of repolymerization in the white dextrins makes the suspensions susceptible to retrogradation, and thus the suspensions must be used soon after preparation.

2. *Yellow Dextrins*

Yellow dextrins are prepared at higher temperatures (135–160°C) and longer roasting times (8–14 h) in the presence of less acid catalyst than are the white dextrins. These conditions promote further repolymerization, yielding a yellow or tan powder with a degree of polymerization between 20 and 50. The yellow dextrins are, for the most part, water soluble; less than 1 part water to 1 part dextrin is required for a working suspension. Yellow dextrin suspensions exhibit good viscosity stability, so retrogradation is less of a problem.

3. *British Gums*

In British gums, the repolymerization reaction is allowed to proceed to the greatest extent. Dry roasting is carried out for 10–24 h at temperatures between 150 and 180°C, and a very small amount of acid catalyst is used. These dextrins tend to be the darkest in color, which ranges from yellow to dark brown. As with the white dextrins, the British gums exhibit a wide range of solubilities in water depending on the exact reaction conditions used. However, the British gums are not prone to retrogradation, and they tend to give a more viscous suspension at the same concentration.

D. Additives and Formulation Variables

The formulation of starch and dextrin adhesives can be viewed more as an art than the result of rigorous scientific study. Not surprisingly, the purpose for which the adhesive is to be used and the method by which it will be applied greatly determine the properties needed in the resin. Factors that must be controlled include viscosity, solids content, stability, tack, slip, substrate penetration, drying rate, flexibility, water and microbial resistance, and cost. Some of these are determined by the type of starch or modification, while others require the addition of an additive to give the adhesive the desired properties. In the sections below we discuss some of the most common additives that are used with starch-derived adhesives.

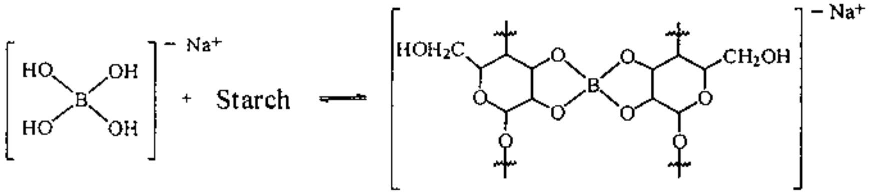


Figure 5 Complexation of starch molecules by the borax in basic solution.

1. *Borax*

Borax (sodium tetraborate) in the presence of small amounts of sodium hydroxide is the most widely used additive to starch-based adhesives. It is commonly used in dextrin adhesives, where it increases the viscosity and acts as a tackifier and viscosity stabilizer. These effects are particularly important in machine application of adhesive to substrate. When used in adhesives, borax is often added in amounts up to 10% based on dry starch before the starch is cooked. Enough sodium hydroxide is added to convert the borax to sodium metaborate, which is the active boron species in thickening. The metaborate is able to hook two starch molecules together, forming a complex (Fig. 5) [10]. If additional sodium hydroxide is added, the complex will dissociate; the viscosity of the suspension will begin to decrease with increasing sodium hydroxide [11].

2. *Plasticizers*

Plasticizers are used to control brittleness of the glue line and to regulate the speed of drying. Commonly used plasticizers act in one of three ways: by forming a solid solution with the dried adhesive, by controlling the moisture in the film, and by lubricating the layers within the dried adhesive. Plasticizers that form a solid solution, such as urea, sodium nitrate, salicylic acid, and formaldehyde, tend to decrease the viscosity of the adhesive preparation. Urea is the most commonly used of these additives, and it may be added at a level of 1–10% based on dry starch. Hygroscopic plasticizers such as glycerol and ethylene glycol are commonly used to decrease the drying rate of the film and ensure that the film does not become brittle. Soaps, polyglycols, and sulfonated oil derivatives are used in small amounts as lubricating adhesives to impart permanent flexibility to the glue line, since they are not affected by changes in humidity.

3. *Additives to Increase Water Resistance*

Starch-based adhesives used in any application that requires water resistance must contain additives that resist water. Commonly used additives of this type are urea–formaldehyde, melamine–formaldehyde, and resorcinol–formaldehyde precondensates, poly(vinyl alcohol), and poly(vinyl acetate). The greatest water resistance is imparted by the formaldehyde-based precondensates; poly(vinyl alcohol) and poly(vinyl acetate) are used for adhesives that are resistant to cold water but can dissolve in hot water.

4. *Viscosity Stabilizers*

As mentioned previously, one problem encountered in starch-based adhesives is retrogradation. Colloid stabilizers such as soaps and sodium chloride are used to retard this tendency. Borax, sodium hydroxide, and several common plasticizers also perform this function to some extent, so viscosity stabilizers may not be necessary if these additives are used for other purposes.

5. *Fillers*

Fillers, in amounts of 5 to 50%, are used to control the penetration of the adhesive into the substrate and to control the setting of the glue. Mineral fillers such as clay and bentonite are commonly used.

6. *Other Additives*

Other additives that may be found in starch-based adhesives include preservatives to retard microbial growth, bleaches to remove colored impurities and prevent discoloration of the glue over time, defoamers to prevent foaming during processing, and organic solvents to enhance bonding to waxed surfaces. The most commonly used preservative is formaldehyde, and common bleaches include sodium bisulfite, hydrogen and sodium peroxide, and sodium perborate. Defoaming agents and solvents to be used in starch adhesives must be matched to the type and use of the adhesive, with special attention to compatibility and toxicity of the components.

E. Applications

The majority of starch-derived adhesives are used in the paper and textile industries as binders and sizing materials. However, the discussion in this chapter is limited to glues and pastes, since paper and textile uses have been covered thoroughly elsewhere [12]. This section provides an overview of several gluing applications, with special attention to the properties required of the glue in each case.

1. *Corrugating Adhesives*

Corrugated board is produced by the adhesion of a fluted layer of paper to a flat layer. A two-phase starch adhesive is commonly used to join the two layers. The liquid phase, a gelled mixture of starch and sodium hydroxide in water, is called the carrier. The solid phase of ungelled starch and borax is suspended in the carrier phase. The mixture is applied to a warm fluted sheet, which is then placed into contact with a hot flat sheet. The ungelled starch gels from the heat of the sheets. Table 2 shows a recipe for a typical corrugating adhesive [13].

2. *Bag Manufacture*

Three types of adhesives are used in the manufacture of paper bags and sacks: side-seam adhesive, bottom paste, and cross paste. During production of a single-layer bag, the paper is first formed into a long tube held together by side-seam adhesive. To be compatible with machinery used in this process, the adhesive needs a viscosity in the range 2–4 Pa s with a solids content of 20–22%. Generally, the side-seam adhesive is made using high-soluble white dextrin or acid-modified starch, so the viscosity of the suspension remains low. Bottom paste adhesive is used to close the bottoms of the paper bags; it is much more viscous and has greater tack than side-seam adhesive. The high tack is necessary to keep the bags from opening after they have been formed. Bottom paste adhesives are usually composed of white dextrins or starch; viscosity may be as high as 140 Pa s at 25°C. Cross paste adhesive is used only for the manufacture of multiwall bags. It is similar to side-seam adhesive, with the added requirement that it must not bleed through the paper to other layers. This is achieved by the addition of mineral fillers or poly(vinyl acetate). Water resistance of bag adhesives can be improved by the addition of urea–formaldehyde or poly(vinyl alcohol). Typical formulations for these adhesives are listed in Table 3.

Table 2 Recipe for Corrugating Adhesive

Starch adhesive phase	Amount (part)
Liquid (carrier)	
Water	11.9
Starch	3.4
40% Aqueous NaOH	2.0
Cook at 71°C for 15 min	—
Cold water	8.5
Solid (suspension)	
Water	56.6
Borax decahydrate	0.54
Stir to dissolve	—
Starch	16.9
Stir to disperse	—
Add carrier solution	—

Table 3 Typical Formulations for Paper Bag Adhesives

Adhesive and component or process	Amount (part)
Side-seam adhesive	
Water	49.7
White dextrin (94% soluble)	39.7
White dextrin (13% to 15% soluble)	5.0
Borax decahydrate	4.0
Preservative	0.01
Antifoam agent	0.03
Cook to 85°C for 20 to 30 min	—
Cool to room temperature	—
50% Aqueous NaOH	1.2
Bottom paste	
Water	76.7
Starch	19.2
Borax decahydrate	3.1
Preservative	0.2
Soap	0.8
Cook to 93°C for 20 to 30 min	—
Adjust solids to 30%	—

Source: Ref. 14, Chap. 26, p. 14.

3. *Laminating Adhesives*

Laminates prepared from paper or paperboard may be bonded with carbohydrate adhesives. The properties of the adhesive used with each will differ greatly depending on the surface of the material and the equipment to be used for laminating. However, all laminating adhesives should exhibit high tack, low penetration into the substrate, and noncurling behavior. White dextrin is often used at about 20% of the total adhesive; a typical formulation is given in Table 4.

4. *Carton Sealing*

Cartons from corrugated board are most often sealed with liquid glues or hot-melt adhesives. However, dextrin adhesives are still used as a result of their low cost and ready availability. Adhesives for sealing cartons must have low and stable viscosity, be able to form strong bonds, and set up quickly. If staining of the carton is not a concern, sodium hydroxide may be added to increase adhesion. A formulation for a white dextrin adhesive is given in Table 5.

Table 4 Typical Formulation for a Laminating Adhesive

Component or process	Amount (part)
Water	54.6
White dextrin (high soluble)	20.2
Clay	13.5
Urea	6.7
Borax decahydrate	5.0
Cook to gel	—

Source: Ref. 14, Chap. 26, p. 4.

Table 5 Formulation of Adhesive for Sealing Cartons

Component or process	Amount (part)
Water	110
White dextrin	80
Preservative	2
Borax	12
Antifoam agent	0.125
Cook at 85°C for 20 min	—
Cool to 50°C	—
Water	10
50% NaOH	0.12

Source: Ref. 14, Chap. 26, p. 4.

Table 6 Formulations for Remoistening Adhesives

Adhesive and component or process	Amount (part)
Envelope adhesive	
Yellow dextrin (95% soluble)	65.7
Water	32.9
Tributyl phosphate	0.2
Heat to 88°C for 30 min	—
Cool to 60°C	—
Corn syrup	1.1
Gummed tape adhesive	
Water	50
Waxy starch (acid-modified)	44
Urea	6

Source: Refs. 15 and 16.

5. *Remoistening Adhesives*

Adhesives for remoistening applications such as tapes, stamps, labels, and envelope flaps must be capable of rewetting. Such adhesives should also be glossy, noncurling, and nonblocking under humid conditions. This requires that the formulation contain acid-modified starch or high-soluble white and yellow dextrins to allow a high solids content. A plasticizer is added to prevent brittleness in the final film. In tape and stamps, the paper with adhesive has traditionally been run over a bar to produce microcracks in the adhesive layer, thus rendering it noncurling. A similar effect has been achieved by solvent deposition of the adhesive. In this process, a cold-water-soluble dextrin is suspended in an organic solvent, where it is insoluble. When this suspension is applied to paper and dries, it leaves behind a layer of discrete dextrin particles, which will not curl. Formulations for two remoistening adhesives are given in Table 6.

IV. ADHESIVES FROM NATURAL GUMS

Gums are hydrophobic or hydrophilic polysaccharides derived from plants or microorganisms that upon dispersing in either hot or cold water produce viscous mixtures or solutions. Natural gums include plant exudates (gum arabic, gum ghatti, gum karaya, gum tragacanth), seed gums (guar gum, locust bean gum, tamarind), plant extracts (arabinogalactan from larch; agar, algin, funoran from seaweed), and the extracellular microbial polysaccharides (xanthan gum, dextran). Gums are used for many industrial purposes, as shown in Table 7. In recent years, synthetic polymers and microbially produced gums increasingly have replaced plant-derived gums.

Historically, several adhesives have been derived from natural carbohydrate polymers. In a few cases, such polymers have been utilized because of their own particular adhesive properties. However, natural carbohydrate polymers are usually used as modifiers for more costly synthetic resins, especially as thickeners, colloidal stabilizers, and flow controllers. Adhesive uses for natural gums include pressure-sensitive tape, denture adhesives, pharmaceutical tablet binders, household products, and label pastes [17].

Table 7 Applications for Natural Gums

Product	Amount (%)
Detergents, laundry products	16
Textiles	14
Adhesives	12
Paper	10
Paint	9
Food	8
Pharmaceuticals, cosmetics	7
Other	24

V. CONCLUSIONS

Carbohydrates, in the form of polymers such as cellulose, starch, and natural gums, are available in large quantities, especially from plant sources. Each of these has potential for utilization as adhesives and in adhesive formulations. This has been true historically and will be increasingly true in the future as petroleum-derived polymeric materials become scarce and their prices rise. However, because the bonds formed by carbohydrate polymer adhesives are generally sensitive to water, future applications of these adhesives will increasingly depend on modifying the natural polymer to give components that can undergo further cross-linking to form water-insensitive bonds.

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Natural Rubber-Based Adhesives

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I. INTRODUCTION

Natural rubber adhesives can be classified into two principal types: latex adhesives and solution adhesives. Natural rubber latex is obtained by tapping the tree *Havea brasiliensis*. The latex consists of about 35% solids. Ammonia is added to the latex immediately after the tapping to prevent bacterial attack and coagulation. Before marketing, the latex is concentrated to a total solids content of about 60 to 70%.

Solution adhesive is obtained from solid rubber obtained by coagulation of latex as acquired from the tree. The coagulation is effected by dilute aqueous solution of organic acids. The solid rubber can be graded in terms of dirt content, ash content, nitrogen content, and volatile matter. It can also be categorized by plasticity retention index and Mooney viscosity. To maintain uniformity it is necessary to choose solid natural rubber of known characteristics.

II. LATEX ADHESIVES

Latex adhesives are made from natural rubber latex by adding stabilizers, wetting agents, and other components. They are applied to the substrate by brush, spray, doctor knife, or reverse roll coater. The adhesive is dried to film near room temperature. The adhesive strength can be improved by vulcanizing the system. The applications of latex adhesives are to porous substances such as paper, leather, and textiles.

Latex adhesives can be handled easily because they are more fluid due to lower solid content. They have little incendiary risk because of the absence of solvent. They are cheaper because they do not contain solvent, which is lost on drying. However, natural rubber solution adhesives possess intrinsically greater adhesion to the substrate than do latex adhesives. Following are some examples of nonvulcanizing natural rubber latex.

1. *Self-seal envelope adhesive*

		Parts by weight (wet)
60%	Natural rubber latex	167
10%	Potassium hydroxide solution	2
50%	Aqueous dispersion of zinc diethyldithiocarbamate (accelerator)	1

2. *Leather adhesive*

		Parts by Weight (wet)
60%	Natural rubber latex	167
20%	Ethylenediaminetetracetic acid solution	2.5
59%	Aqueous dispersion of poly(2,2,4-trimethyl-1,2-dihydroquinoline) (antioxidant)	1

3. *General-purpose pure gum adhesive*

		Parts by weight (wet)
60%	Natural rubber latex	167
50%	Dispersion of zinc dibutylthiocarbamate	2
10%	Solution of ammonium caseinate	10

4. *Adhesives for the carpet industry*. Formulations for backing carpets of hessian and polypropylene staple construction are given below.

	Parts by dry weight	
	A:Primary backing	B:Secondary backing
60% Natural rubber latex	100	100
Stabilizer/wetting agent [sodium lauryl ether sulfate (27%)]	1.5	1.0
10% Aqueous dispersion of thiourea	1.0	1.0
50% Aqueous dispersion of *N*-phenyl, *N*′-cyclohexyl *p*-phenylenediamine (antioxidant)	1.0	1.0
Water	To give 75% solid	
Whiting	400	250
50% Dispersion of polyacrylate thickener	0.2	0.3

Ingredients are to be mixed in the order given above. The stabilizer, thiourea, water, and antioxidant must be completely dispersed in the mix before adding the whiting. The whiting must be completely dispersed in the mix before adding thickeners.

5. *Tire cord adhesive*

	Parts by weight (wet)
60% Natural rubber latex	125
40% Vinyl pyridine latex	62.5
Water	507
Resorcinol–formaldehyde resin solution	266.3
Water	240
Sodium hydroxide	0.3
Resorcinol	11
40% Formaldehyde solution	15

Mature for 6 h at 25°C

III. SOLUTION ADHESIVES

Solution adhesives consist of solid rubber dissolved in a solvent such as toluene, naphtha, or trichloroethane. The solvent used will depend on the drying and flammability considerations in the application. Milled raw rubber can be shredded and agitated in the solvent until a clear solution is obtained. Other components are added at this stage and mixed uniformly. Alternatively, the solid rubber can be compounded with other components and the mix dissolved in the solvent.

Solution adhesives are applied at 10–25% total solids content by spray, doctor knife, reverse roll coater, roller, or by spatula or trowel. The adhesive is dried at room temperature or in air ovens, care being taken to eliminate the fire and health hazards associated with some solvents.

The toughness and durability of the bond may be improved by using vulcanizable rubber solution adhesives. These are normally supplied as two components which are mixed prior to use. Component A is prepared as follows:

	Parts by weight
Natural rubber	10
Zinc oxide	1
Antioxidant	0.1
Sulfur	0.1
Solvent	80

Component B is prepared as follows: To 100 parts of component A, add 4 parts of a 10% solution of a dithiocarbamate accelerator. The mixed adhesive will vulcanize at room temperature or at a higher temperature, if required. Typical vulcanizing time at room temperature is 3–4 days.

IV. PRESSURE-SENSITIVE ADHESIVE TAPES

Solid natural rubber is widely used in adhesive formulations for making electrical insulation tapes, packaging tapes, and surgical tapes and plasters. The backing may be made from paper crepe, cloth, or synthetic materials, depending on the application. The rubber can be applied from solvents or calendered directly onto the backing. The following formulations are for packaging tape and surgical tape adhesives:

	Parts by weight	
	Packing tape	Surgical tape
Natural rubber	100	100
Ester gum (tackifier)	175	100
Lanolin (wool fat)	25	25
Antioxidant	1	1
Zinc oxide	50	100
Solvent (toluene, naphtha, or trichloroethylene)	400	200

Initial shredding or granulation of the rubber aids dissolving. Alternatively, lightly mill the rubber and zinc oxide, then add solvent. Blend the swollen mixture in a Z-blade mixer until homogeneous, then add ester gum, antioxidant, and finally, lanolin.

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Elastomeric Adhesives

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I. INTRODUCTION

At first, there was only natural rubber, a substance "discovered" by Christopher Columbus on his second voyage to the New World. Soft and tacky when solidified from the tree latex, it remained a curiosity for many years, eventually finding use as a "rubber," as Joseph Priestley called it, since it would harden and rub-out pencil markings after it had aged some. The patent literature shows activity after 1791 when the first U.S. patent was issued for a mixture of rubber and solvent that was used to bond two layers of wool fabric together. In 1845, a patent was issued for an adhesive to be used in a self-adhering bandage that contained India Rubber, Gum of Southern Pine, Balsam of Peru, Ground Litharge, Extract of Capsicum Annum, and Turpentine. Just a few years earlier in 1839, Charles Goodyear discovered that the addition to natural rubber of sulfur and certain metallic oxides followed by heating changed the gummy rubber to a stretchable elastic material that, upon release of applied stress, would regain its original shape. Johnson and Johnson developed and patented a pressure sensitive adhesive that contained gum rubber and zinc oxide in 1899.

Also in 1899, Hermann Staudinger graduated from high school in Worms, Germany, continued his studies at several universities, eventually becoming a Professor of Organic Chemistry at the Institute of Chemistry of the Technische Hochschule in Karlsruhe, Germany. In the early 1920s, Professor Staudinger proposed a theory of macromolecular formation. Although his proposals were not immediately widely accepted, a number of researchers pursued certain aspects of his work. And with that research came the foundation of today's synthetic rubber and plastics industries. By the 1930s, a whole host of new, high molecular weight polymers had been developed and were being refined into usable products. In the early to mid-1930s, there was little demand for these new polymers simply because the Southeast Asian natural rubber plantations, which had supplanted the original Brazilian forest collections, supplied all the necessary materials for most elastomeric applications at very low costs. By the late 1930s, that situation had changed, and rather dramatically. War on two continents increased the need for developing sustainable supplies of rubber materials to continue supplying the needs of industry, and eventually, the supplies of the war machines. Japan invaded and took control of Southeast Asia and, with it, the rubber plantations, which immediately threw the rest of the industrial world into disarray. Without natural rubber for tires, gaskets, belting, and hoses, and the rubber-based adhesives used to make those products, modern civilization would have come quickly to a halt.

This situation was recognized immediately by the governments of both Germany and the United States, which embarked on the development of replacement supplies through the building of a synthetic rubber industry. In the United States, polychloroprene (Neoprene), styrene-butadiene rubber [General-purpose Rubber—Styrene (GRS), or Buna S], butyl, and acrylonitrile butadiene [General-purpose Rubber—Nitrile (GRN), or Buna N] were the primary polymers pursued for production. By the early 1940s, synthetic rubber production was underway, while the government instituted strict controls over existing supplies of natural rubber, both in solid bale form and latex, since there were some products that still required the use of natural rubber for manufacture. Even old tires, belting, hoses, molded goods, and other rubber fabricated materials were collected as the rubber reclaim industry grew out of the necessity to recover any usable elastomeric polymer. These controls were maintained in place by the U.S. government through the late 1940s and early 1950s, since the rubber plantations did not immediately recover full capacity and distribution immediately after the war. A limited supply of natural rubber allowed the synthetic rubber industry to grow in industrial markets and prosper into the 1950s, as new developments and continued high rates of production reinforced the stability of this new supply of polymers and kept production costs low.

However, despite all of this burgeoning growth of these new materials, natural rubber could not be replaced for all applications. Natural rubber has a molecular weight of approximately 1 million, solution grade styrene-butadiene rubber is typically only 100,000. Natural rubber does not have the natural chemical resistance of nitrile rubber, but can be compounded for many of the same properties, and is more often less expensive to use. While many synthetic elastomers have unique and special properties, natural rubber had the advantage, in the early years after the war especially, of nearly 150 years of experimentation, development, and production. As the century progressed into the 1960s and 1970s, however, Southeast Asia once again became embroiled in war and, even though the primary supplying countries of Malaysia and Indonesia were not directly involved, changes in supplies and distribution assisted the growth and acceptance of many synthetic polymers. As the synthetic rubber industry continued to grow, so did the products become more economical to use.

II. COMMON PROPERTIES OF ELASTOMERIC ADHESIVES

Since natural rubber is the foundation of the rubber industry, all materials that are so-called elastomers, or rubber, are essentially compared against it. Therefore, elastomers are, generally, high molecular weight polymers that elongate or stretch, are cross-linkable, have the unique cured property of rebound or the ability to snap back to an original configuration upon release of stress, have high resilience and compression strength, and have high tensile strength and modulus when stretched. All uncured rubber materials exhibit the characteristic of viscoelasticity, which combines the properties of both solids and liquids, being both stretchable and “liquid-like,” or viscous, in the solid state. Rubbery polymers, in addition, also have a high degree of resistance to water in both the uncured and cured states, as well as fairly good resistance to heat and cold when properly compounded and cured. The long chain crosslinked polymers also generally have relatively high tear resistance, are usually quite flexible, and highly resistant to fatigue stress.

Now, while many rubber polymers exhibit many of these properties, none of them exhibits all of them, nor equally well. Each polymer type has its own unique set of properties and characteristics, which allows for an expanding array of choices for assembly applications. Listed below are the major areas in which elastomeric adhesives provide an advantage over other polymer types.

Fast strength development Whether used as a base for pressure sensitive adhesives or for contact bond adhesives, most rubber polymer-based adhesives exhibit the characteristic of *green strength*, or the ability to virtually instantaneously develop holding power to a surface. Few other polymer systems have this property to as high a degree, or to as wide an array of surfaces and process conditions. This quick bond feature is a great asset to many assembly processes and manufacturing operations.

Versatility Rubber-based adhesives can be compounded to stick to almost anything under almost any conditions. Bond strength can vary from a temporary holding pressure sensitive product, with a few grams per linear centimeter of peel strength, to a high strength structural bond exhibiting hundreds of kilograms per square centimeter of lap shear strength.

Variety Although there are only a few basic categories of rubber polymers that make up the majority of applications, these polymers come in a wide array of distinct product grades within each category. In addition, most of these polymers are compatible with, and can be mixed freely with, other rubbery polymers to provide even more choices of properties, not to mention the virtually endless numbers of fillers, additives, reinforcing and tackifying resins, other polymer types, plasticizers, and other ingredients that can be used to further modify basic properties.

Economy For many applications, rubber-based adhesives and sealants are inexpensive relative to the base cost of many other polymer systems. In addition, the costs for dispensing and application tooling are often low. The speed of assembly operations with quick-stick adhesives often provides a labor and total cost advantage, and may even lower tooling costs.

Flexibility The inherent resilience of rubber polymers often provides protection in expansion/contraction modes due to product temperature cycling and flex stress from repetitive work cycles. Plus this flexibility improves the assembly's resistance to vibration, fatigue, impact, shear, elongation, and peel forces.

Variety of forms Rubber-based adhesives can be supplied to the user in solvent or water-based formulations, as a solid hot melt or a soft tacky extrusion, as a tape (reinforced or not, single or double-sided), as a film, and even pre-applied to a surface for later solvent or heat activation. Products can be single or multiple component, depending on the application requirements.

Variety of bonding methods The numerous forms and types of rubber-based adhesives and sealants also provide for numerous mechanisms for developing bonds to surfaces. Contact bond, pressure sensitive, wet bond, heat reactivation, and solvent reactivation are all feasible modes of product assembly with these products.

Ease of modification Most elastomeric adhesives can be readily modified in viscosity, tack, drying time (for solvent-based products), strength properties, heat resistance, aging characteristics and other properties to fit process and user requirements, usually without significant changes to basic characteristics or costs.

Thermoplastic or thermosetting A property often available in the same compound. However, typically, low strength requirements and ambient applications usually are solved with thermoplastic noncuring elastomeric adhesives, while high strength and high heat resistance are obtained from rubber polymers that are crosslinked. Thermoplastic adhesives will often begin losing strength at temperatures above 70°C. Some adhesives actually operate as a thermoplastic until the ambient temperature rises, at which time the adhesive will gain strength through a crosslinking mechanism and function as a thermoset thereafter. There is usually a time limit on the ability of an adhesive to function in this manner, since most curing functions are time–temperature dependent and most of these dual type products will achieve some limited crosslinking at ambient conditions. Some curing mechanisms for elastomers do require exposure to elevated temperatures to effect a suitable cure.

III. CHEMICAL TYPES OF ELASTOMERIC ADHESIVES

Many polymers exhibit some of the characteristics of the elastomeric family. Plastics, both thermoplastic and thermoset types, are very close both in terms of chemical structure and physical properties. Under a given set of conditions, plastics and elastomers will react much the same way. In fact, some polymer types are so versatile as to cross over into several different classes of compounds. The acrylic family is one, with rigid plastic compounds familiar to all in clear glass panel replacement applications, reactive two-component versions that provide a structural thermoset adhesive, rubbery polymers that can be used as sealants or adhesives, and soft thermoplastic polymers that can serve as a starting point for pressure sensitive adhesives or construction sealants, both solvent and water based. The polyurethane family is another, ranging from thermoplastic urethanes (TPUs) used in solid rubber and adhesive applications, to water- and solvent-based formulations, to hot-melt reactive systems for high performance applications where flexibility and green strength is a requirement, to rigid, glassy reactive thermoset polymer systems for structural applications. Other families of polymers that exhibit rubberlike properties include several cellulosic materials, a variety of thermoplastic resins such as acrylonitrile butadiene styrene (ABS) and poly(vinyl chloride) (PVC), and a whole host of vinyl acetate-based compounds. In addition, many silicone compounds and polysulfide systems also fall well into the elastomeric property category. And, obviously, natural rubber possesses these properties. But none of these materials will be described here since most will be covered in detail in other chapters of this treatise concentrating on these particular polymers.

Virtually all rubber materials, and plastic materials, can be made into an adhesive or sealant compound. This is because many elastomers begin as monomers dispersed in water or solvent and are polymerized in situ. Latex products can remain so, while solid elastomers that are extracted from either water or solvent systems can be solvated with an appropriate organic solvent system. In addition, most solid elastomers exhibit thermal flow characteristics which can make them suitable for hot-melt formulations. And since there are many different rubber polymer families, it stands to reason that there will be many different rubber-based adhesives to identify and describe. Some, however, have limited usage in the industrial and commercial world, and some have specialty applications because of inherent properties. But for the most part, only a few chemical types make up the majority of rubber-based adhesive and sealant applications. The major rubber families are: Polychloroprene, styrene-butadiene, butyl, and acrylonitrile butadiene. Another class is reclaim rubber, which exhibits many of the properties of the original polymer. The remainder of this chapter will concentrate on providing information on the history, chemistry, forms of use, particular characteristics, and applications of these prime product types.

A. Polychloroprene

At one time, this polymer was one of the most commonly used adhesive types made from a rubber, taking over from natural rubber in the 1950s and 1960s. The primary reason for this high usage was a direct result of the rubber's chemical nature. Structurally, polychloroprene is similar to natural rubber, and in fact was originally described as synthetic natural rubber. The difference between the two is that in the repeat monomer unit that becomes the long chain polymer, polychloroprene has a chlorine atom positioned in one of the positions where natural rubber has a hydrogen atom. This chlorine atom provides the advantage of higher polarity for the polymer molecule, which is a great aid in developing adhesion to a diverse group of surfaces.

Polychloroprene was developed almost by accident. Experimenting with a copper chloride catalyst and acetylene gas in the 1920s, one of the trials by Father Julius Nieuwland of the University of Notre Dame yielded a black tarry substance. Eventually, Dr. Nieuwland was able to synthesize a divinylacetylene polymer and reported his results in a paper. Later, working with DuPont scientists after contact was established following the paper's publication, the reaction conditions were controlled and treatment with hydrochloric acid yielded a chloroprene monomer. Polymerization of that monomer produced a rubberlike polymer that was eventually commercialized as DuPrene, later renamed Neoprene. This new polymer exhibited many of the characteristics of natural rubber in processing, and a number of superior properties in use. Higher chemical resistance, better aging, and improved temperature resistance were just a few properties that were promising. However, since polychloroprene was a manufactured product, it was not competitive with an agricultural product in the 1930s. In addition, for most adhesive applications, higher cost aromatic solvents were required, in part, for dissolution as compared to aliphatic solvents typically used for natural rubber. And in many applications, higher solids contents were required to achieve certain viscosities as compared to natural rubber compounds, which also increased overall cost. During World War II, however, there was high demand for a rubber that matched many of the properties of natural rubber. After the war, polychloroprene retained its popularity because of its exceptional performance in contact bond applications.

Polychloroprene comes in two varieties for manufacturing adhesives: solid rubber, and emulsion or latex. Solid rubber was the preferred form for most of the second half of the twentieth century since it was available in a number of grades, all of which could be intermingled for specific characteristics, and could easily be converted into a solvent-based cement. Most solvents were inexpensive before the oil crisis of the late 1970s, which provided for inexpensive adhesives. Drying times could be controlled with mixtures of solvents, which also allowed for quick process times compared to other adhesive systems. Combination with phenolic resins and metallic oxides yielded improved characteristics that made the compound suitable for myriad applications. However, owing to increasingly stringent environmental laws and regulations, solvent-based polychloroprene adhesives have been losing favor in some applications, even though processing and end use performance are usually superior to that of most water-based polychloroprene systems.

1. *Properties*

While there are significant differences between grades of polychloroprene elastomers due to molecular weight differences and crystallinity characteristics, by and large, processing and performance properties may include:

Superior green strength Applying a thin coat of either water-based or solvent-based adhesive onto each of the substrates to be bonded, drying to a tacky-to-the-touch condition, and mating the surfaces with moderate pressure provides excellent contact bond strength. Often this early strength enables immediate processing in the next part of the assembly, or packaging for shipment.

High ultimate strength Although polychloroprene elastomers can be processed as pressure sensitive adhesives, which are typically low strength applications, typical usage is for high strength requirements. On some surfaces, with a reacted phenolic resin as a formula ingredient, a lap shear strength in excess of $70\,\mathrm{kg/cm^2}$ can be achieved.

Wide surface compatibility The high polarity of the base elastomer aids in developing adhesion to virtually all high polarity surfaces. Solvent-based products often develop good adhesion to low polarity surfaces such as polyolefins and other plastic substrates.

Thermoplastic or thermosetting While many contact bond applications require no curing process because an extra strength requirement is not present, in certain formulations polychloroprene will provide ambient cure for improved properties, and can be cured by several different mechanisms for high performance properties. Ambient cure systems are typically one component, while high performance formulations are often two-part systems, or one-component systems cured in elevated temperature conditions.

Resistance to moisture, chemicals, and oils Service conditions and assembly configuration often play a part in total resistance to end use environment, but polychloroprene exhibits excellent performance for most conditions. Constant immersion in any of these materials is not recommended.

Resistance to temperature Depending on the degree of cure, if required, polychloroprenes will typically provide temperature resistance in the $-50^\circ\mathrm{C}$ to $150^\circ\mathrm{C}$ range, with special formulations capable of even wider ranges.

Resistance to aging While compounding for outdoor exposure is recommended to provide superior performance, the presence of the chlorine atom in the molecule helps provide better resistance to aging than most synthetic elastomers.

2. *End Uses*

As previously noted, the primary use for this elastomer has been as solvent-based adhesives and sealants. Solvent-based products are losing market share to water-based polychloroprenes, to other polymer types such as acrylics and polyurethanes, and to hot melt adhesives. However, where the processing facility is able to contain the vapor emissions, a solvent-based adhesive or sealant is preferred because of better wetting of surfaces, faster drying, and higher performance of the cured or dried product. Many rubber bonding applications for hose and belt manufacture, and for rubber membrane roofing, still recommend a solvent-based product. For applications where high strength is not as big a factor, such as foam fabricating, latex compounds are preferred, sometimes using a two-part system with an acid catalyst to speed processing and bond development. Many leather goods markets, such as belts and shoes, prefer polychloroprene contact bond adhesives because of the fast processing cycles. Polychloroprene adhesives are used to manufacture recreational vehicles, kitchen counter tops, office furniture and partitions, truck and trailer bodies, plastic and composite wood bonding, gasket and trim bonding, floor tile mastics, and many other applications. These polymers can be converted into heat and solvent reactivatible films.

B. Butyl Rubber

Building on technologies first developed in Germany in the early 1930s, Robert M. Thomas and William J. Sparks, both employees of Standard Oil (now ExxonMobil Chemical), patented a new synthetic rubber in 1937. Butyl rubber is characterized by a very saturated linear polymer chain, leaving little space between molecules for transmission of air, vapors, moisture, or water. As such, butyl rubber was successfully used during World War II as a substitute for natural rubber in the manufacture of tire inner tubes and curing bladders.

Butyl rubber is a polymerization product of reacting isobutylene with a portion of an isoprene molecule, thus providing a controlled degree of unsaturation in the resulting polymer chain. The lower the percentage of unsaturation, the more thermoplastic the polymer is; the higher the unsaturation, the more opportunity for crosslinking the polymer into an elastic thermoset. (Unsaturation is a term used to describe the density of carbon–carbon double bonds, i.e., reactive sites.) The level of unsaturation can be polymerized into the base polymer for specific properties. For some applications, the polymer can be halogenated to increase molecular polarity and functionality, increasing the ability of the polymer to bond to polar surfaces or provide for curing by alternative mechanisms. In addition, partially or pre-crosslinked grades of butyl rubber are available which exhibit higher modulus than base grades. Butyl rubber can be blended with many other elastomers and polymers to modify its basic properties, or the properties of the other elastomer formulation, and the polymer is compatible with many kinds of fillers and additives.

Early adhesive uses of butyl rubber generally consisted of solvent-based dispersions, or tape and ‘‘rope’’ extrusion of formulated solid rubber. Extensive use was made of butyl rubber’s inherent tackiness in highly saturated grades of the polymer to make pressure sensitive tapes and precoated films. The polymers are also extensively used as major components of hot-melt adhesives, solid rubber sealing tapes, and caulking grades of sealants and mastics, of which most were high solids content solvent-based formulations.

1. *Properties*

The wide variety of grades available provides for an extremely diverse array of properties that can be developed for butyl rubber adhesives and sealants. However, the following general properties apply to varying degrees.

Superior water and moisture resistance The saturated polymer chain resists passage of water molecules through the chain structure.

Superior resistance to air and gas permeability Also a result of the saturated polymer chain.

High initial tack Even without tackifying resin, the inherent tack of certain grades provides for excellent contact bond and pressure sensitive adhesives.

Good chemical resistance While not as good as polychloroprene-based products, butyl polymers have resistance to vegetable and animal oils, and many other chemicals. Most solvent and petroleum products will cause swelling, even in cured products.

Wide substrate range Even though the base polymers are of relatively low polarity, the inherent tackiness and linear molecules make them bond to most surfaces. Some compounds are suitable for bonding to polyolefins and other highly unsaturated polymers. However, bond strength for most pressure sensitive applications tends to be quite low, leading to creep under sustained stress. Even crosslinked polymers are often limited to low strength applications.

High flexibility and impact resistance Low levels of crosslinking and subsequent chain entanglements provide for stretching and stress absorption.

Variable heat resistance A wide range of heat resistance is available, usually dependent on the degree of unsaturation in the base polymer and the type of cure mechanism used, if any.

Superior aging performance With few sites for oxidation to take place, butyl rubber compounds are typically very resistant to ambient aging, which accounts for its high volume use in sealant compounds.

Wide range of choices Because butyl rubber comes in so many grades and polymer variations, many kinds of compounds can be formulated. Different curing mechanisms can be used, high levels of fillers can be used, and products can range from very soft to hard.

2. *End Uses*

While popular for many years as solvent-based pressure sensitive adhesives and sealant grade compounds, butyl rubber products have been losing favor to water-based acrylics in recent years. Adhesion performance of the thermoplastic acrylics is often quite similar, and even though drying time is longer for water based versus solvent based, many uses have moved to the acrylics. There are, however, many areas where butyl rubber compounds excel, particularly where water resistance and low permeability are required. Specialty adhesive tapes for pipe wrap, surgical tapes, electrical tapes, and similar areas still often use a butyl rubber base. High solids content butyl rubber sealants are quite popular for many construction and repair operations. Hot melt butyls, either as a straight formulation or compounded with other polymers, are used for carton closing, insulated window sealing, appliance manufacture, and prefabricated metal buildings. Extruded tapes come in several grades and are extensively used for auto glass repair, mobile home and recreational vehicle manufacture, rubber roof installation, and marine applications.

Self-curing solvent-based butyl rubber adhesives are used in bonding ethylene-propene diene monomer (EPDM) rubber to itself in rubber roof seaming, laminating polyethylene film, and as a flocking adhesive for bonding short fibers to surfaces, as in auto window inner seals. Butyl rubber adhesives are also used for a variety of applications in belt and hose manufacture and repair. Water-based butyl rubber adhesives are not as popular as the solvent-based grades, but often are used in pressure sensitive adhesives for paper and foil laminating, and for packaging and laminating applications for many other substrates.

C. Nitrile Rubber

First made commercially available in Germany in 1936, this elastomer is officially known as acrylonitrile butadiene, and is usually the product of an emulsion polymerization process that combines the two monomers: acrylonitrile and butadiene. However, the polymer can also be made in a solution process, and with a variety of monomers. As a specialty polymer, and even though several commercial brands were available, Buna N (as it was first known) was little used until World War II, when the polymer's unique oil and plasticizer resistance and high heat resistance became very important for transportation products. Nitrile rubber also exhibits exceptional adhesion to metallic surfaces and is compatible with a wide range of additives and compounding ingredients.

Nitrile polymers used for the manufacture of adhesives generally contain 25% or more acrylonitrile, but in the base polymer the acrylonitrile content can vary from 15% to 50%. Increasing the acrylonitrile content improves the oil and plasticizer resistance and increases the polarity of the compound. However, higher levels of acrylonitrile also increase the hardness and modulus of the polymer, reducing the elasticity of the resulting polymer. Nitrile rubber can be produced by a "cold" (5°C) or "hot" (25–50°C) process, with most adhesive polymers produced by the hot process which induces more chain branching. Nitriles can be combined with other monomers in solution polymerization which increases functionality and improves compatibility with other reactive resins like acrylics, epoxies, and polyurethanes.

For many years following World War II, the primary use for nitrile rubber adhesives was as solvent dispersed compounds, often modified with phenolic resin to increase heat resistance and improve strength properties. Water-based nitrile adhesives have been growing in recent years, but do not match the film strength of the solvent-based compounds. Liquid nitriles, particularly carboxy terminated types, have become a popular reactive resin for flexibilizing rigid polymer systems such as epoxies. Nitrile adhesive coated surfaces can be heat or solvent reactivated within a specified time frame, or before cure occurs. Adhesives can be converted to reinforced or nonreinforced films, usually by casting a solvent-based solution onto release paper, for die cutting to part configuration. After part placement, adhesives can be reactivated and cured.

1. *Properties*

Once again, the wide variety of grades and copolymers available in this polymer make generalizations somewhat difficult, except for the following select properties that are inherent to the polymer.

Superior resistance to oils Nitrile rubber has the highest resistance of any of the generally used elastomers to grease, oil, plasticizers, and most organic solvents, both aliphatic and aromatic. There is limited resistance to some polar solvents, and polymers are generally soluble in ketones.

Excellent high temperature resistance When properly cured at elevated temperatures, nitrile adhesives can withstand temperatures above 150°C, with some compounds capable of limited exposure to temperatures above 200°C.

High strength Lap shear can exceed 200 $\mathrm{kg/cm^2}$ on certain substrates, such as some metals, particularly if combined with other reactive resins, such as phenolic or epoxy.

Good aging Generally requires the addition of antioxidants and ultraviolet (UV) absorbers if exposed for a long term to weathering, but the elastomer has good retention of properties in normal use.

Low building tack Even though used as a contact adhesive for many applications, the adhesive must be freshened with solvent before mating to assure good wet-out; otherwise high contact pressure or the addition of tackifying resins to the formula is required.

Curable Nitrile rubbers can be cured with sulfur or isocyanates, but some formulations exhibit improved properties on elevated temperature cycling, even without curatives. For consistent high performance, the polymer must be cured at elevated temperatures.

Chemical and moisture resistance Like most elastomers, there is a high degree of moisture resistance, and chemical resistance is excellent.

Good processing characteristics Adhesives can be supplied as contact bonding types—either in water- or solvent-based systems—hot-melt, pressure sensitive, or as reactive systems—either 100% solids content or solvent based.

Adhesion properties Exhibits strong bonds to most highly polar surfaces such as metals, but does not bond well to inert surfaces such as polyolefins.

2. *End Uses*

General purpose solvent-based nitrile adhesives are frequently used when resistance to oils and plasticizers is required. Gaskets made from cork, rubber, metal, fiber, and composite blends are often bonded in place with nitrile adhesive. Bonding highly plasticized PVC films to other surfaces and to themselves often requires the superior plasticizer resistance of nitriles, although staining may be a problem with certain combinations of plasticizer and elastomer additives. Nitrile phenolic adhesives have been used for many years for automotive brake and clutch assemblies, for belt and hose manufacture, plastic component assembly, and shoe sole attachment for certain types of outsole materials to leather. In addition, these adhesives have been used for bonding printed circuit wiring boards. Water-based versions are used for laminating vinyl films, and nitrile rubber to fabric and metallic foils. Cast films have been used for bonding honeycomb structures for aircraft assembly, but these films work well for almost any metallic structure.

D. Styrene-Butadiene Rubber

Buna S (as it was first known) was developed in the late 1930s in Germany as a synthetic natural rubber. When the United States needed a synthetic polymer as a replacement for natural rubber as part of the war effort in the early 1940s, chemists at several rubber companies were familiar with that technology and tried to duplicate it. Attempts at developing an emulsion polymerization process failed until Waldo Semon of BF Goodrich consulted with Victor Mills of Procter & Gamble. Ivory soap (99 and 44/100ths pure!) was being used as an emulsifier for the process and it was determined that the small amount of perfume in the soap (part of the other 56/100ths) was a catalyst contaminant. Once the perfume was removed from the soap, the polymerization process was successfully developed, and styrene-butadiene rubber (SBR), which was then called GRS (General-purpose Rubber — Styrene), became the fastest growing of all synthetic rubbers because of its similarity to natural rubber in processing and performance after cure. More than 50 synthetic rubber plants were built by industry during the war period, under the auspices of the federal government, with the most volume allocated to SBR.

While quite similar to natural rubber, there were differences which prevented really high growth for this copolymer after the war. The molecular weight of SBR from those original processes was only about 100,000 compared to over 1 million for natural rubber. Further, differences in tensile strength, cohesive strength, elongation, hot tear strength, aging, and other properties existed which permitted natural rubber to regain most of its earlier market share. The low cost of SBR, however, made it an excellent blending elastomer. Modifications to the base polymers and continued work with compounding, processing and curing conditions improved the performance of these copolymers. New polymerization processes by the 1950s began to improve many of the original polymer properties in comparison to natural rubber.

Standard SBR materials are made from an emulsion polymerization process and are available in more than 100 grades, but only a few are used as a base for adhesives. The two basic processes for producing these many grades can be either a "hot" or "cold" process, depending on the polymerization temperature, with hot polymerization being the preferred process. Hot polymerized SBR typically yields a lower molecular weight polymer, but with a wider molecular weight distribution which provides for a more balanced polymer. The styrene content can also be varied to enhance certain properties. Emulsion process polymers are often called "random" SBR because there is no control of the attachment sites for the styrene monomer when polymerized. These polymers are often blended with other polymers to lower cost and increase compatibility with various resins, plasticizers, and fillers.

In the mid-1960s, a new form of SBR was introduced called a "block" copolymer. Produced by a solution polymerization process, this material exhibited an ordered molecular structure with the styrene monomer located at the ends of the butadiene monomer chain. In addition, other monomers such as isoprene, ethylene, butylene, and others, could be added to the polymer chain, which further modified basic properties. These materials possess a continuous rubber phase for resilience and toughness, and a discontinuous plastic phase for solubility and thermoplasticity. A variety of different grades are also available for this type of SBR, with differences in molecular weight, differences in the types of monomers used, differences in structural configuration, and differences in the ratio of endblock to midblock. Both emulsion and solution polymerized grades of SBR are available as solvent-based and water-based adhesives and sealants. Block copolymers are extensively used for hot melt formulations and both water-based and solvent-based pressure sensitive adhesive applications. Today, SBR elastomers are the most popular elastomers used for the manufacture of adhesives and sealants.

1. *Properties*

The differences between emulsion and solution polymerized SBRs are significant, although they do share the following similarities.

Superior water and moisture resistance While not recommended for immersion applications, and not as resistant as butyl compounds, these polymers are not affected by most aqueous chemicals.

Ease of dispersion Both emulsion and solution grade polymers are easily dispersed in aliphatic and aromatic solvents and solvent blends, and provide low viscosity, high solids content formulations, with low mixing costs. However, the opposite side of this feature is a poor resistance to organic solvents and oils, even when vulcanized.

Good heat resistance Emulsion grade polymers are equal to or better than natural rubber, while block copolymers are superior to natural rubber and emulsion grade SBRs. Block copolymers also are often superior for resistance to cold temperatures.

Low building tack An inherent characteristic of SBR elastomers, which normally requires the addition of tackifying resins, low molecular weight polymers, or plasticizers, or master batch processing.

Excellent substrate compatibility Properly compounded adhesives, sealants, and pressure sensitive materials will adhere to almost any surface. Block copolymers have exhibited superior pressure sensitive adhesion to polyolefin and other low energy surfaces.

Fair to good aging Cured products often will outperform natural rubber products, but uncured products made from emulsion polymers can degrade rather quickly if not compounded for UV, ozone, and oxygen resistance. Block copolymers are typically better in the uncured state than standard SBR, but still require protectant additives for extended exposure conditions.

Good processing characteristics Adhesives are often used as a contact bond type—either in water- or solvent-based systems—as a hot melt, or as a pressure sensitive, in curing systems, or as heat or solvent reactivatible systems. Block copolymers provide superior pressure sensitive adhesives, but can also be compounded for contact bond adhesive or sealant applications.

Curability Typically, these are sulfur cured at elevated temperatures, but can be cured by other mechanisms for higher heat resistance and better strength and aging properties.

Low cost Emulsion polymers are low cost compared to most other synthetic elastomers. Also they can be compounded with a variety of low cost fillers for sealant and low bond strength applications.

2. *End Uses*

The major use for block copolymers is in hot melt and solvent-based pressure sensitive adhesives. These pressure sensitive adhesives are most often used for tapes, and to a lesser degree, for labels. Solids contents of the solvent-based pressure sensitive adhesives are typically in the 40–60% range and are applied by a variety of converting processes, including roll coating, knife coating, and other similar processes. Block copolymers compounded as pressure sensitive adhesives are particularly effective on polyolefin foams, films, and laminates. These products are used in construction applications, automotive padding and insulation, orthopedic devices, packaging, and bookbinding.

Emulsion polymers are typically used in solvent- and water-based formulations, in both curing and noncuring applications. Many applications are similar to those listed for natural rubber applications, being used for bonding paper, fabric, wood, plastic, and other surfaces, often in spray grade formulations. Sulfur curable cements are used in laminating layers of fabric and rubber together for hose, belting, and tire fabrication. Carpets use a major quantity of SBR latex as a binder for backing materials. Emulsions also find extensive use as a binder for nonwoven goods, and in diapers and other personal disposables.

The construction industry uses several kinds of SBR polymers, in both solvent- and water-based compounds. Ceramic and tile bonding for floors and walls is one area, while solvent-based products for subfloor attachment to joists and panels to studs in building construction is a major area.

E. Other Elastomers

As was noted earlier, virtually any elastomeric material can be, and probably is currently, made into an adhesive or sealant. All elastomers are soluble in one or more organic solvents which allows the production of a solvent-based adhesive. Many elastomers are polymerized in an emulsion process, which yields a latex. And a number of elastomers have a low enough glass transition temperature to permit use as a hot-melt polymer, or as one ingredient in a hot melt formulation. Summary statements describing a few of these other polymers follow, but without the detail provided for the primary elastomers.

1. *Reclaim Rubber*

Even before World War II, reclaim rubber was a popular material for many adhesive and sealant applications. At that time, virtually all rubber was natural rubber, which allowed material that had been de-vulcanized to be processed simultaneously with and to extend the new raw materials. Reclaim rubber has the advantage of already containing a selection of oils, fillers, resins, antioxidants, and antiozonants in the original formulation. When delivered in bale or sheeted form, the reclaim rubber will mix and process much the same as original forms of natural rubber. Since the war, however, and particularly since 1970, reclaim rubber has been losing ground in favor of other polymers. Several factors are contributing to this decline, the first of which is polymer purity. As mentioned, when all rubber was natural rubber, it was easy to find different grades of the same polymer for certain applications and use the reclaim in similar operations. The grades included belting regrind, tire regrind, even baby bottle nipple regrind, among others. Today, however, polymers of all different elastomeric bases enter the processing stream and it is extremely difficult, if not impossible, to separate different synthetic polymers in a blend. Coupled with this is the fact that different manufacturers will use different polymer blends for identical applications.

A second major factor contributing to the decline of reclaim rubber adhesives is the fact that factories processing cured rubber materials for reclaim emit strong odors, particularly sulfurous odors. Many reclaim factories discontinued operations as air emissions rules and regulations became more stringent rather than try to contain the odors with different air control devices, which were both expensive to purchase and expensive to operate. A third major factor contributing to the decline of reclaim rubber is the fact that the highest usage of product made for adhesives and sealants was as a solvent-based product. After passage in 1990 of the Clean Air Act, solvent-based products started to decline in total volume for general industrial applications. This decline was accelerated by the difficulty in obtaining suitable reclaim rubber for specific formulations, since many adhesive formulations get “locked” into specific materials from specific sources. The final factor contributing to the decline in use of reclaim rubber adhesives is that most compounds today are black in color (except for baby bottle nipple regrind), whereas in the past a variety of colors were available.

Notwithstanding the factors just mentioned, reclaim rubber still remains a part of the elastomeric adhesive supply chain. Adhesives and sealants made from reclaim rubber are inexpensive, compared to a formulation prepared from new raw materials. Reclaim polymers are very compatible with other elastomers, and often improve overall properties when added to certain formulations. Reclaim elastomers can be processed and cured the same as new polymer, but because of the considerable processing used to produce reclaim rubber, when dispersed in solvents, often provide superior spray and substrate wetting properties. Also of value is that the typical reclaim rubber has improved heat resistance. Reclaim rubber is also very compatible with asphalt; blends of these materials are finding extensive use in construction applications. A new and growing application for reclaim polymers is as an ingredient in high performance polymer mixtures such as epoxies and acrylics. The addition of limited amounts of powdered reclaim rubber serves as a "toughening" polymer, providing a degree of elasticity, resilience, and compression strength to rigid polymers.

In addition to widespread use as a blend in asphalt/rubber sealants for roofing and other construction applications, reclaim rubber adhesives have been used as an insulation adhesive, as a pipe wrap adhesive, and as an ingredient in some pressure sensitive adhesives. Of interest is the fact that virtually every telephone installation in the United States before 1985 that required a cable splice used a reclaim rubber adhesive.

2. *Fluoropolymers*

A small, but ultimately very important, part of the elastomer-based adhesive and sealant market is devoted to fluoropolymers. Most often processed as a solvent-based fluorocarbon rubber mixture, these products are often used as sealants for applications requiring a high degree of chemical resistance, particularly where temperatures may rise above 210°C. These polymers exhibit excellent retention of elastomeric and mechanical properties at elevated temperatures, with some products capable of intermittent exposure to temperatures above 315°C. Another application is as a laminating adhesive for polyimide films for electronic components and flexible circuitry. Fluoropolymer sealants and adhesives are also used for bonding gaskets and seals in high performance aircraft and aerospace vehicles, and in a limited way in high performance automotive applications. Some forms of these products also are listed as fluorosilicones. Some curing grades of fluoropolymers are used as a splice cement in the fabrication of rubber fuel cells, in bonding and sealing tank linings, and in other rubber assemblies made of different grades of fluoropolymer.

3. *Polyisoprene*

A true synthetic natural rubber was introduced in the mid-1960s with the exact same chemical structure as latex tapped from a tree. The difference is that natural rubber comes with a variety of other ingredients in the latex that can both add and detract from performance, while polyisoprene is considered relatively "pure." In addition, there are some differences in molecular weight distribution that impact performance. Available in both latex and solid forms, this elastomer can be directly substituted for natural rubber in many applications. Adhesives which are not cured tend to have higher creep values than natural rubber, but also exhibit lower tack and green strength properties. Vulcanized adhesive products perform equal to cured natural rubber adhesive products.

4. *Ethylene-Propylene Diene Monomer (EPDM)*

EPDM was also introduced in the 1960s. This is a relatively saturated polymer structure with a diene, or double bond carbon monomer, added to provide functionality to the polymer chain. EPDM performs in many respects like butyl rubber in that it has excellent resistance to ozone and oxygen degradation, and has superior UV and weathering resistance. A major difference with butyl polymers is a lower resistance to moisture vapor transmission. The most common use of EPDM is as a sealant for single ply rubber roofing systems, which are themselves made of EPDM rubber. EPDM is available in both emulsion and solid forms, both of which can be easily blended with other elastomers in a formulation. There is also a liquid polymer available for blending and mixing into formulations.

IV. MARKET VALUATION

There are numerous market studies of the adhesive and sealant industry. Some even evaluate subsections of the marketplace, covering, for example, only pressure sensitive products and/or applications, only structural or high performance materials, major end use markets such as packaging or construction, and the raw materials used in making adhesives and sealants. For the most part, none of the studies agree with each other, either in terms of the size of the market, or in the value of individual segments or individual materials. The reasons for this disagreement are typically related to the conduct and parameters of each study, since each research group tends to focus their study a certain way or on a certain segment. In addition, some market segments may even be unknown to some researchers because of so few participants in a tightly defined end user niche. As a consequence, each market study of adhesives and sealants must be gauged on its own merits rather than compared with other studies.

Even so, it is valuable to understand the relative position of individual products in the overall structure of the adhesive and sealant market. Table 1 below provides a good breakdown of elastomeric products in comparison with other major product types. Only the market value of these products is shown, even though most studies, including the one referenced here, include volume data as well. More complete analysis is available from Impact Marketing Consultants, Manchester Center, VT, publisher of the *2000–2002 Rauch Guide to the US Adhesives & Sealants Industry* (see Chap. 2 on Information Resources).

V. CONCLUSIONS

Elastomeric adhesives are formulated from one or more of the many synthetic rubber polymers (or natural rubber) to provide highly flexible, resilient bonds to a variety of substrates. These compounds are based on several basic polymer types and are available in a wide selection of forms for processing by a variety of assembly methods. The most popular synthetic polymer types are: Polychloroprene, styrene-butadiene rubber, nitrile rubber, and butyl rubber. Generally, elastomeric adhesives are characterized by being: Versatile, economical to use, good for quick assembly, available in many standard formulations, easily tailored to process and product requirements, of high peel strength, and thermoplastic or thermosetting.

Table 1 U.S. Consumption of Adhesives and Sealants in 1998

Chemical type	$ (Million)
Elastomers:	
SBR and block copolymers	581
Polychloroprene	150
Butyl rubber	220
Nitrile rubber	77
Reclaim rubber	44
Other elastomerics	30
Total elastomerics	1102
Natural rubber	350
Epoxy	629
Silicone	860
Phenolic	1650
Polyolefins, including ethylene vinyl acetate (EVA) and vinyl acetate ethylene (VAE)	1290
Polyurethane	960
Acrylics	709
Starch and Dextrin	730
Poly(vinyl acetate)	662
All other types	2908
Total market	11,850

Source: Impact Marketing Consultants.
Given economic conditions since 1998, it is likely that the numbers in this table are relatively consistent with the market value of adhesives in 2002.

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Polysulfide Sealants and Adhesives

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I. INTRODUCTION

High-sulfur-containing polymers known as polysulfides were introduced by Thiokol in 1928. The solid polysulfide polymers contain 37 to 82% bound sulfur, but the more important liquid polymers containing about 37% sulfur find application in high-performance sealants and adhesives. These conventional polysulfide polymers are now available from Morton International (United States), Toray Thiokol (Japan), and Chemiewerke (Germany). During the 1960s and 1970s, new mercaptan-terminated polymers were introduced that have varying polymer backbones. The properties, especially the chemical resistance of the polymers, depend on their backbone structures.

Polysulfide sealants account for about 43 million pounds of the total 500 million pounds of the U.S. sealant market. Major fields of polysulfide sealants are aircraft, automotive, construction, and marine. End uses of polysulfides are very diversified: for example, sealing integral fuel tanks, sealing pressurized cabins, potting electrical connectors, sealing bolted steel tanks, glazing of windshields, glazing of rear automotive lights, recreational vehicles, vibration damping in trailers, gas tank liners, curtain walls, building exterior joints, highway joints, airfields, insulated glass, swimming pools, flight decks, decks of pleasure craft, solid-rocket fuel binder, relief maps, printing rolls, dental impressions, hoses, and gaskets.

In this chapter we describe the chemistry and technology of polysulfide polymers; processing and manufacture of polysulfide sealants and adhesives, including their formulations; curing reactions; and characterization and testing. Adhesion considerations are also discussed briefly.

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II. CHEMISTRY OF POLYSULFIDE POLYMERS

A. Preparation of Conventional Polysulfide Polymers

Preparation of liquid polysulfide polymers has been discussed extensively [1–4]. The polymer is synthesized by reacting aqueous sodium polysulfide with bis(2-chloroethyl) formal. Cross-linking is introduced by including a small amount of 1,2,3-tri-chloropropane. The reactions of polymerization done at 100°C produce a mixture of chain lengths in which sulfur is present as $-C-S_2-C-$ or $-C-S_3-C-$. Dihalide monomer is added to aqueous polysulfide solution containing bischlorobutyl formal and bis-4-chlorobutyl ether is used in small amounts where improvement in low-temperature performance is required. Specific emulsifying and nucleating agents (alkyl naphthalene sulfonate and magnesium hydroxide sol) are used in the polymerization. The polymerization reaction is as follows:

$$n\mathrm{ClCH_2CH_2OCH_2OCH_2CH_2Cl} \quad + \quad n\mathrm{Na_2S_{2.25}} \longrightarrow$$
$$\left[\mathrm{CH_2CH_2OCH_2OCH_2CH_2S_{2.25}}\right]_n \quad + \quad 2n\mathrm{NaCl}$$

The high-molecular-weight solid polysulfide polymer is reduced by sodium sulfite, resulting in splitting of the polymer into segments that are simultaneously terminated by mercaptan groups as follows:

$$\mathrm{RSSH + NaSH + NaHSO_3 \longrightarrow 2RSH + Na_2S_2O_3}$$

The concentration of the splitting salts regulates the molecular weight from 1000 to 8000. The extent of cross-linking depends on the mole percent of trichloropropane, a cross-linking agent used in the initial reactions, usually in the range 0.05 to 2.0 mol%. The amount of cross-linking agent regulates modulus and elongation: a decrease gives the lower modulus and higher elongation desirable in applications involving greater movement.

The typical structure of a liquid polysuifide (e.g., Morton's LP-32) is

$$\mathrm{HS}\left[\mathrm{CH_2CH_2OCH_2OCH_2CH_2SS}\right]_{2-3}\mathrm{CH_2CH_2OCH_2OCH_2SH}$$

Use of a mixed dihalide monomer feed will produce random copolymers. During copolymerization, interchange takes place, resulting in randomization. Therefore, block copolymers cannot be prepared by stepwise addition of dihalide monomers. To prepare block copolymers, homopolymers should be made, blended in the desired proportion, and then the blend co-cured by a conventional technique. When cured by mixing an oxidizing agent, water is split off, with the hydrogen coming from the mercaptan groups of two polymer molecules and the oxygen being supplied by the oxidizing curative. The molecules are joined at the sulfurs.

B. Modified Polysulfide

Recent advances have resulted in chemical modification of conventional liquid polysulfide polymers in a one-step reaction with dithiol, as follows:

$$\underset{\text{Liquid polysulfide polymer}}{\mathrm{HS}\left[\mathrm{CH_2CH_2OCH_2OCH_2CH_2{-}S{-}S}\right]_n\mathrm{CH_2CH_2OCH_2OCH_2CH_2SH}} \quad + \quad \underset{\text{Dithiol}}{\mathrm{HSRSH}}$$

$$\Big\downarrow \text{catalyst}$$

$$HS\left[CH_2CH_2OCH_2OCH_2CH_2\text{—}S\text{—}S\right]_{n-m}CH_2CH_2OCH_2OCH_2CH_2SH$$

Segmented lowermolecular-weight liquid polysulfide

$$HS\left[CH_2CH_2OCH_2OCH_2CH_2-S-S\right]_{m}CH_2CH_2OCH_2OCH_2CH_2-SRSH$$

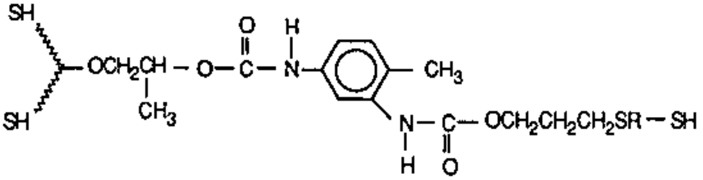
Dithiol-modified liquid polysulfide polymer

These new dithiol-modified liquid polysulfide polymers have lower viscosity and improved compatibility with formulating ingredients (e.g., plasticizers, pigments, and fillers). Thus dithiol-modified liquid polysulfide polymers give more latitude in the formulation of high-performance sealants, adhesives, and coatings. The volatile organic content (VOC) of such products is lower than that of products formulated by conventional liquid polysulfide polymers.

C. Other Mercaptan-Terminated Polymers

In the 1960s Diamond Alkali marketed several polymers having a polyether backbone terminated with mercaptan groups [5,6]. Polymers of poly(oxyalkalene)polyol backbone can be esterified with thio-substituted organic acids to produce terminal mercaptan end groups. These polymers were cured similarly to conventional polysulfides, but gave generally poorer properties and were therefore withdrawn from the market.

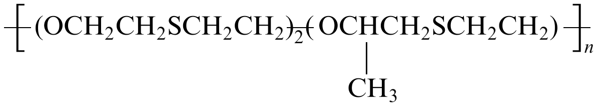
In the mid-1970s, polysulfide polymer chemistry was advanced when Products Research and Chemical Corporation introduced a polyoxypropylene urethane backbone with mercaptan terminal groups [7]. Molecular weight regulation and minimization of side reactions are important features. The backbone is significantly different from that of conventional polysulfide polymers, yet the curing chemistry is the same and the cured product is a polysulfide rubber. A typical structure of this type of resin is shown below.



Mercaptan-terminated polyoxyproplene urethane

D. Polythioether Polymers

This polymer does not contain S–S or forrmal linkages, and these are the weak links in conventional polysulfides. The polythioether polymer has excellent resistance to fuel and organic solvents and has better thermal stability than that of conventional polysulfides. Polythioethers can be terminated with mercaptan, hydroxyl, silyl, and nonreactive end groups. The curing chemistry can thus be varied based on the terminal groups. A typical structure of this class of polymer is



$$\left[(OCH_2CH_2SCH_2CH_2)_2(O\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2SCH_2CH_2)\right]_n$$

polythioether

III. PROPERTIES OF POLYSULFIDE POLYMERS

Liquid polysulfide polymers are available in a series of viscosities and cross-link densities. In general, polymers in the range 400 to 500 P are used in sealants and adhesives, while lower-viscosity polymers are used for coatings and casting compounds. The tensile properties of unfilled polysulfide polymers are poor but are improved by suitable reinforcement with pigments and fillers. Both the molecular weight of the liquid polysulfide polymer and oxidative curing influence the physical properties. Higher tensile strength is obtained with higher-molecular-weight materials.

Cured liquid polysulfide compositions have excellent resistance to many oils and solvents (e.g., hydrocarbons, esters, ketones, dilute acids and alkalis). Systems must be properly formulated and cured to obtain maximum solvent resistance. Swelling tests on cured, filled polysulfides have been reported by Usmani et al. by measuring weight gain versus immersion time [8]. With jet reference fuel (JFR), an equilibrium was quickly reached. During early immersion in water, the weight gain was linear with time. Later, a square-root weight gain versus immersion time was found to exist.

The glass transition temperature (T_g) of polysulfides depends on the hydrocarbon moiety and the length of the polysulfide chain. The amount of cross-linking monomer is small, and therefore it does not influence T_g. Generally, the greater the hydrocarbon content, the lower the T_g. Higher-ranking polysulfides have higher T_g. The thermal stability of polysulfide polymers depends on the polymer backbone and the curative used to vulcanize the polymer. Commercially available polysulfides have an ethyl formal disulfide backbone, and this regulates the upper temperature limits. In an acid-catalyzed hydrolytic attack, formaldehyde is released, which in turn reduces the disulfide bond to mercaptan. The formic acid so generated catalyzes hydrolysis of the formal group. The terminal mercaptan group can react with a hydroxyl group to give a monosulfide bond. The degradation results in weight loss and loss of flexibility due to the monosulfide structure formation. Disulfide and formal groups provide a flexibilizing effect due to free rotation. Calcium oxide can neutralize formic acid and absorb water and is therefore an effective stabilizer. Practical cure rates cannot be achieved in anhydrous formulations by metal dioxide curing agents. Thermal instability can also arise when the mercaptan group reacts with the metal oxide. Sulfur mitigates formation of the mercaptide groups. Polysulfide sealants cured using manganese dioxide and chromate salts provide continuous service at 250°F.

Tobolsky has studied extensively the viscoelastic properties of polysulfide polymers [9]. Polysulfide polymers have the unique ability to relieve internal stress or stress between mercaptan and disulfide linkages. The stress decay of cross-linked polysulfide elastomer follows the equation

$$F(t) = F(0) + e^{-t/T}$$

where $F(t)$ is the final stress, $F(0)$ the initial stress, t the time, and T the relaxation time. The relaxation times (in hours) for polysulfide polymers at 80°C for some curing agents are 0.68 for lead oxide at 7.3 parts by weight of resin (phr), 32 for manganese dioxide at 18.9 phr, and 200 for 2,4-toluene diisocyanate plus *N*-methyl-2-pyrolidone at 7.0 phr. The ability of polysulfide polymers to relieve stress is extremely valuable in maintaining adhesion in joints subjected to joint movement.

IV. COMPOUNDING, PROCESSING, AND MANUFACTURE OF POLYSULFIDE SEALANTS

The polysulfide sealant must be specifically formulated to meet the desired requirements and to obtain optimum properties. Pot life, working properties, and sealant properties should be properly adjusted. Suitable fillers should be dispersed and suitable additives should be incorporated into the formulation. Curing agent, curing modifier, filler, plasticizer, and adhesion additive are discussed briefly below.

Mercaptan-terminated liquid polysulfide polymers are polymerized to rubbery solids by oxidizing agents (e.g., lead dioxide, activated manganese dioxide, calcium peroxide, cumene hydroperoxide, alkaline dichromates, and *p*-quinonedioxime). The curing process involves the oxidation of the terminal mercaptan groups in the polysulfide polymers to form the corresponding disulfide.

$$M^{n+} + H\left[SCH_2CH_2OCH_2OCH_2CH_2S\right]_n S{-}\longrightarrow$$

$$M^{(n-2)+} + \left[SCH_2CH_2OCH_2OCH_2CH_2S\right]_m$$

The process can be written simply as

$$M^{n+}2RSH \longrightarrow M^{(n-2)} + RSSR + 2H^+$$

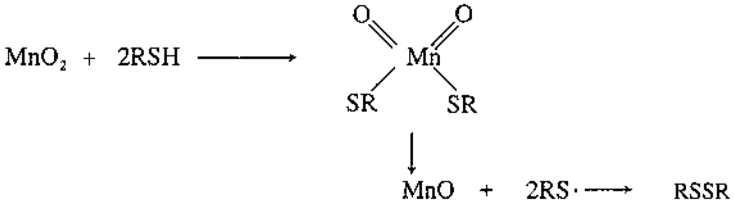
and it involves the net transfer of two electrons per molecule of disulfide. Dichromate oxidation of mercaptans in an aqueous medium may proceed via the following pathway:

$$Cr^{VI} + RSH \rightleftharpoons RSCr^{VI}$$

$$RSCr^{VI} + RSH \longrightarrow Cr^{VI} + RSSR$$

$$RSCr^{VI} \longrightarrow Cr^{VI} + RS\cdot$$

Mercaptan oxidation can proceed through coordination of the mercaptan to manganese dioxide, with the manganite ion providing a base for deprotonation of the mercaptan.



In general, the pH of the system governs the curing rate. Acidic materials retard, whereas alkaline materials accelerate the cure. Thus examples of retarders are stearic acid and metallic stearates. Typical accelerators are amines, inorganic bases, water, dinitrobenzene, and sulfur.

Fillers increase the strength, impart needed rheological properties, and reduce the cost of sealants. Tensile properties are increased significantly, depending on the type of filler, its particle size, and the type of cure. Improper filler selection can ruin the performance of a polysulfide sealant. Calcium carbonates (wet or dry ground limestone, precipitated), carbon blacks (furnace, thermal), calcined clays, silica and silicate fillers, and rutile titanium dioxide are typical fillers used in polysulfide sealants. Generally, combinations of fillers are used in formulation. Plasticizers improve the working properties while

Table 1 Polysulfide Sealant Formulations (wt%)

	Sealant				
Ingredients	One-part	Building	Insulating glass	Aircraft	Casting compound
Polysulfide polymer	20	35	30	65	35
Fillers	50	40	50	25	35
Plasticizers	25	20	15	5	27
Adhesion additives	2	2	2	2	—
Curing agents	3	3	3	3	3

Source: Ref. 10.

Table 2 Chemical Composition of a Typical Aircraft Sealant

Ingredient	Function(s)	Percent
Base component		
Calcium carbonate	Filler, reinforcer	26.15
Titanium dioxide	Filler, opacifier	3.10
Liquid polysulfide polymer	Vehicle	58.50
Volatile diluent	Viscosity adjuster	2.25
Accelerator component		
Manganese dioxide	Curing agent	5.53
Processing oil	Modulus adjuster	3.95
Diluent	Viscosity adjuster	0.51

Source: Ref. 11.

lowering the modulus of the sealant. The plasticizer must be compatible with the cured sealant, should have low volatility, and must be safe. Polymeric and esteric types are commonly used plasticizers.

Sealant adhesion is improved by the incorporation of additives. Typical phenolic resin additives are Methylon AP-108, Durez 16674, Bakelite BRL 2741, and Resinox 468. Epoxies are also good adhesion promoters. Silanes (e.g., A-187 and A-189) are known to increase adhesion. Table 1 lists five types of sealant formulations suggested by Panek that are useful in several end applications [10]. Generally, the integral fuel tank polysulfide sealant consists of two parts: 9 parts by weight of sealant base components mixed with 1 part by weight of accelerator. A typical composition is shown in Table 2.

Most sealants, especially those used in building, applications, contain adhesion additives. Occasionally, to obtain good bonding, primers are used. For metals, a dilute solution of silanes in organic solvents has been used. A film-forming primer is required for porous surfaces. Masonary primers generally contain a chlorinated rubber or a modified phenolic resin either alone or in combination with an additional plasticizer. Thin layers of silanes give good polysulfide adhesion to metals, glass, and ceramic substrates.

Production of polysulfide sealant basically involves mixing and dispersion. Therfore, the equipment used in coating and ink manufacture is applicable to sealant manufacture. Viscosities of up to 60,000 P are common in polysulfide sealant, and therefore heavy equipment is generally used in its manufacture. Typical useful equipment includes sigma blade mixers, kneader–extruders, and high-speed dispersators. A three-roll paint mill gives excellent processing. Transferring and packaging of sealants requires heavy-duty displacement pumps.

V. POLYSULFIDE SEALANT CHARACTERIZATION AND TESTING

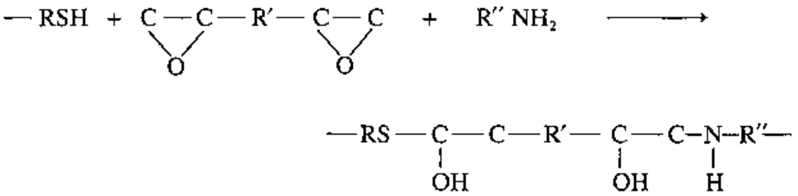
Typical examples of physical, rheological, and mechanical characterization of sealants include specific gravity, percent solid, viscosity, flow, application time, working life, tack-free time, standard curing rate, liquid-immersed curing rate, resistance to rupture, low-temperature flexibility, peel strength, resistance to solvents, tensile strength, elongation modulus, chalking, accelerated storage stability, and hydrolytic stability. Usmani has proposed the use of parallel-plate rheometry (PPR) and dynamic mechanical analysis in the characterization and curing of polysulfide sealants [11–13].

Mechanical and physical quality control tests on polysulfide sealants can produce erroneous and misleading results, especially in predicting long-term performance. Problems such as poor adhesion, inadequate cure, and short working life can frequently occur, resulting in tedious and costly repair.

The composition of polysulfide sealants can be determined by centrifuging thinned polysulfide sealants and resolving them into components. Both quantitative and qualitative analysis can be performed [3,8]. The filler fraction can be analyzed by x-ray analysis and scanning electron microscopy (SEM). Nuclear magnetic resonance spectroscopy and gel permeation chromatography can be used for vehicle analysis. Mazurek and Silva have described a SEM method of analysis for cured polysulfide sealants [14]. Paul has studied the effects of environment on the performance of polysuifide sealants [15]. Numerous data can be obtained by monitoring the effects of various environmental conditions. Understanding chemical processes will assist in improving properties, however.

VI. POLYSULFIDE/EPOXY ADHESIVES

Fettes and Gannon were the first to report reactions of liquid polysulfide polymers with epoxy resins [16]. In these adhesives, the epoxy resin is the major component. The polymer LP-3 in which $n = 8$ has been used most extensively. This polymer has a molecular weight of about 1000 with viscosity in the range 7 to 12 P. The epoxy resins most widely used in adhesive formulations have viscosities the range 80 to 200 P with an epoxy equivalent of 175 to 210. Typical resins are Epon 820 and 828 (Shell), ERL-3794 (Union Carbide), and Araldite 6020 (CIBA). The epoxy–polysulfide reaction is prompted by organic amines (e.g. diethylenetriamine and benzyldimethylamine). The general reaction of a polysulfide polymer, epoxy resin, and amine hardner is



These adhesives are used in the construction, electrical, and transportation industries because of flexibility, adhesion to many substrates, and chemical resistance. They find

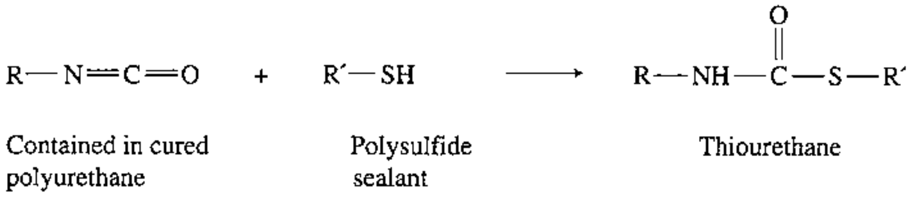
Table 3 Liquid Polysulfide–Epoxy Concrete Adhesive Formulations

Parts by weight	Formulation 1	Formulation 2
Part I		
Thiokol LP-3	100	100
Silica (HDS-100)	80	—
Hydrite 121	—	140
EH 330	20	20
Toluene	—	65
Part II		
Epon 820	200	200
Hydrite 121	—	105
Toluene	—	5
Working and curing properties		
Brush life (h)	0.2	1.4
Trowel life (h)	0.25	—
Setting time for 0.25 mm (h)	0.8	3.5
Tack-free time for 0.25 mm (h)	5.0	—
Cure time for 0.25 mm (h)	—	24
Ratio of part I to part II	1:1 (wt)	1:1 (vol)

application as adhesives for steel, aluminium, ceramics, wood, and glass; for concrete crack repair and patch repair; as a grouting compound; and as an automotive body solder. Fillers (e.g., calcium carbonate, graphite, milled glass fibers, silica, and talc) can be added to polysulfide–epoxy adhesives to extend pot life, reduce exotherm, and increase rigidity and impact strength. Two formulations of liquid polysulfide–epoxy concrete adhesives are shown in Table 3.

VII. ADHESION CONSIDERATIONS

Interfacial aspects and adhesion of polysulfides have been studied extensively and reported by us [3,17]. The epoxy-modified polysulfide has improved adhesion due to chemical reactions that increase electronic attraction forces. Water has been found to be the most potent debonding agent in cured polysulfides. Formation of thiourethane is responsible for excellent adhesion of polysulfide onto polyurethane coatings.



$$R{-}N{=}C{=}O \quad + \quad R'{-}SH \longrightarrow R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}S{-}R'$$

Titanates used as primers interact with polysulfide to produce a tough layer of Ti–S, resulting in enhanced adhesion [17]. We have employed SEM extensively to study polysulfide debonding and events occurring at the interface and have found it to be a very useful tool.

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Phenolic Resin Adhesives

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I. INTRODUCTION

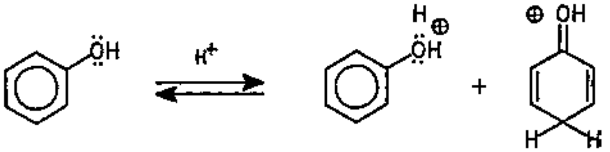
Phenolic resins are the polycondensation products of the reaction of phenol with formaldehyde. Phenolic resins were the first true synthetic polymers to be developed commercially. Notwithstanding this, even now their structure is far from completely clear, because the polymers derived from the reaction of phenol with formaldehyde differ in one important aspect from other polycondensation products. Polyfunctional phenols may react with formaldehyde in both the ortho and para positions to the hydroxyl group. This means that the condensation products exist as numerous positional isomerides for any chain length. This makes the organic chemistry of the reaction particularly complex and tedious to unravel. The result has been that although phenolic resins were developed commercially as early as 1908, were the first completely synthetic resins ever to be developed, and have vast and differentiated industrial uses today, and great strides have been made in both the understanding of their structure and their technology and application, several aspects of their chemistry are still only partially understood.

It may be argued with some justification that such a state of affairs is immaterial, because satisfactory resins for many uses have been developed on purely empirical grounds during the past 90 years. However, it cannot be denied that the gradual understanding of the chemical structure and mechanism of reaction of these resins has helped considerably in introducing commercial phenolic resins designed for certain applications and capable of performances undreamed of in formulations developed earlier by the empirical rather than the scientific approach. Knowledge of phenolic resin chemistry, structure, characteristic reactions, and kinetic behavior remains an invaluable asset to the adhesive formulator in designing resins with specific physical properties. The characteristic that renders these resins invaluable as adhesives is their capability to deliver water, weather, and high-temperature resistance to the cured glue line of the joint bonded with phenolic adhesives, at relatively low cost.

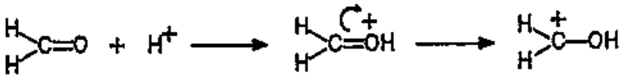
II. CHEMISTRY

Phenols condense initially with formaldehyde in the presence of either acid or alkali to form a methylolphenol or phenolic alcohol, and then dimethylolphenol. The initial attack may be at the 2-, 4-, or 6-position. The second stage of the reaction involves methylol groups with other available phenol or methylolphenol, leading first to the formation of linear polymers [1] and then to the formation of hard-cured, highly branched structures.

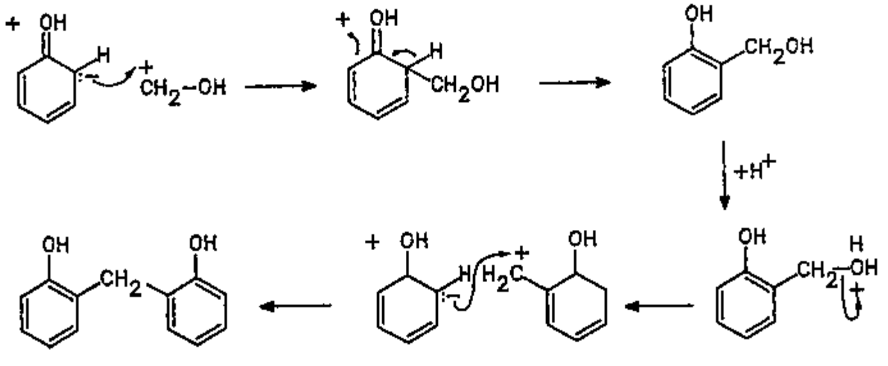
Novolak resins are obtained with acid catalysis, with a deficiency of formaldehyde. A novolak resin has no reactive methylol groups in its molecules and therefore without hardening agents is incapable of condensing with other novolak molecules on heating. To complete resinification, further formaldehyde is added to cross-link the novolak resin. Phenolic rings are considerably less active as necleophilic centers at an acid pH, due to hydroxyl and ring protonation.



However, the aldehyde is activated by protonation, which compensates for this reduction in potential reactivity. The protonated aldehyde is a more effective electrophile.

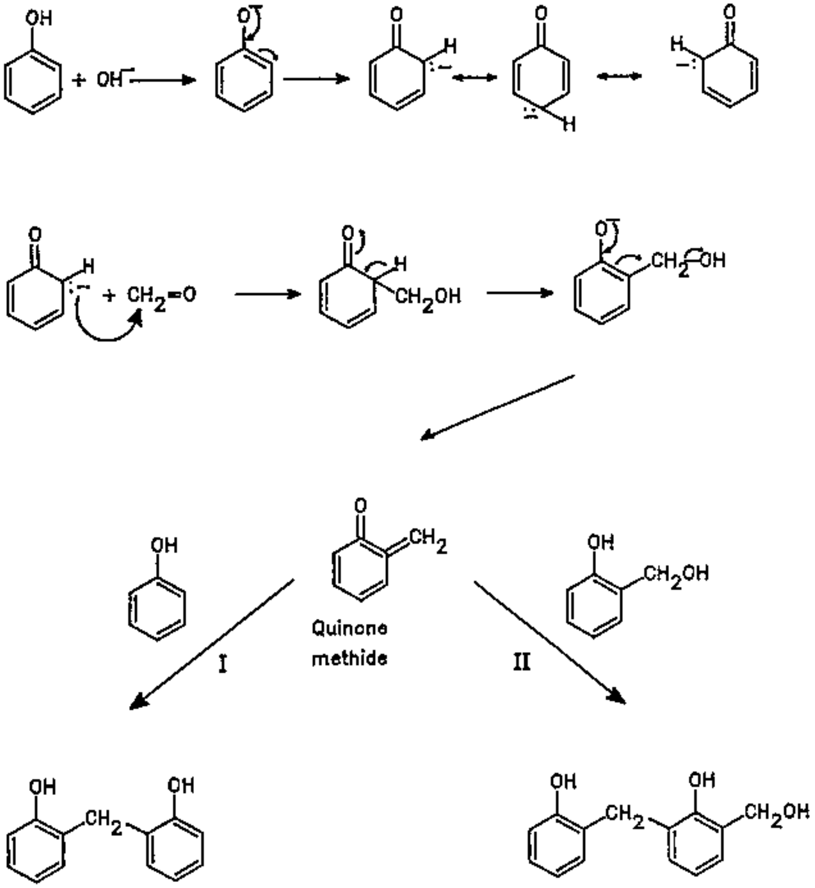


The substitution reaction proceeds slowly and condensation follows as a result of further protonation and the creation of a benzylcarbonium ion that acts as a nucleophile.

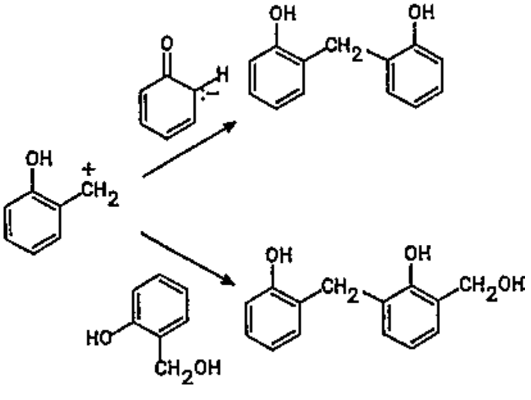


Resols are obtained as a result of alkaline catalysis and an excess of formaldehyde. A resol molecule contains reactive methylol groups. Heating causes the reactive resol molecules to condense to form large molecules, without the addition of a hardener. The function of phenols as nucleophiles is strengthened by ionization of the phenol, without affecting the activity of the aldehyde.

Megson [2] states that reaction II (in which resols are formed by the reaction of quinone methides with dimethylolphenols or other quinone methides) is favored during alkaline catalysis. A carbonium ion mechanism is, however, more likely to occur. Megson [2] also states that phenolic nuclei can be linked not only by simple methylene bridges but also by methylene ether bridges. The latter generally revert to methylene bridges if heated during curing with the elimination of formaldehyde.



The differences between acid-catalyzed and base-catalyzed process are (1) in the rate of aldehyde attack on the phenol, (2) in the subsequent condensation of the phenolic alcohols, and (3) to some extent in the nature of the condensation reaction. With acid catalysis, phenolic alcohol formation is relatively slow. Therefore, this is the step that determines the rate of the total reaction. The condensation of phenolic alcohols and phenols forming compounds of the dihydroxydiphenylmethane type is, instead, rapid. The latter are therefore predominant intermediates in novolak resins.



Novolaks are mixtures of isomeric polynuclear phenols of various chain lengths with an average of five to six phenolic nuclei per molecule. They contain no reactive methylol groups and consequently cross-link and harden to form infusible and insoluble resins only when mixed with compounds that can release formaldehyde and form methylene bridges (such as paraformaldehyde or hexamethylenetetramine).

In the condensation of phenols and formaldehyde using basic catalysts, the initial substitution reaction (i.e., the formaldehyde attack on the phenol) is faster than the subsequent condensation reaction. Consequently, phenolic alcohols are initially the predominant intermediate compounds. These phenolic alcohols, which contain reactive methylol groups, condense either with other methylol groups to form ether links, or more commonly, with reactive positions in the phenolic ring (ortho or para to the hydroxyl group) to form methylene bridges. In both cases water is eliminated.

Mildly condensed liquid resols, which are the more important of the two types of phenolic resins in the formulation of wood adhesives, have an average of fewer than two phenolic nuclei in the molecule. The solid resols average three to four phenolic nuclei but with a wider distribution of molecular size. Small amounts of simple phenol, phenolic alcohols, formaldehyde, and water are also present in resols. Heating or acidification of these resins causes cross-linking through uncondensed phenolic alcohol groups, and possibly also through reaction of formaldehyde liberated by the breakdown of the ether links.

As with novolaks, the methylolphenols formed condense with more phenols to form methylene-bridged polyphenols. The latter, however, quickly react in an alkaline system with more formaldehyde to produce methylol derivatives of the polyphenols. In addition to this method of growth in molecular size, methylol groups may interact with one another, liberating water and forming dimethylene ether links ($-CH_2-O-CH_2-$). This is particularly evident if the ratio of formaldehyde to phenol is high. The average molecular weight of the resins obtained by acid condensation of phenol and formaldehyde decreases hyperbolically from over 1000 to 200, with increases in the molar ratio of phenol to formaldehyde from 1.25:1 to 10:1.

Thermomechanical analysis (TMA) on wood joints bonded with phenol–formaldehyde (PF) adhesives has shown that, frequently, the joint increase in modulus does not proceed in a single step but in two steps, yielding an increase in the modulus first derivative curve presenting two major peaks rather than the single peak obtained for mathematically smoothed modulus increase curves [3]. This behavior has been found to be due to the initial growth of the polycondensation polymer leading first to linear polymers of critical length for the formation of entanglement networks. The reaching of this critical length is greatly facilitated by the marked increase in concentration of the PF polymer due to the loss of water on absorbent substrates such as wood, coupled to the linear increase in the average length of the polymer due to the initial phase of the polycondensation reaction. The combination of these two effects lowers markedly the level of the critical length needed for entanglement. Two modulus steps and two first derivative major peaks then occur, with the first peak due to the formation of linear PF oligomer entanglement networks, and the second one due to the formation of the final covalent cross-linked network. The faster the reaction of phenolic monomers with formaldehyde, or the higher the reactivity of a PF resin, the earlier and at lower temperature the entanglement network occurs, and the higher is its modulus value in relation to the joint modulus obtained with the final, covalently cross-linked resin (Fig. 1).

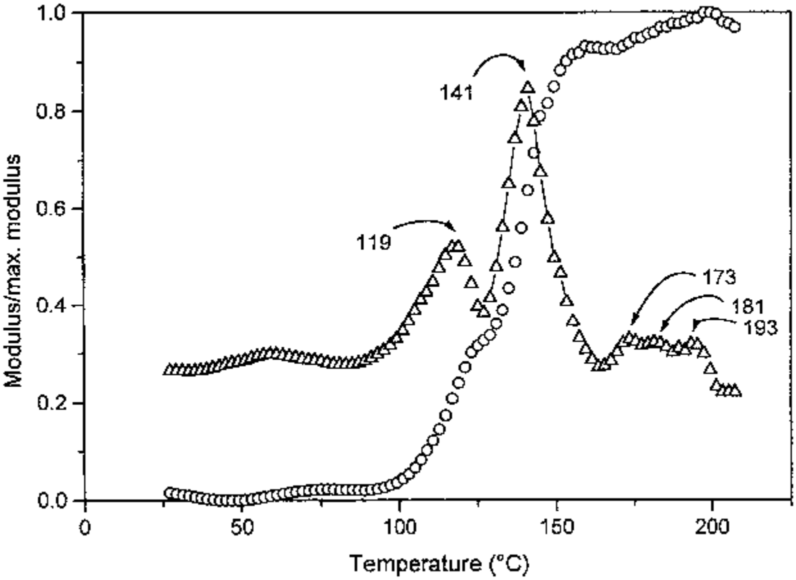
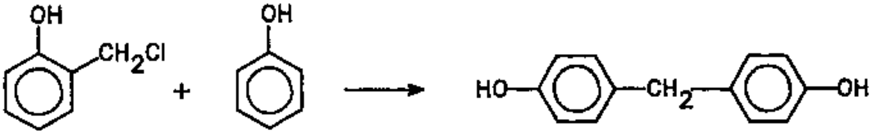


Figure 1 Thermomechanical analysis (TMA) of the hardening of a PF resin in situ in a wood joint. Increase of modulus of elasticity (MOE) of the joint as a function of temperature at a 10°C/min constant heating rate (○); first derivative (△).

A. Acid Catalysis

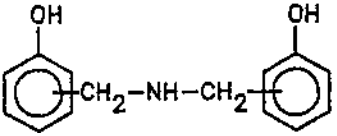
Consideration must be given to the possibility of direct intervention by the catalyst in the reaction. Hydrochloric acid is the most interesting case of an acid catalyst, as is ammonia of an alkaline catalyst. When the PF reaction is catalyzed by hydrochloric acid, two mechanisms may come into operation. Vorozhtov has proposed a reaction route that passes through the formation of bischloromethyl ether ($Cl–CH_2–O–CH_2–Cl$) [4]. Ziegler has suggested a route through the formation of a chloromethyl alcohol ($Cl–CH_2–OH$) as intermediate [5,6]. The second route appears to be the more probable. Both hypotheses agree that chloromethylphenols are the principal intermediates. The chloromethylphenols have been prepared and isolated by various means. They are highly reactive compounds which, with phenols, form dihydroxydiphenylmethanes and complex methylene-linked multiring polyphenols. Reaction is highly selective and takes place in the para position.

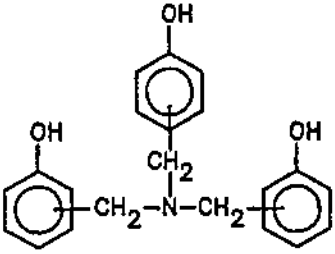


B. Alkaline Catalysis

Different mechanisms of alkaline catalysis have been suggested according to the alkali used. When caustic soda is used as the catalyst, the type of mechanism which seems the most likely is that which involves the formation of a chelate ring similar to that suggested by Caesar and Sachanen [7]. The chelating mechanism was thought to initially cause the formation of a sodium–formaldehyde complex or of a formaldehyde–sodium phenate complex and is similar in concept to the mechanisms advanced for metal ion catalysis of phenolic resins in the pH range 3 to 7. However, while the cyclic metallic ion catalysis ring complexes have even been isolated [8], this is not the case for the sodium ring complex, evidence for its existence being rather controversial, the predominant indication being that it does not form [9].

When ammonia is used as a catalyst, the resins formed are very different in some of their characteristics from other alkali-catalyzed resins: the reaction mechanism appears to be quite different from the of sodium hydroxide-catalyzed resins. An obvious deduction is that intermediates containing nitrogen are formed. Several such intermediates have been isolated from ammonia-catalyzed PF reactions [10–12] and hexamine prepared resins [13–16] by various researchers. Similar types of intermediates are formed when amines or hexamethylenetetramine (hexamine) are used instead of ammonia. In the case of ammonia the main intermediates are dihydroxybenzylamines and trihydroxybenzylamines, such benzylamine bridges having been shown to be much more temperature stable than previously thought and to impart particular characteristics to the resin [13–16].



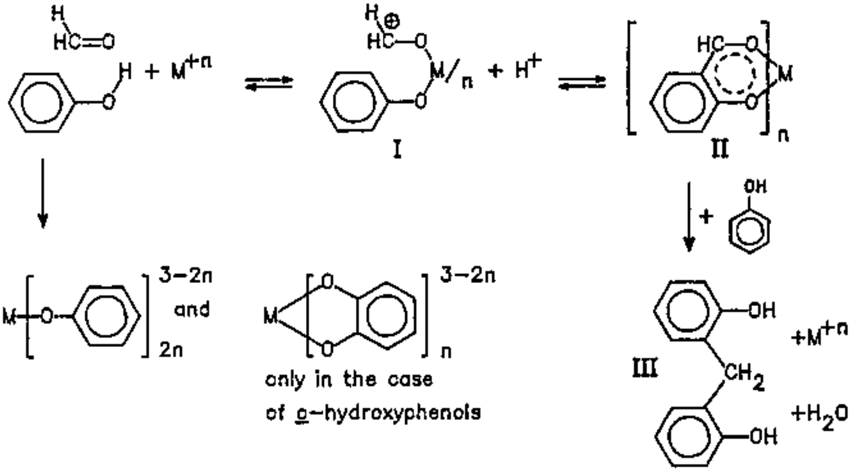


These intermediates contain nitrogen and have polybenzylamine chains. They react further with more phenol causing splitting and elimination of the nitrogen as ammonia or producing eventually nitrogen-free resins. However, as benzylamine bridges have been shown to be much more temperature stable than previously thought, this requires a considerable excess of phenol and a high temperature, or heating for a rather long time. With phenol–hexamethylenetetramine resins of molar ratio 3:1, the nitrogen content of the resin cannot be reduced to less than 7% when heated at 210°C. When the ratio is increased to 7:1, the nitrogen content on heating at 210°C can be reduced to less than 1%. Contrary to what was widely believed it has been clearly demonstrated that in the preparation of PF resins starting from hexamethylenetetramine the di- and trihydroxybenzylamine bridges which are initially formed are very stable and are able to tolerate for a considerable length of time a temperature as high as 100°C [13] yielding in certain aspects (only) resins of upgraded characteristics. This behavior is closely tied to the reactions characteristic of hexamethylenetetramine to form iminomethylene bases [14–16], which are discussed in the melamine resins chapter in this volume (Chap. 32).

Ammonia-, ammine-, and amide-catalyzed phenolic resins are characterized by greater insolubility in water than that of sodium hydroxide-catalyzed phenolic resins. The more ammonia that is used, the higher the molecular weight and melting point that are obtained without cross-linking. This is probably due to the inhibiting effect of the nitrogen-carrying groups (i.e., –CH_2–NH–CH_3 or –CH_2–NH_2), which is caused by their slow rate of subsequent condensation and loss of ammonia. Ammonia, amines, and amides are sometimes used as accelerators during the curing of phenolic adhesives for wood products.

C. Metallic Ion Catalysis and Reaction Orientation

In the pH range 3 to 7 the higher rate of curing of phenolic resins prepared by metallic ion catalysis is due to preferential ortho methylolation [17] and therefore also to the high proportion of ortho–ortho links of the uncured phenolic resins prepared by metallic ion catalysis. The faster curing rates of phenolic resins prepared by metallic ion catalysis is then due to the higher proportion of the free higher-reactive para positions available for further reaction during curing of the resin. The mechanism of the reaction [8] involves the formation of chelate rings between metal, formaldehyde, and phenols or phenol nuclei in a resin.



The rate of metal exchange is solution [8,18] and the instability of the complex formed determine the accelerating or inhibiting effect of the metal in the reaction of phenol with formaldehyde. The more stable complex II is, the slower the reaction proceeds, to the formation of resin III. A completely stable complex II should stop the reaction from proceeding to resin III. If complex II is not stable, the reaction will proceed to form PF resins of type III. The rate of reaction is directly proportional to the instability or the rate of metal exchange in solution of complex II. The acid catalysis due to the metal ion differs only in degree from that of the hydrogen ion [19].

The effect of the metal is stronger than that of hydrogen ions, because of higher charge and greater covalence, since its interaction with donor groups is often much greater [19]. This allows phenolic resin adhesives to set in milder acid conditions. Most covalent metals ions accelerate the PF reaction. The extent of acceleration depends on the type of metal ion and the amount of it that is present. The capability of acceleration in order of decreasing acceleration effectiveness has been reported to be [11] Pb^{II}, Zn^{II}, Cd^{II}, $Ni^{II} > Mn^{II}$, Mg^{II}, Cu^{II}, Co^{II}, $Co^{III} > Mn^{III}$, $Fe^{III} \gg Be^{II}$, $Al^{III} > Cr^{III}$, Co^{II}. The most important conclusion to be drawn is that the accelerating effect is indeed present in both the manufacture of PF resin and its curing. Therefore, the fast rate of curing of high-ortho phenolic resins can be ascribed only partially to the high proportion of para positions available. The other reason for the fast rate of curing is that the metallic ion catalyst is still present, and free to act, in the resin at the time of curing. In such a resin, a considerable number of ortho positions (especially of methylol groups in ortho positions to the phenolic hydroxyls) are still available for reaction and capable of complexing.

III. CHEMISTRY AND TECHNOLOGY OF APPLICATION OF PHENOLIC RESIN ADHESIVES FOR WOOD

A. General Principles of Manufacture

A typical phenolic resin is made in batches, in a jacketed, stainless steel reactor equipped with an anchor-type or turbine-blade agitator, a reflux condenser, vaccum equipment, and heating and cooling facilities. Molten phenol and formalin (containing 37 to 42% formaldehyde or paraformaldehyde), in molar proportions between 1:1.1 and 1:2, along with water, and methanol are charged into the reactor and mechanical stirring is begun. To make a resol-type resin (such as those used in wood adhesives manufacture), an alkaline catalyst such as sodium hydroxide is added to the batch, which is then heated to 80 to 100°C. Reaction temperatures are kept under 95 to 100°C by applying vacuum to the reactor, or by cooling water in the reactor jacket. Reaction times vary between 1 and 8 h according to the pH, the phenol/formaldehyde ratio, the presence or absence of reaction retarders (such as alcohols), and the temperature of the reaction.

Since a resol can gel in the reactor, dehydration temperatures are kept well below 100°C, by applying vacuum. Tests have to be done to determine first, the degree of advancement of the resin, and second, when the batch should be discharged. Examples of methods of such tests are the measurement of the gel time of a resin in a 150°C hot plate or at 100°C in a water bath. Another method is measuring the turbidity point, that is, precipitating the resin in water or solutions of a certain concentration.

Resins that are water soluble and have a low molecular weight are finished at as low a temperature as possible, usually around 40 to 60°C. It is important that the liquid, water-soluble resols retain their ability to mix with water easily when they are used as wood adhesives. Resols based on phenol are considered to be stable for 3 to 9 months. Properties of a typical resin are a viscosity of 100 to 200 cP at 20°C, a solids content of 55 to 60%, a water mixibility of a minimum of 2500%, and a pH of 7 to 13, according to the application for which the resin is destined.

Phenol–formaldehyde (PF) resins present lower reactivity at a pH of about 4. The accepted effect of the pH and of the phenol/formaldehyde molar ratio on the rate of polymerization and rate of hardening of phenolic resols is shown in Fig. 2. Recently, however [9], the concepts expressed in the graph have been found to be only partially correct, at least with regard to the dependence of the PF adhesive rate of curing as a function of pH. The expected asympthotic acceleration expected over pH 7 to 8 and due to the formation of phenate ions has been proven not to be the only effect present. At first acceleration occurs, but after a pH of approximately 8 to 9, the rate of hardening of the resin slows down considerably [9], as shown in Fig. 3, contrary to accepted wisdom. There are several reasons for this behavior [9], the easier of these to accept being the formation of a ring involving phenol, the methylol group, and Na ions, which was postulated already 50 years ago [7]. The existence of this ring has been shown to be untrue [9] and the persistence of the concept is due to the ease with which the behavior shown in Fig. 3 can be explained. The reason for the acceleration, however, was ascribed to and proved to be due to the existence of and equilibria pertaining to quinone methides [9,20]. The structure of the elusive oligomeric quinone methides in PF resins has also been elucidated [21] (see page 549).

The probable reason why the behavior in Fig. 3 was not noticed earlier appears to be due to the slow gel times of PF resins, which makes it very tedious to check reactivity effectively.

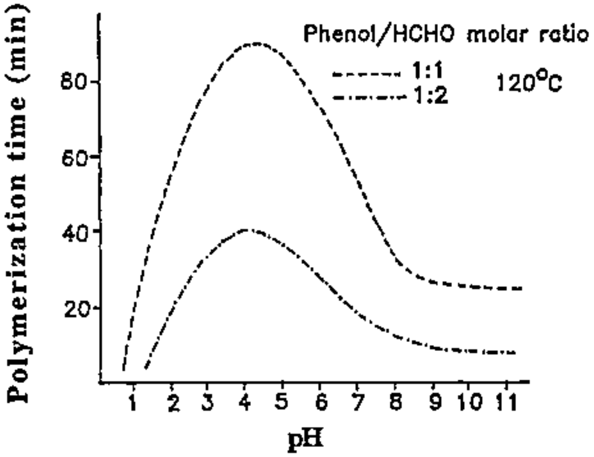
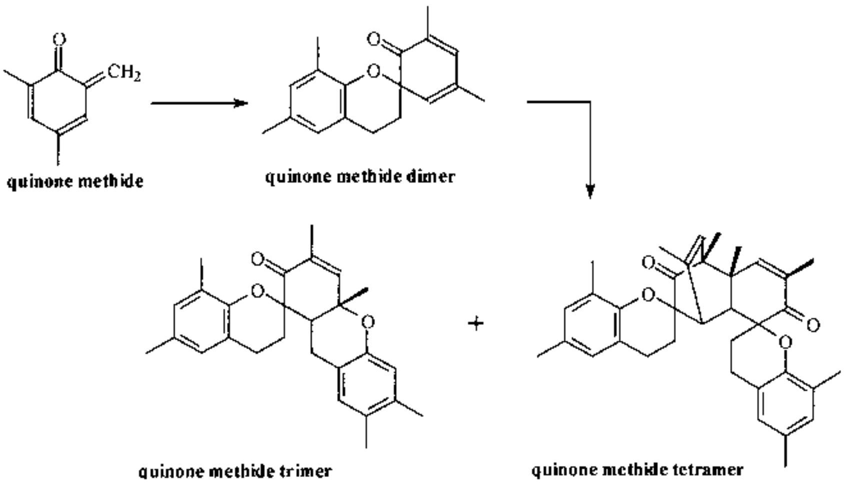


Figure 2 Rate of polymerization as a function of pH for phenolic resols of different molar ratios at 120°C (old concept).



B. Curing Acceleration Under Alkaline Conditions

1. *α- and β-Set Acceleration*

The so-called α- and β-set acceleration of curing for very alkaline PF resins for foundry core binders was pioneered in the early 1970s [22], although it had been discovered in the early 1950s [22]. In this application the addition of considerable amounts of esters or other chemicals in liquid form (α-set) or as a gas (β-set), such as propylene carbonate, methyl formate, glycerol triacetate, and others, was found to accelerate resin curing to extremely short times. This technique is now used extensively around the world for foundry core PF binders [22] and is being considered for wood adhesives [9] and rigid alkaline PF foams. The technique is applicable in the approximate pH range 7 to 14. The mechanism that makes PF curing acceleration possible has only been explained recently [9] and different explanations exist (see below); it is based on the carbanion behavior of the aromatic nuclei

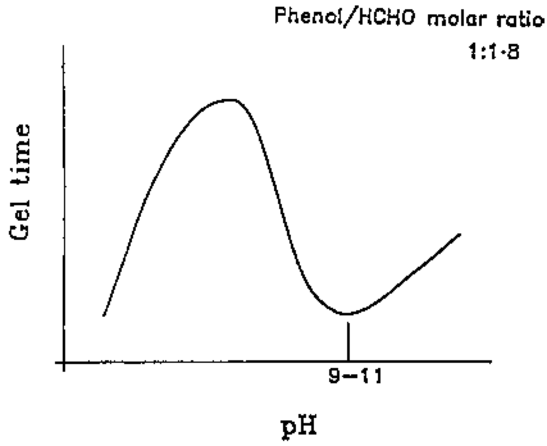


Figure 3 Schematic relationship of gel time to pH for phenolic resols (new concept).

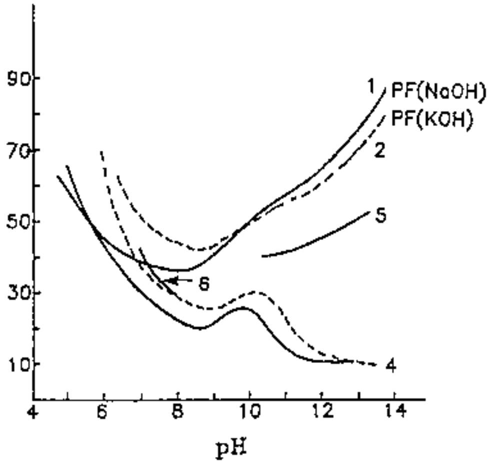


Figure 4 Cure retarding at high pH and ester acceleration effect of NaOH and KOH-catalysed PF resins (ester = propylene carbonate). Note curve 5, the effect of 4 months aging of the PF resin of curve 1 on the extent and starting pH of the retardation effect. Compare the start of acceleration for curves 4 and 6, showing the differences between propylene carbonate and triacetin esters, and compare the starting point of acceleration at pH 5.5 and pH 7.1. The "bumps" on the curves at pH 8–11 are caused by methylene ether formation, decomposition, and rearrangement [9].

of phenate ions, leading to a more complex variant of the Kolbe–Schmitt reaction. The ester, or residue of its decomposition, attacks the negatively charged phenolic nuclei, and its reaction is not limited to the ortho and para sites, transforming the phenolic nuclei in a temporary condensation reagent of functionality higher than 3, leading to much earlier gelling. Furthermore, temporary condensation occurs not only according to the PF mechanism but also according to a second reaction superimposed on it [9,23] (Fig. 4).

Other explanations and mechanisms for this occurrence have also been advanced: determination by TMA of the average number of freedom of polymer segments between cross-linking nodes of PF resin hardened networks indicate that additive accelerated PF resin polycondensations and hardening present several different acceleration mechanisms. [23]. Some additives such as sodium carbonate appear to present a purely catalytic effect on the polycondensation reaction [23]. Other additives such as propylene carbonate present both a catalytic effect as well as including an increase in the average functionality of the system, due to further cross-linking, or alternative reactions in which the accelerator itself participates, leading to a tighter final network [23]. These alternative cross-linking reactions could be of a different nature, such as the propylene carbonate case in which the reaction appears to be related to a Kolbe–Schmitt reaction, or they could be similar to the accelerating effect due to the hydrolysis of formamide to formic acid and ammonia with the subsequent rapid reaction of the latter with two or more hydroxybenzyl alcohol groups of PF resols [23]. The rapid reaction of the -NH2 group of formamide with two hydroxybenzyl alcohol groups of PF resols, a reaction which is also characteristic of urea and methylamine, also appears likely to occur. In some cases such as in formamide none of the two acceleration mechanisms detected appear to be due to catalytic action only, but both appear to be related to additional cross-linking reactions. Both liquid and solid phase ^{13}C nuclear magnetic resonance (NMR) supporting evidence of the mechanisms proposed has been presented [23].

Further proof of complex reactions between propylene carbonate and phenolic nuclei leading to compounds in which the carbonic acid has attacked the phenolic ring has been presented [23] based on the ^{13}C NMR spectrum of the product of the reaction of resorcinol with propylene carbonate, in the absence of formaldehyde. Resorcinol was chosen as its aromatic ring is a stronger nucleophile than that of phenol and thus if any reaction had occurred this would be less elusive and much more easily observed [23]. The reaction products which appeared to be formed were carboxylic and dicarboxylic species. That they might be present was also derived by NMR [23]. It must be pointed out that such structures need to be only transitory and not permanent to obtain the same effects noted experimentally. Such a subsequent lability could be the reason why it is difficult to observe such linkages in the hardened resin except for faster reacting phenols where they can be observed due to early immobilization of the network which surely occurs.

It must also be remembered that in hot temperature curing of phenolic resins, their polycondensation is accelerated particularly on a wood substrate surface, first by heterogeneous catalysis effect by the cellulose [24], and secondly by the substrates subtracting water from the system and thus increasing its effective concentration, always a very important effect in polycondensation reactions [3,25]. Under these conditions the existence of the additional cross-linking mechanism will then be even more marked. It is also clear that if the anhydride exists it might decompose at higher temperature curing, with what type of further reactions it is not possible to say with the data available.

Once defined the nature of the accelerating mechanism induced by increased cross-linking and its existence through the determination of the increased tightness of the PF networks formed [9,23], it is necessary to address the nature of the other accelerating mechanism that appears to be common to both sodium carbonate and propylene carbonate. The apparent failure by different analyses [26] such ^{13}C NMR to find any trace of $C{=}O$ after purification of sodium carbonate accelerated PF resins indicates quite clearly that the sodium carbonate effect may well be purely catalytic and that the $C{=}O$ is transformed during the reaction to another group, or even more likely that the $C{=}O$ disappears from the system as CO_2 or precipitates completely away as sodium hydrogen carbonate. The presence of the $C{=}O$ has been clearly noticed in non purified samples of accelerated PF resins [9,23,27] but strictly speaking this in only proof of the additional cross-linking mechanism just discussed above or it could just be due to any carbonic acid salts still present in the system. That this mechanism exists is proven by the acceleration of hardening being marked for high molar ratio (formaldehyde/phenol ≥ 2.5) PF resins in which all available ortho and para sites on the phenol are blocked by methylene or methylol groups. In this case a soft gel, and no subsequent rapid hardening is obtained. The mechanism involved could then be one of the two proposed up to now, namely the hydrogen carbonate ion intermediate activated complex and derived mechanisms [26,28] which present inherent disadvantages that have been outlined [23], which have been proposed without any evidence, and for which direct evidence would be rather difficult to gather, and the mechanism [23] based on rapid transesterification reactions of the hydroxybenzyl alcohol group of a PF resol. This latter mechanism is based on the very facile transesterification of propylene carbonate with methanol through which dimethyl carbonate is rapidly obtained [23].

It is interesting to remark that other reactive materials which will readily undergo transesterification analogous to that of propylene carbonate with methanol are trialkyl borates, tetraalkyl titanates, and trialkyl phosphates in an alkaline environment. Also gas injection of methyl borate (and carbon dioxide) has been found to enhance the results of wood composites bonded with formaldehyde-based resins [29], just as the addition of propylene carbonate and glycerol triacetate have been shown to do in wood composites bonded with phenolic resins.

In the case of wood adhesives, first glycerol triacetate (triacetin) and secondly guanidine carbonate are the accelerating esters of choice yielding long pot-lives at ambient temperature and fast cure times at higher temperature, and are used in proportions variable between 3% and 10% of adhesive resin solids [30–32]. Propylene carbonate is unsuitable for wood adhesives application as it yields far too short pot-lives at ambient temperature. Methyl formate and other esters, including propylene carbonate, are used instead in foundry core binders where sometimes the proportion of ester accelerator used is up to an equal amount of the resin solids; hence the accelerator application technology is rather different from one field to another. Most other esters are much less effective accelerators at higher temperature, or they shorten the ambient temperature life of the resin to such an extent that in practice the resin cannot be used [30–32]. Triacetin gives long pot-lives and short cure times instead due, among other reasons to its lower rate of hydrolysis at ambient temperature. Another series of compounds, some of which where finally found to yield sufficiently rapid acceleration at higher temperatures still coupled with increased strength of the cured resin as well as sufficiently long shelf-life at ambient temperature, were the salts of guanidine. Guanidine carbonate, guanidine hydrochloride, and guanidine sulphate were tried with positive results [32]. Guanidine carbonate appeared to be the best PF accelerator; both its accelerating capability remained acceptable, while the shelf life at ambient temperature of the PF and phenol–urea–formaldehyde (PUF) resins to which it had been added in different proportions was much longer and the performance in particleboard preparation was the same as triacetin [32]. Even in the case of some industrial higher condensation resins, their pot-life was as long as three weeks with the guanidine carbonate already incorporated in the resin [32].

It has repeatedly been established that the energy of activation of the reaction of polycondensation of PF resins, and also of urea–formaldehyde (UF), melamine–formaldehyde (MF), and other resins, is markedly influenced by the presence of wood [24,33–39]. In the presence of wood as a substrate, the energy of activation of the polycondensation reaction, and hence of the hardening of PF and other resins is considerably lowered. This implies that resin polymerization and cross-linking proceeds at a much faster rate when the resin is in molecular contact with one or more of the wood constituents [24,33]. It was indeed shown that catalytic activation of the hardening and advancement of a PF and other polycondensation resins induced by the wood substrate did exist and was a rather marked effect. The reason for the effect has been found to be due to the mass of secondary attraction forces binding the resin to the substrate [24,33]. These cause variations in the strength of bonds and intensity of reactive sites within the PF oligomer considered, an effect well known in heterogeneous catalysis for a variety of other chemical systems [40], bond cleavage and formation within a molecule being greatly facilitated by chemisorption onto a catalyst surface. This work indicated also which bonds in the PF resin were involves and what was the extent of the acceleration of the hardening reaction caused by such an effect [33].

2. *Addition of Acetals and Transacetalization Reactions*

Another recent approach which has shown considerable promise in markedly decreasing the percentage of PF adhesive solids on a board has been found almost by chance. It is based on the addition to the resin of certain additives capable of decreasing the percentage of any PF resin needed for bonding while still conserving the same adhesive and joint performance. These additives work best for melamine–urea–formaldehyde (MUF) adhesives, but give acceptable results for PF resins too. These additives are the acetals [41,42], methylal and ethylal being the two most suitable due to their cost to performance ratio, which do not release formaldehyde at pHs higher than 1 [43]. Methylal has according to results reported by the Enviromental Protection Agency (EPA) an LD_{50} value of 10,000 against that of 100 for formaldehyde, and is thus classed as nontoxic. The addition of these materials to the glue mix of a formaldehyde-based resin improves considerably its mechanical resistance and the performance of the bonded joint, mainly through its solvent action on the higher molecular weight colloidal fraction of the resin. Molecular, colloidal interactions causing diffusional hindrance problems are thus overcome and minimized by bringing the resin system to a homogeneous phase and as a consequence higher resin strengths are obtained. It has also been shown that the supposed existence of transacetilization reactions forming bridges in the resin hardened network which are better able to optimize the glue line and bonded joint viscoelastic dissipation of energy did not occur [44]. This is in general valid for MUFs, some UFs, and PFs, but the effect is particularly evident and particularly marked for the MUF resins [44]. However, still respectable (but more modest than MUFs) increases in PF resin strength of up to 25%, or alternatively decreases in PF resin solids content of as much as 20% while conserving the same performance, have been obtained in the case of wood particleboard [44].

3. *Urea Acceleration and Phenol-Urea-Formaldehyde Exterior-Grade Resins*

Low condensation PF resins have been coreacted under alkaline conditions with up to 42% molar urea on phenol during resin preparation to yield PUF resins capable of faster hardening times and presenting better performance than equivalent pure PF resins prepared under identical conditions [31–34]. The reason that urea reacts with relative ease with PF resols under alkaline reaction conditions can be ascribed to the relative reactivities toward methylol groups of urea and phenolic nuclei. A study has shown that there are definite pH ranges in which the reaction of urea unreacted $–NH_2$ and –NH– groups with formaldehyde in competition with phenol or with the methylol groups carried by a PF resin, is more favorable than is autocondensation of the PF resin itself [31,33,45] (Fig. 5).

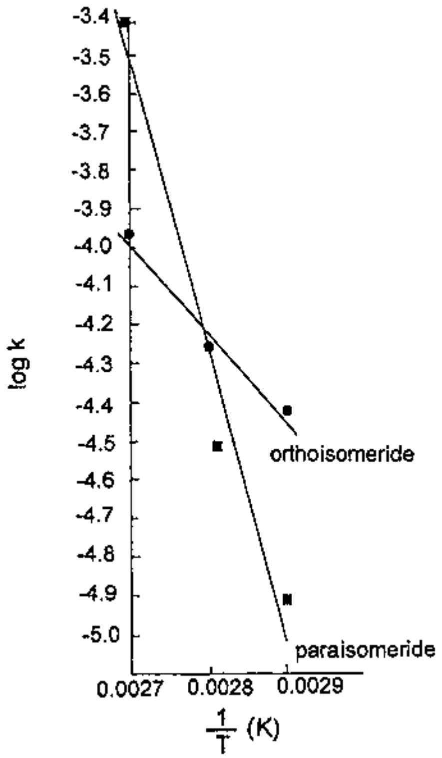
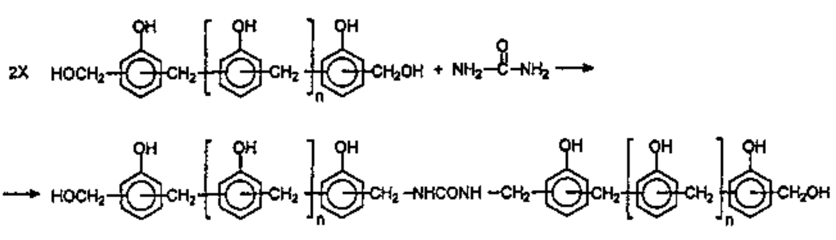


Figure 5 Log of reaction rate constant versus $1/T$ (T in kelvins) for the reaction of ortho and para hydroxybenzyl alcohol with urea, detailing the relative rates of condensation with urea of ortho and para phenolic methylols in a PF resin.

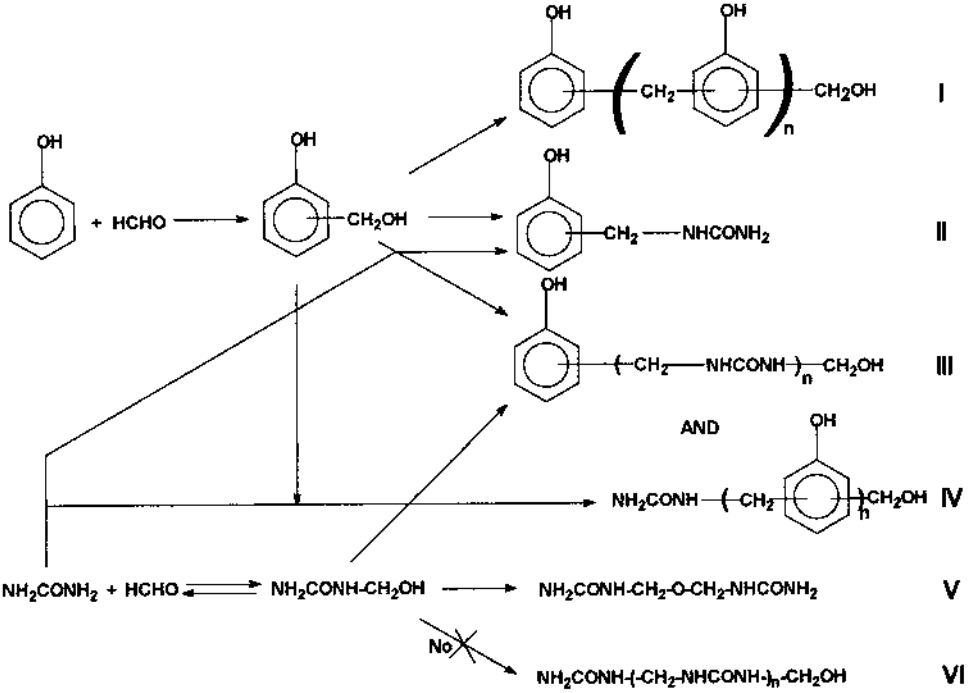
It is the urea which contributes to the acceleration of resin cure by allowing the following.

(i) The preparation of greater molecular mass linear oligomers needing fewer steps to cure, hence curing faster. Copolymerization up to a certain level of urea addition brings an easier and much faster reaction to the mainly linear higher molecular weight oligomers; in a sense this is just a way to molecularly double very quickly the molecular weight of a PF resin while still maintaining the linearity of the higher molecular weight oligomers formed. The extent of copolymerization, however, needs to be limited and cannot be brought to an excess otherwise the viscosity of the resin becomes unmanageable, although the presence of free urea is able to control this trend.



(ii) The faster reaction of urea than phenol with the phenolic methylol group under alkaline conditions as well as the possibility of reaction with phenol of the methylol groups formed by the additional attack of HCHO on urea; the latter reaction drives the reaction of HCHO on urea, an equilibrium, in favor of methylol ureas and subsequent products [31,32].

The water resistance of these PUF resins is comparable to that of pure PF resins when used as adhesives for wood particleboard. Part of the urea (between 18 and 24% molar on phenol at a phenol:HCHO molar ratio of 1:1.7, but higher at higher HCHO proportions) was found by ^{13}C NMR to be copolymerized to yield the alkaline PUF resin while, especially at the higher levels of urea addition, unreacted urea is still present in the resin. Increasing the initial formaldehyde to phenol molar ratio decreases considerably the proportion of unreacted urea and increases the proportion of the PUF copolymer. A coreaction scheme of phenolic and aminoplastic methylol groups with reactive phenol and urea sites based on previous model compounds work has been proposed, copolymerised urea functioning as a prebranching molecule in the formation of a hardened resin network [31].



The PUF resins prepared are capable of further noticeable curing acceleration by addition of ester accelerators, namely glycerol triacetate (triacetin), to reach gel times as fast as those of catalyzed aminoplastic resins, but at wet strength values characteristic of exterior PF resins [31,32]. Guanidine carbonate has also been shown to be an accelerator of PF resins which, while yielding slightly slower gel times than triacetin when just added to a PF resin glue-mix, is also capable of giving glue-mix pot-lives on the order of several days, hence long enough to be premixed with the resin well before use [32]. Both triacetin and guanidine carbonate used as simple glue-mix additives increase the ultimate strength of the resin bond whatever the length of the curing time used for the purpose, this being confirmed both by thermomechanical analysis as well as by application to wood particleboard. Synergy between the relative amounts of copolymerized urea and ester accelerator is very noticeable at the lower levels of the two parameters, but this effect decreases in intensity towards the higher percentages of urea and triacetin [31,32]. The relative performance of the different PUF resins prepared under different conditions, allowed the preparation of wood particleboard bonded with accelerated PUF resins with the ability to achieve press times as fast as those of aminoplastic (UF and others) resins [31,32].

C. Physical Properties of Phenol-Formaldehyde Resins

Hardened PF resin have a specific gravity of approximately 1.2 to 1.3, a refractive index of 1.6, and a specific heat of 0.5. They are typically brown in color, and novolaks are lighter in color than resols. Resols are dark yellow, orange reddish, or brownish even when made with pure raw materials. However, if the alkali is neutralized resols become almost colorless. The best results were obtained with citric, lactic, and phosphoric acids. Pale-colored, hardened resins can be prepared with them [46]. Phenolic resins are relatively stable up to about 200 to 250°C, although oxidative degradation takes the form of attack at the methylene bridges to produce substituted, dihydroxy benzophenones [47]. Above this temperature, they begin to char slowly, and at higher temperatures charring is more rapid. At about 400°C decomposition is rapid, yielding phenols and aldehydes, and leaving a cokelike residue.

In the A stage, simple PF resins are readily soluble in alcohol, esters, ketones, phenols, and some ethers, and insoluble in hydrocarbons and oils. As a class, resols tend to be more soluble in alcohols and water, and novolaks tend to be more soluble in hydrocarbons. In the early stages of condensation, resols are often soluble in water, owing to the presence of methylolphenols, especially polyalcohol. This is more pronounced with resols that are derived from phenol. Cresilic resols are less soluble, and xylenolic resols are almost insoluble in water. The solubility of A-stage resins in dilute aqueous sodium hydroxide or in mixtures of water and alcohols follows the same trend.

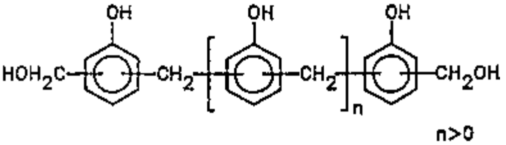
Solubility in alcohols and insolubility in hydrocarbons appear to go together. The alcohol and water solubility can be reduced only by using acetaldehyde or other aldehydes in the place of formaldehyde, and by introducing hydrocarbon chains, particularly in the ortho or para positions in the aromatic ring. B-stage resins are soluble in only a few solvents, such as boiling phenols, acetone, aqueous sodium hydroxide, and deca- and tetrahydronaphthalenes. Resins in the hardened or C stage are very resistant to most chemical reagents. They are unaffected by all ordinary organic solvents and water, although a few percent of water may be absorbed in filled material, mainly by the filler, thus causing slight swelling. The C-stage resins dissolve slowly in boiling phenols such as naphthols. Resins from the simplest phenols can also be broken down and dissolved by hot, strong alkali solutions.

Simple PF resins are readily attacked by sodium hydroxide. However, cresol–formaldehyde, and especially xylenol–formaldehyde resins, are much less susceptible to attack. Resins are often more resistant to strong alkaline solutions (i.e., 15 to 20%) than to dilute solutions (i.e., 5%). The filler has a considerable influence on the chemical resistance of the resins. Inert mineral fillers have a better resistance than cellulosic fillers. C-stage resins are resistant to most acids, except sulfuric acid stronger than 50%, formic acid, and oxidizing acids such as nitric and chromic acids. The insolubility of hardened resins in acetone is used to test the degree of cure of the resin. The curing temperature influences the amount of matter that is insoluble in acetone after prolonged heating [48]. The higher the hardening temperature, the lower the amount of acetone extractives. The mechanical properties of hardened PF resins are greatly influenced by the moisture content. This applies even more to resins containing fillers, plasticizers, and other ingredients. The rate of water absorption decreases with time, but thick samples may not reach an equilibrium even after several months in water. Therefore, in measuring the mechanical properties of resins, it is necessary to condition the test pieces under carefully controlled temperature and humidity prior to making the tests. In many cases, the mechanical properties of hardened resins are largely dependent on the type and orientation of the filler. This applies particularly to water absorption, tensile strength, and impact strength. It also applies to shear strength, with the condition that in the plane of the laminations the shear strength depends on the adhesion between the laminae of sheet material. The properties of the resin are more important than those of the filler in determining the compression strength.

IV. APPLICATIONS

A. Phenol–Formaldehyde Wood Binders

Phenolic resins are used as binders for exterior-grade plywood and particleboard, which need the superior water resistance provided by these resins. In the manufacture of plywood, the phenolic resin adhesive is usually applied to the wood veneers by roller or extrusion coating. The coated veneer is then cross-grained, stacked, and cured in a multi-daylight press for 5 to 10 min at 120 to 130°C and at 11 to 16 kg/cm^2. In the manufacture of particleboard, the phenolic resin adhesives are sprayed onto the wood chips, or sprayed plus spread by continuous blenders. The glued wood chips are formed into a mat and then pressed for 5 to 12 s/mm, according to thickness, press temperature and moisture content, at 190 to 230°C and 25 to 35 kg/cm2. The only type of phenolic resins used commercially for this application are resol-type resins, which have the following structure:



These are hardened by heating after the addition of small amounts of wax emulsion and insecticide solution in the case of particleboard, and of vegetable or mineral fillers and tackifiers in the case of plywood. Accelerators are sometimes added in both types of glue mixes. The pH of these resins varies between 10 and 13.5 and is generally between 12 and 12.5.

In dealing with wood related factors that affect glue bonds, it is important to remember that adhesion is at least 95% physicochemical in nature. The mechanical aspects of bond formation (such as keying cured adhesive solid in the wood surface) contribute negligibly to the bond strength or wood failure. The main chemical forces in thermosetting resin adhesion are primary valence bonds, covalent bonds, and hydrogen bonds, plus secondary forces such as van der Waals and London forces and any other types of electrostatic, dipolar, and associative forces. It is therefore essential that the resin contains a significant number of functional groups and that the wood surface presents a significant number of reactive sites to enable the resin to bond. Any factors that limit resin functionality or block reactive sites on the wood structure necessarily impede adhesion.

1. *Properties of Phenolic Adhesives for Plywood [49]*

Certain attributes of phenolic resins have been designed to give the strongest and most durable plywood bonds. Laboratory and field experience have demonstrated that certain types of PF plywood resins perform significantly better on veneers than do others. These superior resins have several properties in common:

1. They are relatively low in alkali content, generally about one-third to not more than one-half molar.
2. They have a lower molecular weight for hardwood veneers than do phenolic resins designed for softwood gluing.
3. They are high in methylol group content. Alternatively, they may contain free formaldehyde or require a matching catalyst that contains paraformaldehyde
4. Even in dried adhesive carrier films or powdered resins, phenolic resins for hardwoods shares the B-stage characteristic of reliquefying briefly under heat and pressure to allow transfer and flow on the glue lines of a plywood panel. This liquefaction can occur without water. This is unlike all but the most recently developed softwood phenolic resins.
5. Phenolic resins for hardwoods have higher thermal softening points than those of many other conventionally prepared resins. This indicates a network that has more cross-links after final cure and also greater durability.
6. They have a 40 to 45% solids content and 150 to 600 cP of viscosity at 25°C.

In general, lower resin alkali content and lower molecular weight are associated with slower cure, which explains why softwood plywood adhesive resins are both more alkaline and more condensed. Adequate exterior-grade adhesion can be attained on softwood veneer if these considerably condensed phenolic resins, which also cure more quickly, are used. Conversely, the increased functionality of hardwood adhesive resins partially compensates for their inherently slower cure rate. Hardwood phenolic resins require about 30% longer press times for adequate cure.

Notwithstanding their good adhesive capability, phenolic resins for hardwood gluing carry one distinct disadvantage: they do not prepress as well as softwood phenolic resins. Their lower condensation and longer flow are not assets. Prepressing is important because it is done to minimize face veneer losses and to reduce precure times on hot platens. Therefore, other means can be employed to obtain the required tackiness. Additives and adhesive formulations for this purpose are available. To increase the prepress capacity of low alkali, long-flow phenolic resins suitable for hardwood gluing, small amounts of starch or poly(vinyl alcohol) can be added to the resin glue mix just before use.

The finished resin viscosity is increased to allow for the thickening effect of these additives without reducing the average molecular weight of the phenolic resin. Water-soluble thickeners (such as hydroxyethyl cellulose, polyethylene glycols, and maleic anhydride copolymers) contribute to prepress tack. However, they cause a large increase in resin viscosity, and the amount added must be small. Consequently, the benefit to prepressing is limited. Most animal-and vegetable-based thickeners, such as gum arabic, are subject to hydrolysis in alkaline phenolic resins, and lose effectiveness in a matter of hours.

2. *Additives*

A number of additives and modifiers contribute useful properties to phenolic resins used for wood gluing. Multipurpose additives are the amino resins and urea–formaldehyde and melamine–formaldehyde polymers. These include not only urea and melamine plywood adhesive resins, but also dimethylol urea, trimethylol melamine, and hexamethylol melamine. Added in amounts from 5 to 15% of phenolic resin solids, they improve resin tack and prepressing, increase long-assembly-time tolerance, shorten pressing times, and enhance resin functionality. This results in stronger bonds on wood veneers. As long as they are used in limited quantities, they have a negligible effect on long-term phenolic bond durability. They appear to be well protected from hydrolytic degradation by the cured phenolic polymer network. The dispersion of the amino resin molecules in the alkaline medium of the phenolic resin glue mix inhibits their curing reaction, which is acid catalyzed. It causes them to function as methylolated cross-linking units for the PF polymer.

Urea by itself can be used in great amounts in the system for producing PF resins of very high molecular weight and such a high viscosity as to be almost solid at ambient (but not higher) temperature: such a resin while still hot is "drowned" in up to 40% of urea (based on resin solids) to decrease the viscosity of the resin to a perfectly manageable level. These PF in urea solutions have high reactivity and fast curing time thanks to the great advancement of the resin [31,50]. They show little copolymerization with the PF in their liquid state and some copolymerization in the hardened network, the majority of the urea still remaining free to leach out after curing. For these reasons they must not be confused with copolymerized PUFs of high urea proportion which also are operative in fast hardening time applications and are described more fully elsewhere in this chapter [31,32].

Formaldehyde in liquid solution or solid form and formaldehyde-generating compounds are also phenolic resin additives that improve functionality and decrease curing times. Paraformaldehyde is used most frequently, but hexamethylenetetramine, formaldehyde/sodium bisulfite complexes, tris(hydroxymethyl)nitromethane, and glyoxal are also used. Significant effects are obtained when 3 to 5% is added, based on phenolic resin solids. Further reduction in curing time is possible if 1 to 2% resorcinol is added or resorcinol-acting natural extractives such as condensed (flavonoid) tannin extracts (wattle, mimosa, and others). This can be either mixed or not mixed with paraformaldehyde and added to the liquid phenolic resin glue mix. Equally ester accelerators such as glycerol acetate (triacetin), guanidine carbonate, and other esters are also used as very effective cure accelerators and to improve the final hardened strength (See Section III.B.1 on α- and β-set acceleration).

Formaldehyde additions overcome the effect of phenolic extractives in certain hardwood species, which prevent proper cure or adhesion of PF resins. Free formaldehyde appears to react rapidly with these phenolic extractives before they can interfere with the phenolic resin curing mechanism. With certain wood species that are rich in extractives, this technique has been used to increase bond durability from interior-grade to true exterior-grade performance.

Natural phenolic compounds are used as both replacements for substantial portions of synthetic phenol in plywood adhesive resins and as glue mix additives to improve performance; 4 to 6% is added, based on phenolic resin solids. They bring about improvements in assembly time tolerance and flow with no significant change in adhesion. Glue mix additions of wattle tannin or other condensed flavonoid tannin extracts with or without additional formaldehyde produce faster hot-pressing cycles. However, some assembly time tolerance and pot life, has to be sacrificed in the process, but full exterior-grade durability is retained.

The lignin residues from wood pulp production are another class of extractives currently receiving attention as phenolic resin additives. Substituted phenols, such as cresols and xylenols, have been used as glue mix additives for phenolic adhesive resins to improve assembly time tolerance. They are also used as solvents to remove oleoresinous deposits on the surface of pitchy softwood veneers. They can be used as flow promoters in phenolic hardwood adhesives. To avoid interference with the rate of resin curing, the amount added should not exceed 3 to 4% of the phenolic resin solids content.

Complexing additives commonly include the soluble salts of boron, chromium, zinc, cobalt, lead, manganese, magnesium, and others. When added to phenolic resin adhesives, some of these compounds have been successful in reducing pressing times and in improving prepress performance [51]. Borax is widely used in North America to shorten the prepress cycles of phenolic plywood glues for softwoods. However, these compounds tend to increase the molecular weight of a phenolic resin by complexing several molecules together through their phenolic hydroxyl groups. The gain in the resin molecular weight and prepress tack is sometimes accompanied by a reduction in assembly time tolerance and the loss of the B-stage melt-flow behavior. In hardwood gluing, this is sometimes not advantageous, and the addition of complexing salts should be approached with caution.

Mixed borate salts are very effective as a treatment for the preservation of wood products against fungi and most insects. However, the boron salts, which become localized in high concentration on the veneer surface, tend to gel the phenol resin before it can reach the wood surface and bond to it. However, very dilute aqueous solutions of borates (i.e., 0.25%) applied to softwood veneers in their green state decrease their thermal degradation during high-temperature drying and preserve their reactive sites for bonding with phenolic adhesives.

3. *Formulation of Plywood Glue Mixes*

The guiding principles for the preparation of plywood adhesive glue mixes are:

1. To maintain the highest possible phenolic solids content in the mixed glue (preferably in the range 30 to 40%).
2. To incorporate a cellulosic filler, such as a nutshell flour of 200 mesh or finer, in a proportion of about 20 to 40% of phenolic solids. Nonabrasive inorganic fillers may also be satisfactory.
3. Alternatively, to add about half this amount of unrefined starchy material, such as wheat flour.
4. To add no alkali, or at the most only 1 to 2% to disperse and stabilize the starchy material.
5. To add only enough water to produce a glue viscosity that can be handled by the gluing equipment. The preferred viscosity range is 1500 to 2500 cP, measured at 25°C.
6. To ensure proper wetting of the veneer by the glue film, a surface active agent should be added (about 0.1 to 0.25% of resin solids).

Examples of glue mixes incorporating these principles are listed in Table 1.

Table 1 Examples of Glue Mixes

Material	Composition		
40–45% Solids PF resin	100	100	100
300-Mesh coconut (or walnut) shell flour	12	14	10
Industrial wheat flour	6	—	—
50% Sodium hydroxide	2	—	—
Surfactant	0.1	0.1	0.1
Water	10	5	
Total parts	130.1	119.1	110.1
Phenolic solids	31–35%	33–38%	36–41%

4. *General Observations on Particleboard Manufacture [51]*

In the case of the application of phenolic adhesives to the manufacture of exterior-grade particleboard, the closest attention must be focused on the application of the resin rather than on its formulation. A good phenolic resin for plywood can be used successfully for the manufacture of particleboard once the various conditions of application have been understood. The pressing time of the board varies according to the type of adhesive, its reactivity, and the moisture content of the glued particles. In many cases a light water spray is applied to the top surfaces of the board before prepressing to shorten the pressing time. The light film of water covering the surface is vaporized when it comes in contact with the hot caul sheet of the press and migrates from the surfaces toward the core of the panel, causing a faster increase in temperature and a faster cure.

The water spray prevents precuring of the adhesive on the surface of the board during closure of the press before contact with the hot top caul sheet. The wood undergoes a partially irreversible plastic deformation during pressing, caused by the combined action of pressure and heat. Different products can be obtained by varying the type of pressing cycle of the board. Different pressing procedures and diagrams are available. A diagram for industrial three-layer particleboards may read as follows:

1. *Maximum Pressure* A pressure of 23 to 27 kg/m^2 is reached as fast as possible after pressure closure (i.e., after 35 to 50 s; other processes use pressure as high as 35 kg/cm^2).
2. *Contact with the Gauge Bars* As a rule, contact is made after 60 to 120 s from the start of the press closure. The higher the density, the longer the time it takes. This, however, can be reduced by increasing the moisture content of the glued mat.
3. *Steam Escape* This is expected to begin 1 to 3 min after making contact with the gauge bars.
4. *Pressure Decrease* After approximately 1½ to 2 min of maximum pressure, the pressure is slowly decreased until the final pressure on the panel is as low as 2 to 3 kg/cm^2. This takes place toward the end of the cycle, just before press opening.

This pressing diagram produces a board with high-density face layers and the shortest possible pressing time, at a given temperature and a low power consumption. The main properties of panels with high-density face layers are the stiffness of the panel; better warp resistance; high dimensional stability; hard, glossy, and shockproof surfaces that need less adhesive for subsequent veneering; and narrow thickness tolerances.

Considerable variation in the properties of the final board can be obtained by varying the moisture contents of surface and core layers, and by using faster resins in the core layer and slower reacting resins in the surface layer; these variations, among others, intending to increase the board core density and to improve the density profile of the panel as a function of its thickness. This is one of the contributory factors to improving properties based on the adhesive application technology rather than on the characteristics of the adhesive itself. In wood particleboard manufacture, factors derived from the application/pressing technology contribute as much as 50% to the final performance, the rest being due to how good the adhesive itself is. This can also be achieved by varying the geometry and sizes of the wood chips, the density of the board, and so on. Small variations in the manufacture and characteristics of the phenolic resin used do not affect the property of the finished particleboard as extensively as do the factors listed above. Experiments [51] on the correlation of curing and bonding properties of particleboard glued with resol-type phenolic resins by differential scanning calorimetry show that resols tend to reach two endotherm peaks; the first at 65 to 80°C and the second at 150 to 170°C. Resols used for particleboard have been shown to begin curing at lower temperatures than those for novolak resins. Resol-glued particleboard shows no bond formation at 120°C. At 130°C the resol-glued panels show internal bond strengths of 0.55 to 0.7 Mpa. The internal bond strength for the wet tests increases as the board core temperature goes over 120°C during pressing. The normal press platen temperatures for 12- to 13-mm-thick board glued with phenolic adhesives are 170 to 230°C. The pressing time is 18 to 12 s/mm for standard PF resins but today PUFs [31], and ester-accelerated [31,32], tannin-accelerated [51], and urea-drowned PF resin [50] adhesives can reach pressing times as fast as 5 s/mm at 190–210°C in industrial applications [30,31]. Typical results obtained using PF adhesives for particleboard are shown in Table 2.

5. *Dry-Out Resistance*

One of the more common difficulties in bonding pine veneers and chips is adhesive dry-out. Dry-out is associated with the high liquid absorbancy of pine sapwood and it appears especially during long assembly times. This problem can be overcome by using resins modified through reaction with alkylated phenols, especially 3,4-xylenol [52]. Another technique used to achieve similar results is the manipulation of synthesis procedures used in preparing a standard PF resin [52]. The dry-out resistance imparted by alkylated phenols is due to an initial semithermoplastic character in the resin. This is derived from their monomer bifunctionality and the linear polymer that is consequently formed.

If a linear and essentially non-cross-linking prepolymer is prepared from phenol and formaldehyde, it can be coreacted with a nonlinear and cross-linking prepolymer to form a resin. The latter resin will have some initially semithermoplastic or dry flow character but will be primarily thermosetting. The product is an alkaline novolak–resol copolymer.

Table 2 Results Obtained Using PF Adhesives for Particleboard

	Swelling after 2 h boil		Internal bond strength		
Density (g/cm^3)	Measured wet (%)	Measured dry (%)	Dry (kg/cm^2)	After 2 h boil (kg/cm^2)	Cold-water swelling (%)
± 0.700	± 15	2–3	10–11	5–8	9–11

Evaluation of this copolymer concept has shown that many resins possess a controlled initial semithermoplastic character which improves resistance to dry-out. Good dry-out resistance is achieved without loss of press-time efficiency or broad-range bonding ability. Such resins perform noticeably better than other types of resins that are resistant to dry-out.

Such a resin of the alkaline novolak–resol type can be prepared by coreacting a prepolymer, prepared by reacting formaldehyde and phenol in the molar ratio of 2.6:1.0, and a prepolymer obtained by reacting formaldehyde and phenol in the molar ratio of 1:1. The two prepolymers are then mixed in 50:50 proportions by mass and coreacted.

B. Foundry Sand Binders and Mineral Fiber Binders

Phenolic resins are also extensively used in the binding of foundry molds. Both resol and novolak resins are used for this application. The sand is coated with the phenolic resin at a rate of 3 to 4%. The PF resin can be used both as an organic solvent solution and in powder form. Coating of the substrate can be done both at ambient or at higher temperature. In higher-temperature coatings novolaks are the preferred resins and in this application, waterborne resins (75% resin) can also be used. Hexamethylenetetramine as well as wax are added. Hexamine is often added separately from the resin to avoid precuring.

Another equally important field of application of phenolic resins is in the binding of mineral fibers such as glassfiber and rock wool. These are used for thermal and acoustic insulation at densities in the range 2.5 to 70 kg/m^3. Both powder and liquid resins, generally in water solution, are used for this purpose. Liquid resins are generally applied at about 10% concentration in water; the water evaporates, cooling the fiber and avoiding decomposition of the resins, and the resinated mat is then cured in a hot-air circulation oven at 175 to 200°C for 2 to 5 min.

Acid-setting (but not only) PF resins are extensively used in these fields, resins that cannot be used to bind wood or to impregnate paper for laminates due to the acid hydrolysis of the cellulose they would cause. However, even in the wood bonding field self-neutralizing acid-setting PF resins have been developed, although these are not used industrially. Self-neutralizing systems for the hardened glue line are based on special hardeners that allow rapid curing of the resin and equally quick return to neutrality of the hardened glue line on joint cooling. A good joint bonded with a rapidly self-neutralizing PF resin shows high strength and high levels of adhesion and this system shows some promise in some applications of wood bonding [33].

C. Binders from PF Copolymers with Other Resins

The characteristics of PF resins and the reactive chemical groups they present render them particularly suitable for the preparation of binders by coreaction with other resins. This is still a relatively young field, and the most interesting and relevant co-resins that are being used or explored in this respect are the aminoplastic resins, in particular urea–formaldehyde (UF) and melamine–formaldehyde (MF) (the copolymerization with the latter being a somewhat older use), and the diisocyanates.

While MF resins have been known for a long time to be able to form true copolymers with PF resins, this has not been the case for UF resins. Until quite recently, copolymerization between PF and UF resins or urea was not thought to be likely [53], the system curing as a polymer blend only. However, applications of this type have been shown to be useful also [31,45,54]. Such a deduction was based on the lack of detection of any methylene bridge between the phenolic nuclei and the amido group of urea. Recently, PUF resins of two different types and for two different purposes have been shown to be able to copolymerize. First, Tomita [54] has shown that copolymerization between PF and urea resins occurs under acid conditions, the driving force of this work being the aim to produce a PUF copolymer in which the methylol groups are on the amido group of urea, and thus able to cure rapidly at very mild acidic pH values as a UF resin while the resin retains a level of water resistance. Second, in the alkaline pH range PF resins were shown to be able to copolymerize rapidly with urea, doubling the PF linear degree of polymerization while presenting full water resistance of the cured resin [45]. This latter approach was extended to copolymerize fairly high molar amounts of urea and to form a true PUF of excellent exterior performance, much lower cost, and much faster curing and pressing time while still curing at the alkaline pH characteristic of true PF resins [31,32]. The PUF resin showed higher strength of the finished network and increasing hardened strength when the proportion of urea is progressively increased. In this reported work the proportion of urea capable of copolymerizing to form the PUF was shown to depend on the formaldehyde to phenol molar ratio of the resin; within certain limits, the higher the molar ratio the higher the proportion of urea capable of copolymerizing. The upper proportion of urea was limited by the relative increase in viscosity and related pot-life shortening of the resin and no other factors [31,32].

Both behaviors are easily explained by the relative rates of PF condensation and of urea hydroxymethylation and subsequent combination. Thus in Fig. 6 the relative gel times of PF and UF resins are shown, as well as taking in consideration the relative rate constants of PF autocondensation and urea hydroxymethylation and self-condensation, indicating quite clearly in which pH ranges copolymerization is possible and with which species [55]. Figure 6 shows that urea and PF resin, with little free formaldehyde or methylol ureas, will easily copolymerize at pH higher than 7; in Fig. 6, PF and UF resins copolymerize in the pH range 6–9. The type of reactions and mechanisms involved have been worked out and summarized in a scheme (shown on page 555) indicating all the main reactions occurring in the formation of PUF resins [31] even taking in consideration that the urea hydroxymethylation reaction is an equilibrium and that reversible reactions do occur.

PF resols in water solution have been shown [56] to react rapidly and readily with polymeric 4,4′-diphenylmethane diisocyanate (MDI) with minimal deactivation of the

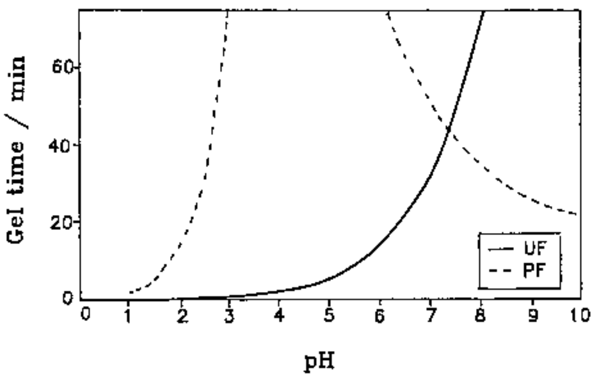
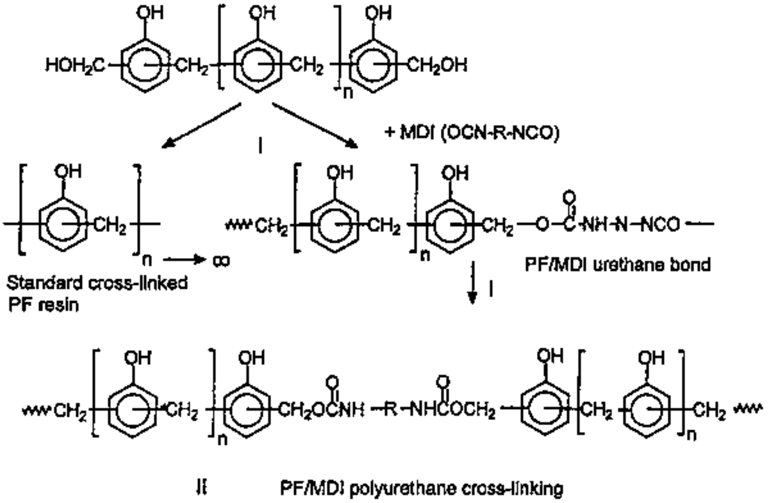
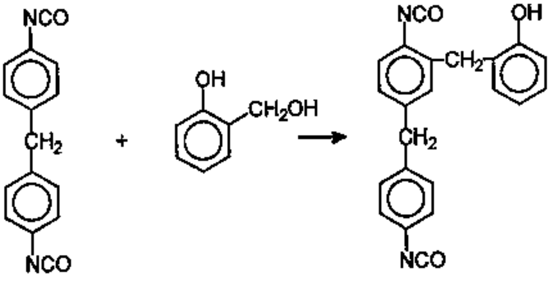


Figure 6 Relationship of gel time to pH for PF and UF resins.

isocyanate groups by water. This peculiar behavior is based on the much faster rate of reaction of the isocyanate group with the PF methylol groups (hydroxybenzyl alcohol groups) than with water [56]. Such adhesives are now used industrially to a limited extent, for bonding difficult to glue hardwood veneer species into exterior-grade plywood [57], and present exceptional adhesion, ease of bonding, adequately long pot life, and very high adhesive strength. There is now more industrial interest in using these adhesives for particleboard and for wood panels other than plywood since it has been perceived that they are an excellent and viable alternative to both pure isocyanates as well as pure phenolics. The reactions which bring network cross-linking of these copolymers (proportions between 5 and 30% of isocyanate on PF resin solids are used when the two are mixed in the glue mix and coreacted in the hot press while pressing the wood panel; 1–2% are used when they are prereacted, but this latter approach is not as yet used industrially and might present some problems) are:



(i) The formation of urethane bridges derived by the reaction of the isocyanate group with the methylol group of the PF resin [33,56], which is perhaps one of the two dominant reactions introducing better dissipation of energy at the interface and hence contributing to strength improvement; (ii) the classical formation of methylene bridges in the PF resin only [33,56,57]; (iii) the formation of polyurea networks due to the reaction of the polymeric polyisocyanate with the water carrier of the PF resin [33,56,57]; and (iv) the reaction of the PF methylol group to form methylene bridges on the aromatic nuclei of polymeric MDI [56].



This latter reaction was also observed to occur between the methylol groups of lignin and the aromatic nuclei of the polymeric MDI which had been proven to be able to penetrate the wood cellular walls [58].

D. Time–Temperature-Transformation and Continuous-Heating-Transformation Curing Diagrams of PF Resins in situ in the Joint

The use of TMA techniques has allowed for the first time the determination of time–temperature-transformation (TTT) and continuous-heating-transformation (CHT) diagrams for UF and PF [59,60] adhesives and for MUF and phenol–resorcinol–formaldehyde (PRF) [41] adhesives hardening directly within wood joints and allowed the quantification of the wood/adhesive interface characteristics and parameter limits. Until then, such diagrams had been obtained only for epoxy resins on glassfiber braid. In Figs. 7, 8, and 9 are shown PF resins on wood isothermal TTT and constant heating rate CHT diagrams as compared to what was previously known about the same diagrams of epoxy resins on glassfiber (a noninterfering substrate) [61,62].

Different trends to those reported in the literature for TTT and CHT diagrams of epoxy resins in the literature, occur in the higher and lower temperature zones of the diagrams of waterborne formaldehyde-based resins hardening on wood. CHT and TTT diagrams have been reported for PF, UF, MUF, PRF, and tannin–formaldehyde thermosetting resins [59,60]. The experimental TTT diagram in Fig. 8 shows quite a different trend from the CHT diagram for the same resins and for the TTT diagrams reported in the literature for epoxies on glassfiber. To start to understand the trend shown in Fig. 8 it is first necessary to observe what happens to the modulus of the wood substrate alone (without a resin being present) when examined under the same conditions of a wood

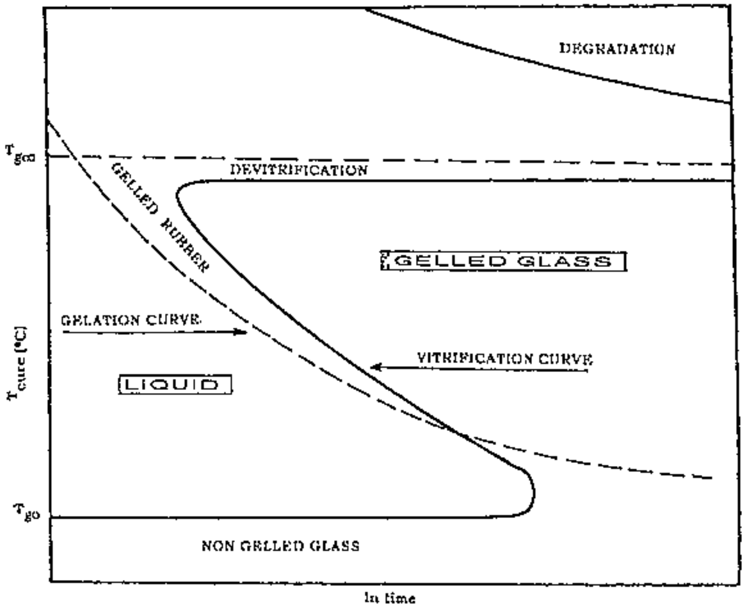


Figure 7 Higher temperature zone detail of the TTT diagram of epoxy resin adhesives on non-interacting glass fiber substrate.

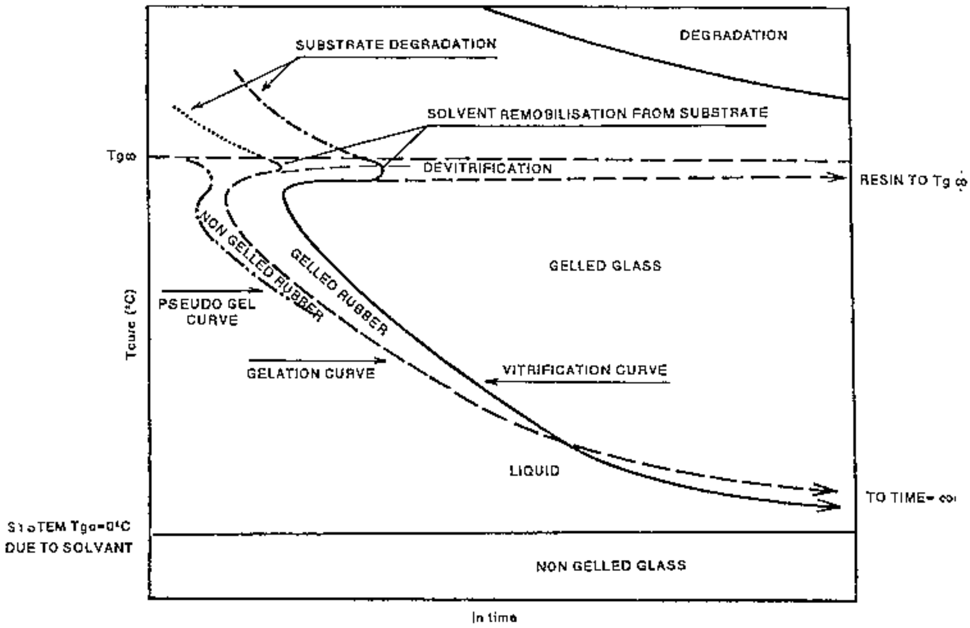


Figure 8 Total generalized TTT diagram of PF resin adhesives on interacting lignocellulosic substrate.

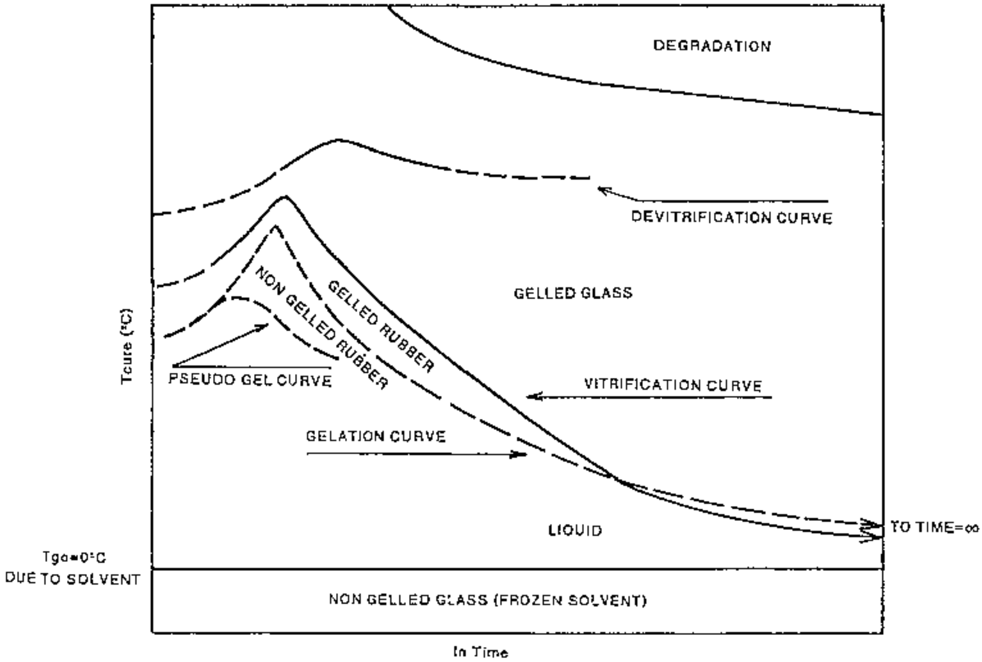


Figure 9 Total generalized CHT diagram of PF resin adhesives on interacting lignocellulosic substrate.

joint during bonding. No significant degradation occurs up to a temperature of 180°C as shown by the relative stability of the value of the elastic modulus as a function of time. Some slight degradation starts to occur at 200°C, but after some initial degradation the elastic modulus again settles to a steady value as a function of time and at a value rather comparable to the steady value obtained at lower temperatures. Evident degradation starts to be noticeable in the 220–240°C range and this becomes even more noticeable at higher temperatures. The effect of substrate degradation on the TTT diagram in Fig. 8 can then only start to influence the trends in the gel and vitrification curves at temperatures higher than 200°C and it is for this reason that the regions of the curves above 200°C are indicated by dashed lines in Fig. 8. At a temperature $\leq 200°$C the trends observed are only due to the resin. In this temperature range the eventual change to longer time and more stable temperature of the vitrification curve, characteristic of the TTT diagrams of epoxy resins (Fig. 7), becomes also evident for the TTT diagrams of the waterborne PF and other formaldehyde resins on lignocellulosic substrates, indicating that diffusion hindrance at a higher degree of conversion becomes for these resins too the determinant parameter defining the reaction rate. However, what differs from previous diagrams is that the trend of all the curves, namely the gel curve, initial pseudogel (entanglement) curve, and start and end of the vitrification curve, is the same. In epoxy resin TTT diagrams the trend of the gelation curve is completely different from that reported here. The result shown in Fig. 8 is, however, rather logical because if diffusion problems alter the trend of the vitrification curve, then the same diffusional problem should also alter the gel and pseudogel curves. This is indeed what the experimental results in Fig. 8 indicate. It may well be that in waterborne resins the effect is more noticeable than in epoxy resins. This is the reason why it is possible to observe it for PF, UF, PRF, and MUF resins. With the data available and with the limitation imposed by the start of wood substrate degradation at higher temperatures it is not really possible to say if the gel curve and the vitrification curve run asymptotically towards the same value of temperature at time of infinity, although the indications are that this is quite likely to be the case. What is also evident in the trend of the two curves is the turn to the left, hence the inverse trend of their asymptotic tendency towards $T_{g\infty}$. This turn cannot be ascribed to substrate degradation because for very reactive resins, such as PRFs, such a turn already occurs at a temperature lower than 150°C, hence much lower than the temperature at which substrate degradation becomes significant. This inverse trend can only be attributed to movements of water coming from the substrate towards the resin layer as the trend of the curves indicates an easing of the diffusional problem already proven to occur at such a high degree of conversion [59,60].

Two other aspects of the TTT diagrams in Fig. 7, 8, and 9 must be discussed, these being the trend of the curves at temperatures higher than 200°C and the trend of the devitrification (or resin degradation) curve. The trend indicated by the dashed lines and the experimental points of all the curves at temperatures above 200°C is clearly only an effect caused by the ever more severe degradation of the substrate; degradation of the substrate implies a greater mobility of the polymer network constituting the substrate, hence the continuation of the curves as shown in their dashed part. That this is the case is also supported by the virtual negative times yielded by the TMA equipment when the temperature becomes extreme, as well as by the trend of the resin's higher degradation curve which tends to intersect the vitrification curve at about 200–220°C or higher, this being a clear indication that one is measuring the changes in the reference system, the substrate itself, and that these are at this stage much more important than the small changes occurring in the resin and so dominate the whole complex system of the bonded joint. The CHT and TTT diagrams pertaining to waterborne formaldehyde-based polycondensation resins on a lignocellulosic substrate should then appear in their entirety as shown in Figs. 8 (TTT) and 9 (CHT).

E. Prediction of Properties

Only a small amount of work has been done up to now concerning the prediction of bond strengths and other properties based on the results of the analysis of the PF resin. Correlation equations evaluating the chemical structures in various PF resins with different formaldehyde/phenol molar ratios and different types of preparation on the one hand and the achievable internal bond as well as the subsequent formaldehyde emission on the other hand have been developed [63]. These equations are valid only for well defined series of resins. The basic aim of such equations is the prediction of the properties of the wood-based panels on the basis of the composition and the properties of the resins used. For this purpose various structural components of the liquid resin are determined by means of ^{13}C nuclear magnetic resonance (NMR) and their ratios related to board results, so to the strength results of the hardened resin. Various papers in the chemical literature describe examples of such correlations, in particular for UF, MF, MUF, and PF resins [63–67]. For example, one type of equation correlating the dry internal bond (IB) strength (tensile strength perpendicular to the plane of the panel) of a particleboard bonded with PF adhesive resins is as follows [33,63]

$$\text{Resin cross-linking} \approx \text{IB} = a\,A/(A+B+C) + b\,Mo/(A+B+C) + c\,Me/(A+B+C) \tag{1}$$

where the IB strength is expressed in MPa; A is the sum of the peak areas of phenolic ortho and para sites still free to react (110 to 122 ppm), B is the sum of the peak areas of phenolic meta sites (125 to 137 ppm), C is the sum of the peak areas of phenolic ortho and para sites already reacted (125 to 137 ppm), Mo is the sum of the peak areas of phenolic methylol groups (59 to 66 ppm), and Me is the sum of the peak areas of methylene bridges connecting phenolic nuclei (30 to 45 ppm). The coefficients a, b, and c are characteristic of the type of resin and depend on a variety of manufacturing parameters. Equation (1) is one of the simpler equations of this type, the equations for UF resins in particular being in general more complex. Similar equations correlating the level of crystallinity of hardened aminoplastic resin, the IB strength of the board prepared with it, the level of cross-linking of the resin and the formaldehyde emission of the panel and resin with the ^{13}C NMR spectrum of the liquid resin have also been presented [33, 64–67].

For certain boards, good correlation exists. However, it must be assumed that a general correlation for various resins and various panels will not exist and that maybe other correlation equations should be used. Nevertheless, these results are rather important, because they show that at least for a special combination of resin type and board type, correlation between analysis of the resin in its liquid state and the strength of the same resin in hardened form exists, and that forecast of performance can be done based on just the analysis of the liquid resin. Furthermore the various parameters corresponding to chemical and physical groups in the liquid resin will also be the decisive parameters for other resin combinations and manufacturing procedures, although the values of the coefficients within the individual equations might differ. However, it also must be considered that the range of molar ratio under investigation in the papers mentioned above is rather broad. At the moment it is not possible to use these equations for predictions within too narrow a range of molar ratios.

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Natural Phenolic Adhesives I: Tannin

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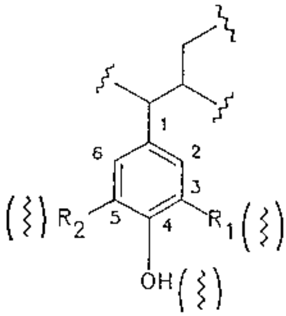
I. INTRODUCTION

The loose term *renewable resources adhesives* has been used to identify polymeric compounds of natural, vegetable origin that have been modified and/or adapted to the same use as some classes of purely synthetic adhesives [1]. At present two classes of these adhesives exist: one already extensively commercialized in the southern hemisphere and the other on the slow way to commercialization. These two types of resins are tannin-based adhesives [2] and lignin adhesives [3–6]. Both types are aimed primarily at substituting synthetic phenolic resins. In some aspects, such as performance, they closely mimic, or are even superior to, synthetic phenolic adhesives, while in others they behave in a vastly different manner from their synthetic counterparts. In this chapter we focus primarily on tannin-based adhesives because they have already been in extensive industrial use in the southern hemisphere, in certain fields of application, for the past 20 years. These adhesives are of some interest not only for their excellent performance in some applications but also for their mostly environmentally friendly composition. Lignin adhesives are treated briefly here and in detail in Chap. 28.

II. LIGNIN ADHESIVES

Lignin is a phenolic polymer that is one of the main polymeric constituents of wood formula (1). It is generally produced in great quantities as waste from paper pulp mills. It is composed of repeating phenylpropane units. Considerable research has been carried out on lignin adhesives and binders. While for certain applications, such as binders for nontarred rough rural roads, lignin derivatives have been used for many years, in the main area of potential application—wood adhesives—industrial use has been lagging. A variety of effective lignin adhesive formulations exist and have already been reviewed extensively [3], some of them having been used for some length of time in some particleboard or plywood mills. Not all these formulations are used today because all of them always come up against two broad problems: the formulation tends to be corrosive or hard on equipment in the plant, or the lignin in the formulation tends to noticeably slow down panel pressing time, with consequent loss of mill productivity. In North America there are now encouraging indications that premethylolated lignin (prereacted with formaldehyde) can be added in place of up to 20 to 30% of synthetic phenolic resins for plywood without lengthening panel pressing times, and a few mills already appear to have been using such a system for some time [4]. Recent claims that industrial use of wood adhesive formulations containing up to 50% lignin has occurred for some years but has now been discontinued purely on economical grounds have proven to be true and reliable [7]. Considering their very limited application, the reader is referred to more extensive reviews on this subject [3,6].



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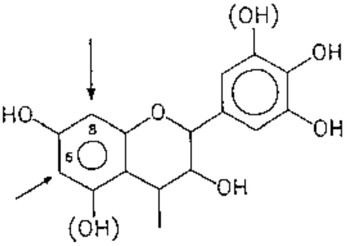
III. TANNIN-BASED ADHESIVES

The word tannin has been used loosely to define two different classes of chemical compounds of mainly phenolic nature: hydrolyzable tannins and condensed tannins. The former, including chestnut, myrabalans (*Terminalia* and *Phyllantus* tree species), and divi-divi (*Caesalpina coriaria*) extracts, are mixtures of simple phenols such as pyrogallol and ellagic acid and of esters of a sugar, mainly glucose, with gallic and digallic acids [2]. They can and have been used successfully as partial substitutes (up to 50%) for phenol in the manufacture of phenol–formaldehyde resins [8,9]. Their chemical behavior towards formaldehyde is analogous to that of simple phenols of low reactivity and their moderate use as phenol substitutes in the above-mentioned resins does not present difficulties. Their lack of macromolecular structure in their natural state, the low level of phenol substitution they allow, their low nucleophilicity, limited worldwide production, and their higher price somewhat decrease their chemical and economical interest.

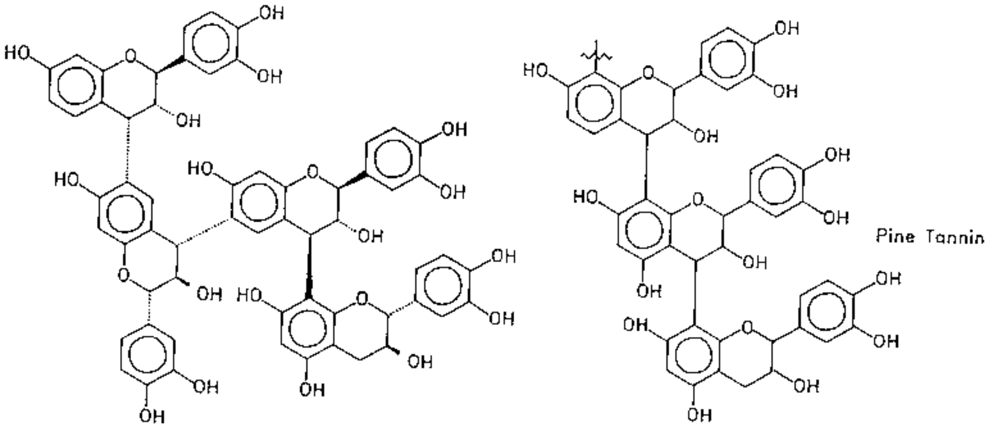
Condensed tannins, on the other hand, constituting more than 90% of the total world production of commercial tannins (200,000 tons per year), are both chemically and economically more interesting for the preparation of adhesives and resins. Condensed tannins and their flavonoid precursors are known for their wide distribution in nature and particularly for their substantial concentration in the wood and bark of various trees. These include various *Acacia* (wattle or mimosa bark extract), *Schinopsis* (quebracho wood extract), *Tsuga* (hemlock bark extract), and *Rhus* (sumach extract) species, from which commercial tannin extracts are manufactured, and various *Pinus* bark extract species. Where the bark and wood of trees were found to be particularly rich sources of condensed tannins, commercial development ensued through large-scale afforestation and/or industrial extraction, mainly for use in leather tanning. The production of tannins for leather manufacture reached its peak immediately after World War II and has since progressively declined. This decline of their traditional market, coupled with the increased price and decreased availability of synthetic phenolic materials due to the advent of the energy crisis of the early 1970s, stimulated fundamental and applied research on the use of such tannins as a source of condensed phenolics.

A. Condensed Tannins

The structure of the flavonoid constituting the main monomer of condensed tannins may be represented as follows:



this flavonoid unit is repeated 2 to 11 times in mimosa tannin, with an average degree of polymerization of 4 to 5, and up to 30 times for pine tannins, with an average degree of polymerization of 6 to 7 for their soluble extract fraction [10–12].



The nucleophilic centers on the A ring of a flavonoid unit tend to be more reactive than those found on the B ring. This is due to the vicinal hydroxyl substituents, which cause general activation in the B ring without any localized effects such as those found in the A ring.

Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages at reactive positions on the flavonoid molecules, mainly the A rings. The reactive positions of the A rings are one of positions 6 or 8 (according to the type of tannin) of all the flavonoid units and both positions 6 and 8 of the upper terminal flavonoid units. The A rings of mimosa and quebracho tannins show reactivity toward formaldehyde comparable to that of resorcinol [13–15]. Assuming the reactivity of phenol to be 1 and that of resorcinol to be 10, the A rings have a reactivity of 8 to 9. However, because of their size and shape, the tannin molecules become immobile at a low level of condensation with formaldehyde, so that the available reactive sites are too far apart for further methylene bridge formation. The result may be incomplete polymerization and therefore weakness. Bridging agents with longer molecules should be capable of bridging the distances that are too long for methylene bridges. Alternatively, other techniques can be used to solve this problem.

In condensed tannins from mimosa bark the main polyphenolic pattern is represented by flavonoid analogs based on resorcinol A rings and pyrogallol B rings. These constitute about 70% of the tannins. The secondary but parallel pattern is based on resorcinol A rings and catechol B rings [2,14]. These tannins represent about 25% of the total of the mimosa bark tannin fraction. The remaining part of the condensed tannin extract is the “nontannins” [14]. They may be subdivided into carbohydrates, hydrocolloid gums, and small amino and imino acid fractions [2,14]. The hydrocolloid gums vary in concentration from 3 to 6% and contribute significantly to the viscosity of the extract despite their low concentration [2,14]. Similar flavonoid A- and B-ring patterns also exist in quebracho wood extract (*Schinopsis balansae* and *Schinopsis lorentzii*) [13–15], but no phloroglucinol A-ring pattern, or probably a much lower quantity of it, exists in quebracho extract [15–17]. Similar patterns to wattle (mimosa) and quebracho are followed by hemlock and Douglas fir bark extracts. Completely different patterns and relationships do instead exist in the case of pine tannins [18–20] which present instead only two main patterns: one represented by flavonoid analogs based on phloroglucinol A rings and catechol B rings [18,20]. The other pattern, present in much lower proportion, is represented by phloroglucinol A rings and phenol B rings [18,20]. The A rings of pine tannins then possess only the phloroglucinol type of structure, much more reactive toward formaldehyde than a resorcinol-type structure, with important consequences in the use of these tannins for adhesives.

In condensed polyflavonoid tannin molecules the A rings of the constituent flavonoid units retain only one highly reactive nucleophilic center, the remainder accommodating the interflavonoid bonds. Resorcinolic A rings (wattle) show reactivity toward formaldehyde comparable to, though slightly lower than that of resorcinol [21]. Phloroglucinolic A rings (pine) behave instead as phloroglucinol [22]. Pyrogallol or catechol B rings are by comparison unreactive and may be activated by anion formation only at relatively high pH [16]. Hence the B rings do not participate in the reaction except at high pH values (pH 10), where the reactivity toward formaldehyde of the A rings is so high that the tannin–formaldehyde adhesives prepared have unacceptably short pot lives [21]. In general tannin adhesive practice, only the A rings are used to cross-link the network. With regard to the pH dependence of the reaction with formaldehyde, it is generally accepted that the reaction rate of wattle tannins with formaldehyde is slowest in the pH range 4.0 to 4.5 [23]; for pine tannins, the range is between 3.3 and 3.9.

Formaldehyde is generally the aldehyde used in the preparation, setting, and curing of tannin adhesives. It is normally added to the tannin extract solution at the required pH, preferably in its polymeric form of paraformaldehyde, which is capable of fairly rapid depolymerization under alkaline conditions, and as urea–formalin concentrates. Hexamethylenetetramine (hexamine) may also be added to resins due to its potential formaldehyde releasing action under heat. Hexamine is, however, unstable in acid media [24] but becomes more stable with increased pH values. Hence under alkaline conditions the liberation of formaldehyde might not be as rapid and as efficient as wanted. Also, it has been fairly widely reported, with a few notable exceptions [25], that bonds formed with hexamine as hardener are not as boil resistant [26] as those formed by paraformaldehyde. The reaction of formaldehyde with tannins may be controlled by the addition of alcohols to the system. Under these circumstances some of the formaldehyde is stabilized by the formation of hemiacetals [e.g., $CH_2(OH)(OCH_3)$] if methanol is used [2,22]. When the adhesive is cured at an elevated temperature, the alcohol is driven off at a fairly constant rate and formaldehyde is progressively released from the hemiacetal. This ensures that less formaldehyde is volatilized when the reactants reach curing temperature and that the pot life of the adhesive is extended. Other aldehydes have also been substituted for formaldehyde [2,21,23,25].

In the reaction of polyflavonoid tannins with formaldehyde two competitive reactions are present:

1. The reaction of the aldehyde with tannin and with low-molecular-weight tannin–aldehyde condensates, which are responsible for the aldehyde consumption.
2. The liberation of aldehyde, available again for reaction. This reaction is probably due to the passage of unstable $–CH_2–O–CH_2–$ ether bridges initially formed to $–CH_2–$ linked compounds.

In the case of some tannins, namely quebracho tannin, a third reaction of importance is present,

3. The simultaneous hydrolysis of some interflavonoid bonds, hence a depolymerization reaction, partly counteracting and hence slowing down hardening [26–28]. Notwithstanding that the two major industrial polyflavonoid tannins which exist, namely mimosa and quebracho tannins, are very similar and both composed of mixed prorobinetinidins and profisetinidins one could not explain this anomalous behavior of quebracho tannin. It has now been possible to determine by both nuclear magnetic resonance (NMR) [26] and particularly by laser desorption mass spectrometry (MALDI-TOF) for mimosa and quebracho tannins and some of their modified derivatives [28] that: (i) mimosa tannin is predominantly composed of prorobinetinidins while quebracho is predominantly composed of profisetinidins, (ii) mimosa tannin is heavily branched due to the presence of considerable proportions of "angular" units in its structure while quebracho tannin is almost completely linear [28]. This latter structural difference contributes to the considerable differences in viscosity of water solutions of the two tannins and which (iii) induces the interflavonoid link of quebracho to be more easily hydrolyzable, due to the linear structure of this tannin, confirming NMR findings [26,28] that this tannin is subject to polymerization/depolymerization equilibria. This also showed that the decrease of viscosity due to acid/base treatments to yield tannin adhesive intermediates does also depend in quebracho on a certain level of hydrolysis of the tannin itself and not only of the carbohydrates present in the extract (see Section IV). This tannin hydrolysis does not appear to occur in mimosa tannin in which the interflavonoid link is completely stable to hydrolysis.

It is interesting to note that while $–CH_2–O–CH_2–$ ether bridged compounds have been isolated for the phenol–formaldehyde [24] reaction, their existence for fast-reacting phenols such as resorcinol and phloroglucinol has been postulated, but they have not been isolated, as these two phenols have always been considered too reactive with formaldehyde. They are detected by a surge in the concentration of formaldehyde observed in kinetic curves due to methylene ether bridge decomposition [19].

When heated in the presence of strong mineral acids, condensed tannins are subject to two competitive reactions. One is degradative leading to lower-molecular-weight products, and the second is condensative as a result of hydrolysis of heterocyclic rings (*p*-hydroxybenzyl ether links) [16]. The *p*-hydroxybenzylcarbonium ions created condense randomly with nucleophilic centers on other tannin units to form "phlobaphenes" or "tanner's red" [16,29–31]. Other modes of condensation (e.g. free radical coupling of B-ring catechol units) cannot be excluded in the presence of atmospheric oxygen. In predominantly aqueous conditions, phlobaphene formation or formation of insoluble condensates predominates. These reactions, characteristic of tannins and not of synthetic phenolic resins, must be taken into account when formulating tannin adhesives.

Sulfitation of tannin in one of the oldest and most useful reactions in flavonoid chemistry. Slightly sulfited water is sometimes used to increase tannin extraction from the bark containing it. In certain types of adhesives, the total effect of sulfitation, while affording the important advantages of higher concentration of tannin phenolics in adhesive applications due to enhanced solubility and decreased viscosity, and of higher moisture retention by the tannin resins, allowing slower adhesive film dry-out, hence longer assembly times [32], also represents a distinct disadvantage in that sulfonate groups promote sensitivity to moisture with adhesive deterioration and poor water resistance of the cured glue line even with adequate cross-linking [32–35].

In recent years the importance of the marked colloidal nature of tannin extract solutions has come to the fore [27,36–45]. It is the presence of both polymeric carbohydrates in the extract as well as of the higher molecular fraction of the polyphenolic tannins which determines the colloidal state of tannin extract solutions in water [26,36]. The realization of the existence of the tannin in this particular state affects many of the reactions that lead to the formation and curing of tannin adhesives, to the point that reactions not thought possible in solution become instead not only possible but the favored ones [26,36], while reactions mooted to be of determinant importance when found on models not in the colloidal state have in reality been shown to be inconsequential to tannin adhesives and their tannin applications [43,44].

IV. TECHNOLOGY OF INDUSTRIAL TANNIN ADHESIVES

The purity of vegetable tannin extracts varies considerably. Commercial wattle bark extracts normally contain 70 to 80% active phenolic ingredients. The nontannin fraction, consisting mainly of simple sugars and high-molecular-weight hydrocolloid gums, does not participate in the resin formation with formaldehyde. Sugars reduce the strength and water resistance in direct proportion to the amount added. Their effect is a mere dilution of the adhesive resin solids, with consequent proportional worsening of adhesive properties. The hydrocolloid gums, instead, have a much more marked effect on both original strength and water resistance of the adhesive [2,22,42]. If it is assumed that the nontannins in tannin extracts have a similar influence on adhesive properties, it can expected that unfortified tannin–formaldehyde networks can achieve only 70 to 80% of the performance shown by synthetic adhesives. In many glued wood products, the demands on the glue line are so high that unmodified tannin adhesives are unsuitable. The possibility of refining extracts has proved fruitless largely because the intimate association between the various constituents makes industrial fractionation difficult. Fortification is in many cases the most practical approach to reducing the effect of impurities. Fortification generally consists of copolymerization of the tannin with phenolic or aminoplastic resins [21,22,42,46]. It can be carried out during manufacture of the adhesive resin, during glue mix assembly, just before use, or during adhesive use. If added in sufficient quantity, various synthetic resins have been found effective in reducing the nontannin fraction to below 20% and in overcoming other structural problems [21,22]. The main resins used are phenol–formaldehyde and urea–formaldehyde resols with a medium to high methylol group content. These resins can fulfill the functions of hardeners, fortifiers, or both. Generally, they are used as fortifiers in between 10 and 20% of total adhesive solids, and paraformaldehyde is used as a hardener. Such an approach is the favorite one for marine-grade plywood adhesives. These fortifiers are particularly suitable for the resorcinolic types of condensed tannins, such as mimosa. They can be copolymerized with the tannins during resin manufacture, during use, or both [2,21,22,42,44]. Copolymerization and curing are based on the condensation of the tannin with the methylol groups carried by the synthetic resin. Since tannin molecules are generally large, the rate of molecular growth in relation to the rate of linkage is high, so that tannin adhesives generally tend to have fast gelling and curing times and shorter pot lives than those of synthetic phenolic adhesives. From the point of view of reactivity, phloroglucinol tannins such as pine tannins are much faster than mainly resorcinol tannins such as mimosa. The usual ways of slowing them down and, for instance, of lengthening adhesive pot life are:

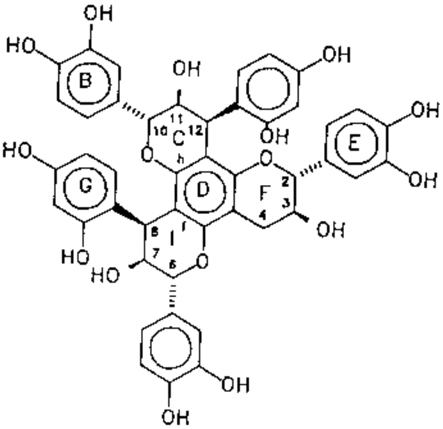
1. To add alcohols to the adhesive mix to form hemiacetals with formaldehyde and therefore act as retardants of the tannin–formaldehyde reaction.
2. To adjust the adhesive's pH to have the required pot life and rate of curing.
3. To use hexamine as a hardener, which under the current conditions gives a very long pot life at ambient temperature but still fast curing time at higher temperatures.

The viscosity of bark extracts is strongly dependent on concentration. The viscosity increases very rapidly above a concentration of 50%. Compared to synthetic resins, tannin extracts are more viscous at the concentrations normally required in adhesives. The high viscosity of aqueous solutions of condensed tannins is due to the following causes, in order of importance:

1. *Presence of high-molecular-weight hydrocolloid gums in the tannin extract* [42,45]. The viscosity is directly proportional to the amount of gums present in the extract [42,45].
2. *Tannin–tannin, tannin–gum, and gum–gum hydrogen bonds*. Aqueous tannin extract solutions are not true solutions but, rather, colloidal suspensions in which water access to all parts of the molecules present is very slow. As a consequence, it is difficult to eliminate intermolecular hydrogen bonds by dilution only [42,45].
3. *Presence of high-molecular-weight tannins in the extract* [28,42,45].

The high viscosity of tannin extract solutions has also been correlated with the proportion of very-high-molecular-weight tannins present in the extract. This effect is not well defined. In most adhesive applications such as in plywood adhesives, the viscosity is not critical and can be manipulated by dilution.

In the case of particleboard adhesives decrease of viscosity is, instead, an important prerequisite. When reacted with formaldehyde, unmodified condensed tannins give adhesives having characteristics that do not suit particleboard manufacture: namely, high viscosity, low strength, and poor water resistance. The most commonly used process to eliminate these disadvantages in the preparation of tannin-based particleboard adhesives consists of a series of subsequent acid and alkaline treatments of the tannin extract, causing hydrolysis of the gums to simple sugars and some tannin structural changes, thus improving the viscosity, strength, and water resistance of the unfortified tannin–formaldehyde adhesive [2,44]. Furthermore, such treatments may cause partial rearrangement of the flavonoid molecules that causes liberation of some resorcinol in situ in the tannin, rendering it more reactive, allowing better cross-linking with formaldehyde, and ultimately yielding an adhesive which without addition of any fortifier resins gives truly excellent performance for exterior-grade particleboard [1,2,44]. Such rearranged "phlobatannin" structures have formula as follows:



This modification cannot be carried out too extensively, but only to a limited extent to avoid precipitation of the tannin from solution by the formation of "phlobaphenes." Typical results obtained are shown in Table 1.

Particular gluing and pressing techniques have been developed for tannin particleboard adhesives [47,48] to achieve pressing times much faster than those traditionally obtained with synthetic phenol–formaldehyde adhesives, although recent advances in synthetic phenol–formaldehyde resins have markedly limited such an advantage [49,50]. Pressing times of 7 s/mm of panel thickness have been achieved and pressing times of 9 s/mm at 190 to 200°C press temperature are in daily operation: these are pressing times comparable to what is obtainable with urea–formaldehyde or melamine–formaldehyde resins at the same pressing temperatures. The success of these simple types of particleboard adhesives relies heavily on industrial application technology rather than just on the preparation technology of the adhesive itself [42,47,51]. A considerable advantage is the much higher moisture content of the resinated chips tolerable with these adhesives than with any of the synthetic phenolic and amino resin adhesives. In the case of wood particleboard and of oriented strandboard (OSB) panels the technology so developed allows hot pressing at moisture contents of around 24% against values of 12% for traditional synthetic adhesives, and presents other advantages as well [42,51,52].

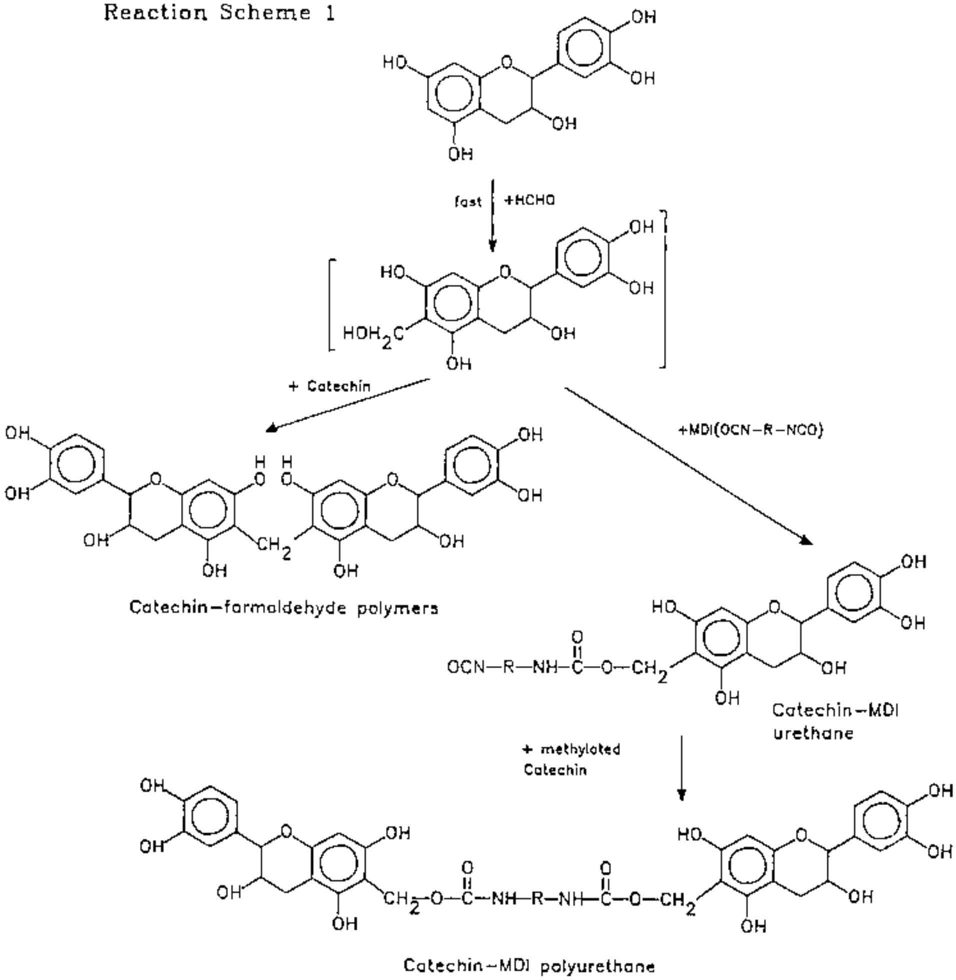
Table 1 Unfortified Tannin–Formaldehyde Adhesives Obtained by Acid–Alkali Treatment for Exterior-Grade Particleboard: Example of Industrial Board Results

	Swelling after a 2-h boil				
Panel density (g/cm^3)	Measured wet (%)	Measured dry (irreversible swelling) (%)	Original IB, tensile perpendicular (kg/cm^2)	IB after a 2-h boil (kg/cm^2)	Cyclic test after five cycles measured (%)
0.700	11.0	0.0	13.0	9.0	3.0

IB, internal bond.

The best adhesive formulation for phloroglucinolic tannins such as pine tannin extracts is, instead, a comparatively new adhesive formulation that is also capable of giving excellent results when using resorcinolic tannins such as a wattle tannin extract [53–56]. The adhesive glue mix consists only of a mix of an unmodified tannin extract in 50% solution to which has been added paraformaldehyde and polymeric nonemulsifiable 4,4′-diphenylmethane diisocyanate (commercial pMDI) [53–56]. The proportion of tannin extract solids to pMDI can be as high as 70:30 based on mass, but can be much lower in pMDI content. This adhesive is based on the following peculiar mechanism, by which the MDI, in water, is hardly deactivated to polyureas [54,56]:

Reaction Scheme 1



The properties of the particleboard manufactured with this system using pine tannin adhesives are listed in Table 2. The results obtainable with this system are then quite good and not too different from the results obtainable with some of the other tannin adhesives already described. In the case of phloroglucinolic tannin extracts being used, no pH adjustment of the solution is needed. One point that was given close consideration is the deactivating effect of water on the isocyanate group of pMDI. It has been found

Table 2 Properties of Particleboard Manufactured Using Pine Tannin Adhesives

	Swelling after a 2-h boil				
Panel density (g/cm^3)	Measured wet (%)	Measured dry (irreversible swelling) (%)	Original IB, tensile perpendicular (kg/cm^2)	IB after a 2-h boil (kg/cm^2)	IB retention after a 2-h boil (%)
0.690	15.0	4.3	8.4	4.3	51

IB, internal bond.

that the amount of deactivation by water of this group when in a concentrated solution (50% or over) of a phenol is much lower than previously thought [53–56]. This is the reason that aqueous tannin extract solutions and pMDI can be reacted without substantial pMDI deactivation by the water present.

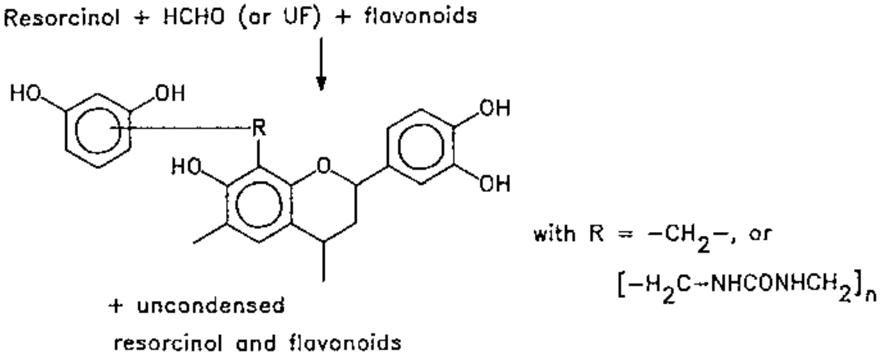
The quest to decrease or completely eliminate formaldehyde emission from wood panels bonded with adhesives, although not really necessary in tannin adhesives due to their very low emission (as most phenolic adhesives), has nonetheless promoted some research to further improve formaldehyde emission. This has centered on two lines of investigation: (i) autocondensation of tannins (see Section IV. D below), and (ii) the use of hardeners that do not emit at all simply because no aldehyde has been added to the tannin. Methylolated nitroparaffins and in particular the simpler and least expensive exponent of their class, namely trishydroxymethyl nitromethane [57,58], function well as hardeners of a variety of tannin-based adhesives while affording considerable side advantages to the adhesive and to the bonded wood joint. In panel products such as particleboard, medium density fiberboard (MDF), and plywood the joint performance that is obtained is of the exterior/marine grade type, while a very advantageous considerable lengthening in glue mix pot life is obtained. Furthermore, the use of this hardener is coupled with such a marked reduction in formaldehyde emission from the bonded wood panel as to reduce emission exclusively to the formaldehyde emitted by heating just the wood (and slightly less, thus functioning as a mild depressant of emission from the wood itself). Furthermore, trishydroxymethyl nitromethane can be mixed in any proportion with traditional formaldehyde-based hardeners for tannin adhesives, its proportional substitution of such hardeners inducing a proportionally marked decrease in the formaldehyde emission of the wood panel without affecting the exterior/marine grade performance of the panel. Medium density fiberboard industrial plant trials confirmed all the properties reported above and the trial conditions and results are reported [57,58]. A cheaper but as equally effective alternative to hydroxymethylated nitroparaffins is the use of hexamine as a tannin hardener. This sometimes causes problems of early agglomeration in some tannins [59] and a better solution proposed which overcame such problems was rather to use as a hardener a mix of formaldehyde coupled with an ammonium salt.

A. Corrugated Cardboard Adhesives

The adhesive developed for the manufacture of damp-ply-resistant corrugated cardboard are based on the addition of spray-dried wattle extract, urea–formaldehyde resin, and formaldehyde to a typical Stein–Hall starch formula of 18 to 22% starch content [60,61]. The wattle tannin–urea–formaldehyde copolymer formed in situ, and any free formaldehyde left in the glue line is absorbed by the wattle tannin extract. The wattle extract powder should be added at a level of 4 to 5% of the total starch content of the mix (i.e., carrier plus slurry). Successful results can be achieved in the range of 2 to 12% of the total starch content, but 4% is the recommended starting level. The final level is determined by the degree of water hardness and desired bond quality. This wattle extract–urea–formaldehyde fortifier system is highly flexible and can be adopted to dampproof a multitude of basic starch formulations.

B. Cold-Setting Laminating and Fingerjointing Adhesives for Wood

A series of different novolak-like materials are prepared by copolymerization of resorcinol with resorcinolic A rings of polyflavonoids, such as condensed tannins [62–64]. The copolymers formed have been used as cold-setting exterior-grade wood adhesives, complying with the relevant international specifications. Several formulations are used. The system most commonly used commercially relies on the simultaneous copolymerization of resorcinol and of the resorcinolic A rings of the tannin, due to their comparable reactivities toward formaldehyde.



The final mixture of the products of this system is an adhesive that can be set and cured at ambient temperature by the addition of paraformaldehyde. Other cold-set systems exist and are described in the more specialized literature [2,62–64]. The typical results obtainable with these adhesives are indicated in Table 3.

A particularly interesting system now used extensively in several southern hemisphere countries is the so-called "honeymoon" fast-setting, separate-application system [66,67]. In this system one of the surfaces to be mated in the joint is spread with a standard synthetic phenol–resorcinol–formaldehyde adhesive plus paraformaldehyde hardener. The second surface is spread with a 50% tannin solution at pH 12. When the two surfaces are

Table 3 Typical Results of Tannin–Resorcinol–Formaldehyde Cold-Setting Adhesives used on Beech Strips according to British Standard BS 1204 [65]

	Dry	After a 24-h cold-water soak	After a 6-h boil
Tensile strength (N)	3200–3800	2300–2900	2200–2800
Wood failure (%)	90–100	75–100	80–100

jointed, fingerjoints develop enough strength to be installed within 30 min and laminated beams (glulam) need to be clamped for only 2.5 to 3 h instead of the traditional 16 to 24 h, with a consequent considerable increase of factory productivity. This adhesive system also provides full weather- and boil-proof capabilities.

C. Tire Cord Adhesives

Another application of condensed tannin extracts that has proved technically successful is as tire cord adhesives. Both thermosetting tannin formulations [68] and tannin–resorcinol–formaldehyde formulations have been experimented with successfully.

D. New Concepts and Principles

1. *Surface Catalysis*

As in the case of other formaldehyde-based resins the interaction energies of tannins with cellulose obtained by molecular mechanics calculations [43] tend to confirm the effect of surface catalysis induced by cellulose on the curing and hardening reaction of tannin adhesives. The considerable energies of interactions obtained can effectively explain the weakening of the heterocyclic ether bond leading to accelerated and easier opening of the pyran ring in a flavonoid unit, as well as the facility with which hardening by autocondensation can occur. As in synthetic formaldehyde-based resins the same effect explains the decrease in energy of activation of the condensation of polyflavonoids with formaldehyde leading to exterior wood adhesives curing and hardening [69].

2. *Hardening by Autocondensation of Tannins*

The autocondensation reactions characteristic of polyflavonoid tannins have only recently been used to prepare adhesive polycondensates hardening in the absence of aldehydes [70]. This autocondensation reaction is based on the opening under alkaline and acid conditions of the O1–C2 bond of the flavonoid repeating unit and the subsequent condensation of the reactive center formed at C2 with the free C6 or C8 sites of a flavonoid unit on another tannin chain [70–74]. Although this reaction may lead to considerable increases in viscosity, gelling does not generally occur. However, gelling occurs when the reaction occurs (i) in the presence of small amounts of dissolved silica (silicic acid or silicate) catalyst and some other catalysts [70–75], and (ii) on a lignocellulosic surface [74]. In the case of the more reactive procyanidin and prodelphinidin type tannins, such as pine tannin, cellulose catalysis is more than enough to cause hardening and to produce boards of strength satisfying the relevant standards for interior-grade panels [74]. In the case of the less reactive tannins, such as mimosa and quebracho, the presence of a dissolved silica or silicate catalyst of some type is essential to achieve panel strength as required by the relevant standards. Autocondensation reactions have been shown to contribute considerably to the dry strength of wood panels bonded with tannins, but to be relatively inconsequential in contributing to the bonded panels' exterior-grade properties which are rather determined by polycondensation reactions with aldehydes [74–76]. Combinations of tannin autocondensation and reactions with aldehydes, and combinations of radical with ionic reactions have been used both to decrease the proportion of aldehyde hardener used as well as to decrease considerably more the already low formaldehyde emission yielded by the use of tannin adhesives [74–76].

V. ANALYSIS

Various methods of analysis are available for the determination of tannin content. These methods can generally be grouped into two broad classes:

1. *Methods aimed at the determination of tannin material content in the extract.* The classical method of this type still used is the hide-power and derived methods. These methods were devised to determine which percentage of the extract would participate in leather tanning. The main drawback for their use for adhesives in their inability to detect and determine the approximate 3 to 6% of monoflavonoids and biflavonoids, or phenolic "nontannins," present in the extract which do not contribute to tanning capacity but which do definitely react with formaldehyde and contribute to adhesive preparation.
2. *Methods aimed at the determination of phenolic material present in the extract that can be reacted with formaldehyde.* These methods were devised particularly for tanning extracts used in adhesives and are all based on the determination of some of the products of reaction of the flavonoids with formaldehyde.

Accepted methods of the first type comprise the hide-power method [77], the refractometric method, and various visible, ultraviolet, and infrared spectrometric methods. Accepted methods of the second type include comparative methods such as the Stiasny–Orth method [78,79] and its modifications, all these being gravimetric methods largely obsolete today due to the lack of reliability consequent to coprecipitation of some carbohydrates together with the phenolic material of the tannin extract and to the results being expressed in an absolute value which is never reportable to a percentage of useful material in the extract, the Lemme [80] sodium bisulfite backtitration method, the ultraviolet spectrophotometric molybdate ion method [77,81], and infrared spectrophotometric methods [82].

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28

Natural Phenolic Adhesives II: Lignin

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I. INTRODUCTION

The occurrence of lignin as a waste product in pulp mills has made it an attractive raw material for adhesives ever since the beginning of the sulfite pulping of wood. The first patents dealing with the application of spent sulfite liquor (SSL) as an adhesive for paper, wood, and other lignocellulosic materials date back to the end of the nineteenth century [1], and since then have shown an ever-growing number. On the other hand, technical utilization of lignin on a large scale is still at a very low level for the amount produced worldwide. Presently, most of the spent liquors in pulp mills are burned. Only about 20% is used for various purposes, such as dispersants, oil-well-drilling muds, pelletizing materials, molding stabilizers, and concrete grinding additives.

As a major wood component, native lignin is neither hygroscopic nor soluble in water. However, during technical sulfite pulping, lignin becomes soluble in water, due to partial degradation and introduction of sulfonic acid groups ($-SO_3H$). In applying SSL as an adhesive, it has to be converted to an insoluble state during the curing period. Cross-linking in lignin can be achieved either by condensation or by radical coupling reactions. A great number of patents have become known during the past four decades [2] dealing with the application of SSL as a wood adhesive, in which the lignin is cross-linked by condensation reactions. However, either high temperatures and long heating times or mineral acids are required for these condensation reactions, which cause structural changes or charring in the wood particles. Recently, cross-linking of the lignosulfonate molecules by radical combinations, which avoids mineral acids and high temperatures, has been developed, but this presents disadvantages as well, since the use of peroxides is not favored in wood processing plants, for a variety of reasons. The use of lignin by polycondensation reactions with formaldehyde also presents the disadvantage of slower pressing time in their application to panel products.

II. CHEMICAL BACKGROUND OF THE CURING REACTION OF LIGNIN

Lignin is composed of phenylpropane (C_9) units that are linked together by carbon-to-carbon as well as carbon-to-oxygen (ether) bonds. Our present knowledge of the lignin

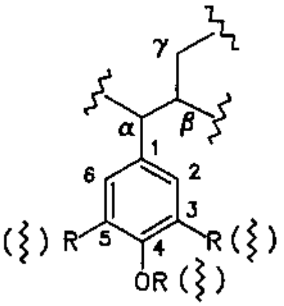

Figure 1 Phenyl propanoid units of lignin: R, $R_2 = H, OCH_3$; $R_3 = H, CH_3, CH_2$; (≀) = possible linkage to other phenyl propanoid units.

structure is based on the assumption that it is formed from *p*-hydroxycinnamyl alcohols by oxidative coupling [2,3] oxidized by hydrogen peroxide and peroxidase to a phenoxy radical (R). The unpaired electron in R is delocalized and reacts at three different sites of the radical, indicated by four resonance structures, leading to dilignols.

A. Cross-Linking by Condensation Reactions

When lignosulfonate is treated with strong mineral acids at elevated temperatures or heated at temperatures above 180°C, condensation reactions leading to diphenylmethanes and sulfones take place. The reactivity of lignosulfonates depends to some extent on the cation. Of the four lignosulfonates obtained technically, the calcium-based exhibit the lowest and the ammonium-based the highest reactivity; the sodium and magnesium lignosulfonates show a medium reactivity.

Hydrobenzyl alcohol groups as well as sulfonic acid groups on the carbon α to the aromatic rings of some of the phenylpropane units of the random polymer react in the presence of strong mineral acids with the aromatic nuclei of other phenylpropane units. This reaction, leading to diphenylmethanes, is of the same type as the formation of phenolic resins from phenol and formaldehyde. Lignin also reacts with formaldehyde and can be cross-linked by it in the same manner as that of synthetic polyphenolic resins.

B. Cross-Linking by Oxidative Coupling [2]

Lignosulfonic acid in technical SSL contains about 0.4 of a free phenolic hydroxy group per C_9 unit. Therefore, like the formation of lignin in plants, cross-linking of lignosulfonate is possible by oxidative coupling. Oxidants such as hydrogen peroxide, and catalysts such as sulfur dioxide or potassium ferricyanide, are most effective. Treatment of a 50% technical SSL with this redox system leads to a very vigorous exothermic reaction under evaporation of water. The yield of the resin under certain conditions exceeds 70%, indicating that some carbohydrates must also have been enclosed in the resin. The advantage of this type of cross-linking compared with condensation reactions is that it needs neither mineral acids nor high temperatures, due to the recombination of radicals, for which the activation energy is very low. The strongly exothermic reaction causes a uniform temperature profile during pressing of particleboard without external heat.

III. APPLICATION OF LIGNIN AS AN ADHESIVE FOR PARTICLEBOARD, PLYWOOD, AND FIBERBOARD

According to its structure as a polyphenol, lignin as an adhesive should be similar to phenol–formaldehyde (PF) resins. This is true for native lignin in wood; to transfer them into insoluble resins, technical lignins (lignosulfonate and black liquor) have to be additionally cross-linked. However, condensation reactions in lignin by heat or mineral acids cannot be as effective as in synthetic PF resins, due to the lower number of free positions in the aromatic nuclei of lignin and their considerably lower reactivity than in PF resins. First, there is only 0.5 of a free 5-position (ortho to the phenolic groups) per C_9 unit; positions 6 and 2 are less reactive. Second, there is less than one benzyl alcohol or ether group per C_9 unit in lignin, whereas in synthetic PF resins up to three methylol groups can be introduced into one phenolic ring. Finally, the aromatics in lignin are considerably less reactive toward hydroxybenzyl alcohol groups than is phenol, due to the presence of methoxy or methoxy-equivalent groups rather than hydroxy groups on the lignin aromatic rings. For these reasons, lignin in technical spent liquors cannot be as effectively cross-linked as synthetic PF resins. At least higher press temperatures at longer heating times or higher acid concentrations are necessary.

Quite a number of patents have been pending during the past four decades dealing with lignin as adhesive for particleboard, plywood, and fiberboard in the absence of conventional PF or urea–formaldehyde (UF) adhesives [2]. Besides lignin, in most cases additional cross-linking agents for lignin are necessary, such as epoxides, polyisocyanates, polyols, polyacrylamides, polyethyleneimine, aldehydes, maleic anhydride, amines, proteins, melamine, hydrazine, and so on. So far, these procedures, for different reasons, have not led to any major practical application. Very few procedures, such as those of Pelikan et al. (1954), Pedersen and Jul-Rasmussen (1963), Shen (1973), Nimz et al. (1972), and others, use lignosulfonates or SSL without integrated cross-linking chemicals [2]. The patent of Pelikan et al. describes ways of using lignin as an adhesive for floor layers by cross-linking it oxidatively with chromium trioxide. The mechanism of cross-linking is the same as with hydrogen peroxide (Nimz, 1972) [2], but it is much less effective. Its applicability to particleboards has been tried, but the boards exhibited low tensile strengths and disintegrated in water at 20°C in less than 2 h.

A. Curing Lignin Boards by Long Pressing Time and Postheating Treatment

According to Pedersen and Jul-Rasmussen [2], wood chips are mixed with 20 to 25% of their weight with a 50% technical SSL and pressed at 185°C for 30 min, giving a 12-mm-thick board that must be postheated at 195°C for 80 min in an autoclave. The pH value of the SSL had been adjusted to 3 by citric acid. The particleboard obtained has a bending strength of 230 kP/cm^2, a tensile strength perpendicular to the grain of 5.3 kP/cm^2, and a density of 0.7 g/cm^3. Press temperatures may vary between 170 and 235°C and temperatures of the autoclave between 170 and 210°C.

High press and autoclave temperatures as well as long heating times are necessary for effective cross-linking by condensation reactions in lignin, as pointed out above. The color of the boards is dark, due to decomposition reactions and charring caused by the high temperatures, and the density of the boards usually reaches values at around 0.8 g/cm^3 if the required tensile strength is to be obtained. The temperature in the core layer during pressing reaches 140°C. This may also cause condensation reactions between wood and SSL, as well as chemical and physical changes in the wood particles [4].

The relatively high dimensional stability of the particleboard toward water may be caused by these changes. Pedersen and Jul-Rasmussen (1963) found a thickness expansion after a 2-h soaking in water at 20°C of only 1.5% and 13.8% water absorbance. Open-air tests, extending over 5 years, carried out by the wood panel products laboratory of the Technical Research Centre of Finland [5] revealed that SSL boards, obtained according to the Pedersen procedure, were superior in strength and in surface properties to UF as well as to PF particleboard. Roffael [6] has shown that water absorption of Pedersen SSL particleboard at different air humidities is only about half as high as with conventional PF particleboard. Weathering for 1 year gave a nearly constant humidity at around 6% for SSL particleboard, while PF boards gave humidities between 12 and 15%. Also, after soaking the boards in water at 20°C for 24 h, the lignosulfonate boards lost only 25% of their initial tensile strength, while that of conventional PF particleboard decreased by 70%. In contrast, the mechanical strength properties of SSL particleboard were inferior to those of PF board [7].

The Pedersen procedure has been applied to mill-scale tests in Denmark, Switzerland, and Finland, but has been discontinued in all cases. One reason for this failure is the high cost caused by the two-stage heating treatment. The autoclave must consist of refined steel, due to the evolution of corrosive gases such as sulfur dioxide, causing additional high costs. Another reason was the long pressing and curing time needed for manufacture. However, one of the main reasons for the discontinuation of the procedure was the frequent fires induced by the high pressing and posttreatment temperatures [2].

As mentioned above, the condensation rate of lignosulfonates depends on the cation, with ammonium ions exhibiting the highest reactivity. Shen and Calvé [8] used fractionated ammonium-based SSL as a binder for particleboard and found the highest reactivity, leading to the best mechanical board properties, with a low-molecular-weight fraction. Unexpectedly, the tensile strength of dry particleboard obtained with a low-molecular-weight ammonium-based SSL fraction increased with the sugar content of the SSL. The best board properties were obtained with 6% of a low-molecular-weight (0 to 5000) ammonium-based SSL fraction having 50 to 60% sugar. In this case, a pressing time of 8 min at 210°C was sufficient for manufacture of 11-mm-thick waferboard to meet the Canadian standard requirements for exterior-grade particleboard.

Obviously, the sugars take part in the condensation reactions of lignosulfonate by production of furfural. While the bending strength of dry boards increased steadily, with the sugar content of the SSL going up to 80%, the bending strength after a 2-h boiling of the boards reached a maximum at about 50 to 60% carbohydrates, indicating that the condensation between lignin and carbohydrates leads to better water resistance than that between carbohydrates only.

B. Curing Lignosulfonate Particleboard with Sulfuric Acid

In 1973, K.C. Shen of the Eastern Forest Products Laboratory in Ottawa, Canada, proposed sulfuric acid as a curing agent for SSL waferboard. The pressing conditions were the same as those of conventional PF particleboard, when poplar wafers were first sprayed with 1% of 15 to 20% sulfuric acid and then with 4 to 5% SSL powder, which adheres at the surface of the wet wood wafers. Later [9], concentrated sulfuric acid (9%) was added to the SSL before spray drying, and the powder adhered to the wax-coated wafers.

High pressing temperatures of about 205°C were also necessary, the catalytic effect of the sulfuric acid merely reducing the pressing time to that of industrial conditions for PF particleboard.

The strength properties of the boards, having an average specific gravity of 0.67 g/cm^3, were measured by the torsion shear at the center plane of 1 in. × 1 in. specimens, from which the internal bond strength (tensile strength perpendicular to the surface) can be obtained by multiplication with the factor 0.7 [10]. Values obtained for internal bond strength and modulus of rupture (MOR) for dry samples as well as after 2 h of boiling met the Canadian standards for particleboard [11]. The torsion shear strength and MOR of dry boards were independent of the pressing time, while the wet strength increased proportionally with the pressing time. This means that for exterior-grade requirements, distinct pressing times are necessary.

The best board properties were obtained with 1% concentrated sulfuric acid, based on dry wood particles. At higher acid concentrations the strength of dry boards decreased, while that of wet boards showed a further increase. However, charring of the wood particles takes place at acid concentrations higher than 0.9%. The thickness expansion of SSL boards obtained with 1% sulfuric acid lay between 26 and 46%, after soaking in water at 20°C for 1 week, and between 51 and 66% after 2 h of boiling. These values are considerably worse than those of exterior-grade PF particleboard.

The acidity of the particleboard was found to be pH 3, after disintegration of the boards in 10 times their weight of water [12]. It has been reported that the acidity had no longer-term influence on the mechanical board properties, checked by conventional accelerated aging treatments [12]. In this case, 11-mm boards had been pressed for 6 min and a part of them had been postheated at 149°C for 2 h. Of the accelerated aging treatments only 20 days of heating at 149°C showed faster aging of SSL than of PF boards, which is due to the higher acidity of the SSL boards.

On the whole, the SSL particleboard obtained by Shen cannot be compared technically with exterior-grade PF particleboard. The Shen procedure, however, has found no practical application yet, as the results obtained are still far from those obtainable with PF particleboard. In 1977 Shen mentioned that a short production trial run had been carried out at a waferboard plant; although the preliminary results were promising, additional work was still required to modify the binder formulation and production parameters to meet the requirements of plant operation, and to obtain results comparable to those of PF particleboard. The Shen system, however, is used in the manufacture of some types of hardboard (high density fiberboard).

C. Curing SSL Boards with Hydrogen Peroxide

The drawbacks inherent in the Pedersen and Shen procedures—high pressing temperatures and long pressing times or strong mineral acids—can be avoided if cross-linking of the lignin molecules is achieved by radical coupling instead of condensation reactions (Nimz et al. 1972 [2]). In this case, the formation of new carbon–carbon as well as carbon–oxygen bonds between two radicals is a very fast reaction with a low activation energy, which needs no external heating or mineral acids as catalyst. This means that the reaction is very specific, and side reactions such as decompositions and charring can be avoided, while linkages between wood and SSL may also occur.

The essential radicals are formed from phenolic groups in the lignosulfonate molecules by oxidation with hydrogen peroxide in the presence of a catalyst. Out of a number of catalysts, sulfur dioxide (SO_2) has been proven to be the most effective [13]. A 50%

calcium-based SSL containing about 1% SO_2 at pH 2 reacts vehemently with a 35% hydrogen peroxide solution in a strongly exothermic reaction, forming an insoluble gel. The reaction time is less than 1 min but depends on the source and composition of SSL. At higher pH values, the reaction takes some minutes or needs heating up to about 70°C, but after reaching 70°C, the reaction is also very fast.

In has been reported [13] that the SSL containing the catalyst and the hydrogen peroxide solution have to be sprayed separately on the wood chips. Under certain conditions, the hydrogen peroxide can be mixed with the SSL and sprayed together on the wood chips, in a single operation [13]. Another possibility consists of adding half of the SSL as spray-dried powder, lowering the humidity of the blended chips to about 13%, which is the upper limit according to German standards. The powder may either be mixed together with the liquid SSL and the hydrogen peroxide or added separately after the wood chips have been sprayed with the mixture of SSL solution and hydrogen peroxide. The humidity of the wood chips can thus be adjusted to predetermined values. The pot life of the blended wood chips, which is the assembly time between spraying and pressing, would then be extended. Medium-density interior-grade particleboard can be obtained from wood chips with 20% SSL, based as dry material on dry wood chips, at pressing temperatures between 100 and 120°C under otherwise conventional manufacturing conditions for UF particleboard.

There are several reasons why this system has not found industrial favor: (1) the unfavorable situation due to the presence of a peroxide in wood panel plants, such as possible machinery corrosion, and other problems, and (2) the fact that the produced board is often relatively very soft immediately out of the particleboard press, rendering its early handling particularly problematic.

IV. LIGNIN IN COMBINATION WITH PHENOL–FORMALDEHYDE ADHESIVES

The number of patents on lignin as a substitute or extender for phenolic wood adhesives during the past four decades is high [2]. Under certain conditions, up to 40% of PF adhesive can be replaced by lignosulfonate or black liquor without significantly extending the curing time or worsening board properties. Lignin–PF formulations have been used in manufacturing particleboard, fiberboard, and plywood. The reason for their application has to be seen in the lowering of costs, resulting from the difference in cost between PF and lignin. However, in most cases the lignin has to be pretreated by deionization, ultrafiltration, or cation change. Two recent procedures that have become better known are discussed next in more detail.

A. Lignin–PF Formulations

In 1971, Roffael and Rauch [14,15] claimed that the curing time of SSL particleboard could be reduced and, according to Pedersen, the postheating treatment in an autoclave avoided when phenolic resins of the novolak type were added to the SSL [15]. Due to coagulations between calcium-based SSL and PF, the calcium-based SSL has to be transferred into sodium-based SSL. The board properties are strongly dependent on the pH value of the glue: for example, 10% SSL, 4% novolak, and 2.1% hexamethylenetetramine were applied to dry pine wood chips to prepare 9-mm-thick boards at a pressing time of 12 min.

While the highest bending and tensile strengths were obtained between pH 5 and 7, the percentage swelling in water at 20°C, after 24 h, had a minimum at pH 3.5. For this reason, a pH value of 4.7 has been suggested by the authors as a compromise [15]. Both the mechanical strength and the dimensional stability of the particleboard can be improved by higher ratios of novolak in the glue formation or increasing pressing temperatures up to 250°C. Besides conventional contact heating in a flat press, high-frequency heating was applied, raising the temperatures in the core layer during pressing to 220°C for 1 min, which diminished the pressing time. In contrast to their publication in 1971 [15], Roffael and Rauch found in 1973 [16] that phenolic resins of the resol type also improve the binding properties of SSL in particleboard, and the percentage swelling can be improved to meet the German standard specification [17] (6% after 2 h in water at 20°C) by applying a postheating treatment at 200°C for 1 h.

The postheating treatment could be avoided when higher amounts of resol-type resin were used. In conventional PF particleboard the PF resin amounts to about 8%, based on dry wood particles. It has been found [16] that up to 33% of the resol-type adhesive in conventional PF particleboard can be substituted in the surface layers of a three-layer 22-mm board by sodium-based lignosulfonate without major deterioration in the mechanical board properties. In 20-mm one-layer particleboards at pH 9, up to 25% of the PF resin could be replaced by sodium–lignosulfonate under conventional pressing conditions, leading to particleboard meeting the German standard specification [6]. Furthermore, 10% of the PF resin in beech/plywood could be substituted by sodium-based lignosulfonate at a pressing temperature of 165°C, and up to 30% at 190°C [7]. The highest shear strength of the plywood was obtained with an adhesive formulation of pH 12 to 13.

B. Karatex Adhesive

According to Forss and Fuhrmann (1972) [5,18], the amount of lignin in lignin–PF adhesives for particleboard, plywood, and fiberboard can be increased to 40 to 70% if a high-molecular-weight fraction (MW > 5000) of either lignosulfonate or black liquor, obtained from alkaline pulping of wood, is applied. Fractionation of SSL or black liquor can be achieved by ultrafiltration [5,18]. According to the authors, the higher effectivity of high-molecular-weight lignin molecules is due to their higher level of cross-linking, which requires less PF for the formation of an insoluble copolymer than do low-molecular-weight lignin molecules. However, bearing in mind the findings of Shen [8] that low-molecular-weight ammonium-based SSL is more effective, Forss and Fuhrmann appear not to have checked the influence of inorganic salts in SSL or black liquor that are separated off during ultrafiltration [2]. Forss and Fuhrmann assume that condensates between smaller lignin molecules and PF "are unable to contribute to the three-dimensional network" [5], which is unlikely because low-molecular-weight lignin molecules are more reactive than are high-molecular-weight molecules.

In the manufacture of particleboard either high-frequency heating or combined contact high-frequency heating has been applied. In the latter case, the press platen temperature has been 180°C. German standard requirements for weather-resistant particleboards were met at pressing times between 10 and 12 s/mm and 8 to 12% adhesive, based on dry wood particles. One advantage inherent in the fractionation by ultrafiltration is that the lignin becomes more uniform and less dependent on variations in pulping conditions and wood source, which sometimes cause serious problems in the application of technical lignins. Full-scale plywood mill tests, some of them running continuously for several weeks, appear to have been performed in two Finnish plywood mills. Again, this procedure does not appear to be in operation anymore.

C. Methylolated Lignins

The fundamental problem of lignin, slowing of the pressing time obtainable with PF resins, was partly eliminated by Sellers (1990) [19] and by Calvé (1990) [20], who first reacted lignin with formaldehyde in a reactor for a few hours. A methylolated lignin (ML) equivalent to a PF resol was obtained. As in this case the reactivity of the methylol groups of lignin introduced depends on the reactivity of phenolic nuclei available for reaction, mixing with a synthetic PF resin ensures that the reactivity of the PF resin is not impaired. In this manner up to 30% ML could be used to substitute for the PF adhesive, with no drop in performance and pressing times. In plywood industrial plant trials with such PF–ML systems, Sellers and Calvé both obtained excellent results. It is believed that at least one Canadian plywood mill is using such a system industrially today. As plywood pressing time is not the really critical variable in a plywood mill, this system did not itself prove suitable for application to particleboard mills, where the shortness of the pressing time that can be obtained is the determining variable.

Attempts were made to use more reactive lignins, such as bagasse (sugarcane waste) lignins, which present 0.7 to 0.9 of a reactive position for each phenylpropane unit, using the same approach. Although good particleboard could be obtained with a mixture of 67% methylolated bagasse lignin (MBL) and 33% PF resin, these could be obtained only at pressing times of 37 to 50 s/mm, still far too long to be of any interest to a particleboard mill [21]. Thus, for particleboard, the low reactivity of lignins toward formaldehyde and the limited number of sites available for reaction with formaldehyde on most aromatic nuclei of the phenylpropane units of lignin are clearly the limiting factors to utilization of this material.

It then became clear that a different but equally or more efficient cross-linking route to be employed in parallel to formaldehyde cross-linking had to be used if feasible pressing times for particleboard mills were to be achieved. Two parallel approaches toward this end have proved successful. First, MBL and methylolated kraft lignin (MKL) were reacted in water with diisocyanate according to a new reaction and the mechanism observed for PF resins [22]. Combinations of polymeric MDI (4,4′-diphenylmethanediisocyanate), synthetic PF, and MLs yielded particleboard with full exterior-grade properties at pressing times as fast as 20 s/mm when using up to 55% MBL [23]. Pressing times using MKL were also faster but still too slow [23]. Second, as a consequence of the elucidation of PF α-set acceleration mechanisms [24], pressing times as short as 7.5 s/mm for MBL and 10 s/mm for MKL were obtained, at a lignin content of the resin as high as 65% of total adhesive [25]. These pressing times are faster than for synthetic phenolic resins and almost of the same order of magnitude as for UF resins. Industrial plant trials have been held for this system, which appears for the first time to have eliminated the main problem of lignin in wood adhesives for particleboard, that is, the problem of too long pressing times.

V. LIGNIN IN COMBINATION WITH UREA–FORMALDEHYDE RESINS

In 1965, W. Arnold [2] found that the pressing time of SSL particleboard obtained with sulfuric acid as catalyst (see the Shen procedure) can be reduced by 50% and the specific gravity of the boards by 7 to 10% if 10 to 30% of the SSL-blended wood chips are replaced by UF-blended wood chips. However, at pressing times of 0.6 to 1 min/mm board thickness, the pressed particleboard still has to be posttreated at high temperatures to meet German standards for mechanical strength properties. Again, the necessary posttreatment of the boards has hindered the practical application of this finding. On the other hand, small amounts (up to 10% of the UF resin) of SSL improve the cold adherence of blended UF particleboard (Schmidt-Hellerau, 1973, 1977) [2]. This has found practical applications in current industrial use in some western European particleboard mills.

Roffael [6] has shown that 20% of the UF in the surface layers of UF particleboard can be replaced by ammonium-based lignosulfonate without significantly worsening the mechanical board properties. The release of formaldehyde decreased only slightly, which was attributed to the reduction of UF resin rather than to a reaction of formaldehyde with the lignin. The binding of formaldehyde by lignin in UF particleboard is claimed in three Japanese patents [2], together with other patents dealing with lignin UF formulations as wood adhesives. Other improvements achieved by lignosulfonate in UF resins are decrease of adhesive viscosity, increased wettability of wood particles, and improved water resistance of finished boards.

According to a recent report [20], substitution of up to 15% of the UF adhesive in particleboards by SSL does not cause major impairment in particleboard properties. This can be seen from the properties of 17.7-mm-thick one-layer particleboard obtained with 8% UF binder (formaldehyde/urea = 1.27), replaced partially by 10 to 30% magnesium-based SSL. The adhesive contained 0.5% paraffin emulsion and 3% ammonium chloride, and the pressing time was 10 s/mm at 200°C [2]. It is obvious, however, that substitution of 20% or more of the UF binder by magnesium-based SSL worsens both the strength and water resistance of the boards, while the gelling time (pot life) of the adhesive is increased. When three-layer 20-mm particleboard was manufactured with 15% of calcium-based (A), sodium-based (B), or ammonium-based (C and D) lignosulfonate and 85% UF binder, with pressing times of 9 s/mm at 200°C and 10.5% adhesive in the surface layer and 8.5% in the core layer, the board properties were different.

At board densities of about 0.7 g/cm^3, the bending and tensile strengths of the UF–lignosulfonate boards are not decreased compared to boards prepared with 100% UF binder, while the percentage of swelling is increased. The formaldehyde release is considerably decreased by ammonium (C and D)- rather than by calcium- and sodium-based SSLs, indicating that the ammonium ions react with formaldehyde under the conditions existing in the boards, but not the lignin. In the case of calcium- and sodium-based SSLs, the reduction in formaldehyde release lies between 10 and 18%, which corresponds to the amount of SSL in the UF–SSL formulation.

In a patent by Edler (1978) [2] it has been claimed that about 33% of UF binder in particleboards can be replaced by ammonium-based SSL if certain conditions are maintained. First, the UF resin should have a relatively high number of methylol (CH_2OH) groups, characterized by a Witte number of 1 to 1.8, preferably 1.6, which leads to better compatibility between UF and SSL. Second, the concentration of ammonium ions has to be adjusted to 0.2 to 4%. The ammonium ions react with free formaldehyde, forming less reactive hexamethylenetetramine, which leads to excessive sulfonic acid groups in lignin. If the ammonium-ion concentration is higher than 4%, based on dry lignosulfonate, the acidity becomes too high, resulting in very fast curing. The latter causes soft board surfaces and diminished strength properties. On the other hand, if the ammonium ion concentration is below 0.2%, the curing time becomes too long. The properties of four types of particleboard, obtained with three different types of adhesive—A having a Witte number of 1.58, B of 1.50, and C of 1.02, the latter prepared using only UF resin, while types A and B contained 33% lignosulfonate and 67% UF—show pressing times of about 15 s/mm at 160°C. Wood chips consisting of 67% pine and 33% Douglas fir gave different results. The mechanical strength properties of boards obtained with resins of types A and B (33% lignosulfonate) show no major impairment compared with those of conventional UF boards (resin type C). Significant improvements in the water resistance are gained, due to the polyphenolic structure of lignin [2].

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Resorcinol Adhesives

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I. INTRODUCTION

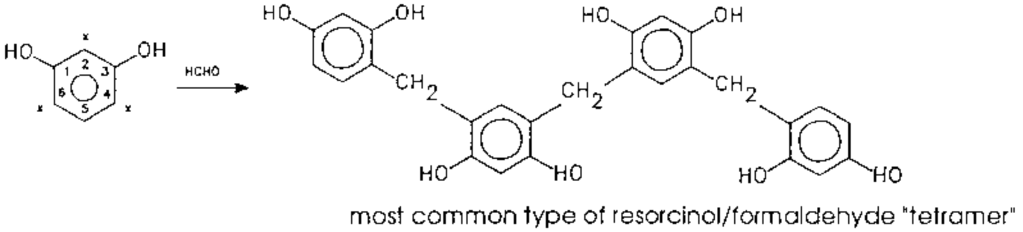
Resorcinol–formaldehyde (RF), and phenol–resorcinol–formaldehyde (PRF) cold-setting adhesives are used primarily in the manufacture of structural, exterior-grade glulam fingerjoints, and other exterior timber structures. They produce bonds not only of high strength, but also of outstanding water and weather resistance when exposed to many climatic conditions [1,2]. PRF resins are prepared mainly by grafting resorcinol onto the active methylol groups of the low-condensation resols obtained by the reaction of phenol with formaldehyde. Resorcinol is the chemical species that gives to these adhesives their characteristic cold-setting behavior. At ambient temperature and on addition of a hardener, it provides accelerated and improved cross-linking not only to RF resins but also to the phenol–formaldehyde (PF) resins onto which resorcinol has been grafted by chemical reaction during resin manufacture. Resorcinol is an expensive chemical, produced in very few locations around the world (to date only three commercial plants are known to be operative: in the United States, Germany, and Japan), and its high price is the determining factor in the cost of RF and PRF adhesives. It is for this reason that the history of RF and PRF resins is closely interwoven, by necessity, with the search for a decrease in their resorcinol content, without loss of adhesive performance.

In the past decades, significant reductions in resorcinol content have been achieved: from pure RF resins, to PRF resins in which phenol and resorcinol were used in equal or comparable amounts, to the modern-day commercial resins for glulam and fingerjointing in which the percentage, by mass, of resorcinol on liquid resins is on the order of 15 to 18%. A step forward has also been the development and commercialization of the "honeymoon" fast-set system [3], either composed of just synthetic PRF resins or of a PRF resin coupled with the use of tannin extracts, which in certain countries are used to obtain PRFs of 8 to 9% resorcinol content without loss of performance and with some other advantages (such as gluing of high moisture content timber). This was a system improvement, not an advance on the basic formulation of PRF resins.

II. CHEMISTRY OF RF RESINS

The same chemical mechanisms and driving forces presented for PF resins apply to resorcinol resins. Resorcinol reacts readily with formaldehyde to produce resins which harden at ambient temperatures if formaldehyde is added. The initial condensation reaction, in which A-stage liquid resins are formed, leads to the formation of linear condensates only when the resorcinol/formaldehyde molar ratio is approximately 1:1 [4]. This reflects the reactivity of the two main reactive sites (positions 4 and 6) of resorcinol [5]. However, reaction with the remaining reactive but sterically hindered site (2-position) between the hydroxyl functions also occurs [4]. In relation to the weights of RF condensates which are isolated and on a molar basis, the proportion of 4- plus 6-linkages relative to 2-linkages is 10.5:1. However, cognizance must be taken of the fact that the first mentioned pair represents two condensation sites relative to one. The difference in reactivity of the two types of sites (i.e., 4- or 6-position relative to the 2-position) is then 5:1 [4]. Linear components always appear to form in preference to branched components in A-stage resins [4]; that is, terminal attack leads to the preferential formation of linear rather than branched condensates. This fact can be attributed to:

1. The presence of two reactive nucleophilic centers on the terminal units, as opposed to single centers of doubly bound units already in the chain.
2. The greater steric hindrance of the available nucleophilic center (nearly always at the 2-position) of the doubly bound units as opposed to the lower steric hindrance of at least one of the nucleophilic centers of the terminal units (a 4- or 6-position always available). The former is less reactive as a result of the increased steric hindrance. The latter are more reactive.
3. The lower mobility of doubly bound units which further limits their availability for reaction (Formula 1)



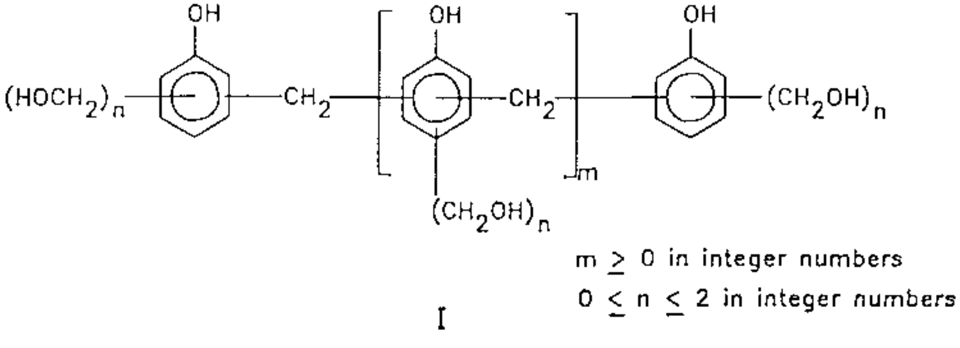
Formula 1

The absence of methylol (–CH_2OH) groups in all six lower-molecular-weight RF condensates which have been isolated [4] reflects the high reactivity of resorcinol under acid or alkaline conditions. It also shows the instability of its para-hydroxybenzyl alcohol groups and their rapid conversion to para-hydroxybenzyl carbonium ions or quinone methides. This explains how identical condensation products are obtained under acid or alkaline reaction conditions [4]. In acid reaction conditions methylene ether-linked condensates are also formed, but they are highly unstable and decompose to form stable methylene links in 0.25 to 1 h at ambient temperature [6,7].

From a kinetic point of view, the initial reaction of condensation to form dimers is much faster than the subsequent condensation of these dimers and higher polymers. The condensation reaction of resorcinol with formaldehyde, on an equal molar basis and under identical conditions, also proceeds at a rate which is approximately 10 to 15 times faster than that of the equivalent PF system [8]. The high reactivity of the RF system renders it impossible to have these adhesives in resol form. Therefore, only RF novolaks, thus resins not containing methylol groups can be produced. Thus all the resorcinol nuclei are linked together through methylene bridges with no methylol groups being present and generally without any presence of methylene–ether bridges either.

The reaction rate of resorcinol with formaldehyde is dependent on the molar ratio of the two constituents, the concentration of the solution, pH, temperature, presence of various catalysts, and amount of certain types of alcohols present [9–12]. The effect of pH and temperature on the reactivity and gel time of the RF system presents the same trend as for all phenolic–formaldehyde reactions, with a minimum of reactivity at around pH 4 and the rate of reaction becoming rapidly faster at progressively more alkaline and more acid pH values [12,13]. Methanol and ethanol slow down the rate of reaction. Other alcohols behave similarly, the extent of their effect being dependent on their structure. Methanol lengthens gel time more than other alcohols, higher alcohols being less effective. The retarding effect on the reaction is due to temporary formation of hemiacetals between the methanol (or other alcohols) and the formaldehyde. This reduces the reaction rate because of the lower concentration of available formaldehyde [10,11]. Other solvents also affect the rate of reaction by forming complexes or by hydrogen bonding with the resorcinol [10,13].

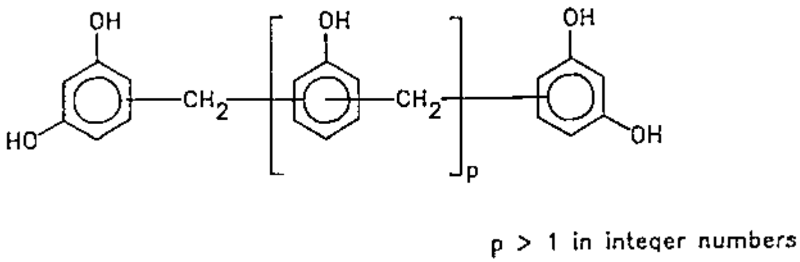
In the manufacture of pure resorcinol resins the reaction would be violently exothermic unless controlled by the addition of alcohols. Because the alcohols perform other useful functions in the glue mix, they are left in the liquid glue. PRF adhesives are generally prepared firstly by reaction of phenol with formaldehyde to form a PF resol polymer that has been proved to be in the greatest percentage, and often completely, linear [4]. This can be represented as follows (Formula 2)



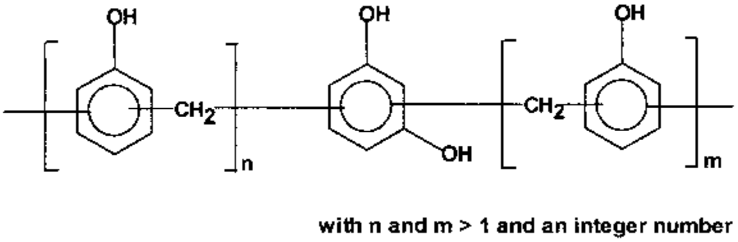
Formula 2

In the reaction that follows the resorcinol chemical is added in excess, in a suitable manner, to polymer I to react with the $-CH_2OH$ groups to form PRF polymers in which the terminal resorcinol groups can be a resorcinol or any type of RF polymer (Formula 3).

In reality, as resorcinol is expensive, the resin manufacturers tend to limit the amount of resorcinol grafted onto the PF resol. This is then generally lower than what is necessary to form structures as shown in Formula 3. Structures as these do occur but the majority of the polymers present in the PRF resin are of the type (Formula 4)



Formula 3



Formula 4

where the residual third reactive site of the resorcinol is still free and is the site through which cross-linking takes place by reaction with the added formaldehyde hardener (see Chapter 8, Fig.1).

Where straight resorcinol adhesives are not suitable, resins can be prepared from modified resorcinol [13]. Characteristic of these types of resins are those used for tire cord adhesives, in which a pure RF resin is used, or alternatively, alkyl resorcinol or oil-soluble resins suitable for rubber compounding are obtained by prereaction of resorcinol with fatty acids in the presence of sulfuric acid at high temperature followed by reaction with formaldehyde. Worldwide more than 90% of resorcinol adhesives are used as cold-setting wood adhesives. The other most notable application is as tire cord adhesives, which constitutes less than 10% of the total use.

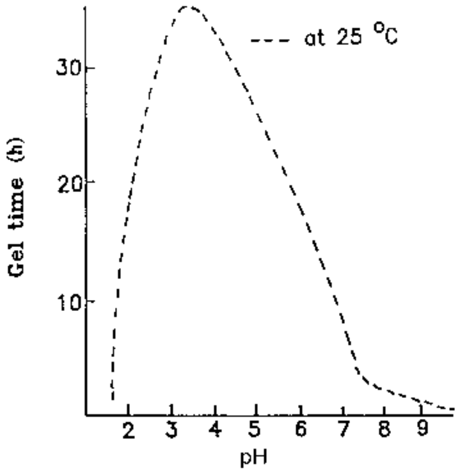


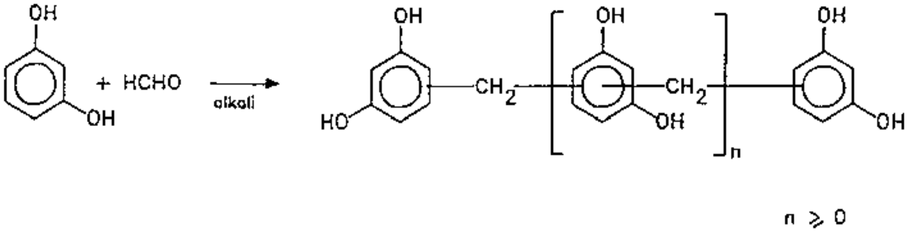
Figure 1 Effect of pH and temperature on the reactivity of the resorcinol–formaldehyde system.

III. WOOD LAMINATING AND FINGERJOINTING ADHESIVES

Various adhesive formulations can be used for the manufacture of laminated wooden beams and fingerjoints for structural purposes. Only those adhesive formulations that at some time or other have been used in industrial applications will be described. All these formulations are based totally or partially on resorcinol, and the hardening process is carried out at ambient temperature, to 50°C [14].

A. Adhesive 1: Resorcinol–Formaldehyde Adhesive

A RF novolak is produced according to the following schematic reaction (Formula 5):



Formula 5

If paraformaldehyde and fillers, generally wood and nutshell flours, are added, the resin becomes capable of setting in 2 to 3 h and curing in 16 to 24 h at ambient temperature.

B. Adhesive 2: Phenol–Resorcinol–Formaldehyde Adhesive and Powder, Liquid, or Sludge Hardener

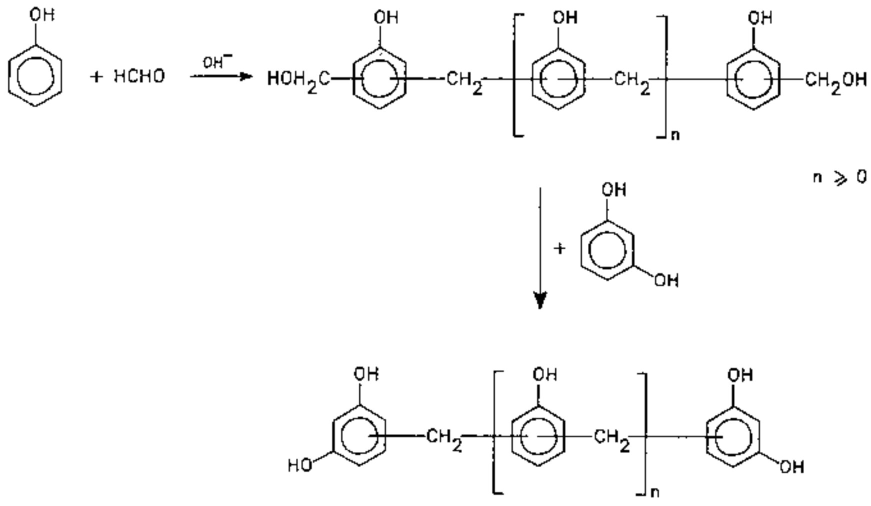
A PF resol is prepared and resorcinol is grafted onto it according to the schematic reaction shown in Formula 6.

The resin produced is capable of setting in 2 to 3 h and cures in 16 to 24 h at ambient temperature once paraformaldehyde and wood and nut flour fillers have been added. This is the most commercially used type of resorcinol cold-set adhesive, variations on the theme concerning mainly the hardener. Thus, sometime and especially in Europe, sludges formed by suspensions of organic or inorganic fillers in water mixed with liquid hardeners such as formalin and urea–formaldehyde precursor concentrates are used as hardeners for this type of adhesive. As these sludges and liquid hardeners have a bad formaldehyde odor during usage, hardeners based on odorless oxazolidines are often used instead of formaldehyde-based ones in these liquid or sludge hardeners.

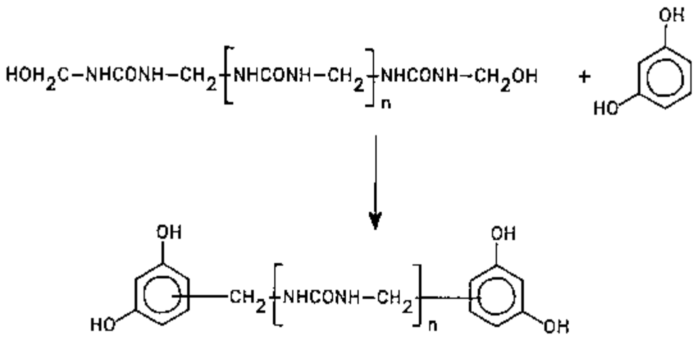
C. Adhesive 3: Urea–Resorcinol–Formaldehyde Adhesive

A urea–formaldehyde resin is prepared and resorcinol is grafted onto it as both terminal units or as middle connecting units leaving each resorcinol to present one or two still reactive sites through which to effect the final cross-linking and hardening of the resin. The schematic reaction is shown in Formula 7.

The behavior of this adhesive is identical to that of adhesive 2, although larger amounts of resorcinol are used. These adhesives have a higher formaldehyde/urea ratio,



Formula 6



Formula 7

are water resistant, and are capable of radiofrequency curing. They can also be used for plywood manufacture, although the high price of resorcinol renders them unsuitable for such an application.

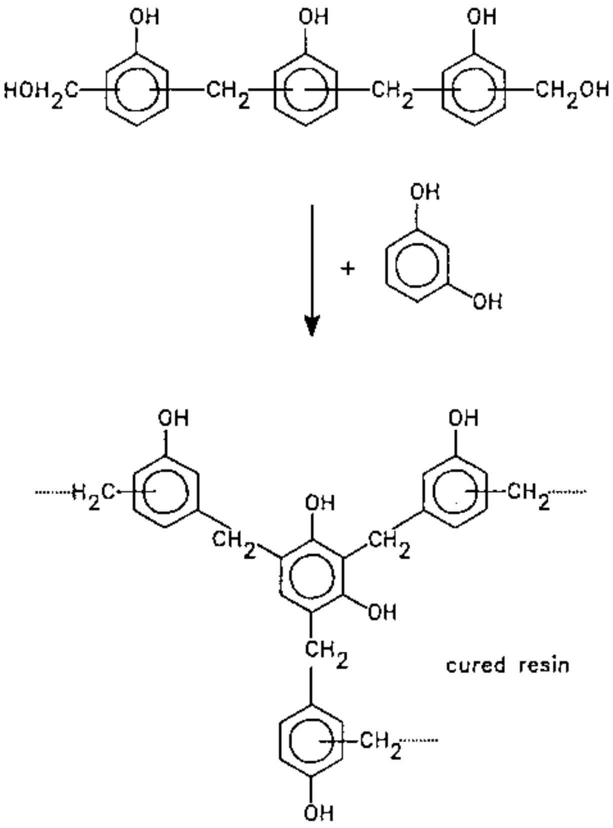
D. Adhesive 4: Phenol–Resorcinol–Formaldehyde and Liquid Hardener

A PF resol is prepared which constitutes the resin. Resorcinol chemicals or RF novolaks, in aqueous or water–alcohol solutions, are used as hardeners according to the scheme in Formula 8.

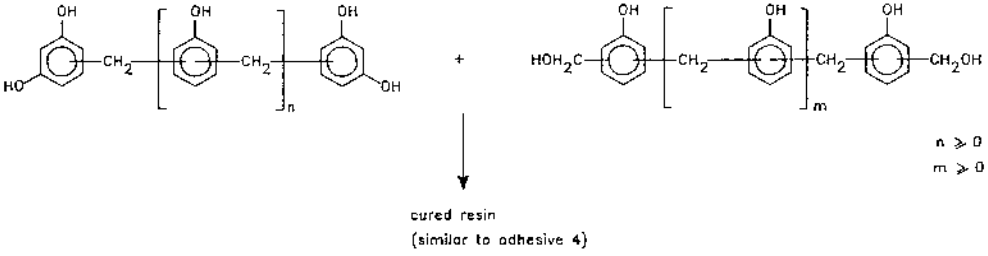
E. Adhesive 5: Phenol–Resorcinol–Formaldehyde and Liquid Hardener

A PRF similar to adhesive 2 is prepared and a PF resol of the same type as adhesive 4 is used as a hardener. The schematic curing reaction is shown in the Formula 9.

The PRF adhesives are always delivered as a liquid and must be blended with a hardener before use. PRF adhesives of type 2 in which a liquid PRF adhesive is mixed with a powder hardener have been the most commonly used industrial systems, although in



Formula 8



Formula 9

Europe the use of sludge hardeners of type 2 above is fairly common too. When using a powder hardener in adhesives of types 1, 2, and 3, they are mixed before use in a mass/mass ratio of liquid adhesive resin (50–60% solid content) to powder hardener of 5:1. The powder hardener is generally a mixture of 10 parts paraformaldehyde and 10% fillers. It is comprised of 200-mesh wood flour or a mixture of wood flour and nutshell flour, also 200 mesh. Adhesives of types 4 and 5 have a liquid resin to liquid hardener ratio of 1:1 by mass. This is so because the hardener is also a resin. Adhesives of types 4 and 5 have been used quite extensively in the past in certain markets but have now been superseded by adhesives of type 2 which have several handling advantages.

Adhesives of type 3, although good, have not really caught on commercially and were developed as an alternative to PRFs of type 2 due to the ever increasing price of oil-derived phenol. In this regard adhesives of type 2 in which the phenol has been completely substituted by a flavonoid tannin have also been developed and have been used commercially in a few southern hemisphere countries for more than 30 years now. Their preparation and performance is detailed in the tannin adhesives chapter (Chap. 27). Pure RF adhesives (type 1) were used extensively earlier (until some 25–35 years ago). They fell into disfavor because of the high price of the resorcinol chemical needed to make them and also due to the shortage of resorcinol supply in 1960 and 1970 (oil crises). They are still used in some industrial applications, particularly at low temperature curing and when difficult wood-gluing problems arise, but they constitute less than 1% of the total market by volume, except in tire cord adhesives which consume in general between 1 and 12% of the resorcinol produced in the world (hence about one sixth of the amount used for wood adhesives). PRF adhesives together with liquid hardeners are used quite extensively in Europe, as they have several handling advantages for this market. These adhesives are mixed before use in a mass/mass ratio of adhesive to liquid hardener from 5 : 1 to 2.5 : 1 of even 1 : 1 (depending on the type). The powder hardener is generally a mixture of equal parts paraformaldehyde fine powder and fillers, these latter comprising 200-mesh wood flour or a mixture of wood flour and nutshell flour, 200–300 mesh. Adhesive types presenting a liquid hardener use as hardeners formaldehyde, paraformaldehyde, formurea, and, when necessary to avoid undue formaldehyde smell, oxazolidine. In addition these hardeners also contain fillers and thickening agents.

All properly formulated resorcinol-based adhesives must have a viscosity low enough in aqueous alcoholic solutions to flow with ease into all the interstices of the wood surface. Wetting ability is promoted by the alcohol. The paraformaldehyde used as a hardener in powder hardener types is an addition polymer composed of a few to over 100 formaldehyde monomers. It dissolves slowly in water, by depolymerization to formaldehyde monomers. The rate of depolymerization depends on the degree of polymerization of the paraformaldehyde, the size of the particles, and the pH. Therefore, the working life or pot life of a glue mix can be adjusted by selecting the type of paraformaldehyde and the pH correctly, but the ratio of resorcinol to phenol will also have an influence on the pH value to be chosen. Fillers are added to give consistency to the glue mix, to control viscosity and thixotropic characteristics, to form a fibrous reinforcement of the adhesive film, and to lessen the cost. Wood flour is used as a filler to obtain better gap filling properties where rough or uneven surfaces must be bonded, or where low bonding pressures must be used. Nutshell flours, such as coconut shell flour, walnut shell flour, peach pip shell flour, macadamia nut shell flour or even olive stone flour are used as fillers to provide smooth-flowing powder mixtures. Inorganic fillers are also used, especially in Europe, although this is a practice to avoid as it is very heavy on saws afterwards. Clays and fumed silica can also be used in very small amounts to control the thixotropic consistency of the glue mix.

As the formaldehyde reacts with the resorcinol-based resin, condensation occurs, with the formation of high-molecular-weight polymers. There is considerable secondary force interaction between the growing resorcinol polymers and the noncrystalline hemicellulosic and lignocellulosic molecules of the substrate. The highly polar methylol groups and the phenolic hydroxy groups link to cellulose and lignin groups by van der Waals, hydrogen, and electrostatic bonds. The growing adhesive polymers continue to interact to form colloidal particles and then a gelatinous film. This mechanism depends

Table 1 Typical Tensile Strength and Percentage Wood Failure Results Obtainable with Synthetic PRF Resins[a]

	Dry test	24-h cold water soak	6-h boil test
Strength (N)	3000–3500	2600–3200	2500–3000
Wood failure (%)	90–100	75–100	75–100

[a] Tested according to Refs. 15 and 16.

strongly on the moisture content of the wood, which determines the rate of water and solvent absorption.

The advantage of ambient-temperature curing is that the moisture escapes gradually from the hard film formed on curing, inducing a minimum of residual stresses on the joint and allowing the glue line to assume the aspect of a molecularly porous solid. As a consequence, the hard film is able to transpire in the same way as wood, which minimizes checking or crazing and allows the glued joint to survive exposure to the extremes of humidity cycles. To shorten the curing time heating chambers (40–60°C) are often used in the manufacturing of glulam, and an even faster curing can be achieved with the use of radiofrequency curing presses. Typical levels of strength and wood failure results obtained in specific standard tests are shown in Table 1.

IV. SPECIAL ADHESIVES OF REDUCED RESORCINOL CONTENT

A. Fast-Setting Adhesive for Fingerjointing and Glulam

Together with the more traditional fingerjointing adhesives that have just been discussed, a series of ambient-temperature fast-setting separate application systems have also been developed. These eliminate the long delays caused by the use of more conventional PRF adhesives, which require lengthy periods to set. These types of resorcinol adhesives are applied separately. They were first developed in the United States [17–20] to bond large components where presses were impractical. Kreibich [20] describes these separate application or “honeymoon” systems as follows: “Component A is a slow-reacting phenol-resorcinol-formaldehyde resin with a reactive hardener. Component B is a fast-reacting resin with a slow-reacting hardener. When A and B are mated, the reactive parts of the component react within minutes to form a joint which can be handled and processed further. Full curing of the slow-reacting part of the system takes place with time.” The *m*-aminophenol used for component B is a frightfully expensive chemical and for this reason these systems were discarded and not used industrially [14]. In their original concept component A is a traditional PRF cold-setting adhesive at its standard pH of between 8 to 8.5 to which formaldehyde hardener has been added. Flour fillers may be added or omitted from the glue mix. Component B is a phenol/meta-aminophenol/formaldehyde resin with a very high pH (and therefore a high reactivity) which contains no hardener or only a very slow hardener.

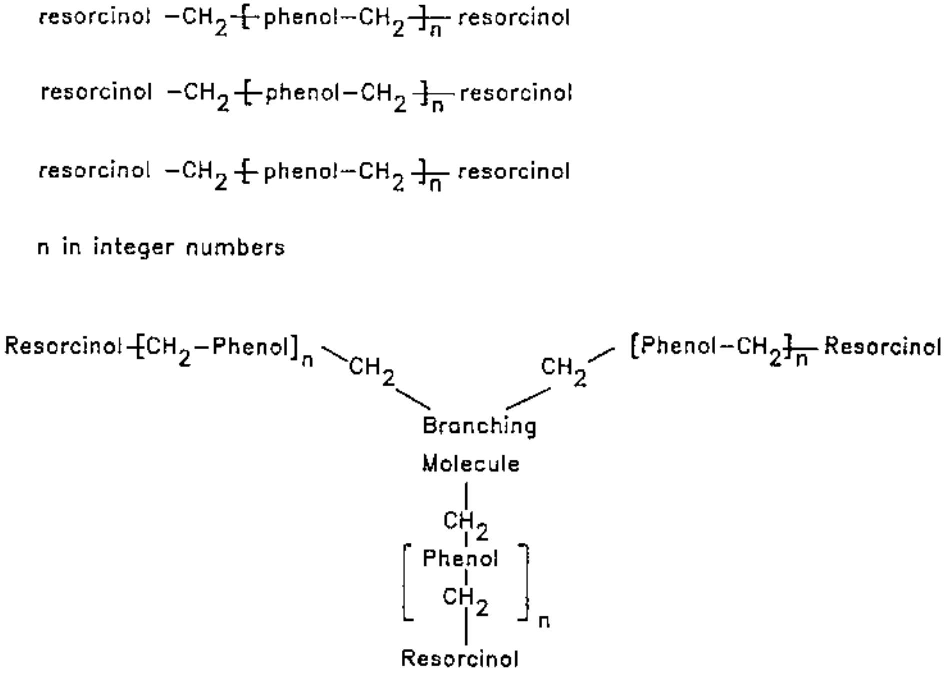
More recently, a modification of the system described by Kreibich has been used extensively in industry with good success. Component A of the adhesive is again a standard PRF cold-setting adhesive with powder hardener added at its standard pH. Component B can be either the same PRF adhesive with no hardener and the pH adjusted to 12 or a 50 to 55% tannin extract solution at a pH of 12–13, provided that the tannin is of the condensed or flavonoid type, such as mimosa, quebracho or pine bark extract with no hardener [3, 21]. The results obtained with these two systems are good and the resin not only has all the advantages desired but also as a result of the use of vegetable tannins and of the halving of the resorcinol content of the entire adhesive system is considerably cheaper [3,21,22].

The adhesive works in the following manner. Once the component A glue mix is spread on one fingerjoint profile and component B on the other fingerjoint profile and the two profiles are joined under pressure, the reaction of component B with the hardener of part A is very fast. In 30 min at 25°C fingerjoints prepared with these adhesives generally reach the levels of strength that fingerjoints glued with more conventional phenolic adhesives are able to reach only after 6 h at 40 to 50°C or in 16 to 24 h at 25°C [3,22]. Clamping of laminated beams (glulam) bonded with these fast-set honeymoon adhesives is an average of only 3 h at ambient temperature compared with the 16 to 24 h necessary with traditional PRF resins [21,22]. These adhesives present also two other advantages, namely (i) they are able to bond without any decrease of performance at temperatures down to 5°C and (ii) they are able to bond "green" timber at high moisture content, a feat which has been used in industrial glulam bonding since their commercial introduction in 1981. Several variations on the theme exist, such as the "Greenweld" system from New Zealand in which component B is a solution composed of just ammonia as a strong accelerator of the PRF plus hardener of component A, and of a thickener; this system, however, suffers from the presence of the odor of ammonia which is unacceptable in some sophisticated markets.

B. Branched PRF Adhesives

Recently another step forward has been taken in the formulation of PRF adhesives of lower resorcinol content. Liquid resorcinol or PRF resins appear to be mostly linear [4]. The original concept in "branching" erroneously maintained that if a chemical molecule capable of extensively branching (three or more effective reaction sites with an aldehyde) is used after, before, or during, but particularly during or after, the preparation of the PF resin, the polymer in the branched PRF adhesive has (1) higher molecular weight than in normal PRF adhesives where branching is not present and (2) higher viscosity in water or water/solvent solutions of the same composition and of the same resin solids content (concentration). It also needs a much lower resorcinol amount on the total phenol to present the same performance as normal linear PRF adhesives. This can be explained schematically and is shown in Formula 10. With $n \geq 1$ and an integer number and comparable to, similar to, or equal to n in formula 9 for the production of PRF resins.

When comparing linear and branched resins, for every n molecules of phenol used a minimum of 2 molecules of resorcinol are used in the case of a normal, traditional linear PRF adhesive, whereas only 1 molecule of resorcinol for n molecules of phenol is used in the case of a "branched" PRF adhesive. The amount of resorcinol has then been halved or approximately halved in the case of the branched PRF resin. A second effect caused by the branching is a noticeable increase in the degree of polymerization of the resin. This causes a considerable increase in the viscosity of the liquid adhesive solution. Because PRF adhesives must be used within fairly narrow viscosity limits, to return the viscosity of the liquid PRF adhesive to within these limits, the resin solids content in the adhesive must be lowered considerably, with a consequent further decrease in the total liquid resin of the amount of resorcinol and of the other materials, except solvents and



Formula 10

water. This decreases the cost of the resin further without decreasing its performance. Thus, to conclude, the decrease in resorcinol by branching of the resin is based on two effects:

1. A decrease in resorcinol percentage in the polymer itself, hence in the resin solids, due to the decrease in the number of the PF terminal sites onto which resorcinol is grafted during PRF manufacture.
2. An increase in molecular weight of the resin, which by the need to decrease the percentage of resin solids content to a workable viscosity decreases the percentage of resorcinol on liquid resin (not on resin solids).

It is clear that in a certain sense a branched PRF will behave as a more advanced, almost precured phenolic resin. While the first effect described is a definite advance on the road to better engineered PRF resins, the second effect can also be obtained with more advanced (reactionwise) linear resins. The contribution of the second effect to the decrease in resorcinol is not less marked than that of the first effect. It is, however, the second effect that accounts for the difference in behavior between branched and linear PRF adhesives.

Branching molecules which can be used could be resorcinol, melamine, urea and others [23]. Urea is the favorite one, because it is much cheaper than the others and needs to be added in only 1.5 to 2% of total resin. When urea is used as a brancher, the adhesive assumes an intense and unusual (for resorcinol resins) blue color, after a few days, hence its nickname, "blueglue." However, later work [24,25] has shown that tridimensional branching has very little to do with the improved performance of these low-resorcinol content adhesives, with tridimensionally branched molecules contributing, at best, no more than 8 to 9% of the total strength [24,25]. In reality, addition of urea causes the reaction as foreseen, but not in three points of branching but rather only in two sites of the branching molecule. This is equivalent to saying that most of the resin doubles linearly in molecular weight and degree of polymerization, while the final effect, good performance at half the resin resorcinol content, is maintained [24,25]. This effect is based on the relative reactivity towards phenolic methylols of urea and of unreacted phenol sites and thus while the macro effect is as wanted, at the molecular level it is only a kinetic effect due to the different relative reactivities of urea and phenol under the reaction conditions used. Thus

$$\begin{gathered}\text{resorcinol}-\text{CH}_2\,[\text{phenol}-\text{CH}_2]_n-\text{resorcinol}\\ \text{resorcinol}-\text{CH}_2\,[\text{phenol}-\text{CH}_2]_n-\text{resorcinol}\\ \downarrow\\ \text{resorcinol}-\text{CH}_2\,[\text{phenol}-\text{CH}_2]_n-\text{urea}-\text{CH}_2+\text{phenol}-\text{CH}_2]_n-\text{resorcinol}\end{gathered}$$

halving of the resorcinol content is still obtained, but between 90 and 100% of the polymers in the resin are still linear. It is noticeable that the same degree of polymerization and "doubling" effect cannot be obtained by lengthening the reaction time of a PF resin without urea addition [24,25].

These liquid resins then work at a resorcinol content of only 9 to 11%, hence considerably lower than that of traditional PRF resins. These resins can also be used with good results for honeymoon fast-setting adhesives in PRF–tannin systems, thus further decreasing the total content of resorcinol in the total resin system at a level as low as 5 to 6%.

C. Cold-Setting PF Adhesives Containing no Resorcinol

As the cost of cold-setting exterior-grade adhesives based on resorcinol is very high due to the high cost of resorcinol itself, the tendency to decrease the amount of resorcinol while maintaining unaltered the performance of the adhesive, when brought to its ultimate conclusion leads to the concept of exterior cold-setting phenolic adhesives of zero level resorcinol. As alkaline PF resins do not have an ambient temperature rate of reaction that is even vaguely sufficient to set and harden the adhesive to a sufficient level, some modifications need to be introduced to overcome in this regard the lack of resorcinol. This can be done in several ways: (i) by using standard PF thermosetting resol resins and hardening them by increasing the glue line temperature by radiofrequency in fingerjointing and glulam manufacture. The system is expensive and needs considerably higher capital outlay and more careful handling of both the equipment and of the joint, for results that are certainly not particularly exciting. (ii) By using resins in which the PF resol of adhesives of type 2 above is terminated by the terminal grafting of a resorcinol substitute, for example a natural polyflavonoid tannin [26], this system being truly cold setting and yielding relatively good results but at best just on the inferior limit of the standard requirements [26]. (iii) By using self-neutralizing acid-setting PF resols. The term "acid-setting" when used in the presence of a lignocellulosic substrate makes wood technologists shudder, conjuring visions of extensive acid-induced substrate degradation and early exterior joint failure. And this is indeed the case! In reality some exterior aminoplastic resins do harden in the moderately acid range without any major substrate degradation problems. PF resins, however, while hardening very rapidly under acid conditions, do need very acid conditions to give a hardened strong network, and this elevated acidity is not really acceptable as regards long term durability of the substrate. The damage due to the acid hydrolysis of

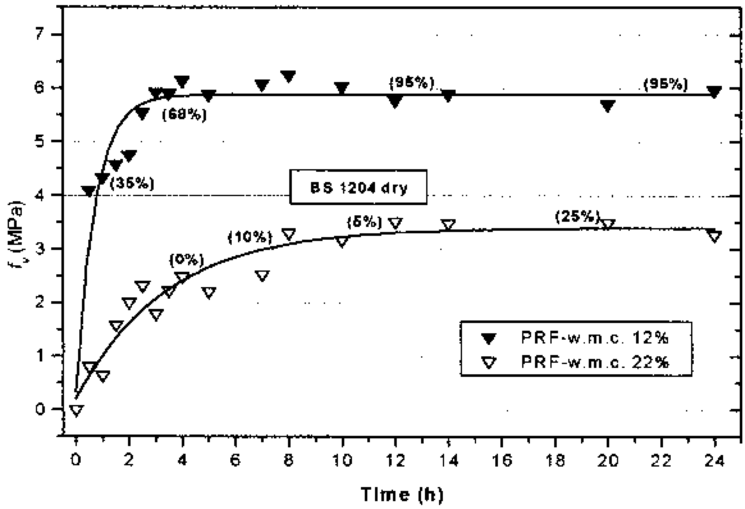


Figure 2 Typical strength and wood failure increase as a function of time of a pure PRF honeymoon adhesive system on timber at 12% and 22% moisture content [26–29]. Note that at the unusually high moisture content of 22% the requirements of the standards are passed in less than 24 h as the timber starts to dry [26–29]. Test on beech strips according to British Standard BS 1204.

cellulose and other wood carbohydrates is particularly aggravated and compounded by the long term effect of the glue line remaining acid after resin hardening. However, the main negative effect due to acid-induced degradation of the substrate has been overcome by using acid-setting PF resins containing no resorcinol but hardened by the use of a self-neutralizing catalyst [27]. According to this principle the adhesive first becomes acid to allow the PF resin to cure and after hardening the hardened glue line self-neutralizes in very short time [27]. The greater majority of the effects of substrate degradation are then avoided and very strong and durable exterior wood joints are produced [27]. The system works well in radiofrequency cured joints, yielding much better results than the alkaline resols of point (i) above, and can work well under purely cold-setting conditions [27] (Fig. 2).

Other rapid setting adhesive systems not containing resorcinol are those based on melamine–urea–formaldehyde resins and on one-component polyurethanes, described in Chap. 32 and Chap. 34, respectively [28,29].

V. FORMULATION FOR ADHESIVES OF TYPE 2 [14]

A basic formulation capable of giving more than adequate results is presented here so that a starter in the field can get aquainted with these types of adhesives. The procedure for the preparation of this resin can be modified in many ways by varying catalysts, concentration, molar ratios, and condensation conditions.

Phenol, 110 parts by mass + 22 parts water
First formalin 37% solution, 49 parts by mass
H_2SO_4 10% solution, 22 parts by mass
First NaOH 40% solution, 4.5 parts by mass

Second NaOH 40% solution, 9.25 parts by mass
Second formalin 37% solution, 90 to 93 parts by mass
Methanol or methylated spirits, 30 parts by mass (at start of reaction)
Resorcinol, 71 parts by mass
Tannin extract, 19 parts by mass (only as a thickener: another thickener can also be used as soon as it is not excessively sensitive to water attack).

Phenol, water, methanol, and the first amount of formalin solution are charged in the reaction vessel and heated mildly until the phenol is dissolved. H_2SO_4 is added and the temperature increased to reflux under continuous mechanical stirring. The mixture is refluxed for 3.5 to 4 h (generally ±4 h) under continuous mechanical stirring. It is cooled to 50 to 60°C and the following is added: the two amounts of NaOH 40% solution (slowly) and the second amount of formalin solution while maintaining the mix under continuous mechanical stirring. The mixture is then refluxed for 4.5 to 4.75 h and then the resorcinol added. The mixture is refluxed for a further 30 to 50 min. Spray-dried mimosa tannin extract is added immediately before or during cooling to adjust the viscosity to the wanted level; the pH must be adjusted to 8.5 to 9.5 according to the pot life required. The reaction must be carried out under continuous mechanical stirring throughout the whole reaction period. The hardener is a 50 : 50 mixture of paraformaldehyde 96% (usually a fast grade) fine powder and 180- to 200-mesh softwood flour (60 : 40 mass proportion) which is added to the liquid resin generally in the proportions by mass of liquid resin: powder hardener = 100 : 20 to 100 : 25.

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Furan-Based Adhesives

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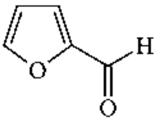
I. INTRODUCTION

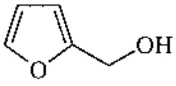
The dwindling availability of fossil reserves constitutes a driving force towards finding alternative resources which can substitute them, totally or partially, in order to prepare chemicals and materials that are normally produced from petroleum and coal. In this context, vegetable biomass represents a very promising source since it offers a large variety of potential monomers, oligomers, and polymers, some of which can be extracted and used as such (namely, products such as terpenes, tannins, rosins, lignins, and cellulose) and others which can be suitably transformed to give monomers, solvents, surfactants, and a variety of polymeric materials (e.g., modified sugars, saponified oils, furfural and its derivatives, and cellulose acetates). We tried to show [1] that, besides its extensive use as a source of fibers for papermaking and textiles, vegetable biomass can also lead to interesting chemicals and materials. In a recent review [2], we focused on the use of furanic monomers for the preparation of polymeric materials and showed that different petroleum-based monomers (especially aromatic derivatives) could be replaced by their furanic counterparts. Thus, a variety of totally furanic, aromatic–furanic, and aliphatic–furanic polymers display properties similar to (and sometimes better than) those of currently used polymers derived from petroleum, proving that a whole area of biomass-based materials can be developed from two first-generation compounds which are readily available from a wide spectrum of renewable resources.

Furanic monomers can be obtained from hemicelluloses which are among the main constituents of vegetal biomass and are abundant in trees and agricultural residues of annual plants, such as sugarcane bagasse, oat hulls, corn husks, rice, and wheat straw. The precursors of most industrial furan derivatives are obtained directly from hemicelluloses through the acid-catalyzed hydrolysis of pentosans (e.g., xylans) followed by dehydration and cyclization of the ensuing pentoses leading to the formation of furfural (**1**), which is today the most important first-generation furan derivative, produced industrially at a rate of ca. 200,000 tonnes per year. This output is spread widely among numerous countries, including both industrialized and developing economies, because the process is particularly simple and the raw materials are available and plentiful virtually everywhere and are renewable often on short cycles. An additional advantage of this approach is that it calls upon a rational exploitation of agricultural wastes. Furfural can be used as such, but is mostly (more than 80%) converted into furfuryl alcohol (**2**) using either liquid-phase or vapor-phase hydrogenation in the presence of copper catalysts which were found to be very selective in avoiding the hydrogenation of the heterocycle ring [3].

Furfuryl alcohol finds numerous applications as monomer (see below) and has, therefore, been for decades the most important second-generation furan derivative.



(1)

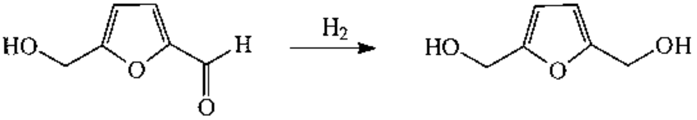


(2)

It is also used to prepare 2,5-bis(hydroxymethyl furan) (**3**) through its reaction with formaldehyde [3], namely:

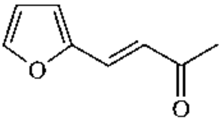
(2) (3)

Compound **3** can also be prepared by the hydrogenation of 5-hydroxymethyl furfural (**4**) which, in turn, is obtained from hexoses following the same acid-catalyzed process described above for furfural [2].

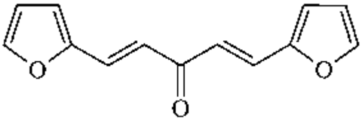


(4) (3)

Compounds **1**, **2**, and **3** are among the most relevant monomers or co-monomers for furan-based adhesives, but so also are furfurylidene acetone (**5**) and its bis-adduct **6**. The synthesis of **5** involves the base-catalyzed reaction between **1** and acetone [2] and, in the same context, the use of an excess of **1** leads to the formation of **6**:



(5)



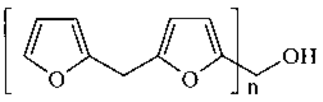
(6)

This chapter is devoted to adhesives and resins prepared from totally furanic monomers or formulations in which furanic compounds are added. In this realm, only a few furanic monomers and resins are involved, namely: **1**, **2**, **3**, **5**, and **6**, as well as liquid oligomers of **2** (**poly2**) and **3** (**poly3**). The properties of these monomers together with the mechanisms of their resinification and the composition of **poly2** and **poly3** will be briefly dealt with before discussing their use in the manufacture of resins for binders and adhesives.

II. PROPERTIES OF FURANIC MONOMERS

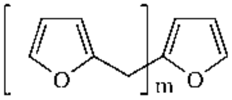
The relevant properties of furanic compounds covered in this review are summarized in Table 1.

The compositions of **poly2** and **poly3** were studied by several groups [2,3] and shown to have mainly the following structures:



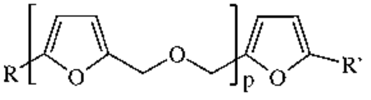
$n = 0, 1, 2\ldots$

(**7**)



$m = 0, 1, 2\ldots$

(**8**)



$p = 1, 2\ldots$

(**9**) $R = H$; $R' = H$ or CH_2OH

(**10**) $R = R' = CH_2OH$

Their relative abundance depends, of course, on the conditions used for their syntheses. A typical composition [3] is given in Table 2.

Table 1 Properties of Furanic Compounds Used in Adhesives

Compound type	**1**	**2**	**3**	**5**	**6**
Molecular weight	96.09	98.10	128.10	136.15	214.22
Boiling point (°C)	161	170	—	116[a]	—
Melting point (°C)				39.7	
Density at 20°C (kg/dm^3)	1.16	1.13	—	1.06[b]	—
Refractive index at 20°C	1.53	1.49	—		—
Viscosity at 25°C (mPa·s)	1.48	4.62	—	—	—
Surface tension (mN/m)	40[c]	38[d]	—	—	—

[a] At 10 mm Hg.
[b] at 45°C.
[c] at 30°C.
[d] at 25°C.

Table 2 Typical Composition (w/w %) of **poly2** and **poly3**

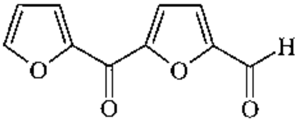
	7	**8**	**9**	**10**
poly2	25	12	35	28
poly3	—	—	5	95

III. HISTORY, ADVANTAGES, AND LIMITATIONS ASSOCIATED WITH THE USE OF FURAN-BASED ADHESIVES

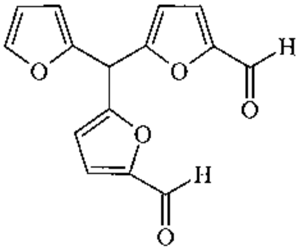
The first synthetic thermosets used as adhesives were phenol–formaldehyde resins produced at the end of the nineteenth century, historically linked to Baekeland's process which attained industrial status at the beginning of the twentieth century [4]. Furanic condensates appeared much later as a result of the marketing of **2**. They were first used as foundry binders by Quaker Oats in 1960. The use of furanic resins in the aerospace industry began ten years later. Although furanic resins represent a mere 1% of the total thermoset production, the high added-value of these materials amply justifies their use. In fact, furan-based adhesives and binders are fire-, solvent-, and acid- or alkali-resistant. They are known, however, to display two main drawbacks related to their sensitivity to shrinkage and oxidation.

IV. RESINIFICATION MECHANISMS

The acid- or heat-initiated cross-linking mechanisms of **1** were extensively studied for decades, but because of the complexity of the reactions involved and the effect of atmospheric conditions (e.g., light, oxygen, and water vapor) intermediate products were not identified until 1975. In that study, **1** was polymerized at 100–250°C in the absence of air and the following intermediates were isolated [5,6]:

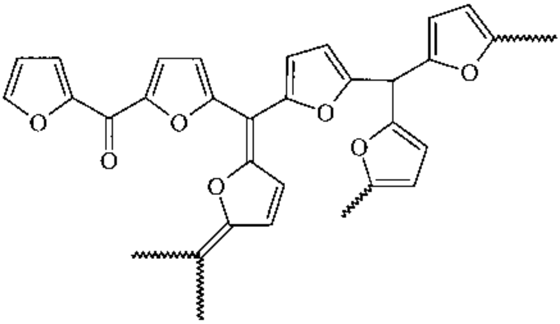


(11)

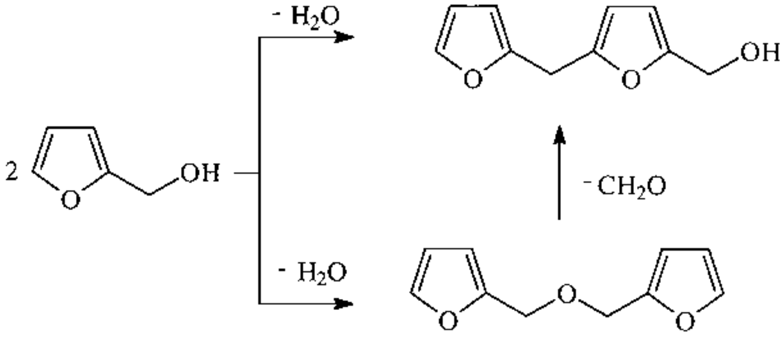


(12)

And for the final product, the following structure was proposed [5,6]:



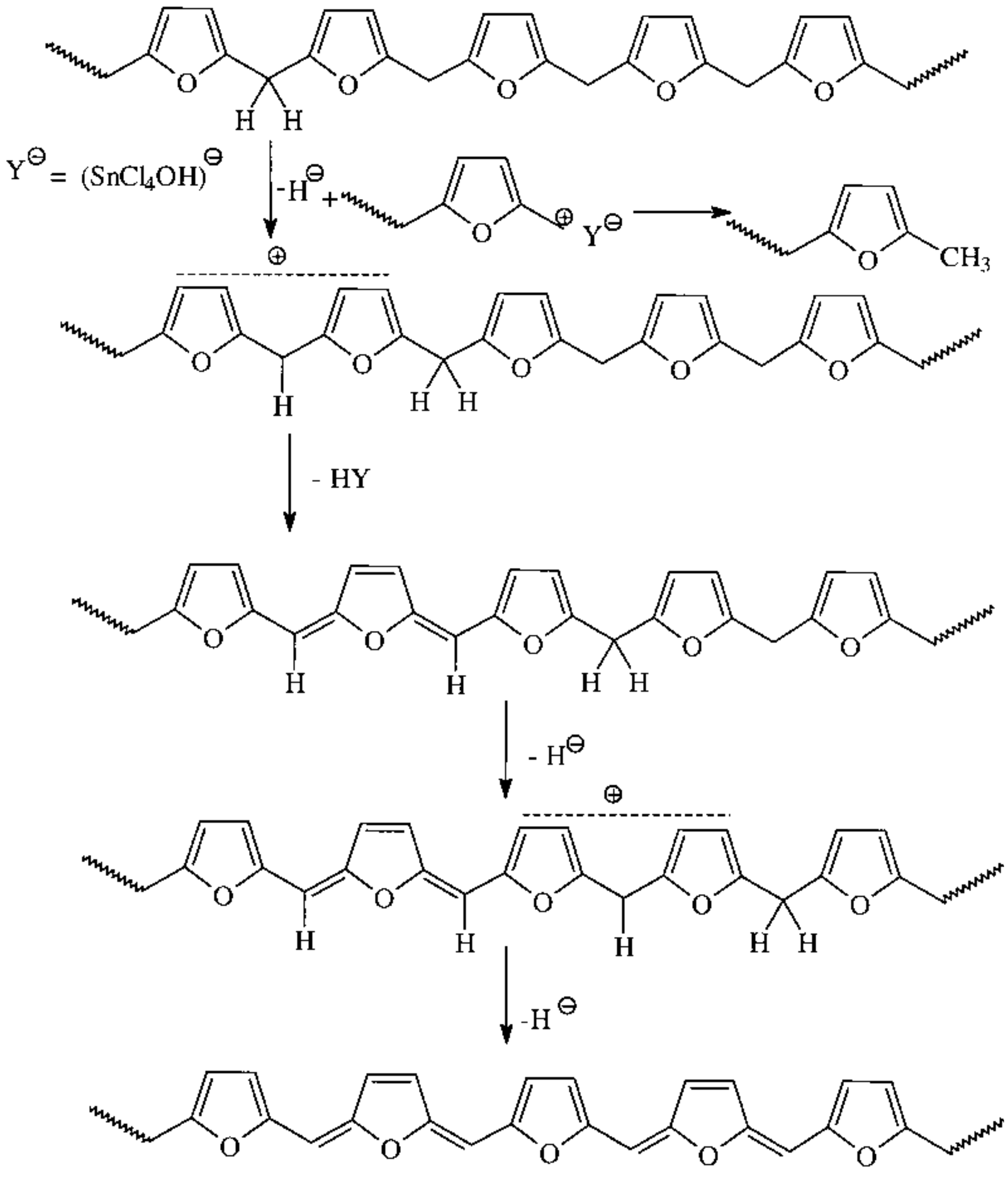
The polycondensation of **2** in acidic media has also been studied for a long time, but only recently was a clear-cut reaction mechanism established from a study in our laboratory [2,7,8]. The success of this investigation stemmed from the fact that a large number of model compounds were synthesized which helped to establish the mechanisms of both cross-linking and color formation in this process. The use of mild catalysts confirmed that the first steps of the polymerization reactions occurred as follows:



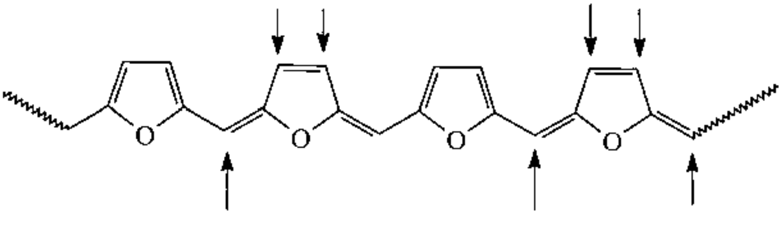
This initial mechanism does not explain, however, these anomalies since both macromolecular structures should give rise to colorless and thermoplastic materials.

It was then shown that only several units actually condensed following this mechanism, since the average degree of polymerization (DP) never exceeded about 5, and cross-linking and color formation rapidly took place thereafter. In the mechanism of color formation, sketched in Scheme 1, we postulated that the formation of highly conjugated sequences resulted from successive hydride-ion/proton abstraction cycles [7]. This mechanism was confirmed by using different model compounds which were treated with an excess of hydride-ion (H^-) abstractors (such as dioxolenium or triphenylmethyl cations) and the ensuing reactions followed by both ultraviolet (UV)–visible and ^1H nuclear magnetic resonance (NMR) spectroscopies. This mechanism also explained the presence of methyl groups already observed by several authors [9–11]. The reaction of **poly2** (obtained at early stages of the polycondensation) with hydride-ion abstractors was again followed by UV–visible spectroscopy and the results confirmed the proposed mechanism. Thus, the presence of conjugated sequences of different lengths was established, since the corresponding carbenium ions absorbed at different wavelengths, namely around 420, 450, 540, 600, and 800 nm.

Having solved the long-standing puzzle related to color formation, we switched to the problem of the occurrence of branching and/or cross-linking reactions [2,7,8]. It was argued that these events could start either from the "irregular" units formed by the mechanism shown in Scheme 1, as illustrated in Scheme 2, and/or by Diels–Alder reactions between two chains, as proposed in Scheme 3. In fact, since the participation of *furanic* hydrogen atoms at C3 and C4 and those of methylene bridges had been clearly excluded on the basis of model reactions, it seemed reasonable to attribute the branching and cross-linking reactions to these two mechanisms. The second alternative, involving the cross-linking through Diels–Alder reactions, was recently confirmed by using 2,5-dimethyl furan as a solvent for the acid-catalyzed polycondensation of **2**. In this experiment, the large excess of dimethyl furan played the role of predominant diene trap for the exo-dihydrofuran dienophiles and thus prevented their coupling with the regular units of **poly2** (Scheme 3). The fact that in these conditions the polymers remained soluble up to long reaction times and high yields was taken as clear evidence of the validity of Scheme 3.



Scheme 1

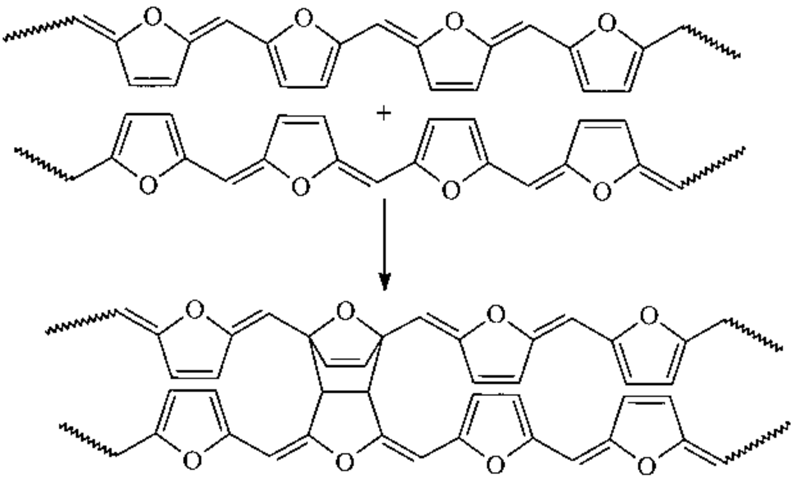


Scheme 2

V. FURAN RESINS AS FOUNDRY BINDERS

Furan resins have been extensively used as foundry binders in combination with formaldehyde, urea, phenol, and casein, for decades [12,13]. The main two monomers used in this field are **1** and **2**. Table 3 summarizes their proportions in different commercial phenolic resins [12].

The main advantages of furan resins are due to their excellent thermal stability, and remarkable resistance to acidic conditions, as well as to fire and corrosion. These resins



Scheme 3

Table 3 Proportions of **1** and **2** in Commercial Phenolic Resins

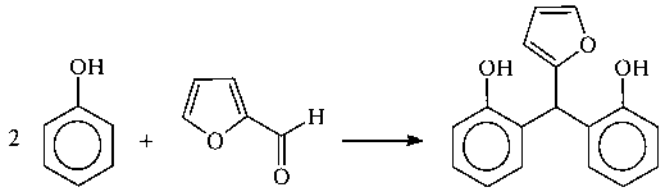
		1		**2**	
	Supplier	Amount added (% w/w)	Amount retained after curing (% of the amount added)	Amount added (% w/w)	Amount retained after curing (% of the amount added)
Bakelite 0215	Quaker Oats Co.	10	90	10	94
Bakelite 0215	Quaker Oats Co.	20	87	20	86
Bakelite 2417	Quaker Oats Co.	20	85	20	83
Durez 7031	OxyChem	20	88	20	85
Durez 8045	OxyChem	—	—	20	77
Durez 14000	OxyChem	—	—	20	87
Durite 278	Contenti Inc.	10	96	10	91
Durite 278	Contenti Inc.	20	96	20	92
Durite 3022	Contenti Inc.	10	95	10	93
Durite 3022	Contenti Inc.	20	92	20	89
Durite 1530	Contenti Inc.	20	93	20	92
Monsanto 795	Monsanto	20	88	—	—
Varcum 1364	OxyChem	20	87	20	84
Varcum 1192	OxyChem	20	69	20	80

have found widespread industrial applications as witnessed by the large number of both patents covering their uses and scientific publications dealing with their chemistry, structures, and properties [3,6,12,14–16].

There are three techniques associated with their production, mostly covered by patent literature, namely: (i) no-bake, (ii) hot-box, and (iii) cold-box processes. The no-bake technique is simple and relatively cheap. It consists in mixing the resin (based on **2**) with the sand in the presence of an acidic catalyst. The reaction starts at room temperature and the curing is accelerated by the heat generated during the polycondensation reaction. The molds thus obtained are withdrawn after 10–30 min and left undisturbed for 3–6 h in order to accomplish a total curing. The hot-box technique is used in light (e.g., aluminum) and heavy (e.g., copper, bronze) metal casting [4,17]. The resins used for light metals are urea-modified furan resins, whereas those used for heavy metals contain only furan components. The hot-box process is well suited for mass production and it consists in mixing the moist sand with a liquid resin and a curing agent. The ensuing mixture is then cured at 180–260°C in heated core boxes. The main limitation of this process is its extremely long bench life. The cold-box (or SO_2–furan) process is based on curing the reactive resin at room temperature in a closed-air system with SO_2. This gas is converted in situ into a mixture of sulfurous and sulfuric acids which catalyze the curing.

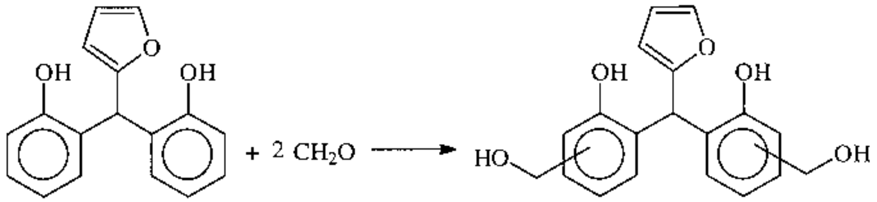
VI. FURAN RESINS AS WOOD ADHESIVES

Regardless of the fact that numerous investigations exist about the possibility of incorporating the furan heterocycle into wood adhesive formulations, their industrial exploitation is still modest. The first suggestion concerning the use of **1** in partial substitution of formaldehyde in phenolic resins was put forward in 1958 by Baxter and Redfern [18] who proposed that the furfural units were incorporated into the polymer skeleton following condensation reactions such as:



(13)

The intermediate oligomers such as **13** were then subjected to methylolation with formaldehyde to form phenolic–furanic–formaldehyde resins, according to:



The interest in this type of process was, of course, the decrease of formaldehyde content and, therefore, its lower release during the life cycle of the resin.

This approach was then extended by Pizzi's group to other phenolic type adhesives such as phenol–resorcinol–formaldehyde networks [19]. In this work, it was shown that the addition of **1** gave cold setting resins with performances and costs comparable to those made using formaldehyde alone. Thus, the phenol–resorcinol–furfural–formaldehyde cold sets obtained appeared to have a lower bulk shrinkage compared to those prepared without **1**. Moreover, it was established that the presence of furfural did not slow down the curing rate of the resins.

Stamm [20] studied the dimensional stabilization of different woods with **2**. Thus, Douglas fir, Engelman spruce, loblolly pine, and yellow poplar woods were treated with **2** in the presence of zinc chloride, citric acid, or formic acid in order to induce their acid-catalyzed polymerization. It was established that the maximum antishrinking efficiency (around 72%) could be reached with a resin level of a minimum of 40% with respect to oven dried (OD) wood. The optimal amount of each acidic catalyst was also determined. The curing time was studied for each system and it was shown that the use of 1% zinc chloride and 6 h of curing time at 120°C gave very satisfactory fracture moduli, toughness, abrasion resistance, and antishrinking behavior. The only limitation associated with the possible uses of these systems is the dark color of the final materials.

Dhamaney [21] showed that the addition of furfural into cashew nut shell liquid adhesives based on phenol–formaldehyde resins, using $CuCl_2$ or $CaCO_3$ as a "hardener," gave good adhesive bonding for ordinary plywood. Johns et al. [22] prepared white fir flakeboards using an aqueous solution containing a mixture of ammonium lignosulfonate, **2**, and maleic acid as a binder. Before bonding, the wood surface was activated by a nitric acid treatment. It was shown that the panels thus obtained possessed a higher elasticity modulus and lower thickness swell and water absorption compared with those prepared using classical phenol–formaldehyde binders. Nevertheless, the internal bonding and the rupture modulus were higher for panels obtained using conventional resins. It was also established that best surface activation was achieved using a 1.5% aqueous solution of nitric acid (25–40%) with respect to OD wood, since it gave the optimal mechanical properties for both high and low density panels.

Gupta et al. [23] prepared plywoods from *Cedrus deodora* and phenol–formaldehyde resins. They showed that the addition of 5% of **1** to this adhesive did not result in any appreciable improvement, but the concomitant addition of 10% of coconut shell powder gave very high failing loads and very low glue failures. Subsequently, in another context, Pizzi et al. [24] tested different aliphatic aldehydes and **1**, in tannin-based adhesives, and showed that furfural could replace formaldehyde in the manufacture of adhesive resins for beam lamination. Roczniak [25] studied the thermal properties of phenol–formaldehyde–**1** resins, as catalyzed by dichlorohydrin of glycerol, boric acid, hexamethylenetetramine (HMTA), or *p*-toluene sulfonic acid. Two main conclusions were drawn from this work: (i) *p*-toluene sulfonic acid gave a faster resinification rate and (ii) HMTA led to the highest thermal resistant resins. Krach and Gos [26] investigated the gluing of large dimension sawn wood structures using urea–melamine–furfural as a binder. They stated that the initial wood moisture (8 to 12%) and the time of adhesive spreading (10 to 90 min) did not influence significantly the strength properties of the glued junction.

Philippou et al. [27] studied the bonding of wood by graft polymerization. They produced white fir, Douglas fir, and bishop pine particleboards using **2** as well as mixtures of ammonium lignosulfonate with **2** or with formaldehyde as cross-linking agents. Before bonding, the wood surface was activated with different amounts of hydrogen peroxide (from 0.5 to 4% with respect to OD wood). The amount of the binder was kept constant in all experiments (7% with respect to OD wood). The internal bond strength of the materials obtained was found to increase with increasing amounts of hydrogen peroxide, whereas the thickness swelling followed the inverse trend. The use of both **2** alone and its mixture with ammonium lignosulfonate showed very good bonding capability. Bishop pine gave the highest internal bonding and white fir yielded the lowest thickness swelling and water absorption when the mixture of ammonium lignosulfonate with **2** was used as a binder. The least efficient adhesive was found to be the formaldehyde–lignosulfonate system. The differences between wood species were attributed to their different contents of extractives. In another study, Philippou et al. [28] studied the effect of the composition of the bonding materials on the properties of Douglas fir particleboards. Thus, the proportion between **2** and ammonium lignosulfonate was varied as follows: 10/0, 9/1, 8/2, 7/3, 6/4, 5/5, 2.5/7.5, and 0/10. In this work, the wood was also activated by hydrogen peroxide (2% w/w with respect to OD wood) and the catalysts used were ferric chloride and maleic acid. Ammonium lignosulfonate without **2** failed to develop resistance to boiling water whereas **2** without ammonium lignosulfonate gave good mechanical and water resistance properties. However, the use of a mixture containing six parts of lignosulfonate and four parts of **2** yielded boards with the highest internal bond strength and water resistance values. Increasing the amount of resin with respect to wood was found to produce an increase in the elasticity and rupture moduli and a decrease in water absorption and thickness swelling. The boards prepared exhibited strength and resistance to cold and boiling water comparable to those made using classical phenol–formaldehyde resins. In a third investigation, Philippou et al. [29] studied the effect of the processing parameters on the mechanical properties of particleboards made from Douglas fir wood treated with ammonium lignosulfonate and **2** as a binder in the presence of maleic acid as a catalyst. They showed that increasing the pressing temperature from 121 to 177°C or the pressing time from 4 to 8 min, progressively enhanced the internal bond strength and the water resistance of the treated boards. The water resistance was found to be further improved by the addition of a small amount of wax (0.5% w/w with respect to OD wood) in the binder mixture.

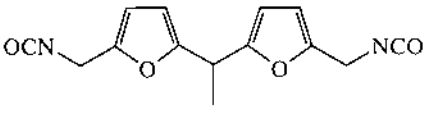
Leitheiser et al. [30] prepared water dilutable furan resins as binders for particleboard and showed that the resulting composites could be used for exterior applications. These resins were readily water dilutable and had low viscosities, which made their application with conventional equipment an easy process. Kelley et al. [31] prepared wood panels from *Acer saccharum var*. Marsh. with various binders. They first activated the surface of the wood by nitric acid and bonded the particles with tannin, **2**, and a mixture of the two, with and without maleic acid. In all cases, the particleboards obtained exhibited shear strengths as high as that obtained from a control system made with a conventional phenol–formaldehyde binder. However, the acidic treatment of wood appeared to have only a slight effect on the mechanical properties of the panels bonded with the tannin–**2**–maleic acid system. Subramanian et al. [32] subjected Douglas fir wood flakes to a nitric acid treatment followed by a grafting reaction with 2(1-aziridinyl)ethyl methacrylate and **2**. They showed that the amount of carboxylic acid groups at the wood surface had increased substantially, thus enhancing its reactivity towards both reagents.

Philippou and Zavarin [33] studied the interactions between lignocellulosic materials, **2**, and maleic acid in the presence or absence of hydrogen peroxide. They used white fir wood flour, microcrystalline cellulose, milled-wood lignin, and ammonium lignosulfonate and followed their interactions with the binder by differential scanning calorimetry (DSC) and concluded that a graft copolymerization between hydrogen peroxide activated wood, **2**, and ammonium lignosulfonate had occurred. Balaba and Subramanian [34] studied the polymerization of **2** catalyzed by the surface acidity resulting from treating wood with nitric acid. They followed the polymerization by intrinsic viscosity measurements and showed that there were two reaction regimes. The first was found to obey zero order kinetics, with an activation energy of 53.4 kJ/mol, whereas the second could not be exploited because of polymer precipitation following the formation of network structures.

In 1985, experiments on an industrial scale were carried out jointly at Quaker Oats Chemicals and Collins Pine Company particleboard plants [35]. In these trials **1** was used as an extender in a polymeric methylene diphenyl isocyanate (MDI) binder (**1**:MDI = 1:3 w/w). The main conclusions which could be reached from these trials were that savings in binder levels, pressing time, and temperature and drying requirements could be obtained compared with the corresponding performances of standard phenol–formaldehyde and urea–formaldehyde systems.

Nguyen and Zavarin [36] studied graft polymerization of **2** on cellulosic materials. They showed that **2** in an aqueous medium at pH 2.0 and 90°C did not copolymerize with the cellulose surface in the presence of H_2O_2/Fe^{2+}. However, under the same conditions, **poly2** was efficiently grafted onto cellulosic fibers and the amount of homopolymer of **2** was negligible. In these conditions, the amount of grafted **poly2** reached 68% w/w with respect to OD fibers. They also showed that working at higher temperature and with more concentrated media yielded higher grafting efficiency. Sellers [37] prepared plywoods from southern pine (major structural species) and yellow poplar (most representative decorative species) using polymeric methyl diphenyl diisocyanate adhesive in the presence of **1** as a reactive diluent in order to reduce the adhesive costs. These formaldehyde-free plywood composites did not suffer delamination after accelerated-aging tests and, although the interfacial failure did not satisfy the requirements for structural plywood, they approached or exceeded requirements for decorative applications. Schultz [38] prepared an exterior plywood resin based on **2** and paraformaldehyde. Three-ply assemblies from yellow pine were bonded at different processing conditions and showed that the curing time necessary for these systems was longer than that which was generally required for conventional gluing systems. The use of veneers with a high moisture content (9.5 instead of 5.1%) had very negative effects on the strength properties of the plywood prepared. Pizzi [39] also prepared particleboard urea–furfural–formaldehyde binders. He concluded that a partial substitution of formaldehyde with **1** led to an enhanced CH_2O emission and explained this unexpected feature in terms of two competitive reactions. In fact, he showed that in the resins which contained both formaldehyde and **1**, the higher stability to hydrolysis of the **1**–urea bonds induced the release of formaldehyde from the final product.

New adhesives from furfural-based diamines and diisocyanates were prepared by Holfinger and coworkers [40,41]. They produced flakeboards alternatively bonded with phenol–formaldehyde, MDI, and 5,5′-ethylidene difurfuryl diisocyanate (**14**) adhesives and showed that the strength properties of flakeboards prepared with **14** were slightly lower than those based on MDI and higher than those prepared with phenol–formaldehyde resins. Thus, the internal bond strength values of flakeboards bonded with MDI and **14** at 3% resin content, were 1.33 and 0.97 MPa, respectively [41], which are much higher than the value required by American standard ANSI/A208.1 (0.41 MPa).

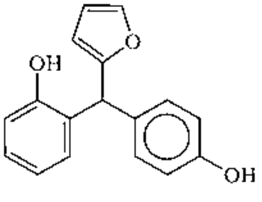


(14)

Joshi and Singh [42] showed that about 30% of formaldehyde could be replaced by **1** (obtained from wheat straw) in the formulation of phenol–formaldehyde adhesives. They used these phenol–**1**–formaldehyde resins in the preparation of plywoods from *Vateria indica* and *Toona ciliata* and obtained materials with good resistance to boiling water. These authors mentioned, however, that **1** slowed down the curing rate of the resin and recommended longer condensation times compared with conventional phenol–formaldehyde thermosets. Motawie et al. [43] prepared **1** by hydrolysis of Egyptian cotton straw and prepared different resins by the copolymerization of the in situ formed furfural with phenol, epichloridrin–phenol, or a bisphenol A-based epoxy prepolymer. The curing of these resins was investigated using phthalic or maleic anhydride at 170–185°C or using diamines at room temperature, both in the presence or absence of kaolin as an inorganic filler. Their properties appeared to be comparable to those of commercially available wood adhesives.

Ellis and Paszner [44] investigated the self-bonding of various lignocellulosic materials possessing high hemicellulose content through the in situ generation of furanic derivatives by acid-catalyzed thermal conversion of some saccharidic units. They used seven different raw materials with increasing pentosan content, i.e., elm, aspen, oak, and birch woods as well as bagasse, sweetcorn cob, and feed corn cob, with pentosan contents of 18.8, 19.4, 20.2, 25.5, 27.2, 39.7, and 42.3%, respectively. The pressing temperatures, pressures, and times tested were in the ranges of 160 to 220°C, 14–20 kg/cm^2 and 2–10 min, respectively. Ammonium sulfate and ammonium chloride were used as catalysts and their amounts were varied from 0 to 6% w/w with respect to the vegetable material. The bending strength of the materials obtained was directly proportional to the xylan content of the initial lignocellulosic source. The optimal amount of catalyst was found to be around 1.5% w/w based on the natural raw material and the optimal pressing time was established to be around 6 min. Increasing the wood particle size induced a drastic decrease in the bending load, whereas an increase in press plate temperature led to a substantial increase in the mechanical properties of these self-bonding composites.

Gos et al. [45] glued spruce wood (*Picea excelsa* L.) using three different adhesives, namely: (i) a phenol–resorcinol binder, (ii) carbamide–melamine–**1** resins, and (iii) a poly(vinyl acetate) glue. They tested the bending elasticity of these glued woods in the temperature range of 20 to 150°C and a minimum loss of bending strength, when the temperature increased from 20 to 150°C, was observed when phenol–resorcinol or carbamide–melamine–**1** resins were used. Kim et al. [46] synthesized **1**-modified phenol–formaldehyde resol resins by partial substitution of formaldehyde by **1**. They tested the performance of these resins using them as adhesives for oriented strandboards. They used ^{13}C-NMR to establish the reaction mechanism between **1** and the other resin components and isolated and identified convincingly structures **15**, **16**, and **17**. The use of **1** with 0.25 mole per mole of phenol in phenol–formaldehyde resol resins gave boards with properties very similar to those obtained by conventional gluing.



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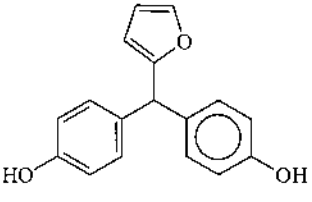

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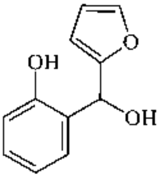
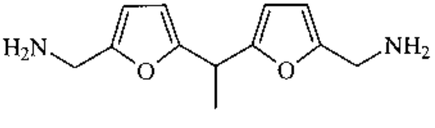


(**17**)

Recently, Schneider et al. [47] fabricated particleboards using **poly2**–urea–formaldehyde adhesives (P2-U-F). They observed that the curing time needed for P2-U-F was double that necessary for classical urea–formaldehyde resins. They also established that P2-U-F produced boards with lower strength properties, but with higher water resistance, if classical processing conditions were used. However, at higher resin contents, P2-U-F gave boards with better mechanical properties. The following optimal conditions were derived to produce particleboards: a blending time of 10 min, a press platen temperature of 150°C, 15% of P2-U-F resin with respect to OD softwood, 1.4 min of pressing time per millimeter thickness, and a board density of 0.67 kg/dm^3.

Dao and Zavarin [48,49] prepared boards using wood powder and **2** or **poly2** as binders. The wood species was white fir (*Abies concolor*) which was used as powder screened to 80 mesh. Compound **2**, **poly2**, and wood were subjected to chemical activation with hydrogen peroxide/ferrous ions or nitric acid. It was established that an increase in the degree of polymerization of **poly2** yielded boards with increased strength properties and that **poly2** gave materials with higher strength and water resistance properties than those obtained using **2**. They also showed that the addition of the activator to **poly2**, rather than to wood, was more efficient. Finally, they also isolated the acetone-soluble fraction of **poly2** (about 73%) and used it as a binder for the same wood samples. They found that the tensile properties of the corresponding boards exceeded, by over 50%, those of composites prepared with conventional phenol–resorcinol–formaldehyde resins.

Abd El Mohsen et al. [50] modified classical urea–formaldehyde resins by adding different amounts of **2** and used them as binders for beech-based plywoods. These modified resins gave materials with higher shear strength properties (100% increase) in comparison to unmodified adhesives. They also established the following optimal formulations: addition of 30, 45, and 60% of **2** to classical urea–formaldehyde resins and 3, 4.5, and 6% of *p*-toluene sulfonic acid as a hardener, respectively. Coppock [51] prepared durable wood adhesives from furfural-based diols, diamines, and diisocyanates. She then made plywoods or particleboards using modified urea–formaldehyde resins, with **3** and **4** as binders and found that the materials thus obtained showed acceptable mechanical properties. These properties were not improved by the addition of further modifiers, such as 5,5′-ethylidene furfuryl amine (**18**). Measurements using DSC showed that **3** did not react under alkaline conditions, but readily resinified at pH values below 3.0. These materials were found to have lower formaldehyde emission compared with those made with unmodified resins. The mechanical performances of flakeboards made with **14** exceeded the industrial standard requirements and were equivalent to those prepared using MDI. Finally, materials based on **14** in the presence of **3** or **18** as modifiers were obtained and found to have better performances in comparison to those prepared without these additives.



(18)

Suzuki et al. [52] prepared wood-meal/plastic composites with an average thickness of 4 mm using urea–**2** and phenol–**1** resins as binders. The molar ratio between urea and **2** was varied from 9:1 to 1:9. The amount of formaldehyde emission decreased with increasing quantities of added **2** and the optimal ratios were found to lie between 2:1 and 1:2. Hexamethylenetetramine was added to phenol–formaldehyde resins which were formulated with a molar ratio of 1:3. The bending strengths of composites prepared using urea–**2** adhesives were substantially higher than those made using phenol–formaldehyde binder. More recently, Raknes [53] studied the natural aging of 14 different commercial adhesives used in plywood manufacturing. He glued spruce (*Picea abies*) pieces and subjected them to 30 years of natural aging! He concluded that the shear strength and the water resistance of samples bonded with "furfurylated" urea–formaldehyde resins (Cascorit 1250 and Dynorit L166, manufactured by Casco Wood Adhesives, Sweden) were still satisfactory.

Kim et al. [54] explored the possibility of using **2** as a cobinder in conventional urea–formaldehyde adhesives. They successfully prepared water-insoluble **poly2** as oil-in-water emulsions and added them to urea–formaldehyde in different proportions. The ensuing mixtures were used to produce particleboards from a mixture of southern pine and hardwoods (75/25). The resin content of these panels was 8% w/w based on OD wood particles and the catalyst used was ammonium sulfate at a level of 0.3% w/w with respect to the dry resins. The optimal quantity of added **2** was found to be in the range of 20–30% with respect to conventional urea–formaldehyde resins. These formulations gave panels with increased strength and low formaldehyde emission. Russian investigators [55–58] used **5** as a binder for fir (*Abies*) plywoods and showed that the properties of these materials met the Russian standard requirements if pressing time of about 10 min, pressing temperature of 160°C, and a platen pressure of 1.8 MPa were used. Thus, the shear strength of the plywoods reached almost 1.5 MPa, and their water uptake did not exceed 39%. The use of clay as a filler (up to 40% w/w with respect to the binder) decreased substantially the final properties of the materials [57]. Mezhov et al. [59] also studied the furfural emission from plywoods prepared using **5** as a binder (produced in situ by reaction of **1** with acetone) and showed that it was much lower than that allowed, i.e., 3–5 mg/100 g of plywood instead of 10 mg/100 g.

VII. FURAN RESINS AS CEMENT ADHESIVES

Furan resins have also been extensively used in formulating mortars, grouts, and "setting beds" for brick lining destined to be exposed to highly corrosive environments, such as concentrated acids or highly alkaline cleaning solutions [3,16,60–62]. Two techniques are used in order to realize assemblies, namely tilesetter's and bricklayer's methods. The first method is based on the use of quarry tiles or pavers with smooth surfaces. The second method consists in using acid-resistant brick linings. Depending on the end use, three types of bricks are used for the installation of this type of assembly, namely:

(i) Red shale bricks which have the highest resistance to chemical attack. They are relatively fragile towards thermal and mechanical shocks. Typically, standard brick dimensions are 20.3 cm by 9.5 cm.
(ii) Fire clay bricks which are less resistant to chemical attack, but much more stable against thermal and physical shocks. Their standard dimensions are 22.8 cm by 11.4 cm.
(iii) Carbon bricks which are used to withstand hydrofluoric acid, fluoride salts, and hot, strong alkaline media. They are also very resistant to thermal shocks.

In 1990, **2** was also used in order to prepare low temperature (−10°C) hardening epoxy resin mortar adhesive [63]. For this, **2** was added as a reactive diluent to classical epoxy resin based on bisphenol A and the adhesive thus obtained was found to have good mechanical properties. These compositions are presently being produced by the Chinese Yanan Chemical plant. More recently, **2** was used in polymer compositions in building and structural repairs and showed properties similar to those obtained with epoxy resins [64].

VIII. FURAN RESINS/GLASS FIBER COMPOSITES

Corrosion-resistant glass fiber reinforced composites were also produced on the basis of furfuryl alcohol thermosetting resins [3,16,60]. Thus, many furan-based glass fiber reinforced materials have been available for many years, particularly for the storage of chlorinated aromatic and aliphatic hydrocarbon solvents. Amongst the commercial units available one finds: (i) very large scrubbing towers packed with Raschig rings. These containers are resistant to hot (up to about 120°C) HCl and organic chlorides; (ii) large brink mist eliminators typically working close to 85°C; (iii) acid wash surge tanks used to store waste liquids with a pH of about 2 at temperatures of 55–60°C; and (iv) dryer exhaust water driven coolers for incoming hot (230°C) acidic HCl and aromatic vapors. These few examples do not cover all the equipment constructed on the basis of furan resin reinforced by fiberglass but they show clearly the usefulness of these materials in different industrial areas. Other applications include the use of **2** as a matrix for fiberglass in the production of wrappings of pipes carrying corrosive liquids and vapors [12]. Thus, steel pipes previously coated with bitumen or coal tar pitch can be wrapped with a bonded glass fiber mat based on this type of resin. In this context, **2** is mixed with water in the presence of an emulsifying agent and an acid catalyst and the ensuing emulsion impregnates the mat. Then, the resulting composite is heated in order to remove the water and induce the acid-catalyzed polycondensation of the matrix.

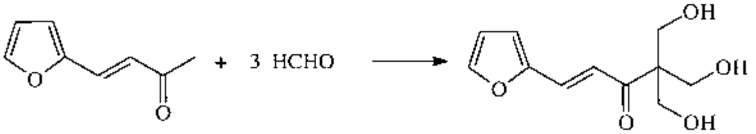
Amongst the composites used one can cite furfuryl alcohol resins reinforced with carbon filled woven glass fiber (commercialized under the name of Permanite, manufactured by the IKO Group, Canada). The main mechanical properties of such composites are: tensile, shear, flexural, and compressive strengths of 15, 20, 39, and 41 MPa, respectively. Their average density, thermal conductivity, and coefficient of thermal expansion are 1.57 kg/dm^3, 3.44 W/(m^{2}K) and 1.8×10^{-5}/°C. Permanite-based pipes are hard, tough, and rigid with exceptional resistance to thermal shocks. They can be used up to 140°C and should be protected against high tensional, torsional, and shear loads.

The combination of furanic derivatives with formaldehyde is also used in order to produce pipes. Haveg 61, manufactured by High Performance Alloys, Inc., Tipton, IN, can be cited as an example of these resins which are usually filled with acid-digested asbestos [16]. These composites are resistant to thermal shocks and have been used continuously at high temperatures (150°C). They have very low electrical and thermal conductivities. The main mechanical properties of these composites are: ultimate tensile, shear, and compressive strengths, at 26°C, of 28, 109, and 72 MPa, respectively. Their coefficient of thermal expansion is 3.2×10^{-5}/°C. The working and hardening times of these resinous cements depend strongly on the working temperature [12]. Thus, for example, for carbon filled **2**-based resin cement, the following critical values are found: at 16, 21, and 27°C the working and hardening times are 90, 60, and 30 min and 48, 20, and 12 h, respectively [12].

IX. MISCELLANEOUS APPLICATIONS OF FURAN RESINS

Azimov et al. [65] compared the performances of furan resins with those of conventional phenol–formaldehyde adhesives. They used these binders to assemble aluminum-to-aluminum and glass-to-glass structures and showed that furanic resins gave much higher rupture moduli in both systems studied. Rassokha and Avramenko [66] studied similar systems, but gave more information about the furan resin used. They used **5**- and **6**-based adhesives both in the presence and absence of zeolite-based fillers, and assembled aluminum-to-aluminum and glass-to-glass structures. They showed that the use of polyethylene-co-vinylacetate as a filler dispersant gave well dispersed suspensions and consequently the best mechanical properties of the assembly. Nikolaev et al. [67] studied the thermal stability of furan resins produced by the reaction between a furfuryl ether of glycerol and 2,4-toluene diisocyanate. They showed clearly that the incorporation of this resin into conventional adhesives improved their thermal stability. The mechanical properties of steel-to-steel assemblies based on these compositions were found to follow the same tendency as that observed for the thermal properties.

Poly(hydroxymethyl furfurylidene-acetone) adhesive resins were synthesized and characterized [68–70] through the **5**-formaldehyde adduct (**19**) and its acid-catalyzed polymerization. The catalysts used were sulfuric, phosphoric, or *p*-toluenesulfonic acid. The authors postulated that the first condensation products resulted from the condensation of two methylol groups of two **19** molecules (adduct **20**). They also proposed a hypothetical structure of the network formed after curing (**21**). It seems, however, difficult to envisage the acid-catalyzed resinification of **19** without the participation of hydrogen atoms at the C5 position of the furanic ring [2].



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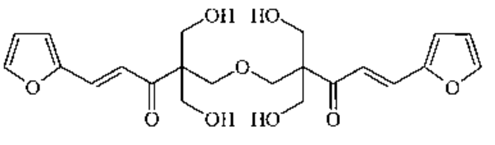

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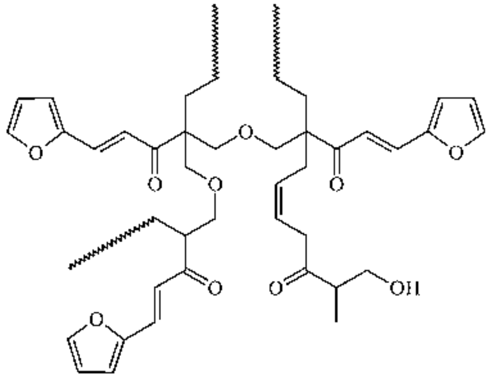

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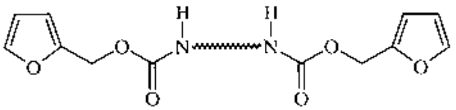

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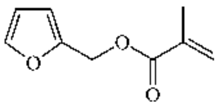

(23)

Macro-diisocyanates based on the reaction of an excess of 2,4-toluene diisocyanate with different poly(dimethylsiloxane)diols of different lengths have been prepared by Nikolaev et al. [71]. These macro-diisocyanates were reacted with **2** in stoichiometric proportions and the resulting adduct (**22**) was cured with a commercial epoxy resin in the presence of what was termed "poly(ethylene)-poly(amine)" at room tempcerature, 80, and 100°C. The mechanical and thermal properties of steel-to-steel assemblies joined by these adhesives were better than those obtained using more common binders.

Bowles et al. [72] studied the copolymerization of different methacrylates with NCO-ethyl methacrylate to obtain dental adhesives. Furfuryl methacrylate (**23**) was among the monomers tested. The main objective of this investigation was to establish a correlation between the solubility parameter of the copolymers and their shear strength. It was moreover shown that the setting time of the furan-based copolymer was very short compared to that of aliphatic homologues, but its shear strength was relatively low.

Dopico et al. [73] prepared **5**- and **6**-based furan resins which, after acid-catalyzed polymerization, were subjected to epoxidation with thiokol in different proportions. In a second series of experiments, 6–7% of **2** was added to the epoxidized resins. They showed that all these resins presented a lower flexure resistance compared to unmodified totally furanic binder. Moreover, the addition of **2** was found to induce negative effects on the mechanical properties of metal-to-metal assemblies.

Furan resins have also been used as binders in grinding wheels [4]. In this field, 5–20% of phenolic resin in combination with **1** as a special wetting agent is added to the abrasive grains and the resulting wheels thereafter coated onto the surfaces of different substrates. Paper, cloth as well as composites based on glass fiber reinforced films, have been used as grinding wheel supports. Acid-catalyzed **poly2** has also been used in the aircraft industry as a low-temperature setting adhesive to bond wood and plastic parts. This adhesive was found to be suitable for assemblies subjected to warping and other deformations at high temperatures [12].

X. CONCLUSIONS AND SUMMARY

From the above survey, it appears that the industrial use of furanic monomers such as furfuryl alcohol and furfural, i.e., chemicals based on renewable resources, as binders in foundry molds is highly successful. Similar furan-based resins can also be used as efficient adhesives in wood–particle composites and thus are interesting alternatives to petroleum-based counterparts. The fact that the substitution of formaldehyde by furfural has not yet met with a reasonable industrial success probably stems from the higher cost of the furan aldehyde. The increasing pressure on the reduction of formaldehyde emission and the renewable character of furfural should play in its favor in the near future.

This chapter has dealt with the use of furanic derivatives as adhesives and binders. It has been shown that the main industrial applications concern the use of furfural and furfuryl alcohol as raw materials for binders for coating different surfaces, namely:

- (i) The storage and the transport of hot and highly corrosive fluids such as chlorinated solvents, acids, and bases. For this purpose, the vessels (e.g., tanks, pipes, or towers) are coated with a composite material based on filled and/or glass fiber reinforced furanic matrix.
- (ii) The molding of liquid metals. In this context, foundry molds are produced from furan derivatives, or in combination with phenolic resins, and are utilized because of their excellent fire resistance and thermal stability.
- (iii) The preparation of highly resistant cements and concretes which are employed when the object is used as a container for chemicals and/or exposed to corrosive cleaning agents.
- (iv) The preparation of grinding wheels in which furan resins are used to bond abrasive grains.

In addition to these well known applications, different studies dealing with the use of furan derivatives as wood adhesives and other miscellaneous applications are presented and discussed.

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Urea–Formaldehyde Adhesives

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I. INTRODUCTION

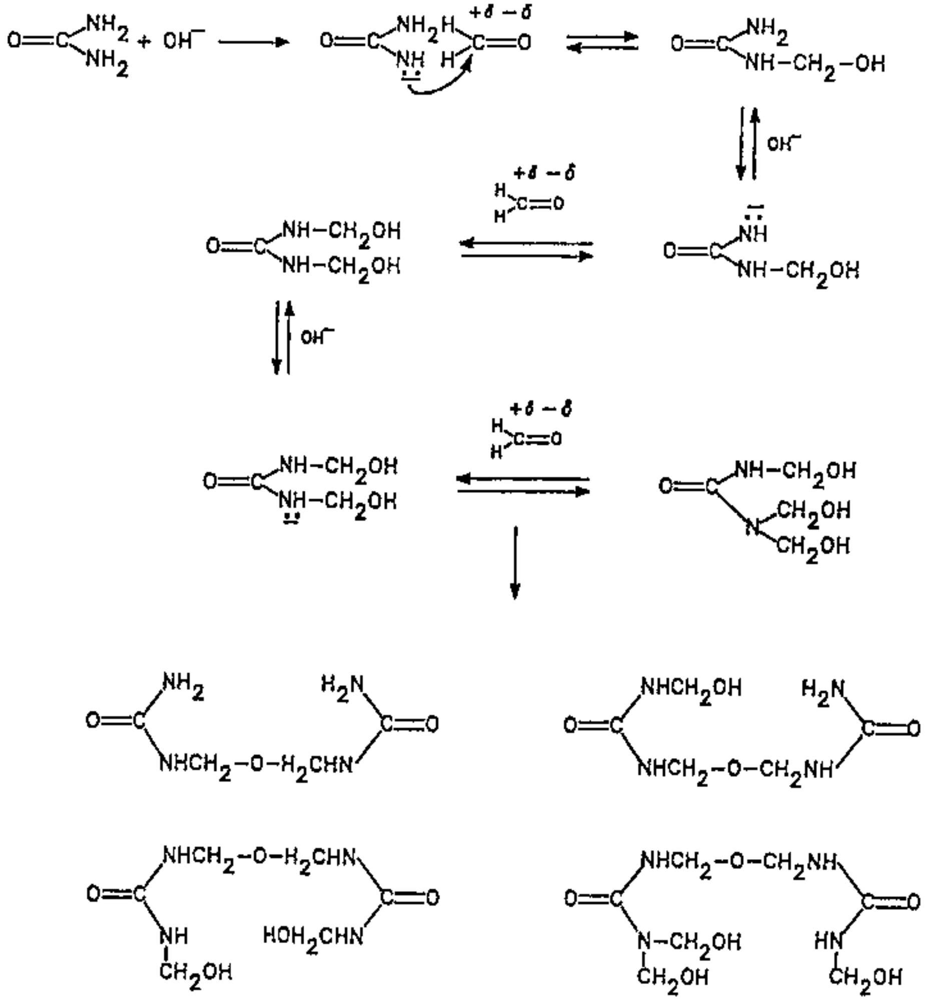
The urea–formaldehydes (UFs) are the most important and most used class of amino resin adhesives. Amino resins are polymeric condensation products of the reaction of aldehydes with compounds carrying aminic or amidic groups. Formaldehyde is by far the primary aldehyde used. The advantage of UF adhesives are their (1) initial water solubility (this renders them eminently suitable for bulk and relatively inexpensive production), (2) hardness, (3) nonflammability, (4) good thermal properties, (5) absence of color in cured polymers, and (6) easy adaptability to a variety of curing conditions [1,2].

Thermosetting amino resins produced from urea are built up by condensation polymerization. Urea is reacted with formaldehyde, which results in the formation of addition products such as methylol compounds. Further reaction and the concurrent elimination of water leads to the formation of low-molecular-weight condensates which are still soluble. Higher-molecular-weight products, which are insoluble and infusible, are obtained by further condensing the low-molecular-weight condensates. The greatest disadvantage of the amino resins is their bond deterioration caused by water and moisture. This is due to the hydrolysis of their aminomethylenic bond. Therefore, pure UF adhesives are used only for interior applications.

II. CHEMISTRY OF UF RESINS: UF CONDENSATION

The reaction between urea and formaldehyde is complex. The combination of these two chemical compounds results in both linear and branched polymers, as well as tridimensional networks, in the cured resin. This is due to a functionality of 4 in urea (due to the presence of four replaceable hydrogen atoms) (in reality urea is only trifunctional as tetramethylolurea has never been isolated, except in the formation of substituted urons [2]) and a functionality of 2 in formaldehyde. The most important factors determining the properties of the reaction products are (1) the relative molar proportion of urea and formaldehyde, (2) the reaction temperature, and (3) the various pH values at which condensation takes place. These factors influence the rate of increase of the molecular weight of the resin. Therefore the characteristics of the reaction products differ considerably when lower and higher condensation stages are compared, especially solubility, viscosity, water retention, and rate of curing of the adhesive. These all depend to a large extent on molecular weights.

The reaction between urea and formaldehyde is divided into two stages. The alkaline condensation to form mono-, di-, and trimethylolureas. (Tetramethylolurea has never been isolated.) The second stage is the acid condensation of the methylolureas, first to soluble and then to insoluble cross-linked resins. On the alkaline side, the reaction of urea and formaldehyde at room temperature leads to the formation of methylolureas. When condensed, they form methylene–ether links between the urea molecules. The alkaline products from urea and formaldehyde, and from mono- and dimethylolureas, are as follows (Formula 1):



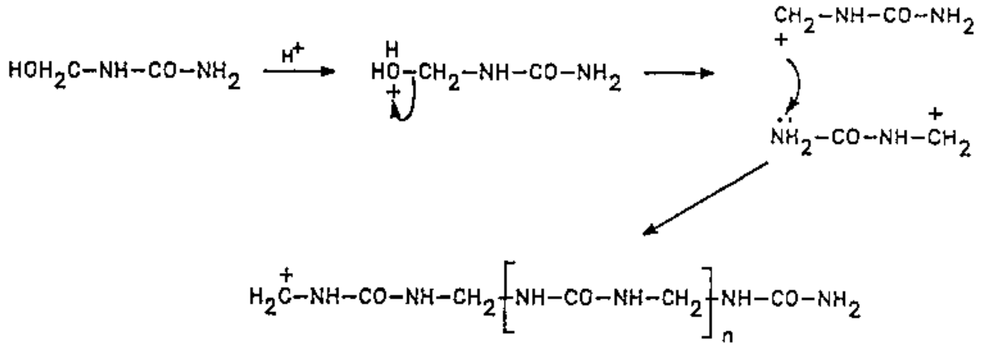
The reaction also produces cyclic derivatives: uron, monomethyloluron, and dimethyloluron.

On the acid side, the products precipitated from aqueous solutions of urea and formaldehyde, or from methylolureas, are low-molecular-weight methyleneureas [3]:

$H_2NCONH(CH_2NHCONH)_nH$

These contain methylol end groups in some cases, through which it is possible to continue the reaction to harden the resin.

The monomethylolureas formed copolymerize by acid catalysis and produce polymers and then highly branched and cured networks (Formula 2):



The kinetics of the formation and condensation of mono- and dimethylolureas and of simple UF condensation products has been studied extensively. The formation of monomethylolurea in weak acid or alkaline aqueous solutions is characterized by an initial fast phase followed by a slow bimolecular reaction [4,5]. The first reaction is reversible and is an equilibrium which proceeds to products due to the uptake of the products, the methylolureas, by the second reaction. The rate of reaction varies according to the pH with a minimum rate of reaction in the pH range 5 to 8 for a urea/formaldehyde molar ratio of 1:1 and a pH of 6.5 for a 1:2 molar ratio [6] (Fig. 1). The 1:2 urea/formaldehyde reaction has been proved to be three times slower than the 1:1 molar ratio reaction [7].

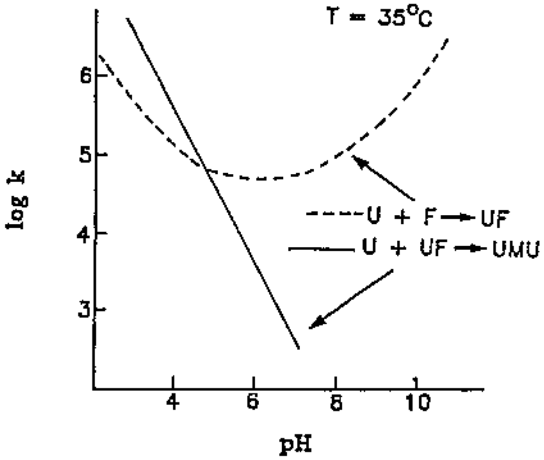


Figure 1 Influence of pH on the addition and condensation reactions of urea and formaldehyde. U, urea; F, HCHO; M, $-CH_2-$.

The rapid initial addition reaction of urea and formaldehyde is followed by a slower condensation, which results in the formation of polymers [7]. The rate of condensation of urea with monomethylolurea to form methylenebisurea (or UF "dimers") is also pH dependent. It decreases exponentially from a pH of 2 to 3 to neutral pH value. No condensation occurs at alkaline pH values.

The initial addition of formaldehyde to urea is reversible and is subject to general acid and base catalysis. Different energies of activation are reported for the forward methylolation and backward demethylolation reaction. The forward bimolecular reaction is reported to have an activation energy of 13 kcal/mol when the reverse unimolecular reaction has an activation energy of 19 kcal/mol [5]. Other sources report values of 17.5 and 17.1 kcal/mol for the same reactions, respectively [8]. If one considers that the reaction of monomethylloation of urea at pH 7 is of the order of 1×10^{-4} $(\text{mol s})^{-1}$ for each site [8] and of the order of 3×10^{-4} $(\text{mol s})^{-1}$ at rather alkaline pH it is possible to deduce what occurs at alkaline pH when urea reacts with formaldehyde to form methylolated ureas. The inverse reaction of decomposition of the methylolurea will limit somewhat, however, the proportion of methylolated urea prepared, the reaction running to completion only as methylolated ureas react to form dimers and higher oligomers when the pH is lowered in the condensation phase. If the condensation phase is not effected a calculation of the degree of advancement of the reaction of methylolation of urea under alkaline conditions can be carried out by the use of the formula [9]

$$p/[2(1-p)] = \exp[(-\Delta G^{\theta})/(2RT)] \tag{1}$$

where p is the degree of conversion at the equilibrium of the methylolation and demethylolation reactions, ΔG^{θ} is the standard Gibbs energy variation, T is the temperature in degrees kelvin, and R is a constant (1.987 cal/g mol K). When introducing the reported activation energies of the urea forward methylolation reaction (17.5 kcal/mol) [8] and of the methylol urea demethylolation reaction (17.1 kcal/mol) [8] one obtains a degree of advancement $p = 0.60$, hence at equilibrium under the conditions used 60% of the urea is present as methylolureas [9]. This compares well with a degree of conversion of 65%, at the equilibrium, of the more reactive melamine extrapolated by reported kinetic values [10] to the same conditions used herewith. The advancement of the reaction may eventually proceed to even higher degrees of conversion, even in alkaline environments, only as a consequence of the subsequent formation of methylene ether-linked oligomers.

The rates of introduction into the urea molecule of one, two, and three methylol groups have been estimated to have the ratio 9:3:1. The formation of N,N'-dimethylolurea from monomethylolurea is three times that of monomethylolurea from urea.

Methylenebisurea and higher oligomers undergo further condensation with formaldehyde [11] and monomethylolurea [12], behaving like urea. The ability of methylenebisurea to hydrolyze to urea and methylolurea in weak acid solutions (pH 3 to 5) indicates the reversibility of the amidomethylene link and its lability in weak acid moisture. It explains the slow release of formaldehyde over a long time in particleboard and other wood products manufactured with UF resins.

III. GENERAL PRINCIPLES OF MANUFACTURE AND APPLICATION

It is very important in the commercial production of UF resins to be able to control the size of the molecules by the condensation reaction, since their properties change continuously as they grow larger. The most perceptible change is the increase in viscosity. Low-viscosity syrups are formed first. These change into high-viscosity syrups, which are clear to turbid. Molecular weight may vary from a few hundred to a few thousand, with a wide range of molecular size. These molecules are built up by water splitting off at random between reactive groups of neighboring molecules, thereby increasing their size. Once their solubility, viscosity, pH, concentration, and so on, have been determined, they constitute the resins available commercially. The most important factors influencing the final properties of aminoplastic resins in industrial manufacture are the purity of the reagents, the molar proportions of the materials used, the preparation process used, and the pH variation and control.

The most common method of preparation for commercial UF resin adhesives is the addition of a second amount of urea during the preparation reaction. This consists of reacting urea and formaldehyde in more than equivalent proportions. Generally, an initial urea/formaldehyde molar ratio of 1:2.0 to 1:2.2 is used. Methylolation can in this case be carried out in a much shorter time, by using temperatures of up to 90 to 95°C. The mixture is then maintained under reflux. When the exotherm subsides (usually after 10 to 30 min), the methylol compounds have formed, and the reaction is completed under reflux by adding a trace of an acid to decrease the pH to the UF polymer-building stage (pH 5.0 to 5.3). As soon as the right viscosity is reached, the pH is increased to stop polymers building and the resin solution is cooled to about 25 to 30°C. More urea (called second urea) is added to consume the excess of formaldehyde, until the molar ratio of urea to formaldehyde is in the range 1:1.1 to 1:1.7. After this addition of urea, the resin is left to react at 25 to 30°C for as long as 24 h. The excess water is eliminated by vacuum distillation until a resin solids concentration of 64 to 65% is reached, and the pH adjusted to achieve suitable shelf life or storage life.

The final addition of urea can be done in one operation, or the urea may be added at suitable intervals in smaller lots. Second or further ureas can be added at a temperature slightly higher than ambient or can be added at higher temperatures, 60 to 90°C, according to the type of final resin wanted [13–16]. Increasing second or further urea additions tends to improve bond quality, especially at low formaldehyde/urea molar ratios [13–16]. Higher-molar-ratio resins tend to exhibit an overall better initial bond quality [14], but present an exponentially increased formaldehyde emission problem [16], most often disqualifying them from many, or most, modern uses. Some UF resins used for joinery are also produced without a final or second urea addition. The pH used during the condensation reaction (not the methylolation) is generally in the range 4.8 to 5.3.

Control of the average molecular size of the finished resin is essential for correct flow in plywood and particleboard applications while in the hot press prior to curing. Too low a level of condensation (i.e., low-molecular-weight resins) may give too much flow; the resin "runs away" from the wood or sinks into it rapidly under pressure, leaving "starved" glue lines. This can be corrected by lowering the pH by adding an acid or acid-producing substance, usually a curing agent, hardening catalyst, or simply, hardener. If a resin of too high a condensation stage (i.e., high-molecular-weight resins) is on hand, its flow under normal pressure and temperature may be too low to produce good results. This can usually be corrected by adding flow agents to it, provided that at least some flow is left in the resin. It is generally an advantage to produce resins with ample flow in the factory. Their storage life is longer and finishing can be done at any time, at short notice, to specification, particularly by adjusting the flow and speed of cure.

Resins that have lost part of their flow during manufacture or storage must be corrected by the addition of a flow agent. The simplest means is often the addition of water sprayed on the compound and mixed in well. If a resin is still capable of flowing, this procedure produces a resin with properties that are still acceptable. In cases where moisture content control is critical, it may be necessary to allow a little more time for "heating" to let the added moisture escape. However, if the flow is very low, and large quantities of water must be used to bring the flow back to normal, this method is not recommended. The large amount of water would cause longer "breathing" times to be necessary due to excessive volatile components, and excessive shrinkage may take place, causing too much stress on the glue lines. It must be kept in mind that excessive water addition causes UF resin precipitation. The best way to correct flow in these cases is to mix the resin with large amounts of an equal resin of the same quality that has a higher flow. Any proportion may be used to bring the flow back to normal. If increased flow is desired, 0.5 to 2.0% of spray-dried UF or melamine–formaldehyde resin can also be added to function as a flow agent. Methylol compounds, such as dimethylolurea, also increase flow, but they increase the water released during reaction more than do spray-dried resins. Lubricating agents such as calcium stearate are also able to give a fair degree of flow increase.

Many substances have been suggested as curing agents. These include the following acid products: (1) boric acid, (2) phosphoric acid, (3) acid sulfates, (4) hydrochlorides, (5) ammonium salts of phosphoric or polyphosphoric acid, (6) sodium or barium ethyl sulfate, (7) acid salts of hexamethylenetetramine, (8) phthalic anhydride, (9) phthalic acid, (10) acid resins such as poly(basic acid)-poly(hydric alcohol), (11) oxalic acid or its ammonium salts, and many others. However, the most widely used curing agents in the wood products industry are still ammonium chloride or ammonium sulfate. Their effect can be altered by retarding the reaction of the resin. This is done by the simultaneous addition of small amounts of ammonia solution (which is eliminated during hot curing) to lengthen the pot life of the glue mix. Latent catalysts that produce acid only on heating may also be used, such as dimethyloxalate and other easily hydrolizable esters, or halogenated substances such as 0.1 to 0.2% of bromohydrocinnamic acid and others (Fig. 2).

The driving force in the use of these salts as hardeners is their capacity to release acid, which decreases the pH of the resin and thereby accelerates curing. The speed of the reaction between the ammonium salt and formaldehyde (or ammonia and formaldehyde when this is present) also determines, together with the amount of heat supplied, the rate of acid release and therefore the rate of curing:

$$4NH_4Cl + 6HCHO \rightarrow 4HCl + \underset{\substack{\text{Hexamethylene}\\ \text{tetramine}}}{(CH_2)_6N_4} + 6H_2O$$

Ammonium chloride is a better hardener than hydrochloric acid, as the latter produces weaker joints. The effect of a fixed amount of ammonium chloride on the pH change and on the rate of resin curing as a function of time and temperature is shown in Fig. 2.

Often, particularly in cold-setting UF resins for joinery, hardeners consisting of mixtures of a salt such as ammonium chloride or ammonium sulfate with an acid such as phosphoric acid, citric acid, or others are used to regulate pot life and rate of curing. Both pot life and rate of curing of the resin can then be regulated (1) by varying the concentration of the hardener in the resin, (2) by changing the relative proportions of acid and salt, and (3) by changing the type of acid and/or salt composing the hardener. Acting on these three principles, setting times of between a few minutes and several hours can easily be obtained.

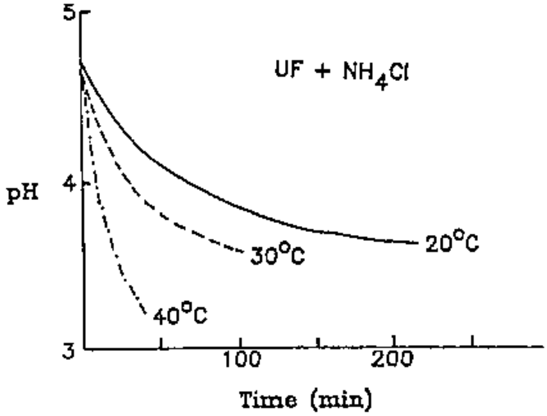


Figure 2 Change of pH of UF resins with ammonium chloride hardener as a function of temperature and time (from Ref. 2).

A. Plywood Adhesives

The UF adhesives for plywood generally contain less than 2 mole of formaldehyde per mole of urea, and most of them are condensed to a slightly viscous, hydrophilic stage and are quite soluble in water. The degree of polymerization, and hence the viscosity under comparable conditions of UF resins for plywood is generally higher than those of UF resins for particleboard.

The application of UF resins for gluing purposes is based on the excellent control that can be exercised on the condensation reaction by varying the pH, a procedure easily applicable to a production scale. A small amount of an acid as hardener is added at ambient temperature. This produces no visible change at first, or possibly for a few hours; finally, thickening sets in, and the resins gels and hardens into an insoluble material. While the adhesive is still in liquid form, it can be spread on the wood surfaces which have to be glued and joined under pressure. These have to be cured either at room temperature for a few days or at elevated temperature for a few minutes. Solutions of ammonium salts, usually ammonium chloride or ammonium sulfate, or mixtures of ammonium chloride with urea, are generally used as resin hardeners. Often, ammonia solution is added to lengthen the usable life of the glue mix. Hydraulic presses with multiple openings are generally used for the production of plywood or flat veneer work. They can operate at pressures of 10 to 16 kg/cm^2, but mostly operate in the range 12 to 14 kg/cm^2, according to the wood species, to avoid destruction of the porous structure of the wood.

The temperature is usually in the range of 120 to 160°C according to the type and moisture content of the veneers. It is chosen according to its capacity for the fastest pressing time and its ability to produce a good joint without blisters. Different pressing conditions are used in different countries, and the resin must be manufactured keeping the differences in the conditions of application in mind. There is quite a difference, for example, between a UF adhesive and glue mix which is capable of giving good joints at 5 to 8% moisture content of the veneer and a pressing temperature of 120°C, and a UF resin and glue mix usable at a veneer moisture content of 0 to 1% and pressing temperatures of 140 to 160°C. The former needs better flow characteristics and faster curing under standard measured conditions than does the latter if optimum pressing times and production schedules are to be maintained. Lower temperatures lengthen the curing time of the resins considerably but have the advantage that when the cured plywood sheets are taken out of the hot press, they tend to warp less on cooling or drying.

The use of fillers with plywood UF adhesives has important economical consequences and is necessary for technical reasons, because the fillers produce "body" in the glue solution and therefore prevent joint "starvation" in porous wood. Without filler it would be difficult to prevent part of the adhesive from flowing away or flowing into the open pores of the wood; or in the gluing of medium to thin veneers, from flowing through them to the other side, thereby causing undesirable resin patches on the outer veneer surfaces. As a rule, 20 to 50% filler is used for joinery and up to 100% for plywood. The most common fillers are wheat flour, corn flour, rye flour, very fine hardwood flour, and gypsum. If gypsum is used, it must be free of calcium hydroxide, because this interferes with the acid curing agent.

B. Particleboard Adhesives

A very important application for UF adhesives is in the manufacture of particleboard. The glue mix is generally composed of a liquid resin to which water has been added to decrease viscosity and to facilitate spraying, plus small amounts of ammonium chloride or sulfate and small amounts of ammonia solution. Small quantities of insecticides, wax emulsion, and fire-retarding agents (such as ammonium phosphates) are added before spraying the adhesive onto the wood chips. Pressing temperatures and maximum pressures used in the cycle are in the range of 150 to 200°C and 2 to 35 kg/cm^2, respectively.

The moisture content of glued furnish chips is 7 to 8% for the board core and 10 to 12% for the surface. The resin contents used (i.e., solids) are 6 to 8% for board core and 10 to 11% for board surfaces, but such proportions might be higher for the weaker low emission adhesives used today and depending for the application envisaged [i.e., particleboard or medium density fiberboard (MDF)].

It must be realized that on curing, the viscosity of UF resins changes, not only at a different rate but also in a different manner according to the temperature. The viscosity gradually increases with the temperature up to $\pm 50°C$. Above 60°C the viscosity quite rapidly reaches a maximum and then decreases. This indicates that the resin tends to degrade under prolonged heating at high temperatures (Fig. 3). To avoid this problem, the UF-bonded particleboard must never be pressed for too long, and must never have a "hotstack" or "postcure" period after pressing. They must preferably be cooled after manufacture to avoid deterioration in strength and quality. The cured UF resins degrade rapidly at any temperature at a pH below 2. The viscosity for a good particleboard resin is on the order of 100 to 450 cP (at 20°C) [17]. While this rule is true, the development that UF resins have undergone in the past 15–20 years in order to decrease drastically the levels of formaldehyde emission has led to new formulations which have very different characteristics and behavior. In some respects, and at least partially some of the old rules are no longer completely valid. This is the case with the rule of trying to avoid hotstacking of UF bonded boards [2,18].

Thus, when a panel is taken out of the press it gives off a considerable amount of moisture and its temperature is quite high. If a board in such a condition is immediately placed in an oven the temperature of which is higher than 75°C some degradation with consequent loss of performance will occur, this being shown to be due mainly by some progressive degradation of the UF adhesive hardened network [2,8]. Conversely, if the board is just cooled down there will not be any further curing of the resin. The predominance of the effect derived from the first of these two considerations has led to the need to

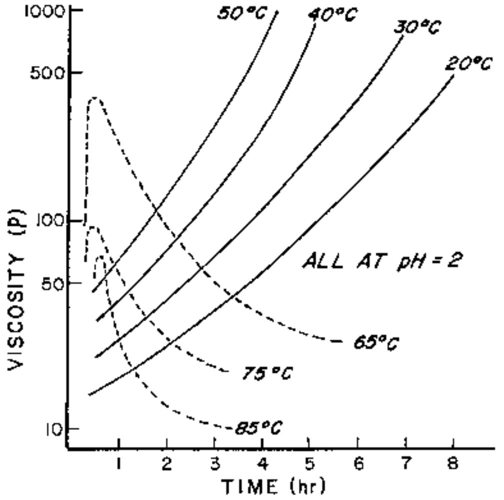


Figure 3 Viscosity of a UF resin as a function of time at different temperatures. Traditional resin of high F/U molar ratio.

limit the heat conservation of UF particleboard after pressing, hence to today's widespread practice of cooling the board after pressing [2,8]. As a consequence, decrease of board performance by resin degradation is in the main avoided but an unexploited reservoir of further potential strength of the resin achievable by further curing is wasted. It has many times been reported that the mechanical performance of aminoplastic resin-bonded particleboard cannot be improved by hot posttreatment with the exception of physical properties such as the homogenizing of the moisture content throughout the board and stress reduction improving the board dimensional stability [19].

Results obtained by a series of techniques for the curing of several resin systems [18,20–24] have indicated, however, that posttreatment and hotstacking (postcuring) conditions capable of improving the mechanical performance of aminoplastic resin-bonded particleboard without any degradation should instead exist. This is of some importance, firstly because the performance of UF- and melamine–urea–formaldehyde (MUF)-bonded particleboard could be improved with very little process change from the present industrial conditions to yield better board performance (or the same performance at lower adhesive content levels), and secondly because at parity of board performance such an approach may well lead to the use of even shorter industrial press cycles than today, even for aminoplastic resins.

From the experimental results obtained [18] it is evident that: (1) postcuring (for example by hotstacking in the simpler cases, by an oven or other heat treatment in more sophisticated cases) can be used in principle and under well-defined conditions to improve the performance of UF-bonded joints and panels without any further joint and hardened adhesive degradation, as the value of strength reached during postcuring is always consistently higher than the value at which the strength stabilizes after complete curing during the "pressing" cycle [18]. (2) Postcuring could also be used in principle and for the same reasons to further shorten the pressing time of UF-bonded joint and panels when well-defined postcuring conditions are used [18]. (3) There is clear indication that even when adhesive degradation starts the application of the posttreatment reestablishes the value of the joint's strength to a value higher than its maximum value obtained during curing [18].

The molecular level reasons for this behavior can be deduced also by bonded wood panel internal bond (IB) behavior. The IB performance improvements for instance are introduced by the series of reactions pertaining to internal methylene ether bridge rearrangements to a tighter methylene bridge network which have already been observed and extensively discussed in thermomechanical analysis (TMA) of aminoplastic and phenolic resins [20–24]. These are able to counterbalance well the degradative trend to which the aminoplastic resin should be subjected. Furthermore, in modern resins of lower formaldehyde/urea molar ratio the amount of methylene ether bridges formed in curing is much lower. Thus, disruption by postcuring of the already formed resin network by internal resin rearrangements will be milder, if at all present, and will definitely not yield the marked degradation and even collapse of the structure of the network which characterizes older resins of much higher molar ratios when postcured under the same conditions [2,8]. In short, notwithstanding the internal rearrangement the network will stand and stand quite strongly: no, or hardly any decrease of IB strength will be noticeable. For modern, lower molar ratio aminoplastic adhesives, since the resin network does not noticeably degrade or collapse with postcuring, only the tightening of the network derived by further bridge formation by reaction within the network of the few formaldehyde molecules released by the now mild internal rearrangement will be noticeable: the IB value will then improve, within certain limits, with postcuring in boards bonded with modern, lower formaldehyde aminoplastic adhesives [18].

A model to describe the decrease in temperature under different conditions of a particleboard after hot pressing has been developed and this model is shown to correlate well with experimental results of board temperature variation after pressing, both on cooling and during postcuring under different conditions [18]. From this, conditions of temperature and time favorable to improve panel performance by postcuring treatments were also determined [18]. The validity of the improvements forecasted under such conditions was then confirmed at molecular level for UF adhesive/wood joints by TMA testing, and finally confirmed by testing the mechanical performance of laboratory boards prepared under the postcuring treatment conditions identified [18]. The improvements in panel performance observed were explained on the basis of already described [24] and well-known molecular level rearrangements of the cured adhesive network and of the shifts in their relative importance in modern, lower formaldehyde content UF adhesives. The conclusion was that modern, lower formaldehyde content UF adhesives can considerably benefit as regards board performance from short period hot postcuring at temperatures in the 60 and 100°C range, a trend in clear contrast with the degradation and loss of performance this practice was known to induce [2,16] in the older, very much higher formaldehyde content aminoplastic resins of the past. Consequences of economical and technical interest derive from this, as the findings also imply lower adhesive consumptions and possibly even faster press cycles at parity with present resin performance, if simple postcuring procedures such as after pressing hotstacking (rather than board cooling as at present) are implemented for UF-bonded particle and other types of boards [18].

Figure 4 [18,20,23] shows that the slower is the heating rate the more evident is the entanglement plateau and the higher is its value of the modulus due initially to entanglement. This confirms that linear growth of the polycondensate can be maximized by decreasing the temperature at which polycondensation is carried out (this is likely to be valid both in the reactor during preparation of the UF resin as well as in the resin curing stages on the substrate). Figure 4 indicates that this effect becomes more marked the slower is the rate of heating applied. It implies that polycondensates grow mostly linearly to a higher degree of polymerization, before tridimensional cross-linking starts, the slower

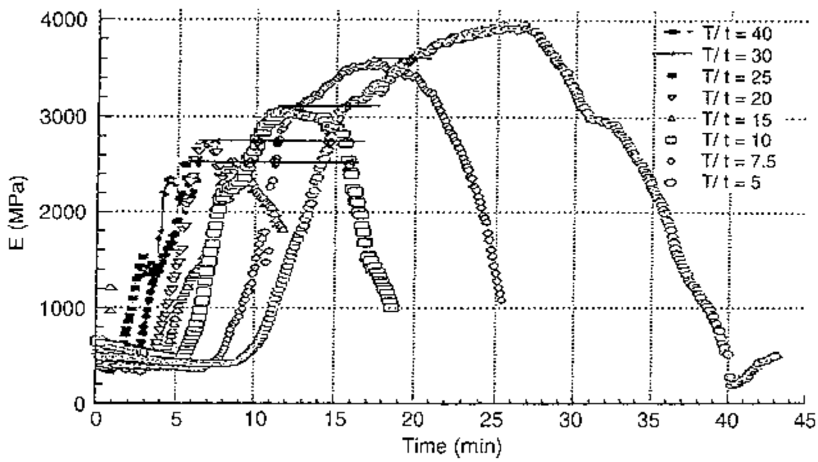


Figure 4 Increase of modulus of elasticity (MOE), at heating rates in the 5°C/min to 40°C/min range, as a function of time for a beech wood joint bonded with a UF resin. Increase of MOE corresponds to resin hardening.

is the rate of heating. This might depend on the reactivities of urea sites with formaldehyde which are in the approximate ratio 9:3:1 respectively for the first-reacted, second-reacted, and third-reacted urea sites [2]. The slower heating rates used decrease molecular movement and hence further decrease the chance of the third urea site reacting, hence favoring more linear growth of the polycondensate. Tridimensional covalent networking will still occur, and a tridimensional cross-linked network will still be the final product of the reaction, but will occur later when the polymer has grown to greater lengths. The most important observation from Fig. 4, however, is the considerably higher value of the modulus at slower heating rates, which must also be viewed in the same context as above: it relates to the polymer having time to adjust by better utilization of empty volume spaces, the same reason that gives a lower value of the glass transition temperature T_g the slower is the rate of heating. The extent of the effect observed is considerable: the maximum value of the modulus once the resin is tridimensionally cross-linked for the 40°C/min case is lower, due to early tridimensional immobilization of the resin in a less tight tridimensional covalent network, than the value of the modulus of just the entanglement network observed for the 15°C/min and slower heating rate curves.

It is important here to point out that the concept widespread in wood panel manufacture that a resin capable of a faster pressing and curing time (a faster curing resin for example) is giving better panel strength is only subjected to the exact definition of the concept of time of curing (and of pressing) in Fig. 4 above. Thus, in Fig. 4 a fast resin, as fast as being able to reproduce the 40 s/mm curve (which is in line with today's rates of curing for wood particleboard panels) will only be able to give to the joint the strength equivalent to 1.5 GPa modulus, while a slower resin which is in principle capable of yielding a modulus three times stronger at 4.5 GPa (reproducing the 5 s/mm curve) has no strength (less than 0.2 GPa) at the same curing time used to maximize the strength result of the faster resin. Thus it is preposterous to define one resin as better than another unless the concept of time is also defined and the two resins are seen in this "time" context. This insight leads also to two consequences. (i) It contributes to explaining why in modern UF resins one can improve strength by after pressing hotstacking: this is equivalent to passing in Fig. 4 from the faster curve to one of the slower curves after hot pressing, one curve that allows the system to reach a higher strength value as shown in the figure. (ii) A faster curing resin needs to be engineered to give not only a faster curing time as this will only yield an ultimate lower strength due to the looser and hence weaker network produced, but also to be able to concomitantly obtain a higher degree of cross-linking of the network to counterbalance the weakening caused by the faster curing rate of the resin: this needs to be introduced by varying resin parameters and by other techniques. To obtain a good yet faster adhesive the two effects must both be taken into account.

As important as viscosity is resin flow, which reflects viscosity under hot-pressing conditions. Resin flow is a determining factor in manufacturing good particleboard. Excessive flow causes the resin to soak into the wood particles and causes glue-line starvation; insufficient flow causes insufficient contact surface. The gel time generally used at 100°C for glue mixes of UF-bonded particleboard is 3 to 12 min, with 30 s to 3 min for board faces and cores, respectively. The actual gel time in the press depends on the press temperature and is considerably shorter.

C. UF Adhesives for Low-Formaldehyde-Emission Particleboard

In their cured state UF resins are nontoxic. Urea itself is also harmless. However, free formaldehyde and formaldehyde generated by slow hydrolysis of the aminoplastic bond are highly reactive and combine easily with proteins in the human body. This may cause a painful inflammation of the mucous membranes of the eyes, nose, and mouth [25]. Even a low concentration of formaldehyde vapor in the air can cause disagreeable irritations of the nose and eyes. However, such irritations usually disappear in a short time without permanent damage. Occasionally, allergic or anaphylactic reactions develop and complete removal from exposure is necessary.

High temperatures and high relative humidity can result in odor problems in a room containing particleboard manufactured with UF resins [25]. The release of formaldehyde from UF particleboard is caused by two factors. It can be due to free formaldehyde present in the board that has not reacted, and it can be due to formaldehyde formed by hydrolysis of the aminoplastic bond as a result of temperature and relative humidity [2,25]. While the first type of release lasts only a short time after manufacture of the particleboard, the second type of release can continue throughout the entire working life of the board. A considerable number of variables influence the emission of formaldehyde from a UF-bonded particleboard. The main ones are the molar ratio of urea to formaldehyde (which influences both types of release), the press temperature, and in service, the ambient temperature and relative humidity.

UF resins for particleboard with urea/formaldehyde molar ratios of 1:1.45, 1:1.32, and 1:1.25 have free formaldehyde contents of 0.8%, 0.3%, and less than 0.2%, respectively [15]. While the current tendency internationally is to use UF resins that have a urea/formaldehyde molar ratio lower than or much lower than 1:1.2, which release much less formaldehyde, these resins perform less well in the production of UF-bonded particleboard [15,17]. In particular, they do not allow as much flexibility in particleboard production as do resins with higher formaldehyde/urea molar ratios. This fact stresses the need for greater control and supervision of the production at particleboard plants where UF resins of low molar ratio are used. An example of the variation in properties between particleboard manufactured with different molar ratio resins is given in Table 1.

Table 1 Comparison of Particleboard Prepared with UF Resins of Various Molar Ratios

Urea/ formaldehyde molar ratio	Approximate density (g/cm^3)	Internal bond (MPa)	Percent water swelling (2 h)	Percent HCHO released, perforator method (mg HCHO/100 g board)
1:1.4–1.5	0.680	0.7–0.8	4	50–70
1:1.3–1.35	0.680	0.6–0.7	4–5	25–30
1:1.1–1.25	0.680	0.45–0.55	5	4–20

Source: Ref. 2.

It is also necessary to use more hardener when working with UF resins of a lower formaldehyde/urea molar ratio, as the gel time of the resin is slower. Up to 5% urea can sometimes be added to the glue mix to decrease the amount of formaldehyde released during pressing and to decrease the initial amount of free formaldehyde present in the finished board immediately after manufacture. Strict norms have been established in many countries with regard to the limits of formaldehyde emission from particleboard bonded with UF resins [25,29,30]. Recent work indicated that good E1-type UF resins of urea/formaldehyde molar ratio lower than 1:1.1 can be prepared in a variety of ways [16,26–28]. Although the theoretical basis of this finding has been discussed in part elsewhere [16], to be able to advance a tentative theory for low-formaldehyde-emission UF resins, it is of interest to apply these findings to the formulation and preparation of UF resins of low formaldehyde emission, initially in the laboratory and then at the industrial level. First, these resins can be divided into two broad classes: (1) those resins based on addition of melamine or melamine–formaldehyde (MF) resins to the UF resin, and (2) those UF resins in which very low formaldehyde emission capability is obtained exclusively by the manipulation of their manufacturing parameters. The former class is simply a subset of the second.

The underlying principle of a low-formaldehyde-emission UF resin is that a certain amount of free urea needs to be present to (1) mop up a large amount of the free formaldehyde that may be present at the end of the preparation, and (2) to mop up the greater part of the free formaldehyde that may be generated during hot curing of the resin. A third possible requirement would be that some free monomeric urea species should still be left to mop up, over a long period of time, some of the formaldehyde that may be liberated during the service life of the board.

Such requirements of a UF resin are fundamentally quite divergent and extreme. They mean that addition of great amounts of urea is needed, possibly at the end of the reaction; such urea will react with the free HCHO present or generated during hot curing, but will also react with the active methylol groups present on the urea resin itself, severely limiting the possibility of cross-linking of the resin and ultimately affecting adversely and diminishing its cured strength. These two sets of divergent requirements indicate that in general, a low-formaldehyde-emission UF formulation must be a compromise between strength and emission requirements. Once this basic conflict of requirements is understood, it can be overcome to attain formulations that give both good strength and low formaldehyde emission. A UF resin is a mixture of molecular species: namely, methylolurea, UF polymers, and methylolated UF polymers. It has already been proven, both theoretically [8,19] and by applied means [14,27,29] that while monomeric and polymeric methylolated species contribute more to the adhesion of the resin to the wood substrate, it is the polymeric fraction (methylolated and nonmethylolated) that contributes most to the cohesion of the resin. Thus, a resin to which great amounts of final urea are added will have a proportionally high amount of urea and monomeric methylolated species, giving both good adhesion and low formaldehyde emission, and proportionally a lower amount of prebuilt polymeric species, giving poor cohesion, hence lower strength. Conversely, a resin of final higher formaldehyde/urea molar ratio such as the classic UF resins used for the last few decades, will have a large number of polymeric species, will still be heavily methylolated—most of the methylolated species will be polymeric, however—and will still have a considerable amount of free and potentially free formaldehyde. These resins will have good cohesion and good adhesion, hence good strength, but very high HCHO emission.

The logical manner to avoid the conflicting requirements of the two properties wanted is then to prebuild in some easy and convenient manner the particular mixture of species that will give the correct balance of strength and emission for the applications required. Thus, although UF resins of very low formaldehyde/urea ratios [16] can be prepared by adding great amounts of second and third ureas, the high predominance of urea and other monomeric species in relation to polymer proportions will give boards of poor strength, albeit of very low HCHO emission. The required balance of chemical species and of properties can then be achieved more easily by preparing two or more UF resins, and/or preresins, which are mixed in various amounts to yield the desired balance of acceptable strength and low emission [16,26].

D. Other UF Adhesive Applications

Although particleboard and plywood are the major users of UF adhesives, two other applications, although consuming much lower proportions of these resins, are also worthy of note. The first is in the furniture and joinery industry, including the manufacture of hollow-core doors. While in the latter application thermosetting resins with characteristics and glue mixes similar to those for plywood are used, often (but not always) cured by radio frequency, the former can be simpler resins of higher urea/formaldehyde molar ratio to which cold setting capability and different pot lives are given by a variety of hardener types; in these, hardeners formed by an acid plus a salt are the norm. The second application of note is in foundry applications as sand core binders. In this application UF resins compete with phenolic and furanic resins. In general, however, the resins used for the hot-box process are UF resins modified with 20 to 50% furfuryl alcohol to obtain a UF–furanic resin copolymer, and phenol–formaldehyde resins modified with urea. Small amounts of paraffin wax and corn flour are often added to facilitate mixing of the resin with the sand (generally between 1 and 2.5% resin on sand).

IV. ANALYSIS

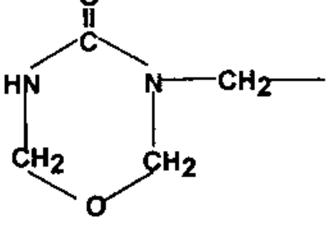
Methods of formaldehyde analysis include the iodometric, sulfite [31], and mercurimetric [32,33] methods. The sulfite method measures only the formaldehyde present, whereas the iodometric method can also estimate the methylol groups. Another method is based on the partition of formaldehyde between water and isoamyl alcohol [34]. Estimation of the formaldehyde in the alcohol phase of a mixture of an aqueous solution of the resin and isoamyl alcohol allows deduction of the amount of free formaldehyde. This procedure has the advantage that no risk of reaction arises between free formaldehyde and the resin components.

Kappelmeier [35] has suggested the use of aniline, benzylamine, and phenyl-ethylamine as reagents for the identification and analysis of urea in UF resins. He has provided evidence that the methylene–ether groups form a bridge between urea residues in UF resins. The use of benzylamine in particular (which yields dibenzylurea from urea derivatives), has been developed as a method of analysis. In determining the ratio of urea to formaldehyde in UF resins, the benzylamine method has been coupled with a process of formaldehyde estimation which involves depolymerization with phosphoric acid, followed by distillation into alkaline potassium cyanide solution [36].

Chow and Steiner [14] advocate the use of bromination in CCl_4 and subsequent x-ray analysis to determine available reactive methylol groups. High-resolution nuclear magnetic resonance (NMR) has also been used to analyze UF resins and to trace their kinetic behavior [37]. Particularly useful is ^{13}C-NMR analysis of liquid UF resins, where clear identification of monomeric species, methylolated or not, methylolureas, methylol groups on the polymer, methylene–ether linkages, methylene bridges, sites of branching, uron, free formaldehyde, and other features can be achieved easily and rapidly [26,38,39]. For example, this technique makes it possible to easily estimate the probable bonding ability and approximate emission class to which the bonded boards are likely to belong [24,26].

V. URONS AND DERIVED RESINS

The potential introduction of an intermediate reaction step at very acid pH inducing the formation of some uron in the preparation of UF resins of lower formaldehyde emission has caused some industrial interest [40], and today industrial UF resins manufactured with the introduction of a rapid, very acid step (pH 1–2) during preparation are available. The only published research work which can be found in the worldwide literature on this subject deals with the introduction of just such a strongly acid condensation step in the preparation of UF resins [40–42]. This work came to the conclusion that introduction of such an acid step can lead to UF resins of improved bonding strength [40–42] and also of lower postcure formaldehyde emission [2,3]. One of the marked effects of the introduction at lower reaction temperatures of the additional strongly acid condensation step was the formation of considerable quantities of uron [40–42], thus of the well-known structure of a cyclic intramolecular urea methylene ether [8,43]. Urons have been found by ^{13}C NMR to be present as methylolurons, methyleneurons, or methylene ether urons, hence as structures of the type shown below [40], and even more interestingly some completely substituted urons appear to exist in the reaction mixture, this being the only case in which the existence of some form of tetrasubstituted urea has been noted [40] (Formula 3)



The favored pH ranges for the formation of urons in UF resin preparation were determined as being at pHs higher than 6 and lower than 4 at which the equilibrium

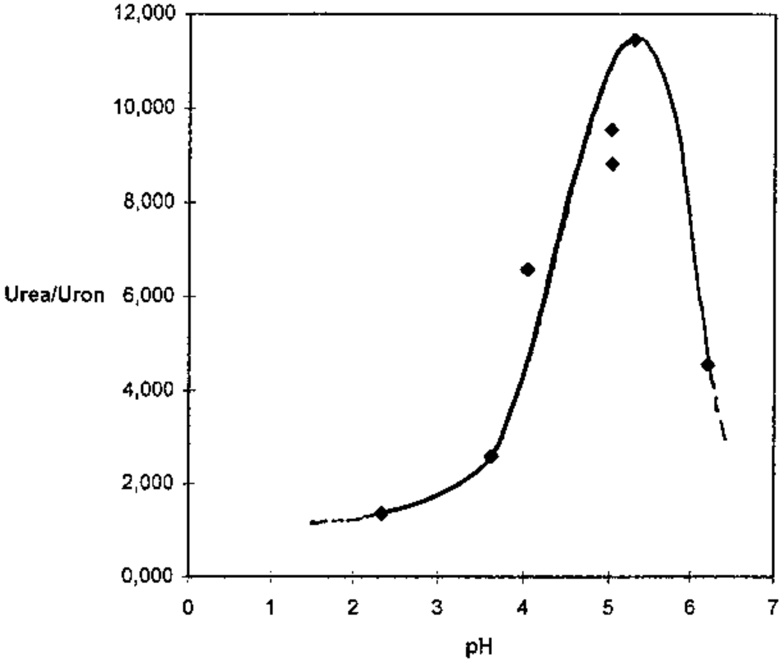
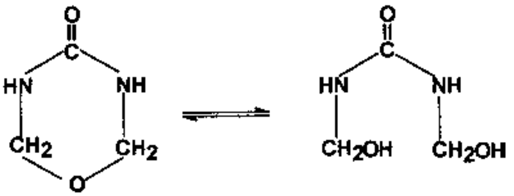


Figure 5 Variation of the urea/uron ratio of the ^{13}C NMR carbonyl peak areas as a function of pH during the total reaction.

urons ↔ *N*,*N*′-dimethylolureas is shifted in favor of the cyclic uron species [40] (Fig. 5). Shifting slowly the pH during the preparation from one favorable range to the other causes a shift in the equilibrium and formation of a majority of methylolurea species, while a rapid change in pH does not cause this to any great extent [40]. Urea–formaldehyde resins in which uron constituted as much as 60% of the resin were prepared and the procedure to maximize the proportion of uron present at the end of the reaction described [40]. Uron has been found to be present in these resins linked by methylene bridges to urea and other urons and also as methylolurons, the reactivity of the methylol group of this latter having been shown to be much lower than that of the same group in methylolureas. Thermomechanical analyses and tests on wood particleboard prepared with uron resins to which relatively small proportions of urea were added at the end of the reaction showed that these were capable of gelling and yielding bonds of considerable strength [40]. Equally, mixing a uron-rich resin with a low formaldehyde/urea molar ratio UF resin yielded resins of greater strength than a simple UF resin of corresponding molar ratio indicating that UF resins of lower formaldehyde emission with still acceptable strength could be prepared in this way [40]. As the "acid-step" industrial resins are not prepared under conditions as extreme as the research on the potential for uron introduction has shown to be possible, it is clear that in this direction there is some room for further improvement for UF adhesives.

The reopened structures reform the intramolecular uron methylene ether cycle as the pH reaches the acid range in which the cyclic structure is again stable. Thus, the uron structure is in equilibrium with the open dimethylolurea form and the pH range determines the direction towards which such an equilibrium is more or less shifted (Formula 4)



The rate of opening or closure of the cycle is not very rapid as, at the end of the reaction, when the pH is rapidly adjusted from the very acid to the alkaline range the proportion of cyclic structures present does not alter much, while during slow descent of the pH during the reaction, passing through the middle pH range causes the disappearance of the greater proportion of the uron cyclic structures, which then form again once the acid pH range is reached.

VI. FORMULATION

An introduction to the typical resin synthesis of a UF resin used as an adhesive for wood products and in industrial applications is given below. It constitutes a handy formulation for those who want to work in this field. It is not a low-formaldehyde-emission formulation. To 1000 parts by mass of 42% formaldehyde solution (methanol $< 1\%$) are added 22% NaOH solution to pH 8.3 to 8.5, 497 parts by mass of 99% urea, and the temperature raised in ± 50 min from ambient to 90°C while maintaining pH in the range 7.3 to 7.6 by small additions of 22% NaOH. The temperature is maintained at 90 to 91°C until the turbidity point is reached (generally another 15 to 20 min). The pH is then corrected to 4.8 to 5.1 by addition of 30% formic acid, and the temperature is raised to 98°C. The water tolerance point is reached in ± 18 min and the pH is then adjusted to 8.7. Vacuum distillation of the reaction water with concomitant cooling is then initiated. After distillation of the wanted amount of water to reach a resin content of 60 to 65%, the resin is cooled to 40°C, 169 parts by mass of second urea is added, the pH is adjusted to 8.5 to 8.7, and the resin is allowed to mature at 30°C for 24 to 48 h; resin characteristics: solids content, 60%; density, 1.268 g/cm^3; free HCHO, 0.4%; viscosity, 200 cP; pH, 8.

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Melamine–Formaldehyde Adhesives

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I. INTRODUCTION

Melamine–formaldehyde (MF) and melamine–urea–formaldehyde (MUF) resins are among the most used adhesives for exterior and semiexterior wood panels and for the preparation and bonding of both low- and high-pressure paper laminates and overlays. Their much higher resistance to water attack is their main distinguishing characteristic from urea–formaldehyde (UF) resins. MF adhesives are expensive. For this reason, MUF resins which have been cheapened by addition of a greater or lesser amount of urea are most often used. Notwithstanding their widespread use and economical importance, the literature on melamine resins is only a small fraction of that dedicated to UF resins. Often MFs and MUFs are described in the literature as a subset of UF amino resins. This is not really the case, as they have peculiar characteristics and properties all of their own which in certain respects are very different from those of UF adhesives.

II. USES FOR MF RESINS

Melamine–formaldehyde resins are used as adhesives for exterior- and semiexterior-grade plywood and particleboard. In this application their handling is very similar to that of UF resins for the same use, with the added advantage of their excellent water and weather resistance. MF resins are also used for the impregnation of paper sheets in the production of self-adhesive overlays for the surface of wood-based panel products and of self-adhesive laminates. In this application the impregnation substrate, α cellulose paper, is thoroughly impregnated by immersing it in the resin solution, squeezing it between rollers, and drying without curing it to proper flow by passing it through an airdraft tunnel oven at 70 to 120°C at ± 10 m/s. The dry MF-impregnated sheets can then be bonded by one of two main processes:

1. The sheets of MF-impregnated paper, consisting of one surface layer or a few surface layers, are bonded together and with a substrate of paper sheets impregnated with phenolic resins to form laminates of variable thickness. In the impregnated papers is the dry but still active MF resin, which functions as the adhesive of the MF-impregnated sheet to both MF-impregnated sheets and at

the interface between MF-impregnated and phenol–formaldehyde (PF)-impregnated layers. These laminates are high-pressure laminates.

2. The MF in an impregnated paper sheet is not completely cured but still has a certain amount of residual activity and is applied directly in a hot press, in a single sheet, on a wood-based panel, to which it bonds by completing the MF adhesive curing process.

Press platens are made from stainless steel or chromium-plated brass and copper. The chromium layer preserves surface quality longer than does ordinary steel. The MF laminates exhibit a remarkable set of characteristics. Because of their unusual chemical inertness, nonporosity, and nonabsorbance, they resist most substances, such as mild alkalies and acids, alcohols, solvents such as benzene, mineral spirits, natural oils, and greases. No stains are produced on MF surfaces by these substances. In addition to almost unlimited coloring and decorating possibilities, this remarkable resistance has resulted in the extensive use of MF laminated wood-based panel products for tabletops, sales counters, laboratory benches, heavy-duty work areas in factories and homes, wall paneling, and so on.

III. CHEMISTRY

A. Condensation Reactions

The condensation reaction of melamine (I) with formaldehyde (Fig. 1) is similar to but different from the reaction of formaldehyde with urea. As for urea, formaldehyde first attacks the amino groups of melamine, forming methylol compounds. However,

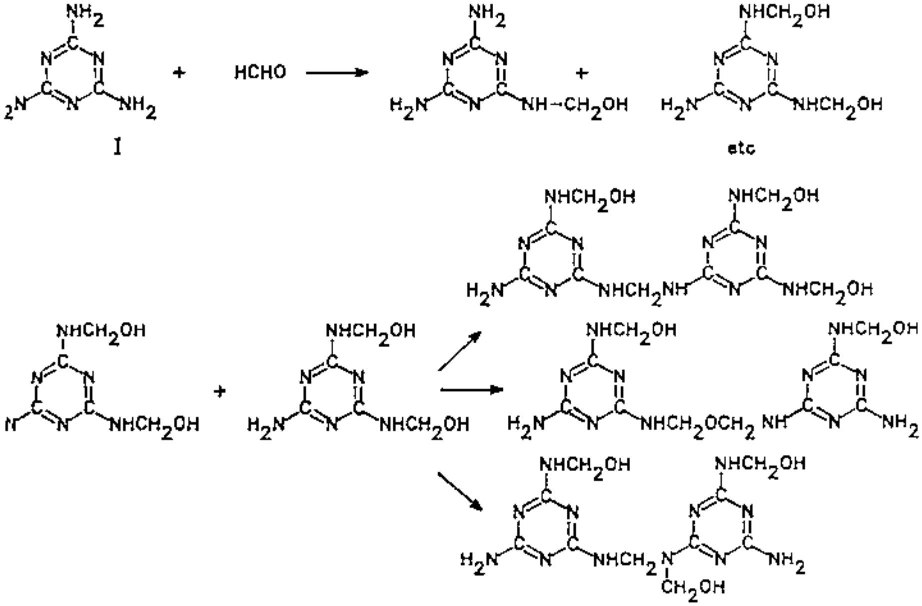
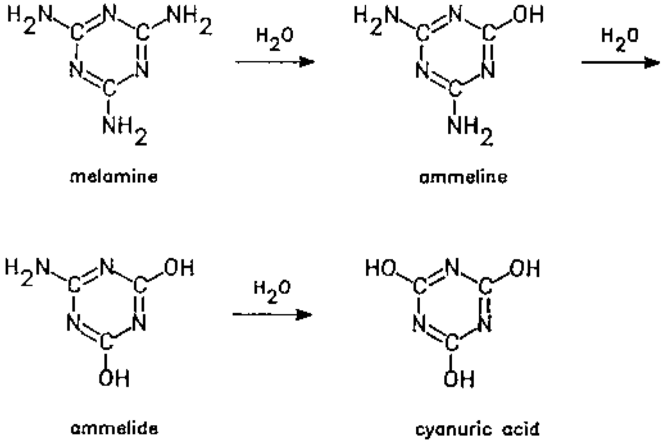


Figure 1 Methylolation (hydroxymethylation) and subsequent condensation reactions to form melamine–formaldehyde adhesive systems.

formaldehyde addition to melamine occurs more easily and completely than does addition to urea. The amino group in melamine accepts easily up to two molecules of formaldehyde. Thus complete methylolation of melamine is possible, which is not the case with urea [1]. Up to six molecules of formaldehyde can be attached to one molecule of melamine. The methylolation step leads to a series of methylol compounds with two to six methylol groups. Because melamine is less soluble than urea in water, the hydrophilic stage proceeds more rapidly in MF resin formation. Therefore, hydrophobic intermediates of the MF condensation appear early in the reaction. Another important difference is that MF condensation to give resins, and their curing, can occur not only under acid conditions, but also under neutral or even slightly alkaline conditions. The mechanism of the further reaction of methylol melamines to form hydrophobic intermediates is the same as for UF resins, with splitting off of water and formaldehyde. Methylene and ether bridges are formed and the molecular size of the resin increases rapidly. These intermediate condensation products constitute the large bulk of the commercial MF resins. The final curing process transforms the intermediates to the desired MF insoluble and infusible resins through the reaction of amino and methylol groups which are still available for reaction.

A simplified schematic formula of cured MF resins has been given by Koehler [2] and Frey [3]. They emphasize the presence of many ether bridges besides unreacted methylol groups and methylene bridges. This is because in curing MF resins at temperatures up to 100°C, no substantial amounts of formaldehyde are liberated. Only small quantities are liberated during curing up to 150°C. However, UF resins curing under the same conditions liberate a great deal of formaldehyde.

At the condensation stage attention must be paid to the formation of hydrolysis products of the melamine before preparation starts. The hydrolysis products of melamine are obtained when the amino groups of melamine are gradually replaced by hydroxyl groups. Complete hydrolysis produces cyanuric acid (Formula 1).



Formula 1

Ammeline and ammelide can be regarded as partial amides of cyanuric acid. They are acid and have no use in resin production. They are very undesirable by-products of the manufacture of melamine because of their catalytic effect in the subsequent MF resin production, due to their acidic nature. If present, both must be removed from crude melamine by an alkali wash and/or crystallization of the crude melamine.

B. Mechanisms and Kinetics

The mechanism of the initial stages of the reaction of melamine with formaldehyde leading to the formation of methylol melamines is very similar to that of urea. The reaction mechanism of the acid-catalyzed condensation reactions of methylol melamines to form polymers and resins has been elucidated by Sato and Naito [4]. Melamine and formaldehyde react similarly to urea and formaldehyde, although basic differences are evident in the reaction rates and mechanism. The primary products of reaction are methylolmelamines, and evidence indicates that such compounds are formed only at ambient or higher temperature except in acid pH ranges. The reaction is reversible throughout the pH range. Its forward rate is proportional to either [melamine][HCHO] or [melamine][H^+CHOH] or [melamine$^+$][HCHO], according to the pH used.

Methylolmelamine forms "dimers" by condensation with melamine under neutral and acid conditions (70°C); this process is irreversible. The initial hydroxymethylation is very rapid. Its rate is determined by the condensation of conjugated acids of methylolmelamines with melamine. The reaction rate is proportional to $[\text{melamine}]^2[\text{HCHO}]$ [5]. When the [mineral acid]/[melamine] ratio is 0.0 to 1.0, the early stage hydroxymethylation of melamine is dependent on the concentration of the melamine molecule (base species) MH and its conjugated acid MH_2^+ in the following manner [6]:

$$\text{rate} = k_{H_2O}[MH][HCHO] + k_H[MH_2^+][HCHO] + k_{MH_{2^+}}[MH_2^+][MH][HCHO] + \\ + k_{MH}[MH]^2[HCHO]$$

in the absence of added acid, when the ratio [mineral acid]/[melamine] is $= 0$, the rate of the reaction can thus be represented as

$$\text{rate} = k_{H_2O}[MH][HCHO] + k_{MH}[MH]^2[HCHO]$$

The condensation reaction has been studied by investigating the kinetics of the initial stage of the condensation of di- and trimethylolmelamine (MF_2 and MF_3) in the pH range 1 to 9. Regardless of pH, the initial rate is equal to [4]:

$$\text{rate} = k[MF_n]^2 \quad (\text{with } n = 2 \text{ or } 3)$$

In the presence of mineral acid, the main reaction at the early stage of the condensation is the reaction between the methylolmelamine molecule and its conjugated acid (MF_nH^+) [7]. This was found at an [acid]/[MF_n] ($n = 2$ or 3) ratio lower than 1.0 (pH 2.7). With an [acid]/[MF_n] ratio higher than 1.0 to 1.2 ($pH < 2$), the main condensation takes place between the conjugated acids themselves.

At equal pH values the condensation rate of trimethylolmelamine is considerably faster than that of dimethylolmelamine. This is the opposite of the rates of mono- and dimethylolurea. This means that while the nitrogen of the amido group in the case of urea is more reactive and therefore more nucleophilic than the nitrogen of the amidomethylol group, the opposite is true in the case of melamine. The reaction for MF_2 is primarily between the carbon of the methylol group next to the nitrogen in HM^+CH_2OH, and the nitrogen of the amino group in MCH_2OH. For MF_3, the condensation is mainly between the carbon of the methylol group next to the charged nitrogen in H^+MCH_2OH, and the nitrogen of the aminomethylol group in MCH_2OH [4]. The condensation rate therefore increases with the increasing electrophilicity of the carbon of the methylol group and the increasing nucleophilicity of the nitrogen of the amino group or aminomethylol group.

Therefore in MF_3 the carbon in HM^+CH_2OH is more electrophilic than the same carbon in MF_2. On the other hand, the nitrogen of the aminomethylol group in

HM^+CH_2OH of MF_3 is less nucleophilic, and therefore less reactive, than the nitrogen of the amino group of MF_2. The effects of the carbon and nitrogen atoms are consequently opposite to each other in the MF_n condensation. Since the effect of the carbon is greater than the effect of the nitrogen on the reaction rate, MF_3 condenses faster than MF_2. At lower pH values the effect of the nitrogen becomes negligible and MF_3 is even faster than MF_2 in condensing to polymers.

The difference between the kinetic behavior of urea and melamine can be ascribed to the different effect of the nitrogen atom in the two compounds. With regard to the formation of methylol compounds as a result of hydroxymethylation, the functionality of melamine has been observed to be 6 against formaldehyde [1,8]. Similarly, melamine reacts easily with formaldehyde to form MF_3; it also forms MF_6 in concentrated formaldehyde [1,4,8]. For example, urea readily forms dimethylolurea, but forms trimethylolurea with marked difficulty [1,8] and never forms tetramethylolurea. These results suggest that the nitrogen of the amidomethylol group in methylolurea is considerably less nucleophilic than the nitrogen of the amido group in urea. However, the nitrogen of the aminomethylol group in methylolmelamine is not markedly less nucleophilic than the nitrogen of the amino group in melamine. Presumably, this is due to the difference in basicity between urea and melamine. The same is also true of their condensation reactions.

C. Mixed Melamine Resins

With regard to melamine–urea–formaldehyde, copolymers can be prepared which are generally used to cheapen the cost of MF resins, but which also show some worsening of properties. Copolymerization was proven by means of model compounds and polycondensates [9]. MUF resins obtained by copolymerization during the resin preparation stage are superior in performance to MUF resins prepared by mixing preformed UF and MF resins, especially because processing of such mixtures is quite difficult [10]. The relative mass proportions of melamine to urea used in these MUF resins is generally in the melamine:urea range 50:50 to 30:70 [11]. Melamine–phenol–formaldehyde resins, which in some respects show better properties than those of their corresponding MF and PF resins, have also been prepared [12–14]. Analysis of the molecular structure of those resins in both their uncured and cured states appeared to show that no co-condensates of phenol and melamine form and that two separate resins coexist. This is due to the difference in reactivity of the phenolic and melamine methylol groups as a function of pH. Also, in their cured state an interpenetrating network of the separate PF and MF resins, as a polymer blend, is formed, not a copolymer of the two [15–18]. Today MUF resins are produced in greater amounts than MF resins in the field of adhesives due to the relatively high cost of melamine: their formulation has progressed to such a level that often no difference in performance exists between a good MUF resin and a pure MF resin. MF resins are still more extensively used at this stage in the paper impregnation/laminates fields although both MUF copolymers as well as separate, double application of UF (paper core) and MF (paper surfaces) resins are making considerable inroads in this area. MUF resins instead totally dominate today in the wood adhesives field. Paper laminates and wood adhesives are the two main application areas of these resins.

A type of resin also used today is the so-called PMUF (or MUPF according to which author is writing) adhesives. These are fundamentally MUF resins in which a minor proportion of phenol (between 3 and 10%; phenol:melamine:urea by weight of 10:30:60 for example) has been assumed to have coreacted with to further upgrade weather resistance of the bonded joint. Unfortunately the alleged superior performance of such resins is

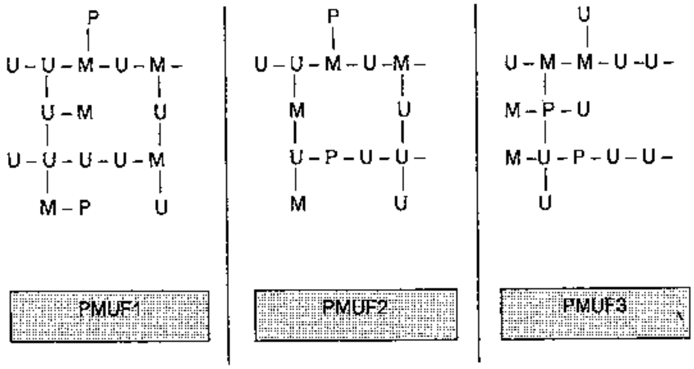


Figure 2 Schematic representation of the dependence on the type of formulation used of the fate of phenol in a PMUF resin. (1) Phenol only present as unlinked free phenol/phenol derivatives but mainly as a pendant group neither participating in resin cross-linking nor contributing to resin performance and water resistance. (2) Intermediate case. (3) Case in which phenol is co-condensed and participating in the cross-linked network.

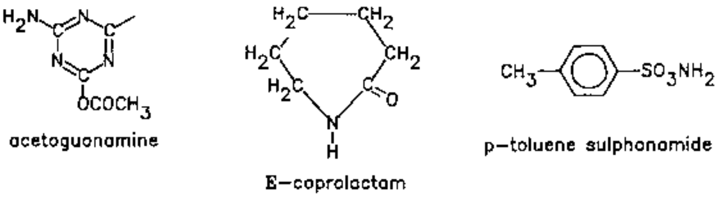
often only wishful thinking as the phenol has frequently not been properly reacted with the other materials, and consequently the PMUF resin will have a worse performance than a comparable top of the range MUF resin. This was confirmed by the demonstration that it depends exclusively on the resin manufacturing parameters and materials reaction order used whether or not the phenol coreacts within many PMUF adhesives, showing that often the phenol remains as a useless pendant group in the hardened aminoplastic (MUF) network without contributing at all to its performance [19,20] (Fig. 2).

The best reaction order necessary to obtain PMUF resins in which phenol makes a positive contribution to the performance of the hardened network has been reported [19]. PMUF resins are still used and some good resins of this type are indeed used in the unrealistic hope that they outperform equivalent MUF resins, when it has been shown clearly that they perform at best as a MUF adhesive presenting the same number of moles of melamine for the total moles of phenol plus melamine of the PMUF itself. The idea that the addition of small percentages of phenol to a MUF resin yields resins of better exterior durability is then an incorrect myth perpetuated in the wood panels industry. Newer formulations of MUF resins always outperform the corresponding PMUF. PMUFs are not bad resins, they are simply resins in which one of the materials, phenol, is often wasted for no purpose.

IV. RESIN PREPARATION, GLUE MIXING, AND HARDENING

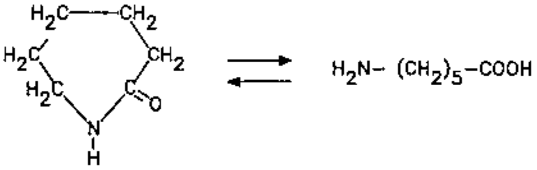
Because of their characteristic rigidity and brittleness in their cured state, when MF resins are used for impregnated paper overlays, small amounts (typically 3 to 5%) of modifying compounds are often copolymerized with the MF resin during its preparation to give better flexibility to the finished product and better viscoelastic dissipation of stress in the joint. Most commonly used are acetoguanamine, ε-caprolactam, and *p*-toluenesulfonamide (Formula 2).

The effect of these is to decrease cross-linking density in the cured resin due to the lower number of amidic or aminic groups in their molecules. Thus in resin segments where



Formula 2

they are included, only linear segments are possible, decreasing the rigidity and brittleness of the resin. Acetoguanamine is most used for modification of resins for high-pressure paper laminates, while caprolactame, which in water is subject to the following equilibrium (Formula 3),



Formula 3

is used primarily for low-pressure overlays for particleboard. Small amounts of noncopolymerized plasticizers such as diethylene glycol can also be used for the same purpose. Due to the peculiar structure of the wood product itself, MF adhesives for particleboard generally do not need the addition of these modifiers. Often, a small amount of dimethylformamide, a good solvent for melamine, is added at the beginning of the reaction to ensure that all the melamine is dissolved and is available for reaction. Sugar is often added to lessen cost of the resin. The aldehyde group of sugars have been proven to be able to condense with the amine groups of melamine and hence to copolymerize in the resin. Their quantity in MF resins must be limited to very low percentages, and if possible, sugars should not be used at all, as with aging they tend to cause yellowing, crazing, and cracking of cured MF paper laminates and to have a bad effect on adhesive long-term water resistance in both plywood and particleboard.

MF adhesive resins for plywood and particleboard must be prepared to quite different characteristics than those for paper impregnation. The latter must have lower viscosity but still high resin solids content because they need to penetrate the paper substrate to a high resin load, to be dried without losing adhesive capability, and only later to be able to bond strongly to a substrate. Instead, MF adhesive resins for plywood and particleboard are generally more condensed, to obtain lower penetrability of the wood substrate (otherwise, some of the adhesive is lost by overpenetration into the substrate). The reverse applies for paper substrates, where the contrasting characteristics desired—good paper penetration and fast curing—can be obtained in several ways during resin preparation. These characteristics can be achieved by producing, for example, a resin with a lower degree of condensation and high methylol group content. Typically, a MF resin of a lower level of condensation with melamine/formaldehyde molar ratio of 1:1.8 to 1:2 will give the desired characteristics. Its high methylol content and somewhat lower degree of polymerization will give low viscosity at a high resin solids content, favoring rapid wetting and impregnation of the paper substrate, while the high proportion of methylol groups will give it fast cross-linking and curing capabilities.

A second, equally successful approach in to produce a MF resin of lower methylol group content and higher degree of condensation to which a small second addition of melamine (typically, 3 to 5% total melamine) is effected toward the end of resin preparation. The shift to lower viscosity and higher solids content given by a second addition of melamine, shifting to lower values the average of the resin molecular mass distribution, yields a resin of rapid impregnation characteristics. Conversely, the higher degree of polymerization of the major part of the resin gives fast cross-linking, and curing, due to the lower number of reaction steps needed to reach gel point. Typical total melamine/formaldehyde molar ratios used in this system are 1:1.5 to 1:1.7.

Figures 3 and 4 show typical temperature and pH diagrams for the industrial manufacture of MF and MUF resins for adhesives and other applications. The important control parameters to take care of during manufacture are the turbidity point (the point during resin preparation at which addition of a drop of MF reaction mixture to a test tube of cold water gives slight turbidity) and the water tolerance or hydrophobicity point, which marks the end of the reaction. The latter is a direct measure of the extent of condensation of the resin and indicates the percentage of water or mass of liquid on the reaction mixture that the MF resin can tolerate before precipitating out. It is typically set for resins of higher formaldehyde/melamine ratios and lower condensation levels at around 170 to 190%, but for resins of lower formaldehyde/melamine molar ratios and higher condensation levels it is set at around 120%. As can be seen from the diagrams in Fig. 3, once maximum reaction temperature is reached, pH is lowered to 9 to 9.5 to accelerate formation of the polymer. Once the turbidity point is reached, pH is again increased to 9.7 to 10.0, to slow down and more finely control the end point, determined by reaching of the wanted value of the water tolerance point. Industrial MF resins are generally manufactured to a 53 to 55% resin solids content with a final pH of 9.9 to 10.4 (but lower pH values are also used for low-condensation resins). To have acceptable rates of curing if higher pH values are used, higher quantities of hardener need to be used, which is clearly uneconomical. For typical MF resins for low pressure (particleboard),

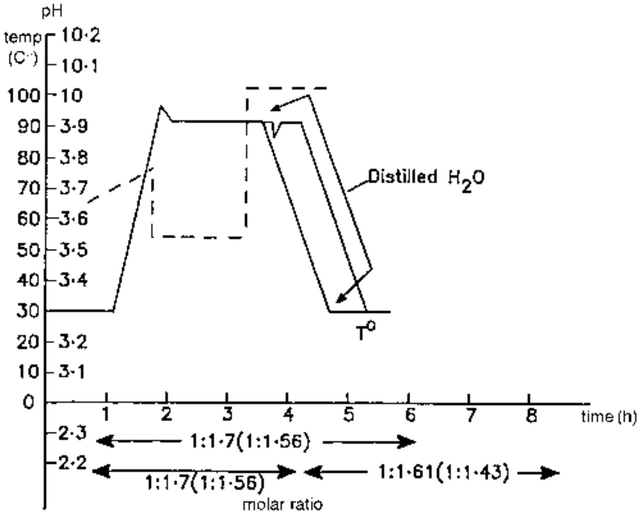


Figure 3 Typical temperature and pH diagrams for the industrial manufacture of MF resins.

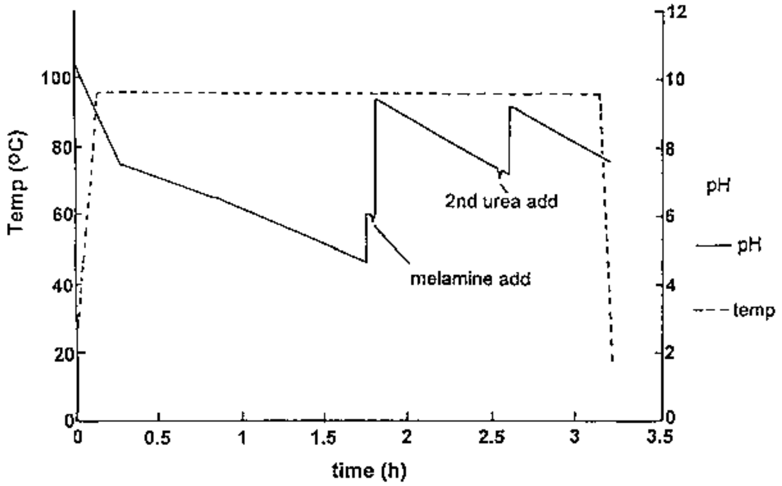
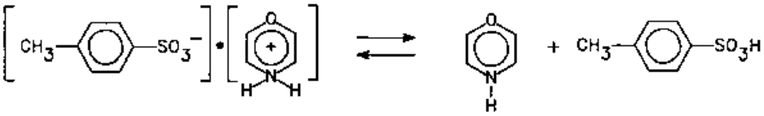


Figure 4 Typical manufacturing diagram for 40:60 to 50:50 melamine/urea weight ratio MUF resins.

self-adhesive overlay pressing times of between 30 and 60 s at 170 to 190°C press temperature are required according to the type of resin used. Pressing conditions for particleboard and plywood adhesives are identical to those used for UF resins.

Glue mixing presents different requirements according to the final use of the MF resin. Hardeners are either acids or materials that will liberate acids on addition to the resin or on heating. In MF and MUF adhesives for bonding particleboard and plywood, the use of small percentages of ammonium salts, such as ammonium chloride or ammonium sulfate, is well established and is indeed identical to standard practice in UF resins. In MF adhesives for low- and high-pressure self-adhesive overlays and laminates the situation is quite different. Ammonium salts cannot be used for the latter application for three main reasons. First, evolution of ammonia gas during drying and subsequent hot curing of the MF impregnated paper would cause high porosity of the cured MF overlay. Second, the stability of ammonium salts, in particular of ammonium chloride, might cause MF liquid resin whitening and the MF-impregnated paper to cure and deactivate at ambient temperature after a short time in storage, causing the resin to have lost its adhesive capability by the time it is needed in hot curing. Third, the elimination of ammonia during drying and curing would leave the cured, finished paper laminate essentially very acid due to the residual acid of the hardener left in the system. This badly affects the resistance to water attack of the cured MF surface defeating the primarily advantage for which such surfaces have justly become so popular. Thus a stable, self-neutralizing, non-gas-releasing hardener is needed for such an application. Several have been prepared and one of the most commonly used is the readily formed complex between morpholine and *p*-toluenesulfonic acid. Morpholine and *p*-toluenesulfonic acid readily react exothermically to form a complex of essentially neutral pH that is stable up to well above 65°C (Formula 4).



Formula 4

Table 1 Typical Paper Impregnation Glue Mix for Self-Adhesive Low-Pressure MF Overlays

Ingredient	Parts by mass
MF resin, 53% solids content	99.1
Release agent	0.08
Wetting agent	0.16
Hardener (morpholine/*p*-toluenesulfonic acid complex)	0.64
Defoamer	0.02

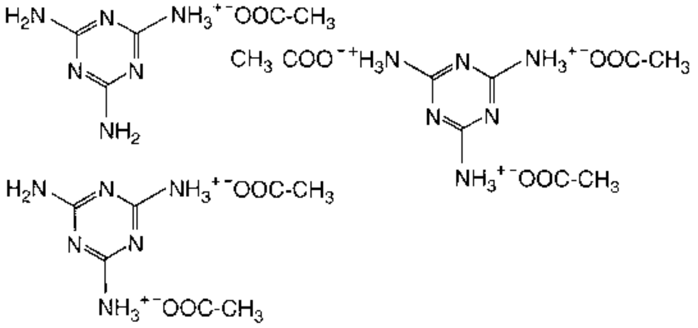
During heat curing of the MF paper overlay in the press, the complex decomposes, the MF resin is hardened by the acid that is liberated, morpholine is not vaporized and lost to the system, and on cooling the complex is reformed, leaving the cured glue line essentially neutral.

In MF glue mixing for overlays and laminates, small amounts of release agents to facilitate release from the hot press of the cured bonded overlay are added. Small amounts of defoamers and wetting agents to further facilitate wetting and penetration of the resin in the paper are always added. A typical glue mix is shown in Table 1.

Two strong trends have appeared reasonably recently in the preparation of melamine-impregnated paper laminates. First, impregnating machines capable of giving papers in which much cheaper UF resin is substituting as much as 50% of the more expensive MF resin have now been in operation for several years. This equipment is based on a double impregnating bath application: the paper passes through a first bath where it absorbs the UF resin first, the excess on the surfaces being scraped off in-line, and then passes through a second bath where it absorbs the MF resin. The concept is to limit the UF resin to the inside of the paper with the MF resin coating the outside of the paper: the hardened surface after final curing will then have all the waterproof characteristics of a MF paper laminate but at a lower price. Good results are obtained and many machines using this type of process are today in industrial operation. A more recent trend has been to develop MUF copolymers to use with the less costly single impregnating bath machines. A few cases of this route to coping with the high cost of melamine are on record.

V. MUF ADHESIVE RESINS OF UPGRADED PERFORMANCE

Several effective techniques to consistently and markedly decrease the melamine content in MUF wood adhesives without any loss of performance have also been recently developed. Some of these formulation systems and techniques are already in the early stages of industrialization. Among these melamine/acid salts, such as melamine acetate (Formula 5), function both as efficient hidden hardeners of UF resins for plywood as well as upgrading the performance of simple UF resins for plywood by approximately 10% by mass melamine grafting to yield comparable strength durability of premanufactured MUF resins of 30 to 40% melamine mass content, hence of resins of much higher mass content of melamine. In short a MUF resin of melamine:urea weight ratio 10:90 will perform in certain applications such as exterior plywood as a premanufactured MUF resin of melamine:urea between 30:70 and 40:60 [21–24]. The system works both (i) by simple addition of the melamine salt in the UF glue mix eliminating the need to premanufacture a MUF resin. The effectiveness of melamine grafting in the glue mix and during hot pressing has been found to depend on the relative solubility of the melamine salt which depends on both the acid strength of the acid as well as the number of acid functions in the salt. (ii) By use of salts in which the excess acid has been eliminated from the salt, hence melamine monoacetate with no loose acid residue. The salt can be added in the resin factory to a UF resin and the mix sold as a MUF resin as pot life is indefinite and the resin needs the addition of a classical hardener for aminoplastic resins such as sodium sulfate or sodium chloride for hardening. The solubility of the salts used increases with increase in temperature. The reasons why traditional, premanufactured MUF resins waste 2/3 or more of the melamine used in them, and why such a melamine salt addition system is so much more effective by not wasting melamine were presented in the same study [21].



Formula 5

How is it possible that addition of a melamine salt to a UF glue mix in a melamine:urea mass ratio of 10:90 yields plywood of comparable water resistance to a prereacted MUF resin of melamine:urea mass ratio in the range 30:70 to 40:60? As a consequence of what is presented above it is now possible to answer such a question. In the preparation of precopolymerized MUF resins, hence of today's normal, commercial MUF resins, during the high temperature preparation reaction the melamine also reacts with formaldehyde to form short MF chains which are then bound to the more abundant UF chains. Hardening of MUF resins has been proven to occur almost exclusively by cross-linking through $-CH_2-$ bridges connecting two melamines [20,25] as, due to its much lower reactivity, urea is not greatly involved. The use of melamine salts at ambient temperature in the glue mix instead ensures that only single melamine molecules are singly and separately grafted on the UF resin chain.

$$—U–CH_2–M–CH_2–M–CH_2–M \text{ against } —U–CH_2–M$$

to yield rather different cross-linked networks than those of a standard MUF reactor-made resin [21–26].

As to cross-link the system only a very small amount of melamine molecules for each UF chain is needed to achieve the same effect, to have several chains of MF as in standard MUF resins does not improve the bond strength because (i) only one of the melamines in the chain will react, the other not participating at all in final cross-linking, and (ii) the bonding strength will also not be improved by having even all the melamines of the MF chain react all in the same space zone of the network as shown in the first network formula above: on the contrary, the highly localized position on vicinal sites in the network of a high density of cross-links might well render the resin far too rigid and far too brittle (which indeed is the case for most melamine-based resins). It is then clear that at least 2/3 of the melamine presently used in MUF resins is actually wasted and does not contribute much to the final results other than in a damaging manner, this being unavoidable as a consequence of the system of preparation used. The new system presented greatly improves on the present situation, not only on ease of handling (only a UF resin and a melamine salt as a hardener are needed rather than a more sophisticated MUF resin), but also on the amount of melamine needed (just approximately 1/3 of present consumption for equal exterior-grade bonding performance) with potentially considerable economic advantages as melamine is generally expensive.

The results of a 2 year field weathering test in Europe have confirmed that a UF resin to which has been added 15% melamine acetate salt at the glue mix stage, to obtain a melamine:urea mass ratio of 10:90 solids on solids, imparts a better durability and better exterior performance to plywood glue lines than traditionally reactor-coreacted MUF resins of melamine:urea mass ratio of 33:66 and even of commercial, prereacted PMUF resin where the relative mass proportions of the materials in the resin are 10:30:60 [23].

Postcuring of aminoplastic-bonded wood joints has always been avoided due to the evident degradation induced by heat and humidity on the aminoplastic resin hardened network. This is a known fact and it is for this reason that boards bonded with UF, MUF, and MF resins are traditionally cooled as rapidly as possible after manufacture. However, tightening of formaldehyde emission regulations has caused considerable progress in aminoplastic formulations, especially much smaller molar ratios, and hence today's aminoplastic adhesives are indeed very different materials than those of 10–20 years ago. A recent study [27,28] has shown that the postulate on the avoidance of postcuring of aminoplastic resin bonded joints is under many conditions no longer valid. Thus, (1) postcuring (for example by hotstacking in the simpler cases, by an oven or other heat treatment in more sophisticated cases) can be used in principle and under well-defined conditions to improve the performance of UF and MUF-bonded joints and panels without any further joint and hardened adhesive degradation, as the value of the modulus reached during postcuring is always consistently higher than the value at which the modulus stabilizes after complete curing during the "pressing" cycle. (2) Postcuring could also be used in principle and for the same reasons to further shorten the pressing time of MUF-bonded joints and panels when well-defined postcuring conditions are used or to decrease the proportion of adhesive used at parity of performance [27,28]. (3) There is clear indication that under certain conditions, even when adhesive degradation starts, the application of the posttreatment reestablishes the value of the joint's strength to a value higher than its maximum value obtained during curing. Some of the best posttreatment schedules have also been presented [27] (Fig. 5).

The performance improvements in the internal bond (IB) strength of bonded wood panels are introduced by the series of reactions pertaining to internal methylene ether bridge rearrangements to a tighter methylene bridge network which have already been observed and extensively discussed in the analysis of aminoplastic and phenolic resins [27,29–31]. These are able to counterbalance well the degradative trend to which the aminoplastic resin should be subjected. Furthermore, in modern resins of lower F:(U + M) molar ratio the amount of methylene ether bridges formed in curing is much lower. Thus, disruption by postcuring of the already formed resin network by internal resin rearrangements will be milder, if at all present, and will definitely not yield the marked degradation and even collapse of the structure of the network which characterizes older resins of much higher molar ratio when postcured under the same conditions [32,33]. In short, notwithstanding the internal rearrangement the network will stand and stand

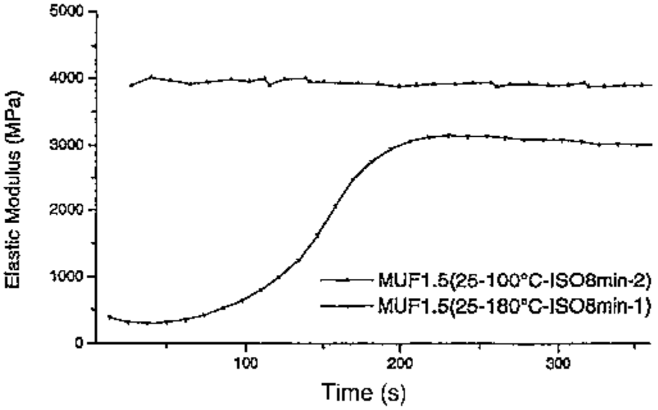
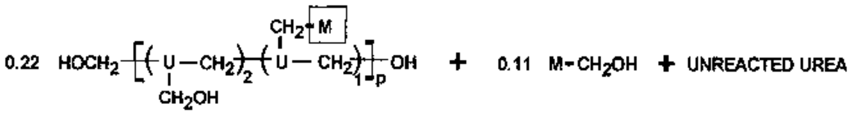


Figure 5 Thermomechanical analysis of a joint glued with a modern MUF adhesive showing the advantage of hot-post-stacking for modern, low molar ratio aminoplastic adhesive bonded panels. Note the maximum modulus achieved during isothermal heating (180°C for 8 min) (lower curve) and maximum modulus achieved after cooling and reheating at 100°C for 8 min (upper curve): the difference in modulus is the potential gain due to hot-post-stacking.

quite strongly: no, or hardly any decrease of IB strength will be noticeable. For modern, lower molar ratio aminoplastic adhesives, since the resin network does not noticeably degrade or collapse with postcuring, only the tightening of the network derived by further bridge formation by reaction within the network of the few formaldehyde molecules released by the now mild internal rearrangement will be noticeable: the IB strength value will then improve with postcuring in boards bonded with modern, lower formaldehyde aminoplastic adhesives.

There are important differences in the behavior of MUF resins prepared in different ways, and hence at the level of their performance as binders of wood panels, due both to their differences at the level of the resin structure and to the type and distribution of the molecular species formed before hardening, as well as to the differences in the structure of the final hardened networks. An example of three types of MUF resins examined can illustrate this point. (i) A sequential MUF in which the UF was prepared first and then melamine coreacted afterwards once the UF polymer had been formed [8], a last small urea addition also being carried out for a final $(M+U)$:F molar ratio of 1:1.5 and M:U weight ratio of 47:53, (ii) a MUF resin in which the great majority of the urea and of the melamine were premixed and then reacted simultaneously to form the resin, followed by addition of small amounts of both last melamine and last urea, for a $(M+U)$:F molar ratio of 1:1.5 and M:U weight ratio of 47:53, and (iii) a UF resin of molar ration 1:1.5 to which has been added 15% by weight on resin solids of monoacetate of melamine in the glue mix for a final $(M+U)$:F molar ratio of 1:1.39 and M:U weight ratio of 14:86. The proportion and type of chemical species formed which can be calculated by the molar proportions of the reagent, the manner in which these are combined during the reaction under different conditions as well as the rate reaction constants of urea and melamine with formaldehyde lead to the conclusion, confirmed by ^{13}C nuclear magnetic resonance (NMR), that the distribution of species for resins (i), (ii), and (iii) are as follows (their relative proportions are indicated in Formulas 6, 7, and 8).

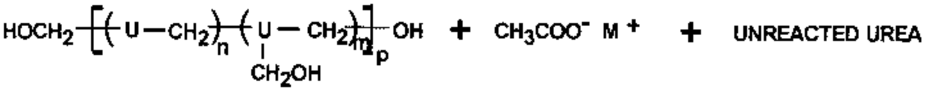
Case (i) above presents the following predominant chemical species (Formula 6), where M attached to the UF polymer is in the form of both a single melamine as well as in the form of a melamine formaldehyde short oligomer.



$$0.22\ \mathrm{HOCH_2}\!\left[\left(\underset{\mathrm{CH_2OH}}{\mathrm{U}}-\mathrm{CH_2}\right)_2\left(\overset{\mathrm{CH_2}-\boxed{\mathrm{M}}}{\mathrm{U}}-\mathrm{CH_2}\right)_1\right]_p\!\mathrm{OH} + 0.11\ \mathrm{M{-}CH_2OH} + \text{UNREACTED UREA}$$

Formula 6

Case (iii) above presents instead just UF oligomers and melamine salts (Formula 7),

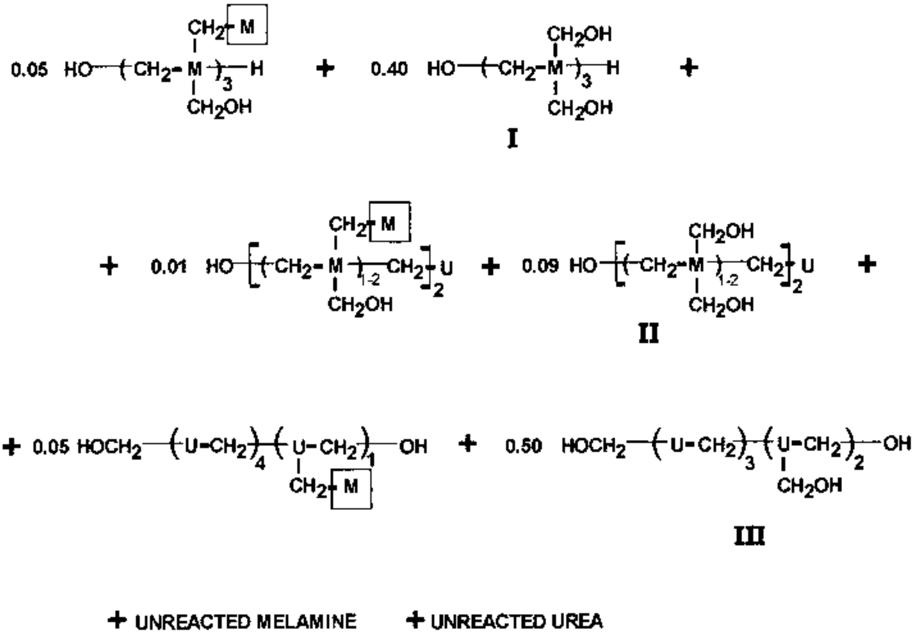


$$\mathrm{HOCH_2}\!\left[\left(\mathrm{U}-\mathrm{CH_2}\right)_n\left(\underset{\mathrm{CH_2OH}}{\mathrm{U}}-\mathrm{CH_2}\right)_m\right]_p\!\mathrm{OH} + \mathrm{CH_3COO^-\ M^+} + \text{UNREACTED UREA}$$

Formula 7

where M is always in the form of a single melamine molecule.

Case (ii) above presents the following predominant chemical species (Formula 8),



$$\begin{aligned}
&0.05\ \mathrm{HO}\!\left(\mathrm{CH_2}-\underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2}-\boxed{\mathrm{M}}}{\mathrm{M}}}\right)_3\!\mathrm{H} + 0.40\ \mathrm{HO}\!\left(\mathrm{CH_2}-\underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{\mathrm{M}}}\right)_3\!\mathrm{H}\ \ \mathbf{I} \ +\\
&+\ 0.01\ \mathrm{HO}\!\left[\left(\mathrm{CH_2}-\underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2}-\boxed{\mathrm{M}}}{\mathrm{M}}}\right)_{1\text{-}2}\!\mathrm{CH_2}\right]_2\!\mathrm{U} + 0.09\ \mathrm{HO}\!\left[\left(\mathrm{CH_2}-\underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{\mathrm{M}}}\right)_{1\text{-}2}\!\mathrm{CH_2}\right]_2\!\mathrm{U}\ \ \mathbf{II} \ +\\
&+\ 0.05\ \mathrm{HOCH_2}\!\left(\mathrm{U{-}CH_2}\right)_4\!\left(\underset{\mathrm{CH_2}-\boxed{\mathrm{M}}}{\mathrm{U}}\mathrm{{-}CH_2}\right)_1\!\mathrm{OH} + 0.50\ \mathrm{HOCH_2}\!\left(\mathrm{U{-}CH_2}\right)_3\!\left(\underset{\mathrm{CH_2OH}}{\mathrm{U}}\mathrm{{-}CH_2}\right)_2\!\mathrm{OH}\ \ \mathbf{III}\\
&+\ \text{UNREACTED MELAMINE} + \text{UNREACTED UREA}
\end{aligned}$$

Formula 8

Thus an MF resin drowned in mostly unreacted urea and where M attached to the UF polymer is in the form of both a single melamine (M and M framed) as well as in the form of a MF short oligomer (M framed).

The structure of the three resins when still in liquid form explains the appearance of their structure after hardening. Thus, hardened MUF resins of formulation type (ii) will present structures as presented in Formula 8 and thus will waste the benefit of a considerable proportion of the melamine used. Hardened MUF resins of type (i) will present structures intermediate between those shown in Formulas 7 and 8 (but tending more to the type of Formula 8) and thus while also wasting a considerable proportion of the melamine used, this will be less than for formulations of type (ii): the strength and water resistance results of MUFs of type (iii) will then be noticeably better at parity of all other conditions than what is obtainable with resins of type (ii), as indeed has been shown to be the case. MUF resin formulations of type (iii), those of melamine acetate type, will give hardened structures according to Formula 7 without wasting much melamine and giving hence the best performance, with the limitation of proportion already mentioned and explained above. This can be seen by comparing the strength results obtained by constant heating rate thermomechanical analysis (TMA) [26]. A MUF formulation of type (iii) containing 20% melamine acetate performs almost as well as a good formulation of type (i) which contains two and a half times more melamine. They both perform much better than a formulation of type (ii) [26] with some notable exceptions [38].

Another recent approach which has shown considerable promise in markedly decreasing the percentage of adhesive solids on a board, and hence in markedly decreasing melamine content, has been found almost by chance. It is based on the addition of certain additives to the MUF resin. Additives have been found that are both able to decrease melamine content in MUF resins at parity of performance, as well as able to decrease the percentage of any MUF resin needed for bonding while still conserving the same adhesive and joint performance. This second class of additives works for UF adhesives too, but less well, while it gives acceptable results for PF resins, but it is at its best in the case of MUF resins. This second class of additives is the acetals [34–36], methylal and ethylal being the two most appropriate due to their cost to performance ratio, which do not release formaldehyde at pHs higher than 1 [35]. Methylal has according to results reported by the Environmental Protection Agency (EPA) an LD_{50} value of 10,000 against that of 100 in the case of formaldehyde, and is thus classed as nontoxic. The addition of these materials to the glue mix of formaldehyde-based resin improves considerably its mechanical resistance and the performance of the bonded joint.

This is in general valid for MUFs, UFs, and PFs, but the effect is particularly evident for the MUF resins [35]. Decreases in MUF resin solids content of as much as 33% while conserving the same performance are reported in the case of wood particleboard. In Fig. 6 are shown the continuous heating rate TMA curves of modulus as a function of temperature for an MUF resin of 1:1.2 (M + U):F molar ratio. Similar but much less extreme

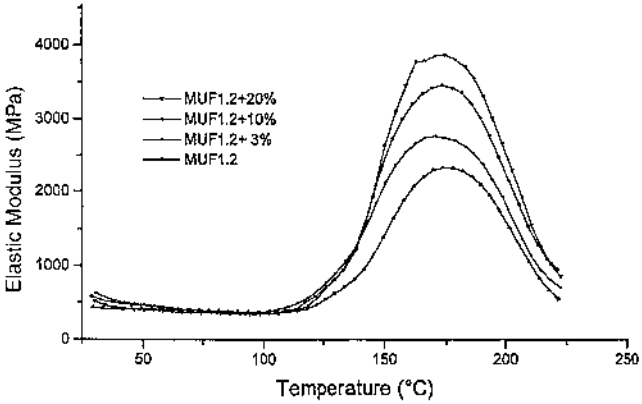


Figure 6 Thermomechanical analysis graph showing the increasing maximum values of the modulus of a MUF-bonded joint with increasing amounts of methylal (an acetal) as an effectiveness upgrading additive.

trends are obtained also for UF and PF resins. In the case of MUF resins the addition of 10% additive on resin solids yields laboratory particleboard in which one can decrease the percentage of resin solids on the board by between 20% and 25% without any loss of performance. Similarly, at equal resin solids the strength of a particleboard is 33% higher when 10% additive on resin solids is added to the glue mix. Addition of 20% methylal on the board yields, in the case of the same resin, the same strength with 30% less adhesive (and hence less melamine) [35].

What is the mechanism of action of methylal, ethylal, and some other acetals to achieve such a feat? Their excellent solvent action on melamine and higher molecular weight ligomers. The cases shown earlier in this chapter referring to melamine salts and the loss of effectiveness due to wastage of melamine are applicable in this case too. Melamine when added to a reacting mixture during resin manufacture is not really soluble. It reacts then in heterogeneous phase with the other components of the resin, some of it being in a transient state in equilibrium between being in solution and being out of solution, and thus its efficacity is partially, but noticeably reduced. The introduction of an excellent solvent, none better than these acetals was known before, brings the totality of the reaction into homogeneous phase with a consequent, noticeable improvement in both the effectiveness of reaction and the effectiveness of melamine utilization.

A different class of additives from those above but also able to decrease melamine content in MUF resins at parity of performance also exist. They are based on the addition in the glue mix of 1 to 5% additive and allow preparation of MUF copolymers, premanufactured in a traditional manner, in which either the proportion of melamine is lower, for example a 20:80 by weight M:U resin to which the additive has been added performing as well as a M:U 50:50 resin, or alternatively to upgrade a top of the range M:U 50:50 MUF adhesive to an exterior performance comparable and even superior to that of PF resins [37–39]. Several different types of additives can achieve this but they are all based on the preparation and acid stabilization of imines, or better of iminomethylene bases [38,39], and of their addition to the MUF resin. Thus, the effect is still the same whether the imines/iminomethylene bases, acid-anion stabilized, are prepared by coreaction of ammonia and formaldehyde [38,39], or for instance as described for acid-anion stabilized decomposition of hexamethylenetetramine [38,39] (Fig. 7). The structure of the imines and the iminomethylene bases yielding this effect are very similar indeed to the structure of the acetal additives presented above, the –NH– bridge of the imines having the same function of the –O– bridge of the acetals. The imines/iminomethylene bases have the added dimension, however, that the nitrogen can function as a knot of tridimensional cross-linking itself, which the oxygen bridge obviously cannot do. The amount of nitrogen-based additive that can be used is limited by its higher sensitivity to water in the hardened network. This is not the case of the possibly less effective oxygen-based additives, which can be used in greater amount: one property balances the other. The oxygen bridge conversely presents perhaps a better longer-term thermal stability than the nitrogen-based bridges. These are only very relative, rather subjective advantages. What is instead important is that the similarity of structure indicates that in the main (but not completely) the mode of action of all these additives may appear to be the same, but often different effects are at work, namely first a considerable improvement of the viscoelastic dissipation of the energy of the glue line and bonded joint without a drop in cross-linking density. The differences between the different additives is then due to additional, although rather important effects such as the solvent effect of the acetals in the MUF resins, and the increase in reaction rate [25] and buffer effect [38] of the iminomethylene basis, as well as others. It is on the basis of

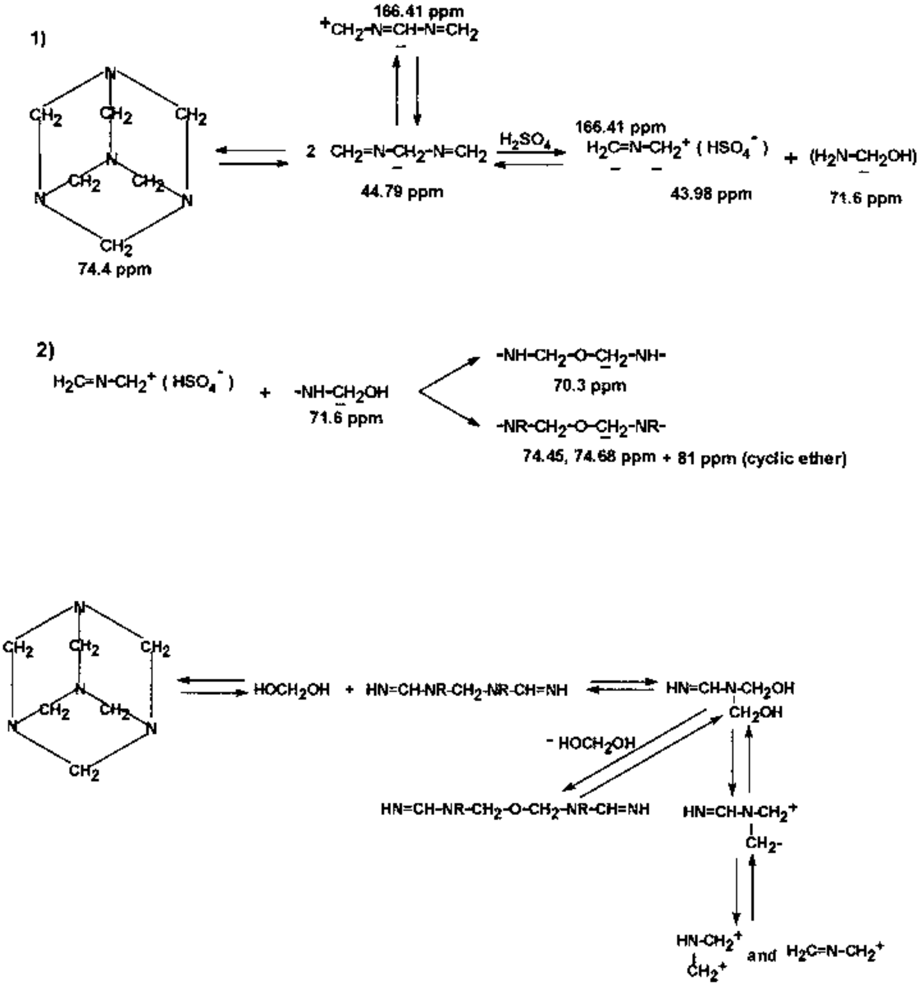
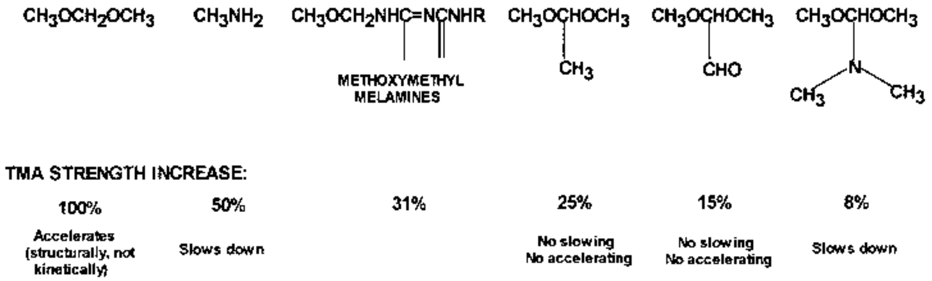


Figure 7 Mechanism of hexamethylenetetramine decomposition leading to the formation of anion-stabilized reactive iminomethylene bases. The same bases can be formed by reaction of ammonium salts such as ammonium sulfate and formaldehyde and constitute a metastable intermediate between hexamine and final decomposition products, and vice versa (after refs 26, 37–39).

this similarity of structure and effect that a scale of additives providing similar effects to different levels has been established (see Formula 9) [40].

It must be pointed out that a TMA strength improvement of 100% on the MUF resin without methylal (this is achieved by addition of 20% methylal on resin solids) corresponds in the actual wood particleboard to an increase of IB strength of 33%. This means that of all the compounds shown above only the acetals, such as methylal and ethylal, as well as the similarly structured imine/iminomethylene bases discussed above (for which the effect on strength is more marked) are capable of marked improvements in IB strength at the actual wood panel level.

These developments are of use for MUF resins not just in the field of wood adhesives, or of other binders in general, but also to improve and upgrade the performance of



Formula 9

resins in other applications such as that of melamine-based impregnated paper laminates, where they have been shown to improve considerably the storage stability of paper impregnating resins [36].

As regards the more application-bound physical aspects of MUF resins these can be applied in different ways, this too sometimes having a bearing on other types of additives used. Thus to the normal case of a MUF plus its hardener one can add cases in which a formaldehyde depressant such as a low condensation MF, UF, or MUF precondensate or one of their mixes is added; sometimes this is in combination with an accelerator based on the same principle. Such an approach is more used in other resins, but it has been shown and reported as being feasible also for MUF resins [41].

VI. TEMPERATURE–TIME-TRANSFORMATION AND CONTINUOUS-HEATING-TRANSFORMATION CURING DIAGRAMS OF MUF RESINS WHEN ALONE AND HARDENING IN A WOOD JOINT (OR OTHER INTERACTIVE SUBSTRATE)

Temperature–time-transformation (TTT) and continuous-heating-transformation (CHT) curing diagrams for polycondensation resins are starting to acquire more importance in the deductions of the behavior of different resins during hardening. They are a type of state diagram. TTT and CHT diagrams of resins by themselves or on noninteracting substrates show similar trends as exemplified by the case of epoxy resins on glass fibers [42,43] (Fig. 8a). Different trends than those for TTT and CHT diagrams of epoxy resins reported in the literature (Fig. 8a) occur, however, in the higher and lower temperature zones of the diagrams of waterborne formaldehyde-based resins hardening on wood. CHT and TTT diagrams have already been reported for PF, UF, MUF, phenol–resorcinol–formaldehyde (PRF), and tannin–formaldehyde thermosetting resins [31,44–46] (Figs. 8b and c). The higher temperature zone of the CHT diagrams for MUF resins in a wood joint, reported in Fig. 8c, shows the same trends (and for the same reasons, namely the interactive nature of the substrate and movement of water from resin to substrate and vice versa) observed for UF and PF resins.

However, the experimental TTT diagram in Fig. 8b shows quite a different trend from the CHT diagram for the same resins and for the TTT diagrams reported in the literature for epoxies on noninteracting substrates such as glass fiber. To start to understand the trend shown in Figs. 8b and c it is first necessary to observe what happens to the modulus of the wood substrate alone (without a resin being present) when examined under

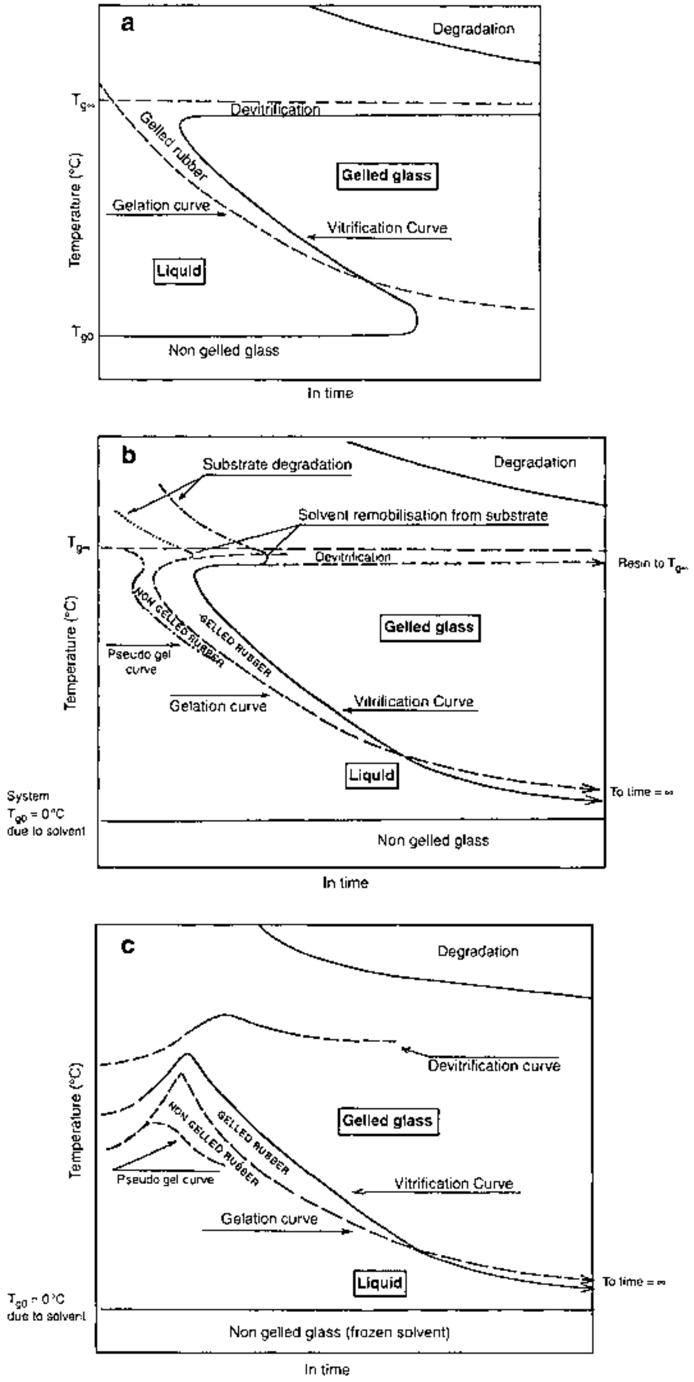


Figure 8 (a) Schematic classical TTT and CHT curing diagrams of epoxy resins and any other polycondensation resin, such as MUFs, on a nonreactive, noninterfering substrate. (b) Schematic TTT curing diagram of MUF, PRF, UF, and PF wood adhesives on wood as an interacting substrate. (c) Schematic CHT curing diagram of PRF, MUF, UF, and PF wood adhesives on wood as an interacting substrate.

the same conditions of a wood joint during bonding. No significant degradation occurs up to a temperature of 180°C as shown by the relative stability of the value of the elastic modulus as a function of time. Some slight degradation starts to occur at 200°C, but after some initial degradation the elastic modulus again settles to a steady value as a function of time and at a value rather comparable to the steady value obtained at lower temperatures. Evident degradation starts to be noticeable in the 220–240°C range and this becomes even more noticeable at higher temperatures. The effect of substrate degradation on the TTT diagram in Fig. 8b can then only start to influence the trends in gel and vitrification curves at temperatures higher than 200°C and it is for this reason that the region of the curves higher than 200°C is indicated by dashed lines in Fig. 8b. At a temperature $\leq 200°C$ the trends observed are due to the resin only. In this range of temperature the eventual turning to longer time and stable temperature of the vitrification curve, characteristic of the TTT diagrams of epoxy resins, becomes also evident for the TTT diagrams of the waterborne PRF and MUF resins on lignocellulosic substrates indicating that diffusion hindrance at a higher degree of conversion becomes for these resins too the determinant parameter defining reaction rate. What differs, however, from previous diagrams is that the trend of all the curves, namely the gelation curve, initial pseudogel (entanglement) curve, and start and end of vitrification curve is the same. In epoxy resin TTT diagrams the trend of the gelation curve is completely different from that reported here. The result shown in Fig. 8b is, however, rather logical because if diffusion problems alter the trend of the vitrification curve, then the same diffusional problem should also alter the gelation and pseudogel curves. This is indeed what the experimental results in Fig. 8b indicate. It may well be that in waterborne resins the effect is more noticeable than in epoxy resins. This is the reason why it is possible to observe it for PF, UF, PRF, and MUF resins. With the data available and with the limitation imposed by the start of wood substrate degradation of higher temperatures it is not really possible to say if the gelation curve and the vitrification curve run asymptotically towards the same value of temperature at time $=\infty$ although the indications are that this is quite likely to be the case. What is also evident in the trend of the two curves is the turn to the left, hence the inverse trend of their asymptotic tendency towards $T_{g\infty}$. This turn cannot be ascribed to substrate degradation because for very reactive resins, such as PRFs, such a turn already occurs at a temperature lower than 150°C, hence much lower than the temperature at which substrate degradation becomes significant. This inverse trend can only be attributed to movements of water coming from the substrate towards the resin layer as the trend of the curves indicates an easing of the diffusional problem already proven to occur at such a high degree of conversion [30,39].

Two other aspects of the TTT diagrams in Figs. 8b and c must be discussed, these being the trend of the curves at temperatures higher than 200°C and the trend of the devitrification (or resin degradation) curve. The dashed line trend and experimental points of all the curves at temperatures higher than 200°C are clearly only an effect caused by the ever more severe degradation of the substrate: degradation of the substrate implies a greater mobility of the polymer network constituting the substrate, hence the continuation of the curves as shown in their segmented part. That this is the case is also supported by the virtual negative times yielded by the TMA equipment when the temperature becomes extreme, as well as by the trend of the resin's higher degradation curve which tends to intersect the vitrification curve at about 200–220°C or higher, this being a clear indication that one is measuring the changes in the reference system, the substrate itself, and that these are at this stage so much more important than the small changes occurring in the resin as to be able to dominate the whole complex system which is the bonded joint.

The CHT and TTT diagrams pertaining to waterborne formaldehyde-based polycondensation resins on a lignocellulosic substrate should then appear in their entirety as shown in Figs. 8b (TTT) and 8c (CHT) rather than as the classical diagrams of epoxies on noninterfering substrates such as glass fiber shown in Fig. 8a.

VII. COLD-SETTING MUF ADHESIVES

MUF resin can be used as a cold-setting wood laminating adhesive for glulam and fingerjointing by the use of adequate acid hardeners. In all semiexterior and protected exterior structural applications where a clear/invisible glue line is preferred for aesthetic reasons then a MUF adhesive is preferred to the classical PRF adhesives used for this purpose. It is then more a question of fashion cycles, but notwithstanding this MUF resins have taken a considerable hold today in Europe (contrary to North America where PRFs are by far preferred) and confidence in them for this application has been steadily growing.

PRF "honeymoon" fast-set, separate application adhesives for exterior-grade structural glulam and fingerjointing have now been used industrially for about twenty years [1,8] in several relevant variations developed over the years. MUF resins are now taking the same "honeymoon" direction: the use of a melamine resin and a resorcinol separate component system [47] has been reported. However, for all the improvements made to the commercial MUF resins of this type in all their different variations, they were still based on some resorcinol or resorcinol-aided component. Thus, using as one component a MUF resin of high melamine content and resorcinol as a second component is just unusual in its use of a MUF rather than a PRF resin; a very acceptable resin concept but for the fact that it is coupled with a phenol such as resorcinol. The coupling of an acid-setting MUF adhesive and of resorcinol might well present no advantages or even some potentially serious disadvantages. It has been shown for example that thermosetting PMUF resins do not present a better performance than equivalent MUF resins and that often, depending on their sequence of manufacture, present instead a much worse performance. There are very well-defined technical and chemical reasons for this [19,20] that boil down to the relevant differences in reactivity of the two materials, namely the phenol (here resorcinol) and melamine. The reactivity of melamine and even urea at the acid-setting pHs they need is much greater than that of any phenol, even resorcinol, as this pH range is that of the lowest reactivity of any phenol. Thus, even resorcinol runs the risk of being linked very little to the MUF matrix, especially in a fast-setting system such as a honeymoon, and at best it will remain as a bypassed pendant side group not able to fully achieve the function for which it has been added.

More recently an exclusively MUF-based honeymoon adhesive for glulam and fingerjoints has been developed and reported in which one component is a high performance MUF resin, while the second separate application component is based on just slightly acidified water thickened to the same viscosity of the first component by the addition of 1.5% carboxymethyl cellulose (CMC) [48,49] (Fig. 9). The system has also been tried successfully in industry for both fast production of fingerjointing (Fig. 10) and glulam and also for the fast production of ambient temperature pressed plywood [48,49]. MUF-based, honeymoon-type, fast-setting, separate application adhesive systems which do not need any resorcinol are then capable of performing as adhesives for structural exterior-grade joints and glulam and of satisfying all the requirements of the relevant adhesive specifications for such an application. The parameters that were shown to be determining are mainly the performance of the MUF resin, if and once an excellent resin formulation is

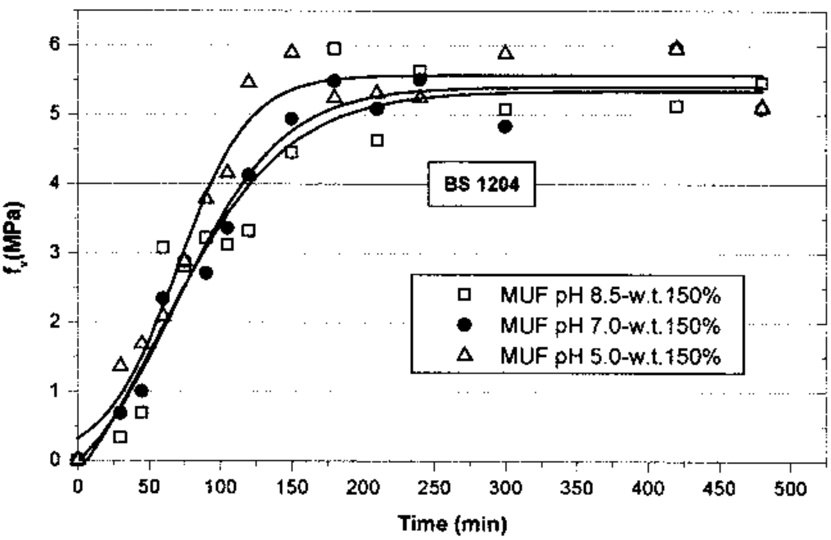


Figure 9 Tensile strength increase as a function of time of beech joints (BS 1204, Part 1) bonded with MUF-based honeymoon adhesive systems: effect of the variation of the initial application pH of the resin (component A).

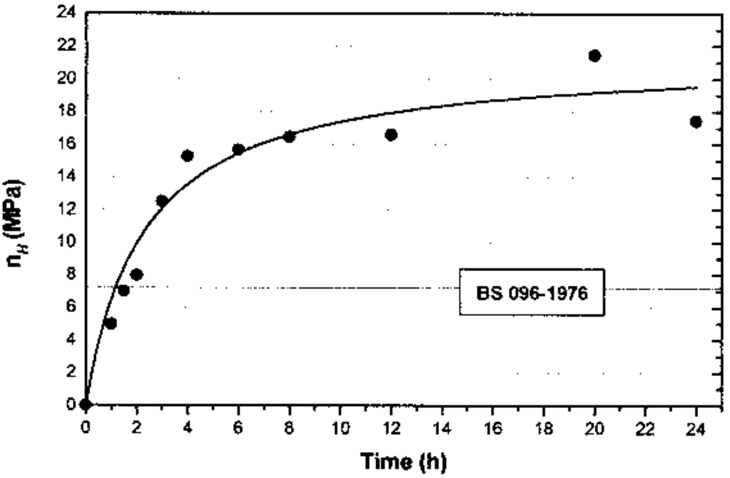


Figure 10 Four-point bending strength increase as a function of time of pine (*Pinus sylvestris*) fingerjoints bonded with MUF-based honeymoon adhesive systems.

available both the ratio of melamine to urea and the molar ratio having a lesser effect, performance only starting to drop lower than the requirements of relevant standards when M:U weight ratios fall well below 20:80 and of the order of 10:90. Addition of resorcinol at these failing levels while improving slightly the performance did not solve the problem; resorcinol addition then does not allow specification requirements to be satisfied [48,49].

At the higher M:U ratios such as M:U = 47:53, but even at lower melamine contents, addition of resorcinol does not improve the results at all, its addition again revealing itself superfluous. The reasons for such a behavior are those already presented and explained above. The MUF honeymoons present all the other usual advantages associated with honeymoon adhesives, namely high curing rate, long pot life, tolerance to higher moisture content of the substrate, and tolerance to even quite severe imbalances in viscosity and proportions between the two components.

VIII. CHEMICAL AND PHYSICAL ANALYSIS

The analysis of these resins is difficult when unknown products, particularly fully cured have to be tested for UF and MF resins. Widmer [50] offers a method for the identification of UF and MF resins in technical products. This involves preparing crystalline products of urea and melamine and identifying them under the microscope. Melamine (in the form of melamine crystals) and urea (in the form of long, crystalline needles of urea dixanthate) can be seen. This method allows one to distinguish between urea and melamine even in a cured adhesive joint.

Quantitative determination of MF resins is also rather difficult. A method was developed by Widmer [50] for the quantitative determination of melamine in MF condensation products. In this method the resins are destroyed under pressure by aminolysis leaving the melamine intact. This is then converted to melamine picrate, which is easily crystallized and weighed. The Widmer method makes it possible to determine quantitatively the presence of urea and melamine in intermediate condensation products and in cured UF and MF resins (even when they have been mixed). Estimations are seldom in error by more than a few percent.

Hirt et al. [51] have published an effective and rapid method for the detection of melamine by ultraviolet spectrophotometry. This method can be used for products containing MF. It makes use of the strong absorption of the melamine ion at 235 nm. The resin is extracted from comminuted MF samples by hydrolyzing to melamine by boiling under reflux in 0.1 N hydrochloric acid. Stafford [52] also gives a method for the identification of melamine in wet-strength paper.

Uncured MF resin analyses are carried out by gel permeation chromatography (GPC) and ^{13}C NMR. GPC was an inconvenient method for MF resins, although it has become much more accepted for this purpose in recent years. Dimethylformamide, dimethylsulfoxide, or salt solutions are generally used as solvents with a differential refractometer as a detector. Derivatives of the resin, such as those obtained by silylation, are generally used to decrease molecular association by hydrogen bonding. ^{13}C NMR is a more convenient technique, and the chemical shifts of the different structural groups in the resin can easily and readily be identified [52,61]. This method is also quite convenient in comparing MF and MUF resin structures obtained by different manufacturing methodologies [52–61].

More recently effective equations correlating the results obtained by liquid-phase ^{13}C NMR of the liquid MF and MUF resin before hardening with the strength and degree of cross-linking of the resin in the hardened state, hence of the IB strength and formaldehyde emission of boards bonded with them were developed and reported by two different groups [41,62–64]. One set of equations applied to different formulations can be used to determine the chemical characteristics of the resin without knowing anything of its manufacturing parameters, procedures or molar ratio [63,64] while a different set of equations from a different group requires the previous knowledge of the molar ratio of the resin [62]. They are both very useful tools for the characterization of such resins.

Recently, thermomechanical analysis (TMA) has been used to characterize the performance of polycondensation resins, including MF and MUF adhesives, by correlating the deflection in bending of a beech wood joint bonded with a thermosetting resin with the IB strength the same resin can give when used to prepare a wood particleboard under given, industrially significant conditions [15,18,48] according to the equation $\mathrm{IB} = a\,(1/f) + b$, where f is the deflection obtained by TMA in three-point bending and a and b are coefficients characteristic of the type of resin used [65–67]. The experiments can be performed on a preprepared joint in isothermal mode or starting with the liquid glue between the veneer substrates in nonisothermal mode and hence following the hardening of the resin in situ within the joint. What is measured is the narrowest deflection of the cured composite joint at whatever temperature this is achieved, this being correlated through a factor with the inverse of the modulus of the bonded joint, as well as the increase of modulus as a function of time or temperature characterizing in situ the kinetic performance of a particular MUF or MF resin. The system can also give the characteristics of the resin-hardened network by calculation of both the energy of adhesion of interaction with the substrate as well as the level of tightness of the hardened network through the average size of segments between cross-linking nodes (and entanglement nodes) [68–70].

MF and today also MUF resins produce high quality plywood and particleboard because their adhesive joints are boilproof. Considerable discussion has occurred and many investigations have been carried out on the weather resistance of MF and MUF adhesives. Many authors uphold the good weather resistance of the more recently developed MF and MUF adhesives, especially those in which small amounts of phenol (PMUF or MUPF) have been incorporated. The more general trend, however, is to consider the wood products manufactured with these resins as capable of resistance to limited weather and water exposure only, such as in flooring applications, rather than being capable of true exterior-grade weather resistance for which phenolic adhesives are preferred. Figure 11 shows the different behavior of traditional older generation MF-bonded and PF-bonded particleboard in a series of wet–dry cycles. Whereas PF-bonded boards initially deteriorate rapidly then stabilize to a constant swelling value, MF particleboards have slower initial deterioration but never stabilize and continue deteriorating with time and additional wet–dry cycles. This indicates that MF-bonded

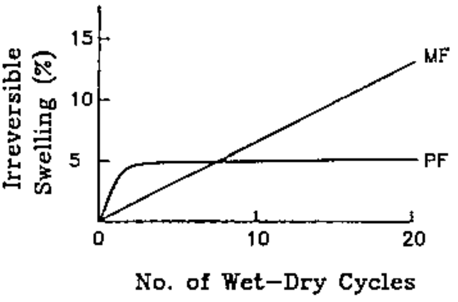


Figure 11 Typical trends of irreversible thickness swelling characteristics of wood particleboard bonded with MF and PF adhesives during a wet–dry cycle test.

wood is not completely impervious to further water attack, indicating the fundamental susceptibility of the aminoplastic bond to water. The rate of deterioration, and therefore bond hydrolysis, increases as the temperature increases. Considering the insolubility of melamine in cold water, this is quite understandable. Recent developments in MUF resins (as indicated in this chapter) have, however, introduced a question mark over this rather conservative definition of the weather resistance of MF and MUF resins in relation to phenolics, and clear indications exist that with wise formulation MUFs can indeed perform as fully fledged, heavy-duty exterior adhesives capable of competing successfully with both phenolic and diisocyanate resins.

IX. FORMULATIONS

For starting experiments in MF resins, the following formulations are suggested.

A. MF Formulation for Exterior Particleboard

In a reaction vessel charge at 25°C, 44.4 parts by mass of water, add 30% NaOH solution to pH 11.2 to 12.0, followed by 15.5 parts of 91% paraformaldehyde prills, 34.4 parts of melamine powder, 2.8 parts of caprolactam, and 2.5 parts of *N*,*N*′-dimethylformamide while maintaining the temperature at 25°C; heat in ± 40 min to 92 to 95°C. When the temperature reaches 80°C, adjust the pH with 30% NaOH solution, if necessary, to pH 9.9. At 93°C, cool to 90°C and maintain the temperature there. Adjust pH to 9.55 to 9.65 with formic acid. Hold the pH at this value while checking, adjusting, and recording the pH value every ± 10 min. Check for the turbidity point at 10-min intervals until the turbidity point is reached. At this time bring pH up to 9.95 to 10.05. Check, adjust, and record the pH every 10 min. Start distilling water under vacuum to a solid of ± 53 to 55%. Check the water tolerance at 10-min intervals until it is 170 to 180%. Then apply full vacuum and cool the resin to 30 to 35°C.

B. Formulation for Low-Pressure MF Paper-Impregnated Overlays

Follow the same procedure as for formulation A, but at the end of the water vacuum distillation add 1.7 to 1.9 parts by mass of the second melamine and heat the reaction mixture to 95°C again and maintain this temperature for 5 to 6 min, then cool rapidly.

C. MUF Formulation for Exterior Particleboard

This sequential MUF formulation can be successfully manufactured at different (M + U):F molar ratios according to exactly the same procedure, and not only for the proportions as indicated in the example that follows. Thus the same formulation gives excellent results for example at (M + U):F molar ratios of 1:1.5 and 1:1.7, but not only these ratios. For more MUF formulations see references [8,11,38].

To 113 parts by weight of Formurea (a formaldehyde concentrate stabilized by urea, of mass content 57% formaldehyde and 23% urea. NB: Formurea comes in other concentrations too) are added 13 parts of urea and 30 parts of water. The pH is set at 10 to 10.4 and the temperature brought to 92 to 93°C under continuous mechanical stirring. The pH is then lowered to 7.8 and the reaction continued at the same temperature, allowing the pH to fall by itself over a period of 1 h 30 min to 1 h 35 min to a pH of 5.2 (one should strictly prevent the pH falling under 5 to avoid both uncontrollable reactions taking hold as well as a decrease in the finished adhesive performance later). To bring the pH back to 9.5 or higher, 22% NaOH water solution was added, followed by 41 parts by weight of melamine premixed with 19 parts of water. One part of dimethylformamide and 2 parts of diethylene glycol are then added to the reaction mixture, maintaining a temperature of 93°C. The water tolerance is checked every 10 min while the pH is allowed to fall by itself. When the water tolerance reached is 180 to 200% (this is often reached after 35 to 40 min, and the pH reached is of 7.2), 6.5 parts by weight of second urea is added and the pH is again brought up to 9.5. The reaction is continued until the water tolerance reached is lower than 150% (the pH has reached generally 7.7 at this stage). The pH is then corrected to 9–10.2 again and the reaction mixture cooled and stored. Resins produced using this procedure have solids contents of 58 to 65%, a density of 1.260 to 1.280 at 20°C, a viscosity of 70 to 150 cP, free formaldehyde of approximately 0.32, and gel times with 3% NH_4Cl of 51 to 57 s at 100°C. Increasing and lowering of pH where the pHs indicated are not reached by the reaction time can be done by addition of 22 to 33% NaOH water solution (pH increases) and by addition of formic or acetic acid (pH decrease). The preparation diagram of this resin is shown in Fig. 4.

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33

Isocyanate Wood Binders

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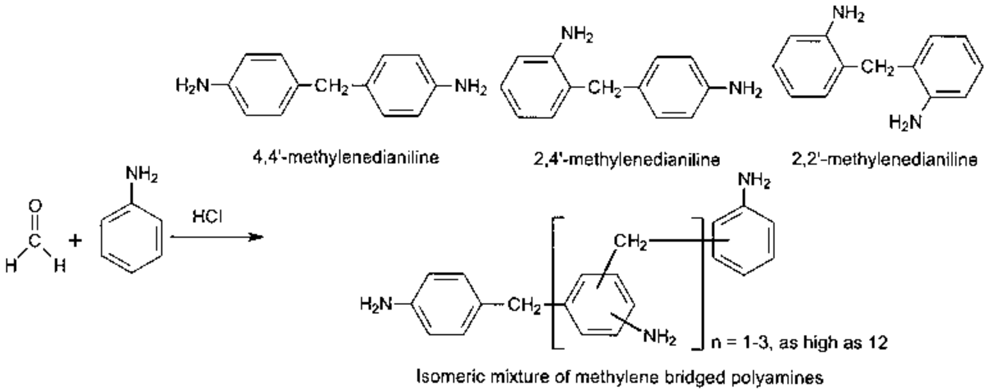
I. INTRODUCTION

Over the last thirty years, the forest products industry has increasingly embraced isocyanate wood binders. This trend is partly due to the tremendous growth of the worldwide polyurethane industry. Central to this growth has been the demand for the aromatic monomer diphenylmethane diisocyanate (MDI), and the associated methylene bridged polyphenyl polyisocyanates known as polymeric MDI (pMDI). Both products are valued for the manufacture of many polyurethane and urethane/urea polymeric products. MDI and pMDI cater to different markets because of differences in functionality, reactivity, and structure. These differences will become evident later. The vast majority of the polyisocyanates are used for the production of rigid foams. However, when polymeric MDI was proven effective for particleboard manufacture (in the late 1960s and early 1970s [1]), a relatively small, but significant, market was born. As the polyurethane industry grew, the forest products industry was developing new composite technologies. In particular, oriented strandboard (OSB) improved wood utilization efficiency because lower quality logs and alternative woods could be used to manufacture panels that were competitive in plywood markets. OSB production grew and stimulated additional technologies, such as laminated strand lumber, and I-beams made with OSB webs. The rapid expansion of strand based composites was an opportunity that the polyurethane industry captured; MDI based polyisocyanates afforded many advantages for strand based wood composites. However, the isocyanate binders have not secured the entire market for reasons that we shall discuss. Currently, isocyanate wood binders are primarily used for the production of OSB and related strand products; however, they may also be used for other materials such as particleboard and medium density fiberboard. The following is an overview of the use of isocyanate wood binders in the forest products industry.

II. CHEMISTRY OF ISOCYANATE WOOD BINDERS

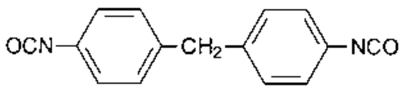
A. Synthesis and Characterization

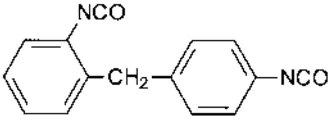
Within the forest products industry, polymeric MDI competes against the formaldehyde based thermosets such as urea–formaldehyde, melamine–urea–formaldehyde, and phenol–formaldehyde. Interestingly, the isocyanate wood binders are also based upon formaldehyde. Their preparation begins with the HCl catalyzed condensation of formaldehyde with aniline, as shown below [2,3].

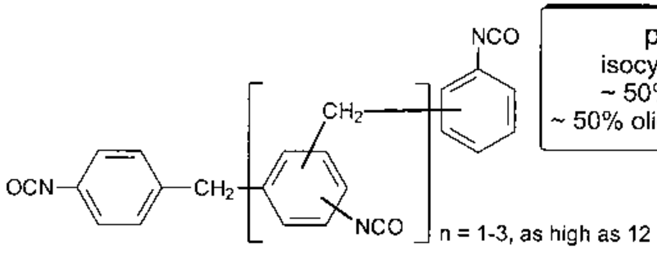


The scheme above belies the complexity of the reaction; see Twitchett's discussion for the detailed mechanism [2]. The overall reaction between formaldehyde and two moles of aniline produces the 4,4′-, 2,4′-, and 2,2′-isomers of methylenedianiline. These diamine isomers will react to form the higher methylene bridged polyphenylene polyamines. It has been stated that 2,4′- and 2,2′-methylenedianiline are preferentially consumed for the production of the higher polyamines [4,5]. The author is unaware of any published work to this effect, but such a preferential reactivity is expected from the steric influence on electrophilic aromatic substitution. It is certainly true that under typical industrial conditions the resulting monomer fraction is mostly 4,4′-methylenedianiline, with 2 to 7% of the 2,4′-isomer and lesser quantities of the 2,2′-isomer. The 2,4′- and 2,2′-isomer levels may be dramatically increased with elevated reaction pressures and heterogeneous catalysis [6,7]. Otherwise, the composition of the polyamine mixture can be altered through several variables including the aniline to formaldehyde ratio, the aniline to HCl ratio, and temperature [2,5].

The acidic polyamine mixture is neutralized and dried in preparation for reaction with phosgene. The phosgene reaction (phosgenation) occurs in high boiling aromatic solvents such as chlorobenzene or 1,2-dichlorobenzene [2,4]. Phosgenation converts the amino groups into isocyanate; so the isocyanate molecular structure is a reflection of the polyamine. Large stoichiometric excesses of phosgene are used to help avoid undesirable side reactions [2,4]. These side reactions may lead to the formation of substituted ureas, biurets, polyurets, carbodiimides, and related chlorine containing compounds [2,4]. Afterwards, the solvent is stripped away and the isocyanate mixture is subjected to distillation for the isolation of the 4,4′-MDI monomer. The remaining nonvolatile residue is the wood binder known as polymeric MDI; it is a mixture of MDI monomer and the related methylene bridged polyphenyl polyisocyanates. In the forest products industry the binder is commonly referred to as MDI or simply as "isocyanate." This confusion of names is further complicated by the fact that polymeric MDI is not at all polymeric. Approximately one half of the resin is diisocyanate monomer, while the rest is a complex oligomeric mixture of polyisocyanates with degree of polymerization less than 12, as depicted below.


4,4'-MDI, typically ~ 95% of monomer fraction


2,4'-MDI

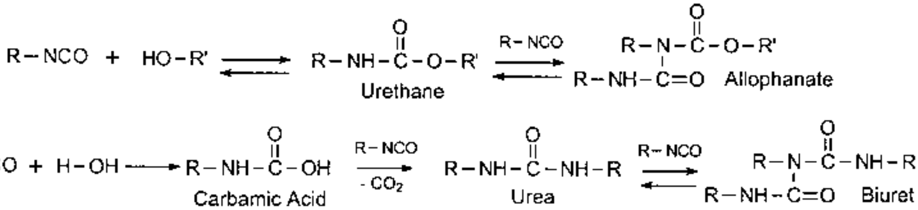

Isomeric mixture of methylene bridged polyisocyanates

polymeric MDI
isocyanate wood binder
~ 50% MDI monomer
~ 50% oligomeric polyisocyanate

Since pMDI is not distilled, phosgenation side reactions not only reduce yield but they may also impact reactivity, as all impurities remain. The best measure of purity is through the determination of the isocyanate content, or percentage–NCO. This is a simple reaction with excess dibutylamine followed by back-titration of the residual [8,9]. The isocyanate content is typically 31 to 32% for industrial pMDI. Other notable wet analytical methods are the determination of hydrolyzable chlorine, and the determination of acidity [9–11]. Both methods quantitate acidic impurities which could create problems in subsequent chemical transformations, for example acid catalysis of isocyanate reactions, or neutralization of the amine catalysts that are often used in the polyurethane industry. The isomer ratio of the monomer fraction (the relative proportions of 4,4′-, 2,4′-, and 2,2′-MDI) is readily determined with gas chromatography. Gel permeation chromatography may be performed on the underivatized resin if a dedicated system is available. Otherwise, cross-reactions between analytes may be avoided by analyzing the *N*,*N*-dibutyl urea derivative of the isocyanate. Molecular weights of typical pMDI wood binders are from about 255 to 280 g/mol number average, and about 470 to 550 g/mol weight average. Typical viscosities are correspondingly low, approximately 0.175–0.25 Pa s (175–250 cP). Finally, pMDI surface tension is approximately 41–46 mN/m. In other words, the 100% organic resin is very low in molecular weight, low in viscosity, and low in surface tension. It is no surprise that this binder wets readily and penetrates deeply into wood, as we shall discuss later.

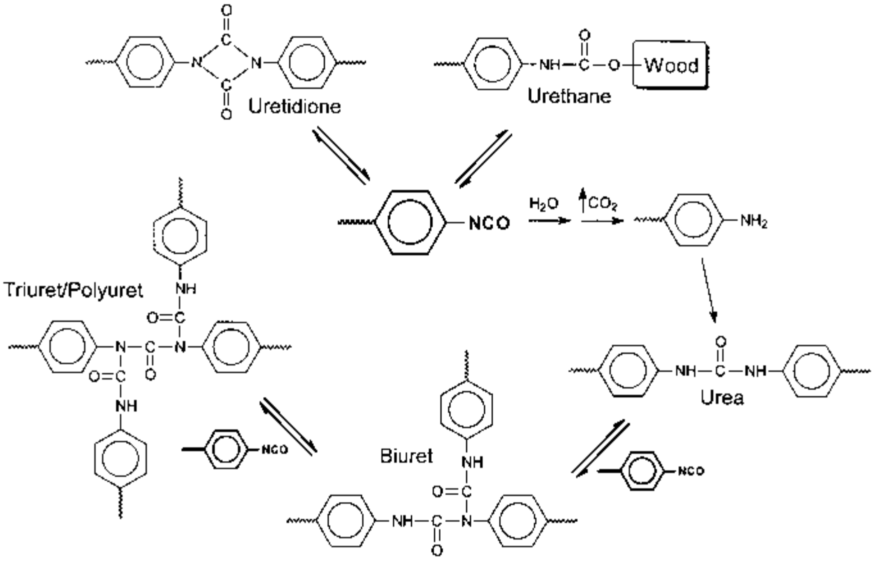
B. Cure Chemistry and Interphase Morphology

Organic isocyanates are very reactive with compounds that possess “active” hydrogens, as in the case of carboxylic acids, primary and secondary amides, primary and secondary amines, alcohols, phenols, and water. The relative reactivity of these compounds with isocyanate depends upon the nucleophilicity and steric structure of the attacking compound. Primary and secondary amines are typically most reactive, followed by primary alcohols, water, secondary alcohols, and phenols in that general order. Carboxylic acids and amides are the least reactive with isocyanate. Of course, deprotonation may increase nucleophilicity. For example, a phenoxide anion will be much more reactive than a phenol, and probably more reactive than a primary alcohol. Regarding the isocyanate, one should realize that the various NCO groups in pMDI also have variable reactivity. Isocyanate groups without ortho substitution (nothing ortho to the NCO group) are more reactive than the ortho substituted NCO groups. Consequently, 4,4′-MDI is more reactive than 2,2′-MDI. Furthermore, and on average, pMDI is less reactive than the pure 4,4′-MDI because the oligomeric polyisocyanates have ortho substituted NCO groups as shown above; this assumes reaction in the liquid state. Reactions most pertinent to wood bonding are with alcohols, phenols, and water, as shown below in general outline.



During urea formation, note that each mole of consumed water leads to an equivalent of CO_2 gas. There has been significant controversy surrounding the precise nature of pMDI–wood cure chemistry, which continues even today. The importance of urethane formation with wood has long been recognized; such a linkage will enhance weather durability. However, the abundance and mobility of water vapor during panel hotpressing could preferentially promote urea formation. The significance of urethane formation has been debated in the literature since 1975, and possibly earlier [12–17]. Some have argued that urethane formation is unlikely [17], while others have predicted some combination of urea and urethane formation [12–16]. Wittman is credited with making one of the first analytical contributions to this issue [18]. By measuring CO_2 production during panel hotpressing, Wittman showed that about 50% of the applied pMDI was consumed by polyurea formation. Thus it has long been established that the essence of pMDI cure is the reaction with water to form a polyurea network. In other words, pMDI wood binders are two-part systems where wood water is the second integral component. However, we are still uncertain of the significance of urethane formation, although this may be a moot point. Polyureas are unsurpassed in their capacity for hydrogen bonding, and they have excellent thermal and hydrolytic stabilities. Consequently, polyurea networks will adhere strongly to wood through secondary forces. Under current industrial practice, it may be safe to say that the incidence of urethane formation is little more than an academic issue. However, the future will no doubt provide ever advanced materials from wood, so the detection and promotion of urethane formation will become more than an academic exercise. A brief review of the search for urethane formation follows immediately.

Some investigators have analyzed wood–pMDI cure using differential scanning calorimetry [19,20]. This method demonstrates that wood has a significant impact on the heat of pMDI cure. However, calorimetry cannot identify cure reactions; so chemical identifications are highly suspect when based upon this method. Others have used infrared (IR) spectroscopy. For example, Weaver and Owen used IR to reveal the reactions of glucose, cellulose, lignin, and wood with phenyl isocyanate and pMDI [21]. They found that urethanes formed more readily with lignin than with cellulose, but that the water reaction was predominant in all cases. Urethanes were only detected when huge excesses of isocyanate were used [21]. Rosthauser et al. conducted a thorough model study and an in situ IR analysis; a remote sensing fiber optic probe was imbedded in laboratory scale particleboard bonded with pMDI [22]. Based upon carbonyl stretching, the authors claim no indication of urethane formation [22]. However, IR identifications within a wood particle mat are complicated by two effects: (1) signal overlap, and (2) the lack of dependable reference spectra that accurately represent conditions within the mat. The study by Rosthauser and colleagues also showed that uretidione formation (isocyanate dimerization) might be more important than previously suspected [22]. Others have used isotopic labeling coupled with nitrogen-15 solid-state nuclear magnetic resonance (NMR) to directly probe the cure chemistry of intact bondlines [7,23–25]. This method reveals that biuret and polyuret formation is very common, that bondline chemistry is very sensitive to cure time and temperature, and that even the wood species may affect cure chemistry. These findings suggest that bondline chemistry (and thus performance) will vary according to the local conditions through the thickness of the wood composite. Unfortunately, nitrogen-15 solid-state NMR cannot clearly detect urethane formation because the urea and urethane nitrogen signals are almost perfectly overlapping. Indirect evidence for urethane formation has been found through relaxation measurements [7]. From the same study, it was suggested that the putative urethane linkages were subject to thermal cleavage, consistent with the thermal instability known of aromatic urethanes. All of the previously described work has a common shortcoming—there is no unambiguous method to detect urethanes. This failing may be resolved with another solid-state NMR strategy that builds upon the nitrogen-15 method. It was recently shown that urethanes were detectable when the pMDI wood binder was prepared with a double isotopic label, e.g., nitrogen-15 and carbon-13 in the isocyanate group [26]. Using small flake samples, this study found: (1) that urethane formation was abundant with cure conditions of 3.45 MPa (500 psi), 22–165°C, and 3 min cure time, (2) that urethane linkages in the wood bondline were subject to thermal cleavage above 165°C, and (3) that the industrial significance of these findings remained to be seen [26]. In other words, the double label method may provide the final answer, but it has yet to be conducted under pilot scale conditions that better reflect industrial practice. Nevertheless, the abundance of urethane seen in this study was striking [26]. The probable cure chemistry of the pMDI–wood bondline is depicted below, but again much is still unknown.



If urethanes are common, we should also expect allophanate formation. However, reliable confirmation of this reaction may never occur due to interference from structurally similar linkages such as biurets. Besides, the extreme thermal instability of allophanates may preclude their contribution to bonding. Biurets and urethanes are substantially more thermally stable, in that order. Furthermore, alkyl urethanes (which arise from alcohols) are more stable than aryl urethanes (arising from phenols). Of course, both alkyl and aryl urethanes are possible with wood. As mentioned, ureas are very stable; their formation is essentially irreversible. While the thermal cleavage of urethane and biuret linkages has been demonstrated, the corresponding effect on bondline performance has not been determined. In any event, it is clear that all of these chemistries promote hydrogen bonding with wood. Regardless of how important urethane formation might be, it is certain that pMDI wood binders promote strong secondary interactions with wood. As with most adhesives, secondary interactions are completely adequate for dry strength properties. In other words, the dry strength of unweathered pMDI bonded composites reveals nothing about urethane formation. Only durability will be impacted by hydrolytically and thermally stable covalent bonding.

The debate over urethane formation in the wood/pMDI bondline may soon yield to studies of the peculiar morphology of this interphase. Recall that pMDI is a low viscosity, low molecular weight, low surface tension organic liquid. Consequently, pMDI wood binders readily wet and deeply penetrate into wood, as demonstrated by Shi and Gardner [27]. In fact the deep penetration of pMDI into wood contradicts traditional views on wood adhesion. The truly polymeric wood binders such as phenol–formaldehyde (PF) and urea–formaldehyde (UF) are formulated for only moderate levels of wood penetration; overpenetration is undesirable with these resins. By traditional standards, pMDI wood binders overpenetrate and yet they perform as well or better than other wood binding thermosets. One then wonders what becomes of the resin that does not span the gap between bonded wood particles? Does it polymerize into a bulk phase within wood cell lumens, providing no benefit? Or does the deep penetration provide some performance gain? How deep is the penetration?

Certainly, pMDI flows into the micrometer size voids of wood via capillary action. Furthermore, it is apparent that penetration occurs down to the angstrom scale. In other words, pMDI actually penetrates into the amorphous components of the wood cell wall, mixing on the molecular level. The wood cell wall plasticization by pMDI was first demonstrated by Marcinko et al. with aspen (*Populus tremula*) wood using solid-state NMR [28]. The corresponding wood swelling caused by pMDI can be measured using a thermomechanical analyzer, an instrument capable of measuring minute dimensional changes. For example, Figure 1 shows a swelling profile of a small block of aspen wood in pMDI. The maximum swelling is slight, about 0.48%; nearly half of this swelling occurs within 5–10 min.

The swelling by pMDI of the amorphous wood polymers has interesting implications for the interphase morphology. With pMDI monomers and oligomers dispersed among amorphous wood chains, the subsequent cure might provide a type of interpenetrating polymer network (IPN) where a synthetic polyurea/biuret network interpenetrates amorphous wood polymers [29]. Urethane formation may then be less important because the disruption of an IPN morphology would require covalent bond cleavage. Proof for the IPN morphology is not yet available, but supporting evidence appears in the literature. For example, Marcinko and coworkers have shown that cured pMDI restricts wood polymer motions according to dynamic mechanical analysis and solid-state NMR [30,31]. Furthermore, the literature suggests that pMDI wood binders impart dimensional

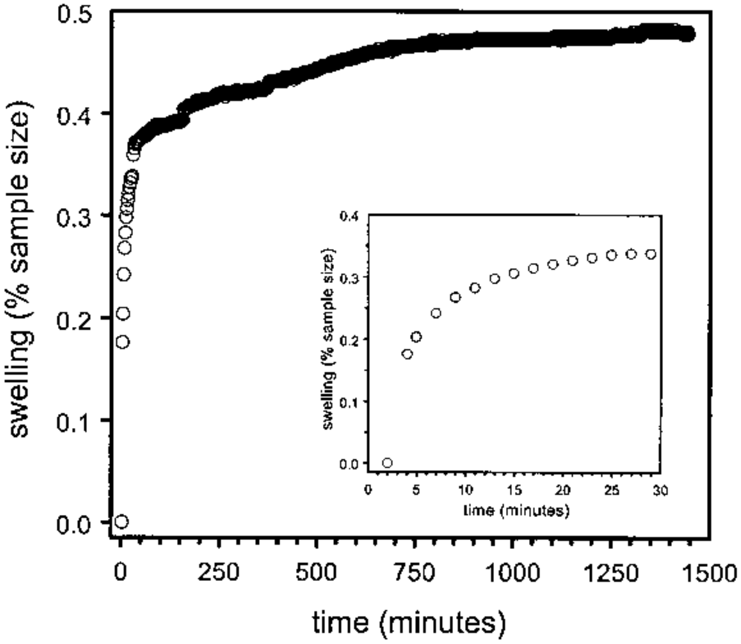


Figure 1 Percentage swelling of a 5 mm × 8 mm × 5 mm oven dry block of aspen wood immersed in liquid pMDI, measured at $24.3 \pm 0.4°C$ in air, in the tangential direction using a thermomechanical analyzer. The inset shows the initial 30 min.

stability and thickness swell resistance to wood panels [13,32,33]. Such moisture resistance would be consistent with the hypothetical IPN interphase morphology, but not proof.

It is also possible that the cured adhesive may exhibit phase heterogeneity that could impact mechanical properties, toughness in particular. The predominant chemical linkages within the pMDI/wood bondline appear to be urea and biuret/polyuret. Nitrogen-15 solid-state NMR studies suggest that these chemical groups may exist separately within nanometer scale phases [7,25]. One study demonstrated the onset of phase heterogeneity only after extended cure times [7]; while another found phase heterogeneity at shorter cure times, more representative of industrial practice [25]. This issue requires additional study because the NMR pulse sequence (which was different in the above-mentioned works) has a strong influence on the detection of phase separation in the wood/pMDI bondline [34]. Finally, recent work raises the possibility that crystallinity may develop during pMDI cure [35,36]. Such crystallinity is known to occur in MDI based elastomers. Since pMDI is about 50% MDI monomer, crystallinity formation in the pMDI/wood bondline is a reasonable hypothesis. Additional research will shed light on this interesting possibility.

III. TECHNOLOGY OF ISOCYANATE WOOD BINDERS

A. General Principles

While pMDI wood binders are derived from formaldehyde, they are distinguished from other wood binders by a total lack of formaldehyde emission. This performance advantage has not displaced the less expensive UF and melamine–urea–formaldehyde

(MUF) adhesives, which are commonly used for particleboard and medium density fiberboard. This is a tribute to the amino resin industry which has successfully reduced formaldehyde emissions while maintaining the excellent performance of UF and MUF binders. The pMDI wood binders are labeled as highly durable exterior grade adhesives; UF and the more durable MUF binders do not receive this designation. Consequently, the higher cost pMDI is often reserved for more demanding specialty applications within the amino resin markets. Another noteworthy difference between pMDI and the amino resins is that isocyanate binders have no cold tack, i.e, no precure stickiness. Consequently, wood particle/fiber mats sprayed with pMDI lack any precure integrity which is required with certain particleboard or MDF handling systems. Also, pMDI binders are not affected by the buffering capacity of wood, which has a significant influence on waterborne amino resins. Similar to the amino resins, pMDI provides a colorless bondline.

A colorless bondline is occasionally a consumer perception benefit as compared to PF resins which produce dark bondlines. PF wood binders are the industry standard exterior grade thermosets. As an older and firmly established technology, PF resins are the primary competition to pMDI. This competition is planted squarely in the OSB industry. Neat pMDI binders do not compete with PF in veneer based products such as plywood and laminated veneer lumber; the gap filling requirements in these products exceed the capabilities of neat pMDI. In contrast, OSB production uses thin wood strands that are compacted under high pressures, conditions which favor the deeply penetrating isocyanate binders. On an equal resin solids basis, pMDI adhesives are equal or superior to PF binders in all aspects of OSB performance. However, in comparison to liquid PF resins, pMDI binders are often used at lower resin solids levels. In commodity OSB manufacture, liquid phenolics may be used at about 3.5% resin solids on dry wood; powdered phenolics may be as low as 2% which is about equal to the lowest levels used for isocyanate binders. The upper limit of pMDI application is about 6–8% on dry wood, which is reserved for certain specialty products. The pMDI binders cure faster than standard single component PF resins, which is a significant advantage in commodity markets where profits hinge upon production rates. These differences (% resin solids and cure speeds) complicate the inevitable comparisons between PF and pMDI. For example, the rapid cure speed of pMDI may result in a 10–25% reduction in hotpress time as compared to PF binders. While this is beneficial for commodity production, one must realize that this also results in a 10–25% reduction in the hygrothermal compression of bulk wood, irrespective of bond formation. Hygrothermal compression of wood (compression of steam plasticized wood under elevated temperature) is known to impact bulk wood properties, often with great benefit [37]. Presently, the benefits of extended OSB hotpress times are not thoroughly understood. The point here is that the effects of rapid cure speed may extend beyond simple reductions in hotpress time, e.g., wood properties may also change, producing effects that are independent of the wood binder.

A clear disadvantage of pMDI wood binders is that they adhere strongly to nearly all surfaces, including steel. Consequently, external release agents are required to prevent adhesion between press platens and boards. The separate application of release agents is a process nuisance which has stimulated research on “internal” release agents, i.e., additives mixed directly into the pMDI binder. Unfortunately, no one has yet developed a truly effective internal release system. This is not surprising; just consider the difficulty in developing selective adhesion. While effective internal release technologies may never become a reality, significant efforts are still directed towards the improvement of external release agents. Current external release agents are based upon waxes or soaps, each having strengths and weaknesses [38,39]. Waxes lead to an organic build-up requiring maintenance downtime for removal and cleaning. While this build-up is undesirable, it is a safeguard against mistakes, misapplications, or incomplete applications of the release agent because the build-up is nonadherent. On the other hand, soaps (simple alkali fatty acid salts) are effective without causing an organic build-up. Unfortunately, soaps are unforgiving release agents; mistakes, misapplications, or incomplete applications will result in adhesion between panel and platen. The adhesion of pMDI to steel has undoubtedly inhibited the growth of this binder in the OSB industry. In fact, this problem has actually resulted in a marriage of PF and pMDI binders. OSB is produced with distinct layers, so manufacturers often use PF resin in the face layers, with pMDI in the core.

Liquid PF resins are particularly effective in the face layers because their close proximity to the platens insures rapid cure, and phenolic resins do not adhere to the platens. Additionally, PF moisture in the face layer is vaporized and driven to the core; this "steam shock" effect improves heat transfer, further accelerating the naturally rapid pMDI cure. This harmony of technologies provides increased production rates with good performance. However, the combination is subject to a pitfall. PF and pMDI incompatibilities may lead to poor bonding and even delamination in the transitional zone. This incompatibility is thought to arise from excessive caustic in the PF face layer resin. Alkali metal ions, particularly potassium, may catalyze isocyanurate formation, and/or aqueous hydroxide anions may directly consume isocyanate yielding (the conjugate base of) the free amine, resulting in urea formation [38]. Neither of these alkali hydroxide catalyzed reactions would seem problematic. However, the reactions could be counterproductive if so rapid that they occur before hotpress compaction. The precise chemical mechanism of how excessive PF caustic causes this incompatibility with pMDI has not been determined. The hypotheses presented above require verification. The PF/pMDI incompatibility is not a common problem because the resin manufacturers are aware of the need to avoid excessive caustic in the phenolic system.

The use of pMDI as an OSB core resin reveals another interesting characteristic of this binder, namely very good moisture tolerance. Core resins require moisture tolerance because steam generated during hotpressing travels to the cooler core and condenses into liquid water. Since pMDI is totally organic and water insoluble, steam and water cannot solubilize the resin; the resin is not diluted and does not suffer from "wash in" or "wash out." These phrases refer to the excessive penetration and flow of liquid PF binders that are diluted and solubilized by steam and water. The good moisture tolerance of pMDI is sometimes erroneously attributed to water consumption by resin cure. The NCO/water reaction has a minor influence on moisture tolerance, if any. The water consumed is but a small fraction of the total. A quick calculation makes this point clear. First, recognize that two moles of NCO react for each mole of water consumed, producing a mole of CO_2 and one urea linkage. Consequently, the NCO/H_2O mole ratio should be halved to estimate the percentage of water consumed; even this is an overestimate because a significant amount of NCO reacts not with water but with ureas, biurets, and probably wood. Table 1 displays the water consumed under conditions that might represent the extremes in conventionally hotpressed panels made with 100% pMDI resin.

It is apparent that water consumed through urea formation is minor under typical industrial conditions. So again, the good moisture tolerance of pMDI reflects that the binder is not water miscible.

One then concludes that pMDI binders could tolerate higher than normal wood moisture during composite manufacture. Indeed this is a desirable goal because higher wood moisture levels translate into reduced drying time with reduced energy costs and lower emissions of volatile organic compounds. Early reports claimed that wood moisture

Table 1 Conservative Estimates of Water Consumption Through Isocyanate Cure During Conventional Hotpressing

	Moles (× 100)		H_2O consumed (% total)
	H_2O	NCO	$(NCO/2H_2O) \times 100$
MC[a] = 4% Resin load[b] = 8%	22.2	6.1	13.7
MC = 4% Resin load = 2.5%	22.2	1.9	4.3
MC = 10% Resin load = 3%	55.5	2.3	2.1

[a] MC, Dry basis moisture content; for simplicity these calculations are based upon 100 g of dry wood.

[b] Resin load as a percentage of dry wood mass, assuming 32% NCO content.

contents could be as high as 25% [13,40]. Subsequent works suggest that lower moisture levels, ranging from 12 to 20%, will yield acceptable board performance [15,16,41–43]. The breadth of this range reflects numerous hotpressing variables and resin loadings. A more conservative approach would suggest that moisture contents from 10 to 15% are realistic upper limits for industrial production using pMDI. While 10 to 15% wood moisture is at the lower range of some claims, this is significantly higher than the levels that formaldehyde binders can tolerate. Wood moisture contents of 4 to 5% are common using liquid PF resins (the resulting total mat moisture is nearly double this because of water in the aqueous adhesive). Powdered PF resins are more moisture tolerant than the corresponding liquids, but they cannot match the moisture tolerance of isocyanate binders. While pMDI resins have superior moisture tolerance, it seems that this capability is not commonly exploited in conventionally hotpressed panels. Many pMDI users dry their wood furnish to moisture levels near 4% [38]. This may reflect the technical challenge of tightly controlling wood furnish moisture; it is easier to minimize moisture variation when drying it towards the minimum. Furthermore, there is a common desire to reduce steam pressure within the mat in order to minimize pressure induced delaminations, or "blows." High moisture and the resulting steam reduce hotpress capacity because venting times must be extended to prevent blows. So the advantages of higher wood moisture are balanced against extended press times [44]. Rapid curing pMDI allows lower press temperatures, thereby reducing steam pressure.

The moisture tolerance of pMDI is utilized in steam injection pressing (SIP), where steam is injected into the flake or strand mat (through the press platens) immediately prior to, and during compaction. SIP accelerates heat transfer and hotpress production, especially for very thick products such as laminated strand lumber. Besides accelerated production, steam processing increases the dimensional stability of the resulting composite [45,46]. Isocyanate resins appear to be the only exterior grade wood binders which can withstand the moisture extremes found in SIP [33,34,47].

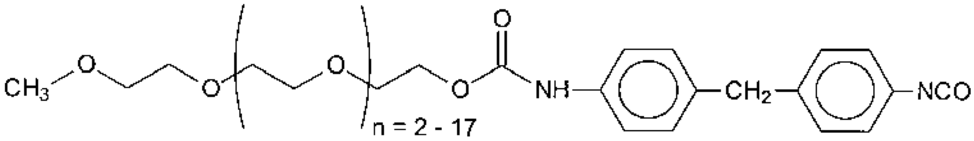
Another noteworthy application of pMDI binders is in the manufacture of "Ag–Fiber" composites, particularly straw-based panels that compete in particleboard and some medium density fiberboard markets [48–50]. The hydrophobic straw cuticle is difficult to wet, and so the low surface tension of pMDI is a clear advantage. The higher surface tension UF resins do not wet the straw surface as well. Furthermore, straw buffering properties may also complicate the application of UF resins to straw-based composites [49,50]. Straw-based composites may represent a significant market for pMDI binders. However, at this time the viability of straw-based panels is unclear because of the extreme competition from particleboard.

B. Industrially Significant Modifications of pMDI

The versatility of isocyanate chemistry provides many avenues for synthetic manipulation and product development. Just a few of many examples are mentioned below.

1. *Emulsifiable pMDI*

Polymeric MDI adhesives are rendered water emulsifiable through reaction with hydrophilic chains such as polyethylene oxide, as shown below.



Monofunctional hydroxyl terminated polyethylene oxide chains with degree of polymerization from 5 to 20 are reacted with pMDI, or simply with MDI, to provide surface active agents. The resulting surface active agent is then mixed with pMDI to provide a resin which is dispersible in water, resulting in an oil-in-water emulsion [51]. Such emulsions are stable for brief periods, 1 to 2 hours, before the water reaction causes gelation. Emulsifiable pMDI could be used where dispersion in water offers some benefit. For example, neat emulsifiable pMDI could be added directly to the blow line for medium density fiberboard production. Water emulsified pMDI has been used for improving resin distribution in particleboard or OSB manufacture; however, this is not common industrial practice.

2. *Urethane Modified pMDI*

As mentioned previously, neat pMDI does not have gap filling capability for wood bonding because of its low viscosity and propensity for deep penetration. Consequently, neat pMDI is not used for applications such as plywood, laminated veneer lumber, etc. However, gap filling properties may be achieved by modifying pMDI with a wide variety of difunctional or polyfunctional polyols. Viscosity and NCO content are easily tailored to meet many application requirements.

3. *PF/pMDI Hybrid Adhesives*

There has been some interest in combining aqueous PF or UF resins directly with pMDI resins [52–54]. The properties of the hybrid depend upon the blend ratio and the method of mixing. The resulting hybrids can be formulated with a wide range of viscosities, appropriate for lamination or spray applications (see Chapter 26, page 565). Presently, it is not clear if these hybrids will yield widespread, economically viable technologies although commercialization has already taken place [53,55].

C. Industrial Hygiene of pMDI Resins

All isocyanate containing compounds are highly reactive and potentially toxic. Care should be taken to prevent stored isocyanates from reacting with water because the resulting CO_2 could produce dangerous pressures in sealed containers. Consequently, isocyanates are often stored under nitrogen gas or anhydrous air. Contact with all isocyanates should be avoided, especially inhalation. Fortunately, pMDI resins have low vapor pressures, which means that inhalation is easy to avoid under typical laboratory conditions. The greatest concern is during industrial processes when the resins are sprayed. Spraying creates aerosols that could lead to allergic sensitization from inhalation. Under current industrial practice, all spraying is conducted in sealed containers so that aerosols are safely controlled. Inhalation exposure is a risk near hotpressing operations due to high temperature volatilization. Consequently, proper ventilation and isolation are required near the hotpress. In practice, ventilation and isolation precautions are also commonly employed at the resin blenders and forming line. It is easy and safe to use pMDI resins when exercising standard precautions to avoid dermal contact and inhalation. Adequate ventilation should be assured when hotpressing pMDI bonded materials under research or pilot scale conditions. Otherwise, respirators and protective clothing are required. Professional industrial hygiene personnel can easily evaluate laboratory and pilot scale operations for airborne pMDI.

IV. SUMMARY

Polymeric MDI is a versatile compound that has grown from the polyurethane industry, and has become an important wood binder in the forest products industry. As a wood binder, pMDI is highly effective and also quite unusual when compared to traditional thermosetting wood adhesives. The isocyanate functionality provides certain advantages which ensures its position in the forest products industry as a strong complement to urea/melamine–formaldehyde and phenol–formaldehyde systems. As wood composite technologies advance, we will certainly observe the growth of isocyanate binders and adhesives. The full potential of isocyanate chemistry has not been realized in the forest products industry, and so we should expect new and interesting technological advances.

ACKNOWLEDGMENTS

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Polyurethane Adhesives

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I. INTRODUCTION

The development of polyurethane adhesives can be traced back more than 60 years to the pioneering efforts of Otto Bayer and co-workers. Bayer extended the chemistry of polyurethanes initiated in 1937 [1] into the realm of adhesives about 1940 [2] by combining polyester polyols with di- and polyisocyanates. He found that these products made excellent adhesives for bonding elastomers to fibers and metals. Early commercial applications included life rafts, vests, airplanes, tires, and tanks [3]. These early developments were soon eclipsed by a multitude of new applications, new technologies, and patents at an exponential rate.

The uses of polyurethane adhesives have expanded to include bonding of numerous substrates, such as glass, wood, plastics, and ceramics. Urethane prepolymers were first used in the early 1950s [4] to bond leather, wood, fabric, and rubber composites. A few years [5] later one of the first two-component urethane adhesives was disclosed for use as a metal-to-metal adhesive. In 1957 [6] the first thermoplastic polyurethane used as a hot-melt adhesive (adhesive strips) was patented for the use of bonding sheet metal containers. This technology was based on linear, hydroxy-terminated polyesters and diisocyanates. Additional thermoplastic polyurethane adhesives began appearing in the 1958–1959 period [7,8]. During this period the first metal-to-plastic urethane adhesives were developed [9]. Waterborne polyurethanes were also being developed, with a polyurethane latex claimed to be useful as an adhesive disclosed in 1961 by du Pont [10]. A commercial urethane latex was available by 1963 (Wyandotte Chemicals Corporation) [11]. The adhesive properties of urethane latexes were explored further by W.R. Grace in 1965 [12]. In the early 1960s, B.F. Goodrich developed thermoplastic polyester polyurethanes that could be used to bond leather and vinyl [13]. In 1968 Goodyear introduced the first structural adhesive for fiberglass reinforced plastic (FRP), used for truck hoods [14].

Polyurethane pressure-sensitive adhesives began appearing in the early 1970s [15]. By 1978 advanced two-component automotive structural adhesives (Goodyear) were commercially available. Waterborne polyurethane adhesives received additional attention during this period [16]. In 1984, Bostik developed reactive hot-melt adhesives [17]. Polyurethane adhesives are sold into an ever-widening array of markets and products, where they are known for their excellent adhesion, flexibility, low-temperature performance, high cohesive strength, and cure speeds that can readily be tailored to the manufacturer's demands [18].

Urethanes make good adhesives for a number of reasons: (1) they effectively wet the surface of most substrates (the energy level of very low energy surfaces such as polyethylene or polypropylene must be raised before good wetting occurs) [19], (2) they readily form hydrogen bonds to the substrate, (3) their small molecular size allows them to permeate porous substrates, and (4) they form covalent bonds with substrates that have active hydrogens. Figure 1 shows the typical mechanism for a urethane adhesive bonding covalently to a polar surface.

Polyurethane adhesive consumption has been estimated at 217 million pounds (1991) having a value of approximately $301 million (see Fig. 2). Applications contributing to this volume are shown in Table 1. It is interesting to note that while the packaging market is the fourth-largest market in terms of pounds of urethane adhesives sold, it is substantially larger than the forest products market and the foundry core binder market in terms of

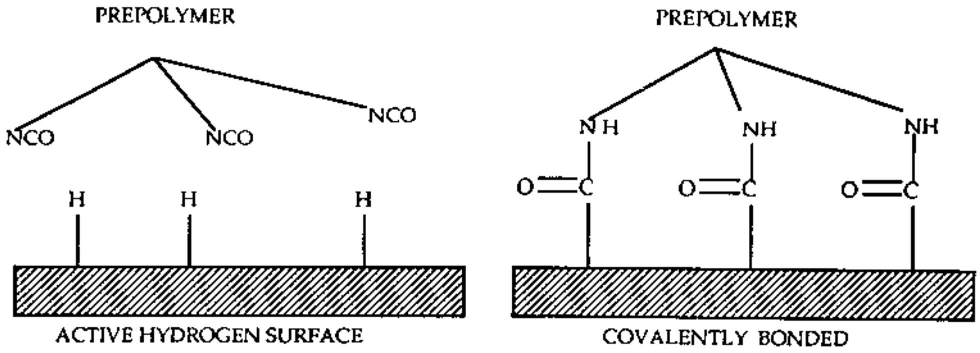


Figure 1 Typical mechanism for a urethane adhesive bonding covalently to a polar surface.

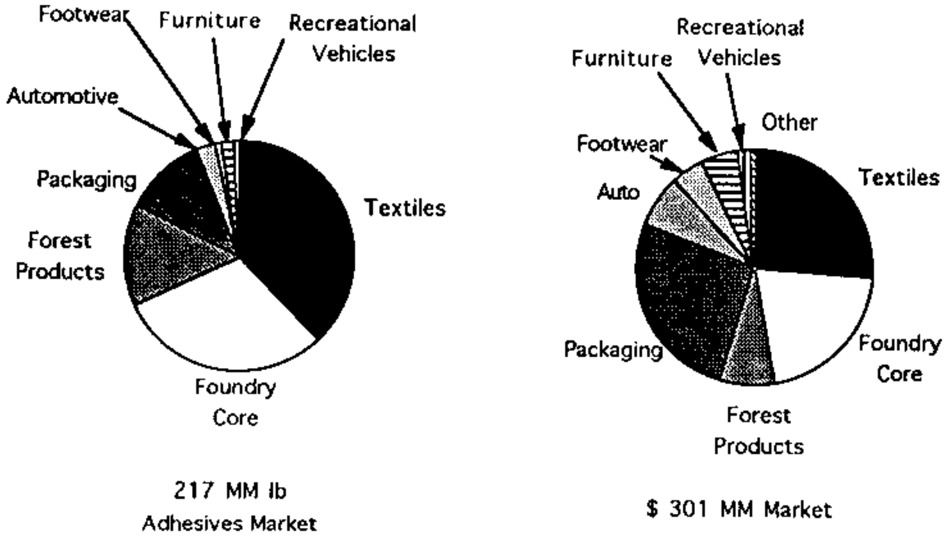


Figure 2 Polyurethane adhesive consumption, 1991.

Table 1 Sales Distribution for Polyurethane Adhesives, 1991

Market segment	Volume (lb × 10^6)	Sales (× 10^6)
Textiles	82.7	$79.6
Foundry core binders	66.0	62.5
Forest products	30.7	22.6
Packaging	25.0	79.7
Automotive[a]	6.2	21.4
Footwear	1.6	13.2
Furniture	3.8	15.4
Recreational vehicles	1.6	5.0
Other	0.35	1.8

[a] Does not include windshield sealant volumes.

dollars. Overall, the polyurethane adhesives market grew at an annual rate of approximately 3% from 1986 to 1991. Specific market segments such as automotive and recreational vehicles easily surpassed the gross national product (GNP) growth rate. In the next few years a number of specific market segments are expected to grow at about 5% per year. These would include vehicle assembly (automotive and recreational vehicles), electronics, furniture, and curtain wall manufacture.

II. APPLICATIONS OVERVIEW

The textile market has traditionally been the largest consumer of polyurethane adhesives. There are a number of high-volume applications, including textile lamination, integral carpet manufacture, and rebonded foam. Textile lamination occurs through either a solution coating process or flame bonding. Flame bonding textile lamination is accomplished by melting a polyurethane foam by flame and then nipping the foam between two textile rolls while it is still tacky. Integral carpet manufacture describes carpeting that is manufactured by attaching either nylon, wool, or polypropylene tufts that are woven through a polypropylene scrim with a urethane adhesive to a polyurethane foam cushion in a continuous process. Rebonded foam is made using scrap polyurethane foam bonded together with a urethane prepolymer and is used primarily as carpet underlay. Durability, flexibility, and fast curing speeds are all critical parameters for these applications.

Foundry core binders are isocyanate-cured alkyd or phenolic adhesives used as binders for sand used to produce foundry sand molds. These sand molds are used to cast iron and steel parts. A fast, economical cure of the sand mold is required under ambient conditions.

Packaging adhesives are adhesives used to laminate film to film, film to foil, and film to paper in a variety of packaging constructions. A broad variety of products are sold to this market, with solvent-based, high solids, 100% solids, and waterborne adhesives all being used. Polyurethane adhesives are considered one of the high-performance products offered to this industry because of their excellence in adhesive properties, heat resistance, chemical resistance, and fast curing properties. Polyurethane adhesives can also be designed to meet U.S. Food and Drug Administration approval, a requirement for food packaging applications.

Solvent-borne adhesives represent the majority of the volume in the packaging market, with both one- and two-component systems being used. Waterborne polyurethane adhesives are a much smaller segment that has been driven by environmental considerations. Growth has slowed in recent years because of generally inferior performance compared to solvent-based adhesives and because most of the major converters have already made capital investments in solvent recovery systems.

Isocyanates are used in the forest products industry to adhesively bond wood chips, which are then pressed to form particleboard and oriented strandboard. Urethanes are also used to fill knotholes and surface defects in finished plywood boards (“plywood patch”). These filled systems must cure rapidly and be sanded easily.

The transportation market has used polyurethane adhesives for such diverse applications as bonding FRP and sheet molding composite (SMC) panels in truck and car applications, polycarbonate headlamp assemblies, door panels, and weatherstrip flocking.

The construction market for polyurethane adhesives consists of a variety of applications, such as laminating thermal sandwich panels, bonding gypsum board to wood ceiling joists is modular and mobile homes, and gluing plywood floors. Early green strength, low shrinkage, and high bond strength are critical properties.

The furniture industry uses polyurethane adhesives to bond veneers of various composition to boardstock and metal substrates. Both waterborne and solvent-based adhesives are used.

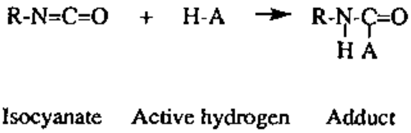
Footwear is a sizable niche for polyurethane adhesives that are used to attach the soles. Polyurethane adhesives compete primarily with neoprene-based adhesives and have replaced much of the neoprene volume due to improved performance. However, the overall market has declined as U.S. manufacturers have moved production overseas.

III. BASIC URETHANE CHEMISTRY

Isocyanates react with active hydrogens as depicted in Fig. 3. This addition reaction occurs with the active hydrogen adding to the nitrogen atom and the electron-rich nucleophile (Lewis base) reacting with the carbonyl group. Generally, the stronger the base, the more readily it reacts with the isocyanate. Table 2 shows typical reaction rates of some active hydrogen-containing compounds.

As expected, the aliphatic amines and aromatic amines (the strongest bases in the table) react the fastest. The urethanes industry has taken advantage of this reactivity in two-component commercial processes, demanding fast cure by using specially designed metering equipment and spray heads.

Alcohols and water react readily at room temperature. Most urethane adhesives depend on the –NCO group reacting with either water or alcohols. Primary OH groups are two to three times as fast as sterically hindered secondary OH groups under equivalent conditions. The reaction rates shown in Table 2 reflect uncatalyzed reaction rates and should be used as an indication of relative reaction rates. Actual rates are dependent on



$$R\text{-}N{=}C{=}O \quad + \quad H\text{-}A \rightarrow R\text{-}\underset{H}{N}\text{-}\underset{A}{C}{=}O$$

Figure 3 Reaction of isocyanate with active hydrogen.

solvent, temperature, and the presence of catalysts. Catalysts can significantly accelerate these reactions and can in some cases alter the order of reactivity [20].

A. Branching Reactions

There are a number of complex reactions that can occur besides the desired reaction of the polyol hydroxyl group with the isocyanate group to form a urethane, as shown in Fig. 4. Isocyanates can continue to react with undesirable consequences under conditions of high heat or strong bases. Basic impurities and excess heat catalyze branching reactions, leading to variations in prepolymer viscosity, gelation, and exotherms. Most basic impurities arise from the polyol, since polyols are typically produced under basic condition. As such, the net acidity of the overall system (contribution of acidic or basic components from the reactants) plays a critical role in determining the final viscosity achieved [21,22].

The presence of water will lead to the formation of ureas and evolve CO_2 as shown in Fig. 5. This mechanism is thought to proceed through the formation of an unstable intermediate, carbamic acid, which then decomposes to give CO_2 and an aromatic amine. The amine will then react further with another isocyanate to give a urea linkage. All common moisture-cured urethanes give off CO_2 upon curing, which can pose problems

Table 2 Typical Reaction Rates for Selected Hydrogen-Containing Compounds

Active hydrogen compound	Typical structure	Relative[a] reaction rate
Aliphatic amine	$R—NH_2$	100,000
Secondary aliphatic amine	$R_2—NH$	20,000–50,000
Primary aromatic amine	$Ar—NH_2$	200–300
Primary hydroxyl	$R—CH_2OH$	100
Water	H—O—H	100
Carboxylic acid	$R—CO_2H$	40
Secondary hydroxyl	$R_2CH—OH$	30
Urea proton	R—NH—CO—NH—R	15
Tertiary hydroxyl	$R_3C—OH$	0.5
Urethane proton	R—NH—CO—OR	0.3
Amide	$R—CO—NH_2$	0.1

[a] Uncatalyzed reaction rate, 80°C [1].

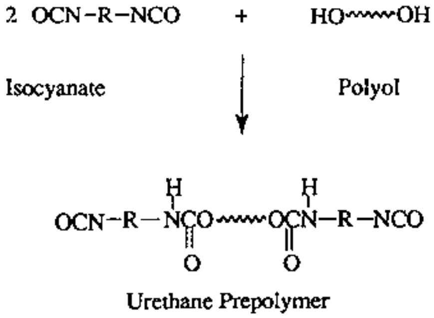


Figure 4 Reaction of polyol hydroxyl group with isocyanate group to form a urethane.

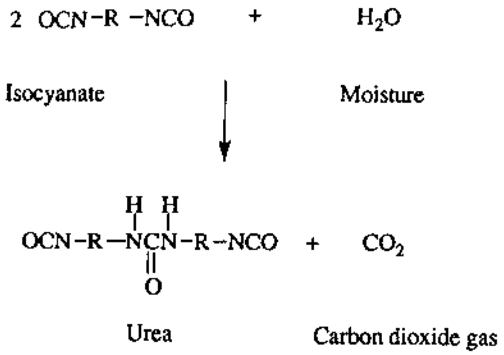


Figure 5 Reaction of isocyanate with water.

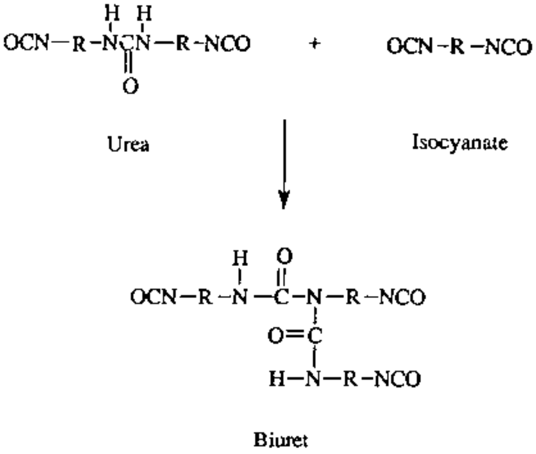


Figure 6 Reaction of urea with isocyanate.

if not properly controlled. Urea groups are known to cause high prepolymer viscosity because of increased hydrogen bonding and because of their ability to react further with excess isocyanate groups to form a biuret, as shown in Fig. 6.

At room temperature the biuret reaction proceeds very slowly; however, elevated temperatures and the presence of trace amounts of basicity will catalyze the biuret reaction as well as other branching reactions. These would include the formation of allophanate groups, as shown in Fig. 7 (due to the reaction of urethane groups with excess isocyanate groups), or trimerization of the terminal NCO group (to form an isocyanurate), as shown in Fig. 8. Biurets and allophanates are not as stable thermally or hydrolytically as branch points achieved through multifunctional polyols and isocyanates. The allophanates shown in Fig. 7 can continue to react with excess isocyanates to form isocyanurates (as shown in Fig. 8), a trimerization reaction that will liberate considerable heat. In most cases the desired reaction product is the simple unbranched urethane or a urea formed by direct reaction of an isocyanate with an amine. Ureas are an important class because they typically have better heat resistance, higher strength, and better adhesion. By controlling the reaction temperature (typically less than 80°C) and stoichiometry, and using a weakly

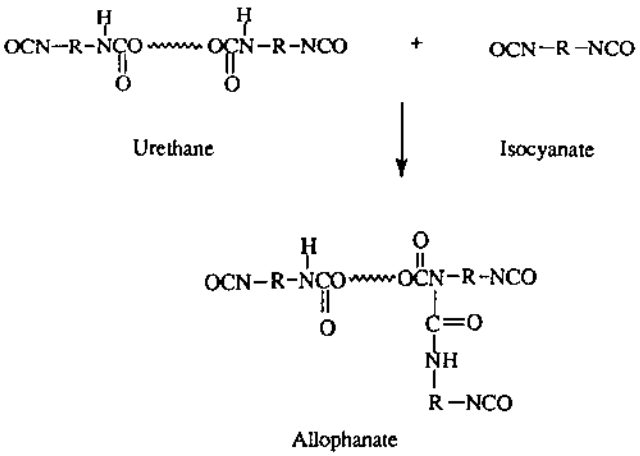


Figure 7 Reaction of urethane with isocyanate.

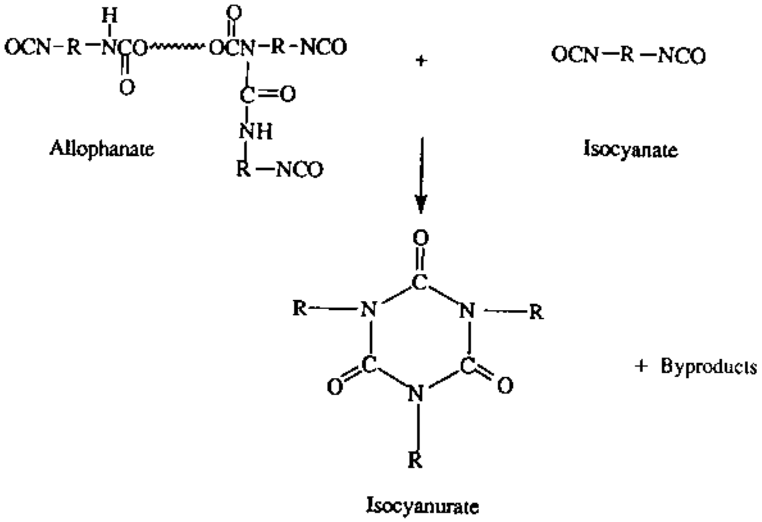


Figure 8 Reaction of allophanate with isocyanate.

basic catalyst (or none at all), the reaction will stop at the urethane or urea product. Increasing the functionality of the polyol or the isocyanate will achieve branching or cross-linking in a more controlled fashion.

B. Catalysts

As noted previously, strong or weak bases that are sometimes present in the polyols will catalyze the urethane reaction. The effect of catalysts on the isocyanate reaction is well documented. Indeed, the first reported examples occur in the literature well before urethanes became a commercially significant class of compounds. The first use of a catalyst with an isocyanate was reported by Leuckart in 1885 [23]. Other early reports

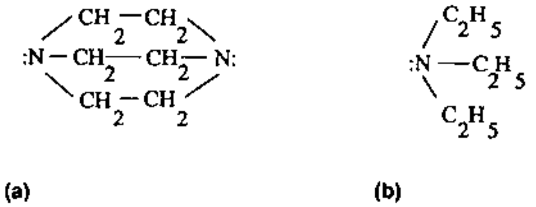


Figure 9 Structure of (a) triethylenediamine and (b) triethylamine.

were from French and Wirtel (1926), who used triethylamine to catalyze the reaction of phenols with 1-naphthylisocyanate [24]. Baker and Holdsworth (1947) detailed the mechanism of the urethane reaction [25].

Commercial catalysts consists of two main classes: organometallics and tertiary amines. Both classes have features in common in that the catalytic activity can be described as a combination of electronic and steric effects. Electronic effects arise as the result of the molecule's ability to donate or accept electrons. For example, in the tertiary amines, the stronger the Lewis base, generally the stronger the polyurethane catalyst. Empty electronic orbitals in transition metals allow reactants to coordinate to the metal center, activating bonds and placing the reactants in close proximity to one another.

Steric effects arise from structural interactions between substituents on the catalyst and the reactants that will influence their interaction. The importance of steric effects can be seen by comparing the activity for triethylenediamine to that of triethylamine. The structure of triethylenediamine (see Fig. 9) forces the nitrogens to direct their lone electron pairs outward in a less shielded position than is true of triethylamine. This results in a rate constant for triethylenediamine that is four times that of triethylamine at 23°C [1].

Organometallic complexes of Sn, Bi, Hg, Zn, Fe, and Co are all potent urethane catalysts, with Sn carboxylates being the most common. Hg catalysts have long induction periods that allow long open times. Hg catalysts also promote the isocyanate–hydroxyl reaction much more strongly than the isocyanate–water reaction. This allows their use in casting applications where pot life and bubble-free parts are critical. Bismuth catalysts are replacing mercury salts in numerous applications as the mercury complexes have come under environmental pressure.

Catalysts will not only accelerate reaction rates but may also change the order of reactivity. Table 3 illustrates this behavior. These data indicate that amines do not affect the relative reactivities of different isocyanates and show that Zn, Fe, and Co complexes actually raise the reactivity of aliphatic isocyanates above aromatic isocyanates.

IV. URETHANE POLYMER MORPHOLOGY

One of the advantages that a formulator has using a polyurethane adhesive is the ability to tailor the adhesive properties to match the substrate. Flexible substrates such as rubber or plastic are obvious matches for polyurethane adhesives because a tough elastomeric product can easily be produced. Polyurethanes derive much of their toughness from their morphology.

Polyurethanes are made up of long polyol chains that are tied together by shorter hard segments formed by the diisocyanate and chain extenders if present. This is depicted schematically in Fig. 10. The polyol chains (typically referred to as soft segments) impart

Table 3 Gelation Times (min) at 70°C

Catalyst	TDI	Isocyanate *m*-xylene diisocyanate	Hexamethylene diisocyanate
None	>240	>240	>240
Triethylamine	120	>240	>240
Triethylenediamine	4	80	>240
Stannous octoate	4	3	4
Dibutyltin di(ethylhexoate)	6	3	3
Bismuth nitrate	1	0.5	0.5
Zinc naphthenate	60	6	10
Ferric chloride	6	0.5	0.5
Ferric 2-ethylhexoate	16	5	4
Cobalt 2-ethylhexoate	12	4	4

TDI, toluene diisocyanate.
Source: Ref. 20.

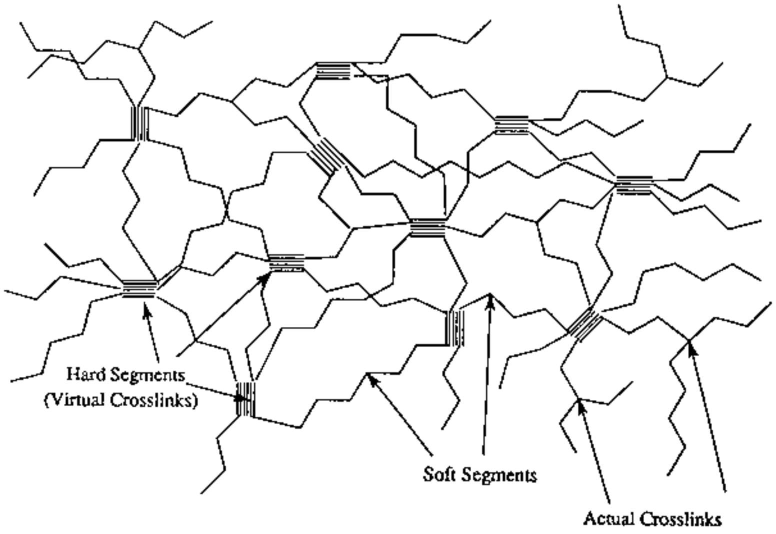


Figure 10 Polyol-chain structure of polyurethane.

low-temperature flexibility and room-temperature elastomeric properties. Typically, the lower-molecular-weight polyols give the best adhesive properties, with most adhesives being based on products of molecular weight less than 2000. Generally, the higher the soft segment concentration, the lower will be modulus, tensile strength, hardness, and tear strength, while elongation will increase. Varying degrees of chemical resistance and heat resistance can be designed by proper choice of the polyol.

Short-chain diols or diamines are typically used as chain extenders. These molecules allow several diisocyanate molecules to link forming longer-segment hard chains with higher glass transition temperatures. The longer-segment hard chains will aggregate together because of similarities in polarity and hydrogen bonding to form a pseudo-cross-linked network structure. These hard domains affect modulus, hardness, and tear strength and also serve to increase resistance to compression and extension. The hard segments will yield under high shear forces or temperature and in fact determine the upper use temperature of the product. Once the temperature or shear stress is reduced, the domains will re-form.

The presence of both hard segment and soft segment domains for polyurethanes gives rise to several glass transition temperatures, one below −30°C which is usually associated with the soft segment, transitions in the range 80 to 150°C, and transitions above 150°C. Transitions in the range 80 to 150°C are associated with the breakup of urethane hydrogen bonds in either the soft segment or the hard segment. Transitions higher than 150°C are associated with the breakdown of hard segment crystallites or aggregates. Linear polyurethane segmented prepolymers can act as thermoplastic adhesives which are heat activated. A typical use for this type of product is in the footwear industry.

By proper choice of either the isocyanate or the polyol, actual chemical cross-links can be introduced in either the hard or soft segments that may be beneficial to some properties. The effectiveness of these cross-links is offset by a disruption of the hydrogen bonding between polymer chains. Highly cross-linked polyurethanes are essentially amorphous in character exhibiting high modulus, hardness, and few elastomeric properties. Many adhesives fall into this category.

V. PREPOLYMER FORMATION

Most urethane adhesives are based on urethane prepolymers. A prepolymer is made by reacting an excess of diisocyanate with a polyol to yield an isocyanate-terminated urethane as shown in Fig. 11. Prepolymers may have excess isocyanate present ("quasi-prepolymers") or they may be made in a 2:1 stoichiometric ratio to minimize the amount of free isocyanate monomer present. Most moisture-cured prepolymers are based on 2:1 stoichiometric ratios. Two-component adhesives generally are based on quasi-prepolymers, which use the excess isocyanate to react with either chain extenders present in the other component or with the substrate surface.

Prepolymers are isocyanates and react like isocyanates, with several important differences. Prepolymers typically are much higher in molecular weight, are higher in viscosity, are lower in isocyanate content by weight percent, and have lower vapor pressures. Prepolymers are important to adhesives for a number of reasons. The desired polymeric structure of the adhesive can be built into the prepolymer, giving a more consistent

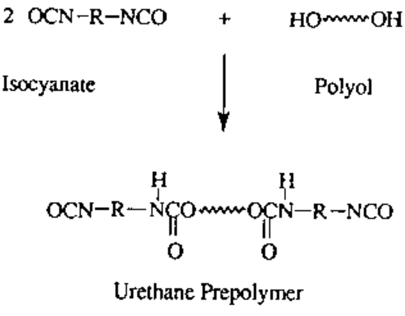


Figure 11 Reaction of isocyanate with polyol.

structure with more reproducible physicals. In addition, since part of the reaction has been completed, reduced exotherms and reduced shrinkage are normally present. For two-component systems, better mixing of components usually occurs, since the viscosity of the two components more closely match. In addition, the ratios of the two components match more closely. Side reactions such as allophanate, biuret, and trimer are lessened. Finally, prepolymers typically react more slowly than does the original diisocyanate, allowing longer pot lives.

VI. ADHESIVE RAW MATERIALS

Polyols for adhesive applications can be generally broken down into three main categories: (1) polyether polyols, (2) polyester polyols, and (3) and polyols based on polybutadiene. Polyether polyols are the most widely used polyols in urethane adhesives because of their combination of performance and economics. They are typically made from the ring-opening polymerization of ethylene, propylene, and butylene oxides, with active proton initiators in the presence of a strong base as shown in Fig. 12.

Polyether polyols are available in a variety of functionalities, molecular weights, and hydrophobicity, depending on the initiator, the amount of oxide fed, and the type of oxide. Capped products are commercially available as well as mixed-oxide feed polyols, as shown in Fig. 13. Polyether polyols typically have glass transitions in the -60°C range, reflecting the ease of rotation about the backbone and little chain interaction. As one would expect from such low glass transition temperatures, they impart very good low-temperature performance. The polyether backbone is resistant to alkaline hydrolysis, which makes them useful for adhesives used on alkaline substrates such as concrete. They are typically very low in viscosity and exhibit excellent substrate wetting. In addition, their low cost and ready availability from a number of suppliers add to their attractiveness.

The more commonly used polyether polyols range in molecular weight from 500 to 2000 for diols and 250 to 3000 for triols. Lower-molecular-weight, higher-functionality polyols are traditionally used in rigid-foam applications but have also been used as cross-linkers for two-component, fast-curing urethane adhesives. Polytetramethylene glycols (PTMOs; see Fig. 14) can be considered a subset of polyether polyols. They offer

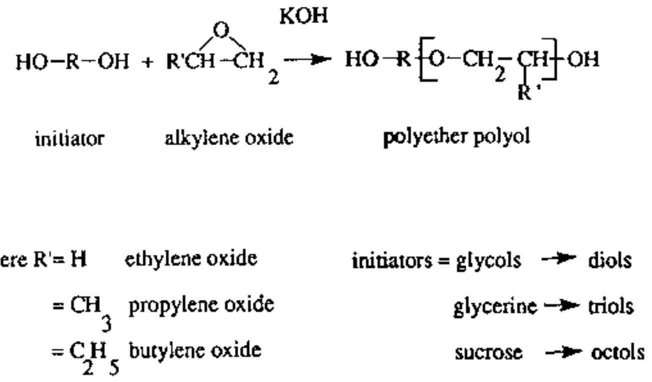


Figure 12 Ring-opening polymerization to form polyether polyols.

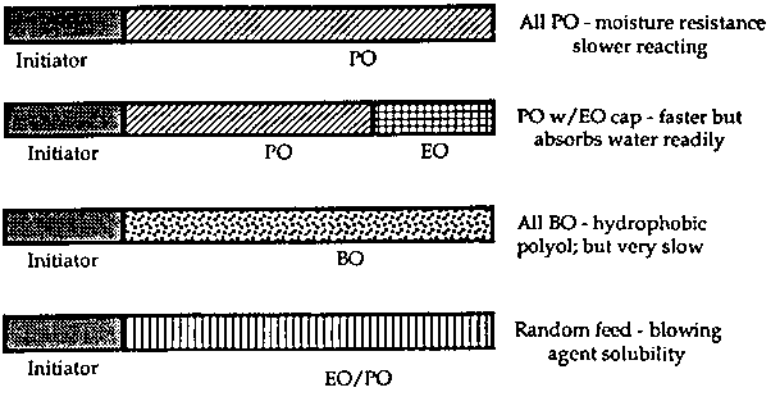
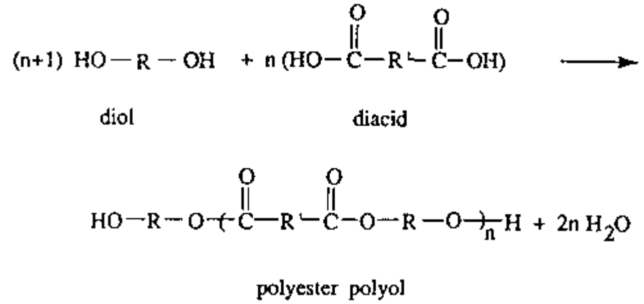


Figure 13 Various commercially available capped products and mixed-oxide feed polyols. BO, butylene oxide; EO, ethylene oxide; PO, propylene oxide.

$$\mathrm{HO{-}\!\left(CH_2{-}CH_2{-}CH_2{-}CH_2{-}O\right)_n\!{-}H}$$

Figure 14 Structure of polytetramethylene oxide.



$$(n+1)\ \mathrm{HO{-}R{-}OH} + n\,(\mathrm{HO{-}\overset{\overset{\large O}{\|}}{C}{-}R'{-}\overset{\overset{\large O}{\|}}{C}{-}OH}) \longrightarrow$$

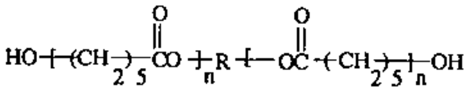
$$\mathrm{HO{-}R{-}O{-}\!\left(\overset{\overset{\large O}{\|}}{C}{-}R'{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}R{-}O\right)_{n}\!{-}H} + 2n\,\mathrm{H_2O}$$

Figure 15 Reaction of diol with diacid to form polyester polyol.

improved physical properties compared to polyethers based on ethylene oxide, propylene oxide, or butylene oxide, combining high tensile strength (due to stress crystallization) with excellent tear resistance. They are also noted for their excellent resistance to hydrolysis. They are typically priced at a premium to other polyols.

Polyester polyols are used widely in urethane adhesives because of their excellent adhesive and cohesive properties. Compared to polyether-based polyols, polyester-based polyol adhesives have higher tensile strengths and improved heat resistance. These benefits come at the sacrifice of hydrolytic resistance, low-temperature performance, and chemical resistance. One of the more important application areas for these products is in the solvent-borne thermoplastic adhesives used in shoe sole binding. These products are typically made from adipic acid and various glycols (see Fig. 15).

Some glycerine or trimethylolpropane may be used to introduce branching structures within the polyester backbone. Phthalic anhydride may also be used to increase hardness and water resistance. Inexpensive terephthalic acid-based polyesters from recycled polyethyleneterephthalate (PET) resins have more recently become popular.



$$HO\text{—}[(CH_2)_5\overset{O}{\overset{\|}{C}}O]_n\text{—}R\text{—}[O\overset{O}{\overset{\|}{C}}(CH_2)_5]_n\text{—}OH$$

Figure 16 Structure of polycaprolactone diol.

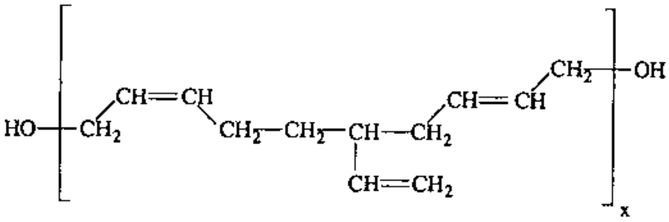


Figure 17 Structure of polybutadiene polyol.

Polycaprolactones (see Fig. 16), another type of polyester polyol, offer improvements in hydrolysis resistance and in tensile strength (can stress crystallize) over adipic acid-based polyester polyols. They are typically higher in viscosity and higher in cost than polyether polyols of comparable molecular weight. When moisture resistance is critical, urethane adhesives incorporating polybutadiene polyols are used. These products are hydroxy-terminated, liquid polybutadiene resins. The hydrocarbon backbone greatly decreases water absorption, imparting excellent hydrolytic stability. Polybutadiene compounds also have exceptional low-temperature properties, with glass transition temperatures being reported below $-70^\circ C$ [26]. These products are priced at a 40 to 50% premium over comparable polyether polyols. The structure of polybutadiene polyols is shown in Fig. 17.

A. Isocyanates for Adhesive Applications

Toluene diisocyanate (TDI) is a colorless, volatile, low-viscosity liquid commonly used in the adhesives area to manufacture low-viscosity prepolymers for flexible substrates. The structure of TDI is shown in Fig. 18. TDI is typically supplied as an 80:20 mixture of the 2,4 and 2,6 isomers, respectively, with two grades of acidity available. Type I TDI is low in acidity (10 to 40 ppm); type II TDI is higher (80 to 120 ppm). Type II TDI is generally used for prepolymer applications because the additional acidity is available to neutralize trace bases found in polyether polyols. These trace bases can cause branching reactions during prepolymer cooks, causing high viscosities and even gelations if not properly controlled (see Section V). The extra acidity present also serves to stabilize the prepolymer, extending the shelf stability. In addition, since TDI is predominately the 2,4 isomer, a reactivity difference is noted for the isocyanate groups. Since the less hindered site reacts first, the sterically hindered site is left when prepolymers are formed, leading to prepolymers that are more shelf stable. TDI prepolymers are used in adhesives for the textile and food packaging laminates industry, where a fit is found for their low viscosity and low cost. The volatility of TDI and additional handling precautions that must be taken when using TDI has limited its growth in adhesive applications.

Methylene diphenyl disiocyanate (MDI) is used where high tensile strength, toughness, and heat resistance are required. MDI is less volatile than TDI, making it

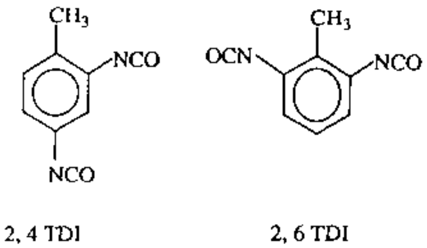


Figure 18 Structure of the 2,4 and 2,6 isomers of toluene diisocyanate.

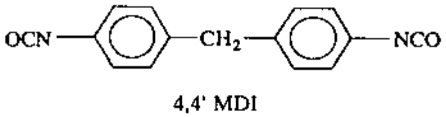


Figure 19 Structure of methylene diphenyl diisocyanate.

less of an inhalation hazard. The acidity levels in MDI are very low, typically on the order of 0 to 10 ppm, so the trace base levels in the polyols are much more critical in prepolymer production than with TDI. The structure of MDI is shown in Fig. 19. There are several commercial suppliers of MDI that typically supply grades with 98% or better 4,4′ isomer. MDI is a solid at room temperature (melting point 38°C, 100°F), requiring handling procedures different from those for TDI. MDI should be stored as a liquid at 115°F or frozen as a solid at (−20°F) to minimize dimer growth rate. MDI reacts faster than TDI, and because the NCO groups in MDI are equivalent, they have the same reactivity, a contrast to TDI. MDI is used in packaging adhesives, structural adhesives, shoe sole adhesives, and construction adhesives.

Several MDI products have been introduced that address the inconvenience of handling a solid. They are seeing increased usage in the adhesives industry and are expected to experience a higher growth rate. Most MDI producers offer a uretonimine-modified form of MDI that is a liquid at room temperature. The uretonimine structure is shown in Fig. 20. In addition, several producers have introduced MDIs containing elevated levels of the 2,4′ isomer, as shown in Fig. 21. At approximately the 35%, 2,4′ isomer level, the product becomes a liquid at room temperature, greatly increasing the handling ease. A number of advantages are seen: slower reactivity, longer pot life, lower-viscosity prepolymers, prepolymers with lower residual monomeric MDI, and improved shelf stability.

Polymeric MDIs are made during the manufacturing of monomeric MDI. These products result as higher-molecular-weight oligomers of aniline and formaldehyde get phosgenated. A typical structure for these products is shown in Fig. 22. These oligomers average 2.3 to 3.1 in functionality and contain 30 to 32% NCO. Much of the hydrolyzable chlorides and color bodies produced in the manufacturing process of MDI is left behind in these products. The acidity levels can be 10 to 50 times the level found in pure MDI, and the products are dark brown in color. The higher acidity level decreases reactivity; however, this decrease is offset somewhat by the higher functionality.

Polymeric MDIs are typically lower in cost than pure MDI and because of the increased asymmetry have a lower freeze point (liquids at room temperature). They are less prone to dimerization, and as a consequence are more storage stable than are pure MDI and derivatives. Polymeric MDIs are used whenever the color of the finished

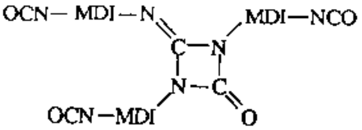


Figure 20 Structure of uretonimine.

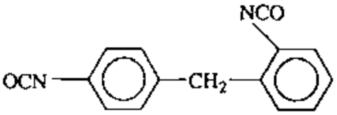


Figure 21 Structure of the 2,4′ isomer of MDI.

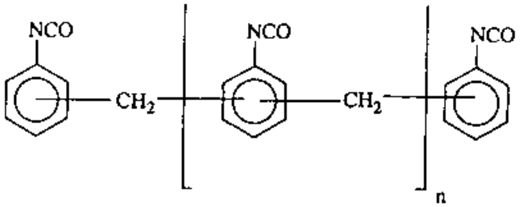


Figure 22 Structure of polymeric MDI.

adhesive is not a concern. They are generally not used for prepolymers because high-viscosity branched structures typically result. They are widely used as adhesives in the foundry core binder area, in oriented strandboard or particleboard, and between rubber products and fabric or cord. It is interesting to note that the polymeric isocyanates used commercially today are structurally very similar to the Desmodur R (trademark, Bayer) products used over 50 years ago [2].

Aliphatic isocyanates are used whenever resistance to ultraviolet light is a critical concern. Examples of aliphatic isocyanates are hexamethylene diisocyanate, hydrogenated MDI, isophorone diisocyanate, and tetramethylxylene diisocyanate. Structures for these molecules are shown in Fig. 23. The aliphatic isocyanates are usually more expensive than aromatic isocyanates and find limited use in adhesive applications. Resistance to ultraviolet light is usually not a critical concern in adhesives because the substrate shields the adhesive from sunlight.

Blocked isocyanates are also used in urethane adhesives. Blocking or "masking" of the isocyanates refers to reacting the isocyanate groups with a material that will prevent the isocyanate from reacting with active hydrogen-containing species at room temperature but will allow that reaction to occur at elevated temperatures. Blocked isocyanates are easily prepared and their chemistry has been developed extensively since their inception by Bayer and co-workers during the early 1940s [27–29]. As an example, the preparation of a methylethylketoxime blocked isocyanate is shown in Fig. 24.

Blocked isocyanates offer a number of advantages to unblocked isocyanates. The traditional concern for moisture sensitivity can be addressed by blocking the isocyanate. Heat activation is then required, but most commercial adhesive applications can meet this requirement. Water-based dispersions and dispersions of the isocyanate in the polyol or other reactive media become possible using blocked isocyanates. There are a number of blocked isocyanates commercially available that could be used in adhesive

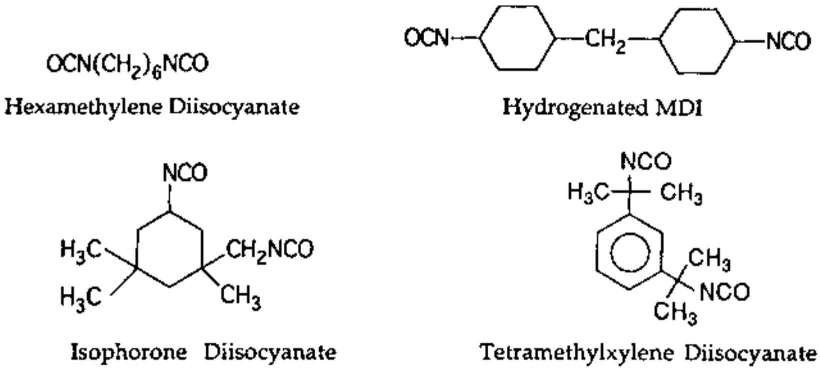


Figure 23 Structure of various aliphatic isocyanates.

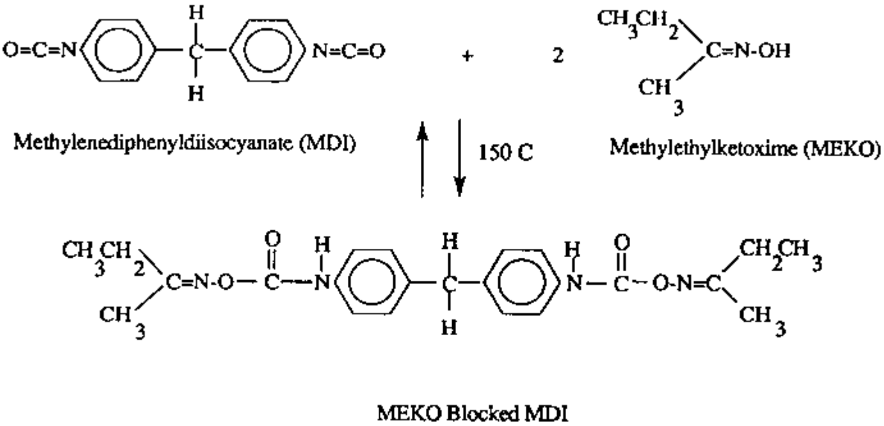


Figure 24 Preparation of a methylethylketoxime blocked isocyanate.

applications. Miles (Bayer) produces a series of aromatic and aliphatic blocked isocyanates marketed for primers, epoxy flexibilizers, wire coatings, and automotive topcoat applications. Blocked isocyanates are widely patented for fabric laminating adhesives [30], fabric coating adhesives [31–34], and tire cord adhesives [35–40].

B. Toxicology

Polyether polyols are generally considered to be low in toxicity with respect to eye and skin irritation; however, amine-initiated polyether polyols have been found to be more irritating to the skin and eyes. The manufacturer's material safety data sheet (MSDS) should always be consulted before use. Oral toxicity is generally a secondary concern in an industrial environment. The vapor pressure of polyols is generally negligible; thus vapor inhalation is not usually a concern [41]. Low-molecular-weight glycols (chain extenders) are considered more problematical than polyether polyols. While generally the vapor pressure of these products is low, there are processes that could potentially result in vapor concentrations close to the exposure limits [41]. The exposure guidelines for chain extenders may be written to differentiate between aerosols and vapors. For more specific handling information the manufacturer should be consulted.

The toxicology of isocyanates is a primary concern when developing or using polyurethane adhesives. Respiratory effects are the primary toxicological manifestation of repeated overexposure to diisocyanates [42–46]. In addition, most of the monomeric isocyanates are eye and skin irritants. Precautions should be taken in the workplace to prevent exposure. The risk of overexposure is primarily (but not limited to) allergic sensitization with asthma-type symptoms. Manufacturers' guidelines (MSDS) should be consulted for the most current information and legal requirements.

C. Fillers and Additives

Fillers are used in adhesives to improve physical properties, to control rheology, and to lower cost. The most common polyurethane fillers are calcium carbonate, talc, silica, clay, and carbon black. A more rigorous treatment of this subject can be found in Katz and Milewski [47]. Fumed silicas and carbon blacks are used primarily as thixotropes in application areas that require a nonsagging bead. Calcium carbonates, clays, and talcs are used to improve the economics of an adhesive formulation. A major concern using fillers with urethane prepolymers is the moisture content associated with the fillers. Fillers typically must be dried prior to use with urethane prepolymers or isocyanates. Hygroscopic fillers should be avoided, as moisture introduced by the filler can lead to poor shelf stability of the finished product.

Pigments are sometimes used in polyurethane adhesive systems, but since most adhesives are generally hidden from view, pigments do not play major roles. Pigments may be used to color the adhesive to match the substrate. Pigments are more typically used to color one side of a two-component system to help the user distinguish between the isocyanate and the polyol. They are also sometimes used as an aid to judge mix ratios. Carbon black and titanium dioxide are two commonly used pigments.

Plasticizers can also be used in polyurethane adhesives to lower viscosity, improve filler loadings, improve low-temperature performance, and plasticize the polyurethane adhesive. Phthalate esters, benzoate esters, phosphates, and aromatic oils are common examples [48]. Plasticizers should be used sparingly, as adhesion will generally decrease as levels increase.

VII. SURFACE PREPARATION AND PRIMERS

Proper surface preparation is the key to obtaining good adhesive bonds having a predictable service life. Substrate surfaces may have dirt, grease, mold-release agents, processing additives, plasticizers, protective oils, oxide scales, and other contaminants that will form a weak boundary layer. When the adhesive fails it is usually through this region, giving a low-strength bond. Some form of surface treatment is necessary to obtain optimum bond strength. The primary goal of surface treatment is to remove any weak surface boundary layer on the substrate [49]. A large number of surface treatments have been developed, with many targeted toward specific substrates. These would include mechanical abrasion, etching, solvent cleaning, detergent washing, flame treatments, chemical treatments, and corona discharges [19,50–55].

Primers are also used in conjunction with a surface treatment either to improve adhesive performance or to increase production flexibility in a bonding operation. Isocyanates have been used for over 50 years as primers on substrates such as rubber, plastic, fibers, and wood [56]. Isocyanates will react with polar groups on the surface and promote bonding.

Silane coupling agents are commonly used as primers for glass, fiber composites, mineral-filled plastics, and cementacious surfaces. The silane coupling agents have been found to be especially effective with glass substrates. One end of the coupling agent is an alkoxysilane that condenses with the silanol groups on the glass surface. The other end of the coupling agent is an amino, mercapto, or epoxy functionality that will react with the isocyanate group in the adhesive. Epoxy silanes have also been used as additives to adhesives to improve water resistance [57]. Other organometallic primers are based on organotitanates, organozirconates, and some chromium complexes [49].

VIII. COMMON ADHESIVE TYPES

A. One-Component Adhesives

The oldest types of one-component polyurethane adhesives were based on di- or triisocyanates that cured by reacting with active hydrogens on the surface of the substrate or moisture present in the air or substrate. The moisture reacts with the isocyanate groups to form urea and biuret linkages, building molecular weight, strength, and adhesive properties. Prepolymers are also used either as 100% solids or solvent-borne one-component adhesives. Moisture-cured adhesives are used today in rebonded foam, tire cord, furniture, and recreational vehicle applications.

A second type of one-component urethane adhesive comprises hydroxypolyurethane polymers based on the reaction products of MDI with linear polyester polyols and chain extenders. There are several commercial suppliers of these types of thermoplastic polyurethanes. The polymers are produced by maintaining the NCO/OH ratio at slightly less than 1:1 to limit molecular weight build to the range 50,000 to 200,000 with a slight hydroxy content (approximately 0.05 to 0.1%). These are typically formulated in solvents for applications to shoe soles or other substrates. After solvent evaporation heat is used to melt the polymer (typically 50 to 70°C; at these temperatures the polymers reach the soft, rubbery, amorphous state), so the shoe upper can be press fit to the sole. Upon cooling, the adhesive recrystallizes to give a strong, flexible bond [58]. More recently, polyisocyanates have been added to these to increase adhesion and other physical properties upon moisture curing. In Section IX.B we discuss this in more detail.

The use of waterborne polyurethane adhesives has grown in recent years as they have replaced solvent-based adhesives in a number of application areas. There are a number of papers and patents covering the use of waterborne polyurethanes in shoe soles, packaging laminates, textile laminates, and as an adhesive binder for the particleboard industry [59–62]. Because waterborne polyurethane adhesives have no VOC (volatile organic content) emissions and are nonflammable, they are more environmentally friendly. Typically they can be blended with other dispersions without problems and exhibit good mechanical strength. Water-based systems are fully reacted, linear polymers that are emulsified or dispersed in water. This is accomplished by building hydrophilicity into the polymer backbone with either cationic or anionic groups or long hydrophilic polyol segments or, less frequently, through the use of external emulsifiers. Figure 25 illustrates the more common functional groups that can be built into the urethane molecule that will confer hydrophilicity.

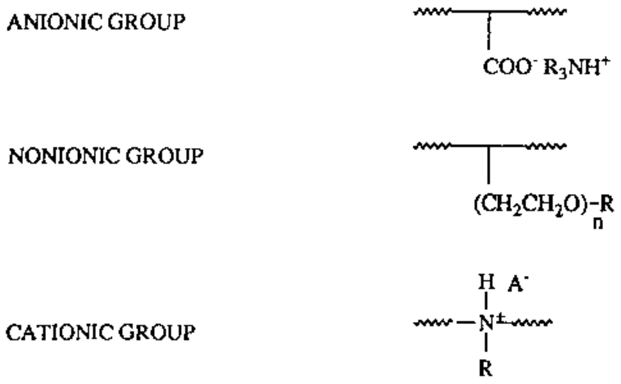


Figure 25 Common functional groups that confer hydrophilicity in the urethane molecule.

A typical example of how these groups are built into the polymer backbone is shown in Fig. 26. A urethane prepolymer is reacted with chain extenders containing either carboxylates or sulfonates in a water-miscible solvent (e.g., acetone). The reaction product is an isocyanate-terminated polyurethane or polyurea with pendant carboxylate or sulfonate groups. These groups can easily be converted to salts, which as water is added to the prepolymer–solvent solution, allows the prepolymer to be dispersed in water. The solvent is then stripped, leaving the dispersed product. There are variations on this theme that allow lower solvent volumes to be used [63]. Long hydrophilic polyol segments can also be introduced. Chain extenders with hydrophilic ethylene oxide groups pendant to the backbone are reacted with the prepolymer to form a nonionic self-emulsifying polyurethane. This reaction is also carried out in a water-miscible solvent that can later be stripped from the solvent–water solution.

Blocked isocyanates can also be considered a one-component adhesive. The use of a blocking agent allows the isocyanate to be used in a reative medium that can be heat activated. One-component adhesives based on blocked isocyanates are thus not amenable to room-temperature curing applications. The chemistry of these products is covered in more detail in Section VI.A.

B. Two-Component Adhesives

The second major classification of common polyurethane adhesives is the two-component system. Two-component polyurethane adhesives are widely used where fast cure speeds are critical, as on OEM (original equipment manufacturers) assembly lines that require quick fixture of parts, especially at ambient or low bake temperatures. Two-component urethanes are required in laminating applications where no substrate moisture is available or where moisture cannot penetrate through to the adhesive bond. Two-component urethanes are also useful where CO_2 (generated by a one-component moisture cure) or a volatile blocking agent would interfere with the adhesive properties.

Two-component adhesives typically consist of low-equivalent-weight isocyanate or prepolymer that is cured with a low-equivalent-weight polyol or polyamine. They may be 100% solids or solvent borne. Since the two components will cure rapidly when mixed, they must be kept separate until just before application. Application is followed quickly by mating of the two substrates to be bonded.

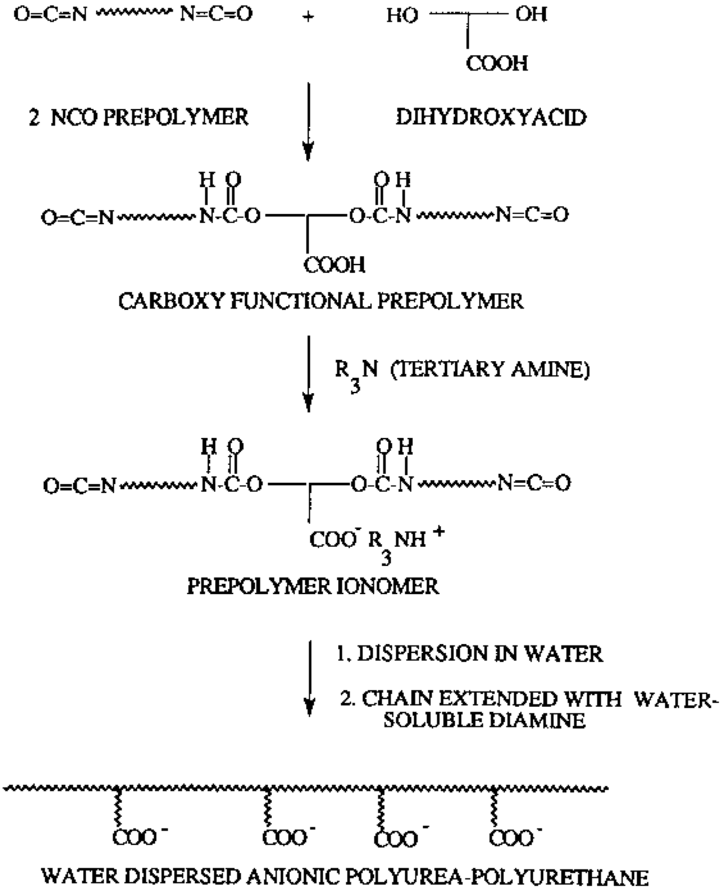


Figure 26 How functional groups are built into the polymer backbone of urethane.

Efficient mixing of the two components is essential for complete reaction and full development of designed adhesive properties. In-line mixing tubes are adequate for low-volume adhesive systems. For larger-volume demands, sophisticated meter mix machines are required that will mix both components just prior to application. Commercial systems for delivering two-component adhesives are segmented based on the viscosity ranges of the components. The ranges can be broken down into low, middle, and high viscosity, with, for example, Liquid Control Corp., Sealant Equipment and Engineering Inc., and Graco Inc., respectively, supplying equipment for the three ranges [64].

In present-day high-speed assembly line operations, adhesives are applied robotically. The adhesive bead is applied quickly and evenly to parts on a conveyor line just prior to being fitted. These operations, especially the need to handle the adhered substrates soon after assembly, demand fast-curing adhesive systems [65]. Two-component adhesives are used to bond metals to plastics in automobiles, to laminate panels in the construction industry, to laminate foams to textiles, to laminate plastic films together, and to bond poly(vinylidene chloride) films to wood for furniture. A commercial waterborne two-component adhesive is sold by Ashland under the trademark ISOSET. This system is used for exterior sandwich panels by recreational vehicle manufacturers and is composed of a water-emulsifiable isocyanate and a hydroxy-functionalized emulsion latex.

IX. RECENT DEVELOPMENTS

A. Hybrid Adhesives

Over the last four decades there have been a number of attempts to wed the unique benefits of polyurethane adhesives with the benefits of other adhesive systems. These attempts have led to the reporting of a variety of urethane hybrids. Early work focused on simple blends; for example, in 1964 Union Carbide blended organic isocyanates with ethylene–vinyl acetate copolymers [66]. These blends were used as an adhesive interlayer in glass laminations, particularly safety glass laminates. Similarly, polylurethane–epoxy blends for safety glass laminates were reported in 1970 [67].

More recent efforts have focused on developments that create true hybrids. For example, blocked isocyanate prepolymers have been mixed with epoxy resins and cured with amines [68–70]. These blocked prepolymers will react initially with the amines to form amine-terminated prepolymers that cross-link the epoxy resin. Several blocked isocyanates are commercially available. The DESMOCAP (Bayer) 11A and 12A products are isocyanates (believed to be blocked with nonylphenol) used as flexibilizing agents for epoxy resins. ANCAREZ (trademark, Pacific Anchor, Inc.) 2150 is a blocked isocyanate epoxy blend used as an adhesion promoter for vinyl plastisols. A one-package, heat-cured hybrid adhesive was reported consisting of isophorone diisocyanate, epoxy resin, and a dispersed solid curative based on the salt of ethylenediamine and bisphenol A [71]. Urethane amines are offered commercially that can be used with epoxy resins to develop hybrid adhesive systems [72].

Urethane acrylic hybrids have been reported based on several approaches. Pacific Anchor has developed a urethane acrylate that is commercially available (ANCAREZ 300A). Acrylic polyols have been synthesized in the presence of polyether polyols by Saunders for use in two-component structural adhesives with improved tensile and impact strength [73,74]. Pressure-sensitive acrylic prepolymers with hydroxyl groups have been formulated with isocyanate prepolymers to give adhesives with improved peel strength [75,76]. Aqueous-based vinyl-to-fiberboard adhesives were reported by Chao using water-dispersible MDI with a functionalized acrylic latex and an aqueous dispersion polyurethane to given improved shear and hot peel strength [77]. Acrylonitrile dispersion graft polyether polyols have also been used in two-component SMC adhesives [78].

Urethanes have also been used to toughen vinyl-terminated acrylic adhesives for improved impact resistance. Thus rubber-toughened urethane acrylates [79,80], water-dispersible urethane acrylates [81], and high-temperature-performance urethane–acrylate structural adhesives have been reported [82]. Polyurethanes terminated with acrylic functionality are also used for anaerobic or radiation-cured adhesives with improved toughness [83].

B. Reactive Hot Melts

Polyurethane reactive hot melts are 100% solid, hot-melt thermoplastic prepolymers that moisture cure slowly after application. Conventional hot melts are known for their quick setting, excellent green strength, ease of application, and low toxicity. Their primary limitation is low heat resistance (at elevated temperatures, the adhesive will soften and flow) and poor adhesion to some substrates, due to insufficient wetting. The use of a polyurethane prepolymer with low levels of free isocyanates as a hot melt offers distinct advantages: initial green strength is still achieved, and in addition, the isocyanate will moisture cure slowly, converting the thermoplastic adhesive to a thermoset. There are a number of recent patents on reactive hot melts [84–87]. The tensile strength of the adhesive increases, heat resistance is improved, and the final cured adhesive will not flow at elevated temperatures [88]. A limitation of this technology is the need for porous substrates or bond designs that will allow the diffusion of moisture into the adhesive so that moisture curing will occur. The adhesive itself must be protected from moisture prior to use. This technology should be applicable to assembly line operations which require an adhesive that gets high initial green strength.

C. Pressure-Sensitive Adhesives

The use of polyurethanes in the pressure-sensitive adhesives market has been relatively small. Polyurethanes have been somewhat limited to being used as additives to pressure-sensitive adhesives to improve their cohesive strength. Recent developments in the institutional carpet backing or automotive carpet floor mat markets suggest that pressure-sensitive urethanes can succeed commercially [89].

X. SUMMARY

Polyurethane adhesives as a class can no longer be perceived as new raw materials. From a base of 217 million pounds, double-digit growth can no longer be expected. Even so, significant growth will continue. Formulators are taking advantage of the tremendous flexibility of urethane chemistry in designing new adhesive products. Specialty niches such as waterbornes and reactive hot melts, for example, will continue to emerge and fuel growth. Exciting times lie ahead for innovative formulators of polyurethane adhesives!

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Polyvinyl and Ethylene–Vinyl Acetates

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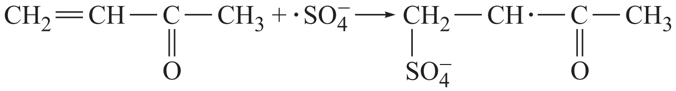
I. INTRODUCTION

Poly(vinyl acetate) (PVA) and ethylene–vinyl acetate (EVA) copolymer adhesives have much in common, yet represent extremes in the degree of sophistication of their production processes. Both products are stable suspensions in water of a film-forming polymer, the particles of which are generally spherical. They are made by emulsion polymerization, which uses a free-radical addition mechanism to polymerize the monomer in the presence of water and stabilizers. Vinyl acetate is the sole or major monomeric raw material.

The major difference between the processes is the incorporation in EVAs of ethylene, an internally plasticizing monomer. The use of ethylene requires production equipment suitable for safe handling of a highly flammable, high-pressure gas. Despite the volatility and very low flash point of vinyl acetate, simple PVAs are manufactured successfully by many small-scale producers in developing countries; EVAs are made only at sophisticated and costly plants where ethylene gas, engineering skills, and a significant demand for the product come together.

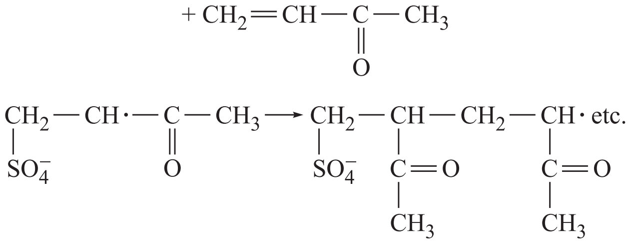
II. CHEMISTRY

Vinyl acetate is characterized by having an activated double bond. While being an acceptably stable material under normal ambient storage, it is readily attacked by a free radical. This simple addition gives another free radical, and the addition of a series of monomer units results in a polymer chain. Thus



$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + \cdot SO_4^- \longrightarrow \underset{\underset{SO_4^-}{|}}{CH_2}{-}CH\cdot{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

Vinyl acetate monomer



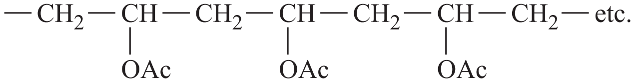
$$+\,CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

$$\underset{\underset{SO_4^-}{|}}{CH_2}{-}CH\cdot{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \longrightarrow \underset{\underset{SO_4^-}{|}}{CH_2}{-}\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{CH}{-}CH_2{-}\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{CH}\cdot\ \text{etc.}$$

III. RESIN PREPARATION

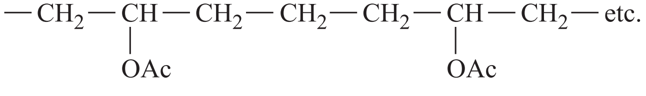
The essential property of any polymer used as an adhesive is that it should have good cohesion and stick to the surfaces it joins. This can occur only if the polymer forms a film on application or at some stage during the joining process. In the case of a water suspension such as a PVA or an EVA adhesive, this involves a smooth coalescence of the polymer particles as the water evaporates. For this to occur, the polymer must be above its minimum filming temperature (MFT). Some applications lend themselves to the application of heat. However, most rely only on the evaporation of water at ambient temperature, coupled with absorbence (or "wicking") into the substrate, if porous.

Poly(vinyl acetate) has a glass transition temperature (GTT) of about 30°C. The GTT marks the change in properties from a material with a glasslike nature to one with rubbery properties. In particular, particles above their GTT may deform, flow, and adhere. This results in the GTT being the greatest factor in determining the minimum temperature for the formation of a coherent film. The GTT of any polymer is dependent on its structure. As the temperature rises, polymer chains vibrate under the influence of the stretching and bending motion of individual bonds. At the GTT the steric and covalent locking of the chain is overcome, allowing the molecule as a whole to bend and rotate, subject to the special constraints of neighboring polymer chains. It is clear that any internally plasticizing copolymerized monomer or external solvent or plasticizer that assists this process by making the main chain of the polymer more flexible, or eases its rotation by spacing adjacent chains of the polymer, reduces the temperature at which film formation can take place. Ethylene acts directly as a polymer backbone plasticizer. A polymer such as poly(vinyl acetate) homopolymer:



$${-}CH_2{-}\underset{\underset{OAc}{|}}{CH}{-}CH_2{-}\underset{\underset{OAc}{|}}{CH}{-}CH_2{-}\underset{\underset{OAc}{|}}{CH}{-}CH_2{-}\ \text{etc.}$$

becomes the much more flexible copolymer with ethylene:



$${-}CH_2{-}\underset{\underset{OAc}{|}}{CH}{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{OAc}{|}}{CH}{-}CH_2{-}\ \text{etc.}$$

In the latter structure the acetate groups are too widely spaced to influence rotation.

PVA adhesives are plasticized externally by smaller molecules that space the chains and minimize chain-to-chain interactions. The classic material for this purpose is dibutyl phthalate (DBP), but any compatible solvent may be chosen. Even water itself acts as a temporary coalescing solvent to some degree. Volatile materials gradually evaporate, allowing the PVA adhesive to harden and gain tensile strength. This is particularly important if strength at high ambient temperatures is required. Conversely, materials less volatile than DBP may be chosen to ensure that a degree of flexibility is retained in the joint, even after many years at high temperatures or repeated rinsing with water. For ultimate stability over time, copolymerization with ethylene must be chosen.

Lowering of the minimum filming temperature and increasing flexibility is not the only reason for introducing other polymerizable monomers into the preparation of the adhesive. A large variety of materials are available, having in common a double bond that is either activated or may become so on the approach of a free radical. Such monomers may modify the behavior of the final polymer, conferring resistance against alkalis, or to improve adhesion in wet conditions. Chain branching to increase molecular weight may be introduced. Stability of the polymer against freezing or mechanical shear are other desirable properties that may be gained by copolymerization.

Because of the simple addition of monomer to growing chains, and because the reaction takes place in the bulk of the polymer or on the surface of polymer particles rather than in solution, molecular weight is very high. Chain growth can cease only when two free-radical-terminated chains collide, an initiator fragment adds to and eliminates a growing chain, or a chain transfer reaction takes place with a small, volatile molecule. In practice, the chances of two growing chains mutually eliminating each other by addition are very low because of their high molecular weight and consequential lack of mobility. One recent theory relies on chain transfer to monomer and subsequent desorption of the small free radical as the only significant mechanism of chain termination. Molecular weight can be increased by the addition of small amounts of monomer with more than one double bond. These are known as chain branching agents. Conversely, molecular weight is decreased by the addition of a material containing a reactive hydrogen such as *n*-dodecyl mercaptan (1-dodecane thiol) as a chain transfer agent. The hydrogen is readily removed from the thiol (—SH) group, giving a terminated chain on the polymer but also a —S• free radical capable of starting a new chain. Formulation factors such as the level of the free-radical initiator used and process factors such as temperature of reaction and the amount of agitation also play a part. Low levels of initiator, low temperatures, and a carefully judged degree of agitation all favor high molecular weight.

Turning to practical considerations, choice of process and formulation is all important in successful production of PVA and EVA adhesives. Some formulation examples are given in a later section, but various aspects are discussed here.

A. Process

Addition polymerization is exothermic, and one of the major constraints to high production rates is the problems associated with heat removal. In processes using ethylene, the pressure of the gas determines solubility in the liquid phases (i.e., water and vinyl acetate monomer droplets) and in the polymer particles. This concentration of ethylene at the point of polymerization determines the ethylene content of the final polymer. Use of high pressures in such systems eliminates refluxing of the vinyl acetate, losing a very effective heat removal mechanism available to simple batch-process PVA production. Refluxing, however, gives condenser vapor losses. Great care has to be taken to ensure that the condenser is adequate to deal with the volume of vapor to be condensed. Returning condensate from an inverted condenser is also a very effective cooling agent, as it is often very much below the reaction temperature. The sensible heat removal adds to the evaporative cooling.

Care also has to be taken not to overcool the reaction. If so, a slowdown in the polymerization rate may occur, with excess free monomer, leading to an exotherm followed by foaming or an overloading of the condenser. A reduction in the monomer feed rate at this time is essential, but again care has to be exercised, as a sudden loss of cooling from the incoming monomer stream coupled with a drop-off in the reflux rate can give an uncontrollable exotherm.

The batch process uses a kettle fitted with an agitator. Other features are temperature probes and a cooling jacket. Simple processes operate at atmospheric pressure and use a condenser. If no condenser is fitted or ethylene gas is to be used, the reactor must be pressurized. On larger kettles, an external heat exchanger may be employed. This system is attractive, as it avoids the need to manage reflux, and the total cooling capability has flexibility through variable rates of pumping through the heat exchanger. Its disadvantage is the need to clean and maintain the heat exchanger. and manufacture of grades of adhesive with poor mechanical stability, high viscosity, or a tendency to foul surfaces can be difficult or uneconomic.

The batch process starts with filling the reactor with most of the water, much or all of the stabilizer [frequently poly(vinyl alcohol) in adhesives], and a small proportion of the monomer. On agitation and raising the temperature to above 65°C, addition of a water-soluble free-radical generator such as ammonium persulfate initiates polymerization. This establishes the number of particles and the average particle size of the emulsion polymer. A continuous stream of vinyl acetate is run or pumped in with additional initiator until the required concentration of polymer is obtained, this coinciding with the maximum working volume of the kettle. It follows that in this process there is a wide spread of residence times within the reactor. The initial polymer is present from the outset, but shells of fresh polymer built around the early particles have a relatively short period within the reactor. The water and the stabilizers are also present at the beginning, which gives maximum time for degradation and grafting reactions. It is, however, energetically inefficient to agitate such viscous solutions over the full period of the process.

One alternative is the *Loop process* [1–3]. This employs a rather simple principle. A small volume of reaction mixture is recirculated, while streams of monomer and water phase [a stabilizer solution such as aqueous poly(vinyl alcohol)] are pumped into the reactor in the correct proportions. The reactor is fully filled and a balancing volume of product is released through a pressure-sustaining valve. Any unreacted monomer remaining in the outlet stream polymerizes on the way to the cooling tank or over a few hours, prior to packing. The volume of this type of reactor is only 40 to 80 L compared to 3000 to 100,000 L for a batch reactor.

The two types of reactor may be compared. The Loop reactor is more efficient energetically as the volume of reaction mixture to be agitated is so much less. It should be said, however, that the savings are not proportional to the volumes involved, as the diameter of the Loop pipes give greater frictional losses. As with many calculations involving viscosity in emulsion polymer production, complications arise due not only to pseudoplasticity of reaction mixtures, but also because of different behavior at different shear rates and temperatures.

One of the greatest contrasts between the processes is the residence time within the reactor. It has already been noted that the poly(vinyl alcohol) in the batch process is usually present from the start. The residence time is therefore several hours. In contrast, the mean residence time of materials in the Loop process is around 2 to 10 min. This has obvious advantages in terms of minimizing degradation of colloids but will also restrict grafting between colloid and monomer.

Aside from process comparisons, the main contrast between the systems is that of size, weight, and cost, especially for pressurized systems. Construction of batch reactors for use with ethylene at pressures of 1000 psi (70 atm) and upward has to be massive. The simple construction of the Loop process—just pumps and pipework—lends itself to use at high pressures. Apart from cost and weight, the small volume of the Loop reactor has obvious safety advantages. Despite these attractions, the Loop reactor system has so far been used successfully only for low-pressure systems such as poly(vinyl acetate) homopolymer for adhesives and copolymers for paint. Large-scale production of ethylene–vinyl acetate copolymers has yet to be demonstrated.

B. Formulation Factors

The majority of standard product formulations for PVA and EVA adhesives use poly(vinyl alcohol) as the main protective colloid and thickener. Poly(vinyl alcohol) can be obtained in a number of grades produced from poly(vinyl acetate) by hydrolysis. As a consequence, almost all products are effectively vinyl acetate/vinyl alcohol copolymers. Lower levels of hydrolysis, 88% most commonly, are readily water soluble in hot or cold water, although in practice care has to be taken in making solutions to avoid clumping of the grains, which can then be difficult to disperse. Eighty-eight percent hydrolyzed material is normally coupled with a "fully hydrolyzed" grade, in which the hydrolysis has been taken into the range 97 to 99.5% of the theoretical maximum.

These grades are not easily soluble in cold water, but once made into a solution by heating, are usually stable. Because of insolubility in cold water, the higher hydrolysis-grade materials have better water resistance as dried films. Their disadvantage is to give less viscous products for poly(vinyl alcohol) of the same molecular weight. This may be associated with the particle size of the polymer formed—the presence of vinyl acetate groups gives some surfactancy, especially if the acetate groups are in blocks. Finer average particle size—and hence more particles—fill the free space more effectively, increasing viscosity. Particle–particle interactions are also important, and particle size distribution has a profound effect on rheology.

Introduction of surfactants, especially anionic surfactants or in mixtures with nonionics, gives wider distributions that often lose viscosity on shearing. This makes pumping and application easier but may bring in the problem of overspreading. For consistency of application between different machines, a more Newtonian rheology is an advantage. Many commercial adhesives are further compounded by the addition of fillers, thickening agents of various kinds, plasticizers, and solvents, although the range of the latter that are acceptable is diminishing rapidly.

IV. ANALYSIS AND TESTING

PVA and EVA products are often sold with rather limited information. Often solids content, viscosity range, and pH are the only real specifications given. Minimum filming temperature (or in some cases, glass transition temperature) may be quoted, together with comonomer type, if any, and some brief application recommendations. Manufacturers may in production test for more properties than they publish, especially grit content, particle size, and unreacted monomer. Grit is the material retained by a standard sieve and comprises oversized particles up to beads, skins, and pieces of reactor wall fouling which have found their way through the system. Most adhesives are filtered prior to packing, but this is less easy and less important than in lower-viscosity paint grades. The high viscosity of many adhesive products makes the use of fine screens an economic impossibility because of the slow speed of filtration.

Viscosity is a property sometimes difficult to assess, as figures can be measured on any one of several types of viscometer. One common type is the rotating disk viscometer, which must be used in a container big enough to eliminate wall effects. The main alternative is the cup-and-bob viscometer, where the viscous drag of the liquid between stationary and rotating concentric cylinders is indicated by a spring-loaded pointer moving over a dial.

For use with high-speed applicators, high shear cone and plate viscometer results may be quoted as secondary information. Many poly(vinyl alcohol)-stabilized products are comparatively insensitive to shear and give broadly similar results with different types of viscometer. This behavior under shear is known as Newtonian and is a feature, inter alia, of large particles with a narrow particle size distribution. High shear viscosity testing also indicates if there is sufficient mechanical stability to allow application by knife or roller, although this is not usually a problem with colloid-stabilized emulsion polymers and adhesives.

Particle size range is often from 200 to 4500 nm or more, with one or more peaks. Multipeak distribution may indicate agglomeration at some stage of the preparation, and microscopy can be used to show if the peaks are of single particles or of an agglomerated mass of smaller ones. Freeze–thaw resistance is called for in many countries. The key here is to avoid the higher degrees of hydrolysis in the poly(vinyl alcohol) (not greater than 98% hydrolyzed), and ensure that sufficient stabilizer is present to cover the surfaces. Nonionic surfactants will act as antifreezes and suppress the freezing point and it is often of value to quote the behavior of the adhesive at −5°C and −20°C. Residual monomer should also be checked for quality control purposes and kept below the specified level. Gas–liquid chromatography is the favored method of analysis, but bromination is also widely used.

Application tests by their nature are often specific to the materials to be bonded and the application machinery in use. For packaging applications it is important that sufficient strength is generated within seconds of the bond being formed to hold the surfaces in position until the adhesive dries. Testers are available that apply a measured, standardized film to a series of kraft paper pieces. A second sheet of kraft paper (or whatever may be appropriate) is applied and the papers are peeled apart at specified time intervals. The time at which the surface of the paper is first torn off (as contrasted to the earlier tests, in which the surfaces are partially covered with adhesive) is noted. Short times are necessary for high-speed machinery. High viscosity, or suitable rheology to create resistance to parting of the adhesive layer, is obviously of value and is called wet tack or "grab." As most of the initial drying is through wicking of the water in the adhesive into the paper or board to be bonded, standardization of the paper used in this test is vital. Wood bond strength is more concerned with ultimate strength and the test pieces are usually allowed to dry thoroughly for 24 to 48 h or more. Small beechwood slips giving a controlled area of overlap are generally used, although end bonding of beech dowels is an alternative. In each case, bond strength is measured using a tensiometer and it should be noted that the overlap method gives the strength to resist shearing in a direction parallel to the wood surface, while the dowel method tests the resistance at right angles to the wood. In both cases the wood should fail before the adhesive, although if the adhesive fails, the strength measured may be a function of the amount of plasticizer or softening comonomer used in the preparation.

Ethylene–vinyl acetate adhesives are used for many of the same applications as externally plasticized PVAs but have especially good performance in the field of poly(vinyl chloride) (PVC) lamination to hardboard and chipboard. Again, an adhesive is sought where the mode of failure is the cohesion of the wood. Drying is slow in this case because the PVC foils are largely impervious to water. Wicking into the substrate and vapor loss are the only modes of water removal. Hence it is essential that bonds be matured for a suitable period prior to test. Various test methods exist; the simplest uses 5-cm-wide strips of PVC foil laminated to plywood. This is dried and matured and suspended inverted with the plywood at 45° to the horizontal. Weights may be suspended from the width of the PVC, using a clamp or a firm clip to which the weights are attached. This is simply extended to high-temperature peel strengths by placing the test piece within an oven, say at 70°C. The distance that the specimen has peeled after 30 min can be measured. Weights employed are usually 350 g or 500 g, but greater weights are possible. Ninety-degree peel tests can be conducted using tensile-strength testing equipment, but they are more difficult to conduct at temperatures above ambient.

V. FORMULATIONS

A. Poly(vinyl acetate) Homopolymers

1. *Batch Process*

A simple formulation by the batch process is as follows:

	Parts by weight (kg)	
1. Initial reactor charge		
Process water	360.5	Presolution
Poly(vinyl alcohol) (88% hydrolyzed)	12.6	
Nonyl phenol (15 M) ethyl oxide condensate	6.6	
Linear C_{12} sulfate, sodium salt	0.3	
Sodium bicarbonate	1.6	
Antifoam (nonsilicone)	0.4	
Water	64.4	Rinse
2. Initial monomer charge		
Vinyl acetate	25.0	
3. First initiator		
Sodium persulfate	1.1	
Water	6.0	
4. Continuous monomer feed		
Vinyl acetate	460.0	
5. Continuous initiator feed		
Sodium persulfate	0.2	
Water	6.0	
6. Final initiator feed		
Sodium persulfate	0.1	
Water	3.0	

	Parts by weight (kg)
7. Plasticizer	
Dibutyl phthalate	50.0
8. Preservative	
Preservative	2.2
	1000.0

Process: Make a presolution of the poly(vinyl alcohol). Add to the polymerization kettle, agitate, and heat to 65°C, meanwhile adding the other ingredients of the initial reactor charge. At 65°C, add the initial vinyl acetate monomer and the first initiator. Heat cautiously to 80°C, during which time the initial vinyl acetate will polymerize (shown by the development of a blue color, a reduction or cessation of reflux, and a slight exotherm).

Start to add the continuous monomer and initiator feeds to go in over 4 h at a steady rate. Monitor temperature and reflux continuously, especially in the early stages of the reaction. Slow the feed of monomer if reflux is excessive or temperature cannot be maintained at 80 to 85°C. Ensure that the agitation is sufficient at all times to give a small vortex that blends in added monomer and condenser return smoothly but does not create foam or splashing. When feeds are complete, add final initiator and allow temperature to rise to 90 ± 2°C (heat if necessary). Hold for 20 min, then cool, adding the dibutyl phthalate at about 65°C and the preservative at 35°C or less.

2. *Loop Process*

A Loop continuous reactor uses a broadly similar formulation to the batch case, but the poly(vinyl alcohol)-containing solution is pumped in continuously rather than added to the reactor initially. Also, a redox initiator is used:

	Parts by weight (kg)
1. Initial reactor filling	
Process water	46.3
Poly(vinyl alcohol) (88% hydrolyzed)	2.2
Poly(vinyl alcohol) (98% hydrolyzed)	1.3
Sodium acetate	0.1
Sodium metabisulfite	0.1
	50.0
2. Water/stabilizer feed	
Process water	489.6
Poly(vinyl alcohol) (88% hydrolyzed)	23.6
Poly(vinyl alcohol) (98% hydrolyzed)	14.1
Sodium acetate	1.1
Sodium metabisulfite	1.0
3. Monomer feed	
Vinyl acetate	419.2
4. Initiator feed	
t-Butyl hydroperoxide	1.1
5. Plasticizer	
Dibutyl phthalate	50.0
6. Preservative/antifoam	
Preservative	0.2
Antifoam	0.1
	1000.0

Process: Pump into the Loop reactor the initial fill. Start the circulation pump. Start to pump the water–stabilizer solution, followed by the monomer feed and the initiator, to give a total feed of raw materials of 500 kg/h. Allow the temperature to rise to 55°C and apply cooling to stabilize the temperature to 55 ± 1°C. Collect the product and add dibutyl phthalate after holding the completed required volume for 20 min at about 50°C. Cool and add the preservative and antifoam at 35°C or less.

B. Vinyl Acetate–Ethylene Copolymers

1. *Batch Reactor Process*

The following formulation illustrates the use of a redox initiator in a batch process. Also, the introduction of *N*-methylol acrylamide increases the molecular weight and chain cross-linking, minimizing the thermoplastic properties of the adhesive and the tendency to cold flow.

	Parts by weight (kg)
1. Initial reactor charge	
Deionized water	380.0
Poly(vinyl alcohol) (88% hydrolyzed)	25.0
Sodium bicarbonate	2.0
Ammonium persulfate	5.0
2. Initial monomer charge	
Vinyl acetate	50.0
Ethylene	(to 250 psi)
3. Reducing initiator	
Sodium formaldehyde sulfoxylate	1.5
Deionized water	25.0
4. Continuous monomer feed (1)	
Vinyl acetate	446.0
5. Continuous monomer feed (2)	
N-Methylol acrylamide	4.5
Deionized water	60.0
6. Preservative, etc.	
Preservative	0.5
Antifoam	0.5
	1000.0*

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*Excluding the weight of the combined ethylene.

Process: Load the reactor with the initial charge, using a presolution of the poly(vinyl alcohol) in 300 g of the water. Rinse in the sodium bicarbonate and ammonium persulfate with the remaining water. Switch on the agitator and purge with nitrogen. Then pump in the initial vinyl acetate and pressurize with ethylene gas. Raise the temperature to 35 to 40°C and maintain at this temperature. Start to add the reducing initiator feed to go in over about 8 h. After 1 h, start to add the continuous monomer feeds (1) and (2) to go in over about 7 h. At all times the unreacted monomer should be kept at 1 to 2% of the reaction mixture to ensure even copolymerization of the *N*-methylol acrylamide.

2. *Loop Process*

A Loop continuous reactor formulation is given below, where the redox initiator is of an unusual manganese type.

	Parts by weight (kg)
1. Initial reactor filling	
Water	50
2. Water/stabilizer solution feed (feed rate: 3.95 kg/min)	
Water	236.66
Poly(vinyl alcohol) (80% hydrolysed)	11.36
Sodium bisulfite	3.79
3. Monomer feed (feed rate: 8.52 kg/min)	
Vinyl acetate	440.18
Ethylene	71.00
4. Initiator feed (feed rate: 3.95 kg/min)	
Manganese^{3+} sulfate/sodium	0.35
pyrophosphate complex	236.66
Water	1000.00
	(Items 2, 3, and 4)

Process: Fill the reactor with water and set the circulation pump to 800 rev/min. Start feeding the water–stabilizer solution at 3.95 kg/min, followed by the Mn^{3+} complex, also at 3.95 kg/min. Then start pumping in the vinyl acetate, finally beginning to feed the ethylene into the vinyl acetate feed at a pressure of 260 psi, the pressure-sustaining valve on the outlet of the Loop reactor being adjusted accordingly. This formulation was found to give a 95% conversion of ethylene with a 13.4% by weight incorporation in the final polymer.

C. Formulated Adhesive

	Parts (%)
PVA homopolymer (58% solids, 10% DBP)	82.6
Dibutyl phthalate (DBP)	5.7
Ethyl acetate	5.5
Calcium carbonate filler (micronized)	4.8
Preservative	0.2
Water	1.2
	100.0

Process: Blend all ingredients except the filler with the PVA. When complete add the filler slowly, blending well between additions.

VI. APPLICATIONS

Applications for poly(vinyl acetate) homopolymers include:

Wood adhesives
Packaging adhesives

General building adhesives; polystyrene tiles, hardboard; plasterboard
Ceramic tile adhesives
Remoistenable adhesives
Concrete patching adhesives
Bookbinding adhesive

Applications for vinyl acetate–ethylene copolymers include:

Bonding plastic foils and films in packaging
Lamination of PVC films to chipboard and plywood
Paper and board
Remoistenables for envelop flaps, paper labels, etc.
Bookbinding
Do-it-yourself (DIY) and household adhesives
Shoe and leather industry
General building adhesives
Nonwovens and flocking adhesives
Cigarette side-seam adhesives
Heat-sealable adhesives
Textiles

VII. SUMMARY

Vinyl acetate homopolymers are simply-made adhesive bases manufactured by addition polymerization in the presence of water and stabilizers. They are made commercially by the batch reactor process or by the Loop reactor continuous process. External plasticizers such as dibutyl phthalate are often added to confer flexibility and to lower the temperature at which they form a film on drying. Higher-quality products may be made by the copolymerization of ethylene with vinyl acetate to form an EVA. This involves the safe handling of ethylene gas under high pressure, and the plant required is more complex and considerably more costly. The Loop process has considerable attraction in the field of pressure polymerization.

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Unsaturated Polyester Adhesives

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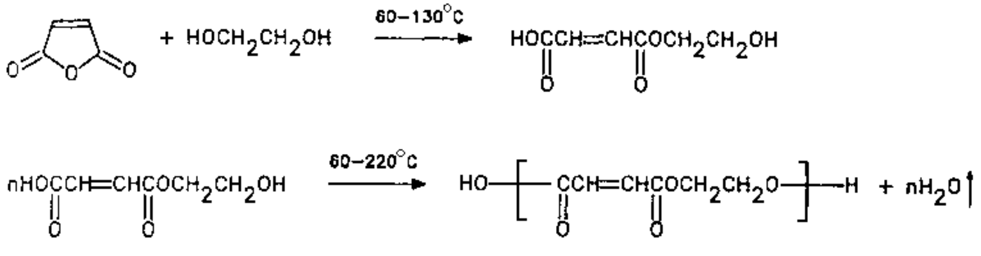
I. INTRODUCTION

Although unsaturated polyester resins are often regarded as casting plastics in at least one important use, glass-fiber lamination, they are used as adhesives. The method of binding glass-fiber mats with unsaturated polyesters started in 1942 by U.S. Rubber [1].

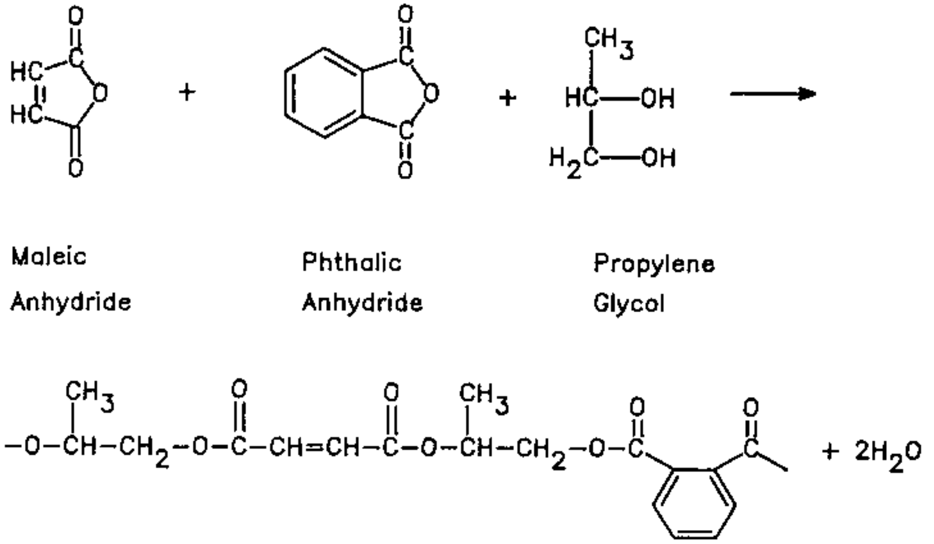
II. SYNTHESIS

A. Reaction Between Dicarboxylic Acids or Anhydrides and Diols

The synthesis of unsaturated polyesters usually involves a bulk reaction at elevated temperatures between dibasic acids or anhydrides and diols. A general reaction scheme for maleic anhydride and 1,2-ethanediol can be illustrated as follows:



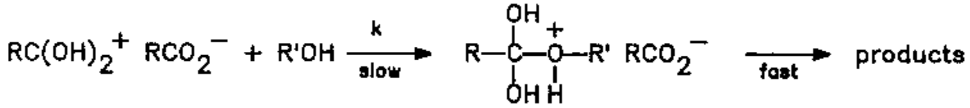
During this reaction most of the maleate groups are isomerized into fumarate groups. Since esterification is a reversible process, reaction water must be removed efficiently, especially in the last stages of the reaction, where the decrease in carboxyl group concentration is slow and the increase in viscosity is fast. These last stages are usually carried out under vacuum. However, to avoid losses of volatile reactants, an azeotropic distillation of reaction water in the presence of added organic solvent such as toluene or xylene may be used [2]. The main drawbacks of this process are the longer reaction time and the difficulty in removing the last traces of solvent. Phthalic anhydride can be used to substitute maleic anhydride partially but extensively. The reaction scheme can be represented as follows:



B. Kinetics and Mechanisms

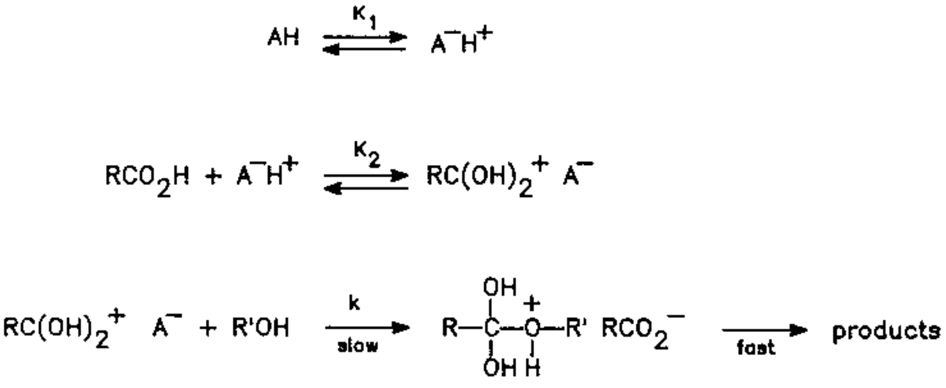
The theoretical analysis of the kinetic data for bulk polyesterification reactions is difficult because of the high concentrations of reactive end groups at the beginning of the reaction and because of the changes in dielectric constant of the medium during the reaction [3]. According to Flory [4], only the experimental results obtained for extents of reaction above 0.8 should be considered, that is when the polarity no longer changes and when the reactive groups form a dilute solution in the polyester. Within these limits, experimental data show that both mono- and polyesterifications are third-order reactions [4], second order in acid and first order in alcohol. A reasonable mechanism involves non-dissociated ion pairs and can be described, and with a protonic catalyst [2], as in the two following schemes:

$$2RCO_2H \overset{K}{\rightleftharpoons} RC(OH)_2^+\ RCO_2^-$$



$$RC(OH)_2^+\ RCO_2^- + R'OH \xrightarrow[\text{slow}]{k} R{-}\overset{\text{OH}}{\underset{\text{OH}}{C}}{-}\overset{+}{\underset{\text{H}}{O}}{-}R'\ RCO_2^- \xrightarrow[\text{fast}]{} \text{products}$$

R, R' = polyester chains $\quad -d[RCO_2H]/dt = kK[RCO_2H]^2[R'OH]$



$$AH \underset{}{\overset{K_1}{\rightleftharpoons}} A^-H^+$$

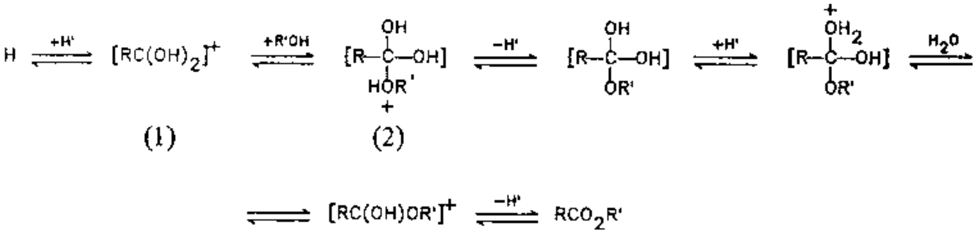
$$RCO_2H + A^-H^+ \overset{K_2}{\rightleftharpoons} RC(OH)_2^+\ A^-$$

$$RC(OH)_2^+\ A^- + R'OH \xrightarrow[\text{slow}]{k} R\text{—}\overset{OH}{\underset{OH}{C}}\text{—}\overset{+}{\underset{H}{O}}\text{—}R'\ RCO_2^- \xrightarrow[\text{fast}]{} \text{products}$$

R, R' = polyester chains $-d[RCO_2H]/dt = kK_1K_2[AH][RCO_2H][R'OH]$

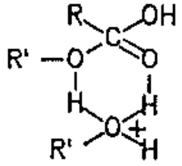
According to classic organic chemistry, direct esterification can be catalyzed by either acidic or basic compounds, and Ingold [4] has proposed eight different mechanisms, four for acid-catalyzed and four for base-catalyzed processes. Basic compounds are seldom used as catalysts for polyesterification, and among the acid-catalyzed mechanisms, $A_{AC}2$ is by far the most frequently observed. Hundreds of compounds have been claimed as effective catalysts in the patent literature; strong protonic acids (H_2SO_4, benzene-, naphthalene-, and *p*-toluenesulfonic acids are the most popular), oxides or salts of heavy metal ions (acetates are often preferred for their higher solubility), and organometallic compounds of titanium, tin, zirconium, and lead are the catalysts most frequently reported.

The mechanisms proposed for direct esterification of low-molecular-weight esters have been investigated in detail by many workers and have been discussed in detail in a review by Bender [4]. According to these investigations, the following scheme is generally accepted for proton-catalyst reactions.

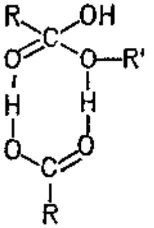


In this scheme, the reaction of the protonated form (1) of the carboxylic acid with the hydroxy compound to give the addition intermediate (2) is usually taken as the rate-controlling step. This mechanism is usually extrapolated to proton-catalyzed direct polyesterification.

Owing to the low basicity of substrates such as carboxylic acids, the concentration of protonated species (1) can be extremely low, and alternative mechanisms, involving a nucleophilic attack assisted by compounds able to form hydrogen bonds in cyclic transition states such as (3) or (4), have also been considered [4].



(3)



(4)

C. Side Reactions

The chemical structure of unsaturated polyester is more complex than expected in view of the chemistry described above. The ^{13}C nuclear magnetic resonance spectra of unsaturated polyesters present many small peaks that cannot be assigned to carboxylic or hydroxylic end groups alone. These are due to a number of side reactions. Of these, the addition of hydroxyl groups to double bonds is one of the most important side reactions in the synthesis of unsaturated polyesters by polycondensation. It leads to the formation of side chains and a modification of the stoichiometry due to diol consumption [4].

D. Catalysts

Selection of the proper catalyst and the amount to be used for any application depends on the resin, the temperature at which the resin is to be cured, the required working or pot life, and the time of gelation. No catalyst is available that can meet all the requirements. Therefore, combinations of catalysts, or of catalysts and accelerators, must be used to obtain the best results.

When it is necessary to start and even cause a complete cure at lower temperatures so that the polymerization heat can readily be dissipated, methyl ethyl ketone peroxide (MEKP) is the catalyst generally used. It does not lead to a full cure by itself at ambient temperatures. However, with the addition of an accelerator, the catalyst will cause gelation and almost complete cure within short periods of time, depending on the percentage of each used with the resin. From 0.5 to 2.0% of MEKP and 0.1 to 1.0% of cobalt naphthenate accelerator can be used, depending on the desired working time of the resin.

It is important that special care be taken to avoid the contamination of organic peroxides with accelerators or promotors used in polymerization reactions. These materials should never be added directly to one another or consecutively to a resin unless one ingredient is thoroughly mixed in before adding the other. In some cases, vigorous or explosive decompositions may result if direct contamination occurs.

E. Resin Reactivity

The maximum exothermic temperature reached, the time required for the reaction to attain peak exothermic temperature, and the time of gelation are important factors to be considered when selecting a resin. Reactivity tests provide a method for determining the behavior, uniformity, and curing characteristics of a resin. The use of a resin for a specific application often depends on the reactivity of the resin. Measurements of reactivity are helpful in the evaluation of accelerator, catalysts, and other materials that must be considered for the correct use of the resin.

The inhibitor in the resin counteracts the catalyst which dissociates into free radicals to initiate polymerization during the induction period. As the inhibitor becomes completely consumed, near the end of the interval, the free radicals from the catalyst initiate polymerization. The beginning of the polymerization is evidenced by the exothermic reaction, which causes the temperature of the resin to rise above the ambient bath temperature and the gelation of the resin. Knowing the time it takes for gelation is very helpful in selecting the correct resin for a particular application.

The time period it takes for the temperature of the resin to rise from 5°F above the bath temperature to its maximum is the propagation interval. The rate of polymerization increases until the rate of heat evolution of the resin equals the rate of heat loss to the bath. Polymerization is complete after the peak exothermic temperature is reached. The maximum exothermic temperature together with the propagation interval indicate the rate at which cure is attained.

F. Cross-Linking Mechanism

1. *Free-Radical Formation*

The decomposition of initiators is induced by heat in the case of molding compounds or by accelerators at temperatures below the decomposition temperature of the initiator in the case of cast polyester resins. Two types of accelerators are used, metal salts—mainly cobalt salts—and amines. The oxidoreduction of metal salts by peroxides produces free radicals. The process is very efficient since both lower and higher valencies of cations participate in the reaction.

$$RO_2H + CO^{2+} \longrightarrow CO^{3+} + RO + OH^-$$

$$RO_2H + CO^{3+} \longrightarrow CO^{2+} + RO_2 + H^+$$

$$CO^{3+} + OH^- \longrightarrow CO^{2+} + OH$$

2. *Free-Radical Cross-Linking*

The free radicals first react with the chemical inhibitor which has previously been added to the resin, since the inhibitor material must be chemically dissipated before any reaction between free radicals and the C=C double bonds can proceed [5]. Apparently, the free radicals serve to open the double bonds in the polyester linear chain to set in motion that portion of the polymerization process designated as initiation. Either the opened double bonds react with the vinyl groups of the monomer, or the free radicals serve to also open (add to) these latter unsaturated C=C bonds, permitting them to perform their cross-linking function, uniting the polyester chains into a three-dimensional network. There is further evidence that free radicals may also, to some degree, react with the unsaturated monomer to form various products of decomposition [5].

Theoretically, the reaction of polyesters should go to completion with all the double bonds reacted upon by free radicals and complete cross-linking established under the most favorable conditions. However, in actual practice, as determined by iodometric analysis, the true amount of residual unsaturation (indicating how far the polymerization has not gone) has been traced in the actual curing of polyesters, and can be summarized as follows:

1. What may be considered as an optimum cure with full-properties potential realized occurs when 92 to 95% of the unsaturation has been converted. Neither extra catalyst nor postcuring will convert this slight amount of remaining unreacted material.
2. The failure of all unsaturated sites to become reacted during final cure accounts for the discoloration of polyesters upon weathering and long-term aging. The unreacted double bonds eventually take up oxygen due to the action of sunlight and other factors, and peroxides are formed, creating a yellowish or amber color.

III. STRUCTURE–PROPERTIES RELATIONSHIPS

For a given polyester formulation, the properties of the final compound are a function of its condensation (e.g., carboxyl and hydroxyl group concentration), viscosity and molecular weight distribution, and the structural features of the three-dimensional network obtained after free-radical copolymerization. An increase in the molecular weight of an unsaturated polyester improves its hardness, tensile and flexural strength, and its heat distortion temperature (HDT) until a plateau value is reached. Carboxyl end groups impart higher viscosities and better physical properties to polyesters than do hydroxyl end groups.

Generally, both the physical and chemical properties of a polyester are affected by the ratio and type of the acid and diol components and of the copolymerizable monomer. To this effect higher proportions of maleic anhydride lead to a higher density of cross-linking and thus greater hardness and heat resistance of the cured resin. Conversely, phthalic anhydride is the most common reagent used to decrease the density of cross-linking, increasing the flexural strength. Equally, a variety of glycol can be used to obtain different resin properties. Propylene and ethylene glycols, diethylene glycol, and neopentyl glycol are commonly used.

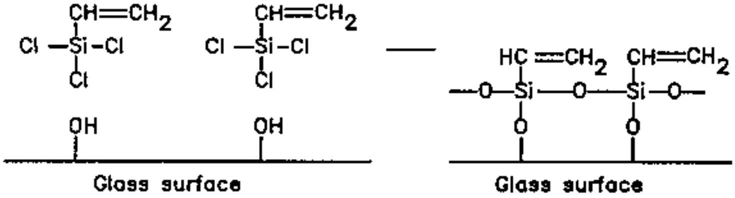
Vinyl monomers are usually added to the polyester resin as solvents of the unsaturated polyester; this is to decrease viscosity within manageable limits, as well as to function as cross-linking reagents. Styrene is the vinyl monomer most commonly used. Thus the degree of cross-linking can be controlled not only by modifying the concentration of unsaturated acid residues in the resin backbone, but also by changing the proportion of vinyl monomer added to the resin. The length of the cross-links can be controlled to a certain extent by modifying the concentration and type of vinyl monomer used.

IV. GLASS-FIBER LAMINATION

One of the main uses of polyester resin is to function as the adhesive for glass-fiber lamination. The cross-linking reaction of unsaturated polyesters is exothermic; that is, it is accompanied by a rise in temperature. Indeed, one of the useful features of an inorganic adherend functioning also as a reinforcing agent in these resins is that the heat of reaction is dissipated efficiently, achieving better temperature control across the width of the laminate. Poor temperature control during curing often gives rise to one or several of the following defects: warpage, shrinkage, motley surface resulting from overcure, and blisters resulting from undercure [6].

Glass fibers are the preferred form of adherend for polyester resins since they provide the strongest laminates. The glass may be of various types: for example, electrical glass, a low-alkali borosilicate glass, or alkali glass with an alkali content of 10 to 15%. The low-alkali borosilicate glass gives laminates with the best weathering and electrical properties, but the alkali glass is cheaper. For good adhesion to be achieved between resin and glass it is necessary to remove any sizing (in the case of woven cloths) and then to apply a finish to the fibers. The function of a finish is to provide a bond between the inorganic glass and the organic resin. Today, the most important of these finishes are based on silane compounds. In a typical system vinyl trichlorosilane is hydrolyzed in the presence of glass fiber, and this condenses with hydroxyl groups on the surface of the glass [7].

The glass-fiber strands are converted into three basic forms: roving, filament yarn, and mat. These fibers have a high tensile strength and differ from natural fibers in that they have no inner cellular structure and therefore do not absorb moisture internally. They do absorb it on the surface, however, and can be wetted with organic liquids. The roving is in a twinelike form, prepared by twisting and collecting 60 simple yarns (12,240 filaments) on a spool. In this form glass is available for chopping into shorter fibers of varying lengths for use in preforming machines or for incorporation into molding compounds. The most common mat is obtained by cutting fibers into 5-cm lengths, collecting them by suction on a moving metal screen, applying a binder, baking, and collecting the bound mat in rolls. The 5-cm fiber length confers optimum properties in respect to manufacture, molding characteristics, and all-round strength properties [7].



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Hot-Melt Adhesives

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I. INTRODUCTION

Hot melts are a widely used class of adhesives that are used for many applications but are rarely used for structural bonding, as seldom are they able to match the tensile strengths of other adhesive classes. Their primary uses are in packaging and in wood for edge veneering and veneer splicing. There are important reasons for employing hot-melt adhesive systems, such as:

1. Ease of Application via high-speed equipment
2. Formation of strong, permanent, and durable bonds within a few seconds of application
3. No environmental hazard and minimal wastage because of 100% solid systems
4. Ease of handling
5. Absence of highly volatile or flammable ingredients
6. Excellent adhesion
7. Wide formulation possibilities to suit individual requirements (e.g., color, viscosity, application temperature, and performance characteristics)
8. Cost-effectiveness

Hot melts are 100% solid thermoplastic materials that are supplied in pellet, slug, block, or irregular-shaped chip form. They require heating via appropriate application equipment, which usually is fairly sophisticated in order to control the required temperature and coverage rate. Upon application, the heat source is removed and the thermoplastics set immediately (within a few seconds). Hot melts are thus well suited to high-speed continuous-bonding operations.

II. ETHYLENE–VINYL ACETATE HOT MELTS FOR EDGING

A. Physical Characteristics

Edge veneering requires use of a hot-melt adhesive that is relatively high in viscosity at application temperatures (usually around 200°C). The reasons for this are as follows:

1. The adhesive must have sufficient body to prevent flowing from vertical surfaces after application.
2. It must not penetrate the substrate surface too deeply, causing glue starvation.
3. It must have easy spreading and excellent wetting characteristics.

Viscosities of these hot melts are on the order of 50,000 to 60,000 mPa s (cP) at 200°C. Viscosity is achieved through the correct selection of ethylene–vinyl acetate (EVA) copolymer grades, coupled with the quantity and type of reinforcing filler that is added to the system. The ball and ring softening point is an early indication of the degree of heat resistance of a particular hot melt. The softening point is influenced by the combination of ingredients, but to a large extent by the grade and quantity of EVA copolymer and tackifying resin contained in the system. Using a 5.1-g lead ball, the average softening points are between 90 to 105°C.

For optimum adhesion, the wetting characteristics (of the hot melt to substrates during application) are vital. Proper wetting is related to viscosity but is again largely influenced by resin selection and quantity. Stability of the adhesive is another important consideration. During prolonged periods at elevated temperature while contained in the hot-melt applicator, the hot melt must resist oxidation and thermal breakdown of components. This often leads to discoloration, charring, and inferior bonds. As a result of charred material, nozzle blockages can also be encountered.

B. Formulation Considerations

EVA hot melts consist basically of the following:

1. EVA copolymer
2. Tackifying and adhesion-promoting resins (e.g., hydrocarbon, rosin esters, coumarone–indene, terpene resins)
3. Fillers, usually barium sulfate (barytes) or calcium carbonate (whiting)
4. Antioxidants

1. *EVA Copolymer*

EVA copolymer is the main binder in the system and largely influences the following: (a) viscosity and rheology characteristics, (b) cohesive strength, (c) flexibility, and (d) adhesive strength. A variety of EVA grades are available, allowing the formulator a choice of varying vinyl acetate contents coupled with varying viscosities (melt index). Higher vinyl acetate contents generate greater adhesion to plastics, coupled with increased flexibility. The higher the vinyl acetate content, however, the higher the cost. Broadly speaking, EVA-based edge-veneering hot melts utilize grades averaging 28% vinyl acetate, and formulations usually contain 40% binder.

2. *Resins*

A certain percentage of resin is almost always incorporated into formulations, with resin content varying from 8 to 25%. Hydrocarbon resins are used most often, but rosin esters, terpenes, and indene resins, which are more heat stable, are also common. Resins provide better flow, hot-tack, adhesion, and wetting characteristics.

3. *Fillers*

The heavy fillers, such as barytes, are used at levels of up to 50% by weight, but more commonly at around 35 to 40%. The filler imparts cohesive strength and body to the adhesive, and also reduces the cost considerably. Barium sulfate is the filler chosen in most cases because of its high density and hence low pigment volume concentration. Barium sulfate grades vary from beige to dark brown, and this assists in formulating specific opaque colors to match color requirements. Finely ground calcium carbonate is sometimes used as a filler where very light colors are required. Titanium dioxide pigment is commonly used as a toner, at levels of 2 to 5%.

4. *Antioxidants*

Antioxidants are added to protect the organic components, especially resins, from oxidation/discoloration at high temperatures. A large choice exists. These materials are usually added at levels of 0.2 to 0.5%.

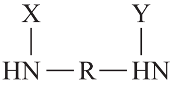
C. Production Technique and Equipment

Because of their relatively high melt viscosities, the EVA hot melts need special manufacturing equipment. For example, a Z-blade mixer such as a Baker Perkins or Winkworth with oil-heated jacketing is required. Mix temperatures are kept as low as possible (± 110°C) to keep bulk thick. The high-viscosity kneading action ensures rapid dissolution of EVA copolymer and resin. Fillers are easily dispersed and a homogeneous mix is achieved rapidly with this type of agitation. Upon completion, the molten product is extruded into ropes approximately 6 mm in diameter, which are cooled through a chilled water trough and then granulated into pellet form. Alternatively, hot-melt slugs are supplied where application equipment utilizes this form. It is essential to ensure that any residual moisture picked up during the cooling process is eliminated via an air-drying cyclone before packing.

III. POLYAMIDE HOT MELTS

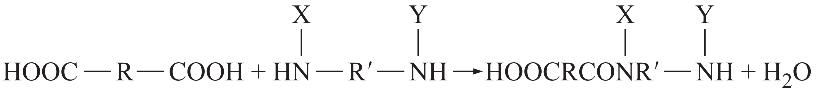
The polyamide hot melts are high-performance systems and are used selectively where good heat resistance is required. Their high cost relative to EVA types makes them rather unattractive for general use. Polyamide resins offer high tensile strengths and high initial tack, often without the need for additional formulating. Their higher melt points ensure good heat-resistance qualities and are responsible for rapid setting on cooling. Their two main drawbacks are cost and the tendency to char easily if kept at high temperatures.

Hot-melt polyamide resins are obtained by the reaction of diamines with diacids. While in their simplest form polyamides are the reaction of a particular diamide with a particular diamine, most of the polyamides used in adhesive formulations are complex reaction products obtained by combining several diacids and diamines to obtain the particular properties required. The most common diacid used is a dibasic acid obtained by polymerizing oleic or linoleic acid or other unsaturated fatty acids. This acid can be represented as HOOC—R—COOH, where R is a hydrocarbon residue of 34 carbon atoms and of indeterminate configuration. Commercial forms of this dimeric diacid also contain preparations of products obtained by polymerization of three or more molecules of unsaturated fatty acids and thus contain varying quantities of trimeric acids and of higher homologs. Monomeric forms are also present. The most used diamine for this type of adhesive is ethylenediamine, $H_2N—(CH_2)_2—NH_2$, but other diamines are also used, responding to the general formula



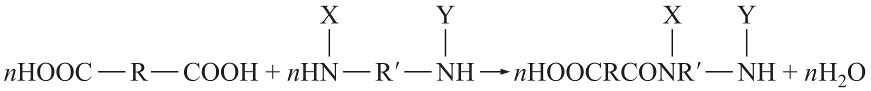
$$\overset{\overset{\mathrm{X}}{|}}{\mathrm{HN}}—\mathrm{R}—\overset{\overset{\mathrm{Y}}{|}}{\mathrm{HN}}$$

where X and Y can be H or other chemical groups. Polyamides are then formed according to the schematic reaction



$$\mathrm{HOOC}—\mathrm{R}—\mathrm{COOH} + \overset{\overset{\mathrm{X}}{|}}{\mathrm{HN}}—\mathrm{R'}—\overset{\overset{\mathrm{Y}}{|}}{\mathrm{NH}} \rightarrow \mathrm{HOOCRCO}\overset{\overset{\mathrm{X}}{|}}{\mathrm{N}}\mathrm{R'}—\overset{\overset{\mathrm{Y}}{|}}{\mathrm{NH}} + \mathrm{H_2O}$$

or simply



$$n\mathrm{HOOC}—\mathrm{R}—\mathrm{COOH} + n\overset{\overset{\mathrm{X}}{|}}{\mathrm{HN}}—\mathrm{R'}—\overset{\overset{\mathrm{Y}}{|}}{\mathrm{NH}} \rightarrow n\mathrm{HOOCRCO}\overset{\overset{\mathrm{X}}{|}}{\mathrm{N}}\mathrm{R'}—\overset{\overset{\mathrm{Y}}{|}}{\mathrm{NH}} + n\mathrm{H_2O}$$

The reaction occurs with the elimination of water of form amide groups. The high polarity of the amide groups contributes to give, by formation of interchain hydrogen bonds, the characteristic polymer strength and adhesive properties to the polyamides.

The basic resins need some form of modification to achieve (1) suitable application viscosities, (2) flexibility, and (3) reduction in costs if possible. Suitable polyamide resins (those of the more flexible variety) are thus frequently modified by the addition of EVA copolymer (high-viscosity, high-melt-point grade). The amount of EVA that can be added is restricted to a maximum of 25% in most cases because of compatibility problems. The blend is then further modified with selected tackifying resin addition and small quantities of filler, to reach an optimum balance of performance properties. To achieve maximum adhesion, it is common for polyamide hot melts of this type to be used in conjunction with a polyamide resin solution primer system for edging material. The primer is invariably a dilute solution of the base polyamide resin.

IV. ADHESIVE APPLICATION GUIDELINES

In general, one should ensure that operation of the machine is in accordance with the manufacturer's instructions, being sure to set the machine according to the adhesive supplier's specifications for line speed, operating temperature, and adhesive coating weight. During application, the following guidelines should be observed:

1. Adhesive reservoir temperature: 204°C
2. Application roller temperature: 191°C (application roller to be 12 to 13°C lower than reservoir temperature)
3. Adhesive application weight: 200 to 250 g/m^2
4. Melting time of adhesive: $1\frac{1}{2}$ to 3 h

Correct application weight and spread of the hot melt can be checked by bonding a transparent poly(vinyl chloride) (PVC) strip and applying at a pressure of 2 to 4 kg/cm^2. If the correct pressure has been applied, the pattern caused by the applicator wheel on the adhesive should disappear, with little or no squeeze-out at the edges. The adhesive reservoir must be filled completely and the lid kept in place, to avoid heat loss. It is necessary to clean gluepots thoroughly at regular intervals, as well as filters, nozzles, and glue lines (every 2 to 4 weeks). Suitable solid hot-melt cleaners, available from adhesive suppliers, have largely replaced the traditional use of cleaning solvents. The applicator wheel or roller is used at a pressure of 2 to 4 kg/cm^2.

V. APPLICATION AREAS

A. Veneer Splicing

Particleboard with a decorative wooden veneer surface usually employs a hot-melt adhesive to effectively mate veneer edges down the length of the joint. Polyamide hot-melt adhesives are widely used for this veneer splicing process. The adhesive is more often than not supplied as a thread and positioned as such in a zigzag configuration. A heated press is employed to activate the adhesive followed by rapid cooling and setting. The rapid set required is best achieved with polyamide hot-melt adhesives, since their setting temperatures are much higher than, for example, those for EVA types, and since the range between application and setting temperatures achievable with polyamides is narrow. Another important feature of polyamide resins in the context of this application is the low melt viscosities achievable, thus ensuring rapid spreading and wetting of the molten film.

B. Edge Veneering and Edge Banding

Edge veneering and edge banding constitute by far the main area employing hot-melt adhesives which are based predominantly on EVA copolymer resins. For some applications, however, formulated polyamide hot melts are also used, particularly where exceptional heat resistance of the bond is required. Modern materials such as decorative surface board products, used in the manufacture of furniture components, require exposed edges to be covered with suitable edging materials. Most laminated surface board products consist of a decorative melamine or PVC layer bonded to a chipboard substrate. These board products have their own performance characteristics, which may influence the edge bond. The choice, application, and fabrication method of edging plays a very important part in the manufacturing and final application of the furniture produced. The choice of correct edging selection, therefore, depends very much on performance requirements and aesthetic value.

VI. GRAVURE APPLICATOR WHEEL TECHNOLOGY

A. Application Process

The gravure applicator wheel is the most important individual component on an edgebander. Adhesive transfer to the substrate takes place when the substrate comes into contact with the gravure wheel applicator, which should rotate at the same speed as the moving track. Fresh adhesive is resupplied to the applicator wheel via the doctor blade in less than one revolution of the wheel.

By adding another doctor blade and reversing the direction of the rotation of the gravure applicator wheel, much more adhesive can be driven onto the substrate. This may be necessary when edging substrates with a low density, wide edges, or edges that require a lot of gap filling (plywood). Worn gravure applicator wheels should be replaced immediately. On replacement, a change in machine performance will take place and equipment adjustments should be carried out.

B. Heating

Where a cartridge heater is mounted in the center of the applicator wheel shaft, a high-temperature grease must be used as a heat-conducting medium between cartridge heater and applicator wheel; otherwise, there will be rapid cartridge heater burnout due to overheating. Adhesive temperature at the applicator wheel should be 12 to 13°C cooler than the adhesive temperature in the reservoir, to increase cartridge heater life.

C. Behavior of Hot-Melt Adhesives on Gravure Wheel Applicators

The single most important component on an edgebander is the gravure wheel applicator. All other components of the machine support the performance of the gravure wheel applicator. It is the gravure wheel application that controls the amount of hot-melt adhesive that is applied to the substrates, which, in turn, determines the number of calories of heat present to keep the hot-melt liquid until the time of bond formation.

Of the hot-melt adhesive that is located between the peaks and the doctor blade, only 1% is transferred to the substrate; the balance becomes nothing more than squeeze-out. The volume of adhesive that is found in the groove area is the actual material that is transferred to the substrate edge. The purpose of the doctor blade is not to act as an adjustment to increase or decrease adhesive transfer to the substrate; rather, it serves to replace in the grooves the adhesive that has transferred to the substrate. An incorrect doctor-blade setting will either cause excess squeeze-out or insufficiently fill the grooves, which will result in less than maximum adhesive transfer. The volume of adhesive that is transferred to the substrate is the single major controlling factor in determining the open time of the hot-melt adhesive. The volume of adhesive that does transfer is preset at the factory and is determined by the actual dimensions and geometry of the groove area.

If the adhesive is too cohesively strong (too cold) or too cohesively weak (too hot), the adhesive will break out of the top of the groove in the gravure applicator wheel, reducing the adhesive transfer. This is exactly why the open time of the hot-melt adhesive is determined by the amount of adhesive transferred, not by raising the application temperature. If the shear force is too low to move the adhesive from the gravure applicator wheel (slow line speed), adhesive transfer is reduced from maximum; too high a shear force (fast line speed) also reduces transfer. Shear force affects the cohesive strength of the hot melt exactly like temperature.

VII. FORMULATIONS FOR TYPICAL EVA EDGE-VENEERING HOT MELTS

Following are formulas for hot melts in various applications. Ingredients are listed in parts by weight.

A. General-Purpose Hot Melts for Both Wood and Plastic Veneers

	White	Natural	Brown
Hydrocarbon resin, 90°C m.p.	5.50	5.50	5.50
Rosin ester, 85°C m.p.	8.00	8.00	8.00
Coumarone indene resin, 105°C m.p.	5.00	5.00	5.00
Butylated hydroxytoluene (BHT) antioxidant	0.20	0.20	0.20

Hot-Melt Adhesives

	White	Natural	Brown
Elvax 250	14.00	14.00	14.00
Elvax 210	10.00	10.00	10.00
Elvax 150	15.00	15.00	15.00
TiO_2 pigment	4.50	0.80	—
Superfine light barytes	37.80	41.50	—
Pink barytes	—	—	42.30
	100.00	100.00	100.00

B. Low-Cost Hot Melt for Wooden Veneer Only, Natural Color

Hydrocarbon resin, 90°C m.p.	12.00
Hydrocarbon resin, 100°C m.p.	10.00
Elvax 250	30.00
BHT antioxidant	0.20
Superfine light barytes	47.20
TiO_2	0.60
	100.00

C. Hot Melt for Difficult Plastic Surfaces (e.g., Deccon, Natural Color)

Polyterpene resin, 115°C m.p.	30.00
BHT antioxidant	0.20
Elvax 260	10.00
Elvax 250	35.00
$CaCO_3$ (15 μm)	24.80
	100.00

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Reactive Acrylic Adhesives

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I. INTRODUCTION

“Curing acrylic adhesives” can be defined as reactive, cross-linked, high strength structural adhesives that cure by way of free radical initiation. They typically contain methacrylate monomers that are generally toughened with elastomeric polymers as part of the formulation.

Curing acrylic adhesives are distinctly different from anaerobics, cyanoacrylates, and acrylic solution adhesives and emulsions. These related chemistries use different formulating materials, cure via different curing mechanisms, and often possess minimal high performance properties over long periods of time, or when exposed to aggressive environments.

Curing acrylic adhesives were first developed in Germany in the late 1960s as an outgrowth of poly(methyl methacrylate) chemistry. Early formulations were simply low molecular weight solutions of poly(methyl methacrylate) dissolved in methyl methacrylate monomer. These simple systems could be cured by way of peroxide initiation and found utility in bonding aluminum windows and doors. Since that time, a considerable amount of research has occurred resulting in the emergence of the very sophisticated adhesive systems that are on the market today. A considerable amount of the most recent work in developing what are now being referred to as “high performance acrylic adhesives” has been conducted in the United States.

This chapter will cover acrylic chemistry, the various types of acrylic adhesives that have come into existence over the years, advantages and limitations of these systems, properties of adhesives, lap shear strength, what makes these systems unique among other types of adhesives, and examples of performance.

II. HARDENING (CURE KINETICS)

Acrylic adhesives cure by addition polymerization reactions. These chain reactions are initiated by the formation of free radicals that result in the adhesive curing by way of a very rapid polymer chain growth. This cure chemistry is significantly more rapid than a typical cure curve (i.e., condensation type) found in epoxy and urethane adhesives. A comparison of the cure profile of condensation (epoxy and urethane) versus addition

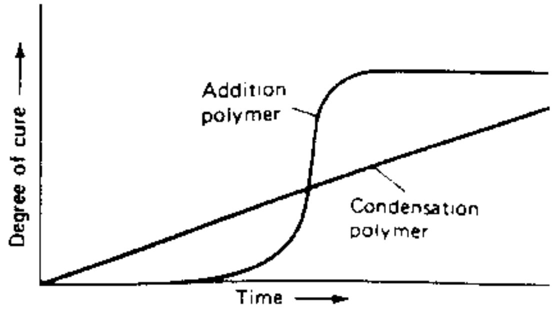


Figure 1 Cure profile of condensation versus addition polymerization.

(acrylic) polymerization is shown in Fig. 1. The free radical reaction or addition polymerization used in acrylic adhesives offers the user certain advantages over other types of adhesives, again, namely epoxies and urethanes.

As can be seen from the cure curve only little polymerization is noticeable in the early stage of the reaction after the adhesive is mixed. This allows the user to position and re-position parts for longer periods of time after the adhesive is mixed. The time to reposition parts is relatively longer for acrylics when considered as a percentage of the overall cure time than is typically possible with other types of adhesives. This can be a significant advantage for some manufacturing methods.

Once cure is initiated with acrylics, it tends to proceed at an increasingly accelerated pace until full cure is reached. This rapid achievement of final properties is in contrast to urethanes and epoxies which tend to more gradually build properties to full cure. The rapid setting (cure) feature of acrylics allows the user to more clearly determine when parts are securely bonded (i.e. the adhesive is fully cured) and finished goods are suitable for shipment. The fact that this rapid setting is possible at room temperature is also a unique feature of acrylic adhesives.

Due to the availability of a large number of formulating tools and choice of polymerization initiators, it has also been possible for formulators to develop systems that have a whole spectrum of cure rates. This allows manufacturing and design engineers to custom-fit specifically designed adhesives to a variety of different production schedules.

III. STORAGE

Like most adhesive types, acrylic adhesives do not have an indefinite shelf life after manufacture. Typically suppliers of acrylic adhesives list shelf lives of at least three months, with some as long as a year.

One difference with acrylic adhesives is the fact that they do often contain large amounts of highly reactive substances (monomers) that are used to achieve some of the unique properties associated with this family of products. In some cases, certain monomers may have a tendency to autopolymerize (cure without the use of externally added accelerators or hardeners). Consequently, shelf stability with some systems can be a problem at relatively low temperatures. Even at as low as 44°C some acrylic formulations will begin to cure and harden in as little as a few weeks if maintained at these temperatures. Large containers [above 5 gallons (ca. 19 L)] can worsen this problem.

This problem with shelf stability above 44°C is largely historic in nature since recently introduced products have much improved stability over early prototypes. Users of these products should, however, consult with suppliers to confirm recommended storage conditions.

IV. PHYSICAL FORM AND HANDLING CHARACTERISTICS

Most acrylic adhesives are supplied as two high viscosity liquids or pastes that are mixed together, called "Mix-in Accelerator" systems. Some types can also optionally be cured by no-mix accelerator lacquers. Accelerators are low viscosity liquids which are brush or spray applied to one or both of the substrates being bonded. Following accelerator application, the unmixed adhesive is applied to the primed substrate. This method eliminates the need for premixing the adhesive and accelerator, which eliminates pot life concerns.

Many acrylic adhesive products also go through a notable color change as they cure, which is unique to these materials. This color change can be used as a rough indicator of cure state and can be utilized in many manufacturing situations as an effective means of verifying the presence of both adhesive components.

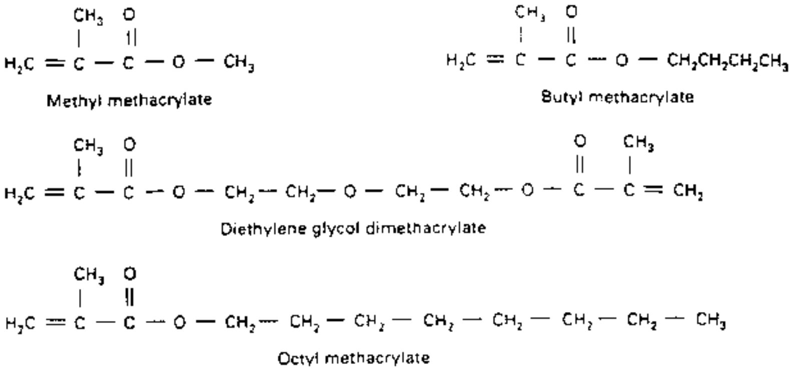
Because many acrylic adhesives cure very rapidly with a significant exotherm, manufacturers generally recommend that quantities greater than a pint (ca. 0.47 L) should not be mixed at one time. As a consequence of the rapid exothermic cure of many acrylic adhesives, the use of dual component cartridges is often ideal. Most products can be purchased in ready-to-use cartridges. For large continuous operations, various automated types of meter-mix-and-dispense equipment are marketed by a number of engineering companies.

One typical concern with acrylic adhesives, specifically those containing methyl methacrylate as a component, is the characteristic odor of the methyl methacrylate monomer. This odor may be objectionable to some people and may result in the use of other types of adhesives instead. Later in this chapter some of the new "low odor" formulations will be briefly discussed as alternative adhesives where odor has been an issue. This new technology offers performance characteristics equal to methyl methacrylate-containing products, albeit at a higher price.

V. PRODUCT COMPOSITION

As with almost all commercially available high performance products on the market today, there are many proprietary, highly formulated products described as "acrylic adhesives." The formulations vary widely with different families and subfamilies of products constantly being introduced, each offering certain advantages over previous "generations." In general, however, they can all be characterized as having a significant portion of the formulation composed of acrylic monomers, used in combination with various other polymers. They all contain ingredients to initiate hardening or curing of the adhesive. In addition, they contain various other organic and inorganic components designed to achieve desired handling properties, flexibility, specific adhesion, and shelf stability.

Methyl methacrylate and some of the other related monomers that are typically used in acrylic adhesives are shown in Fig. 2. These monomers vary in volatility with the lower molecular weight members of this family having a rather high odor and low flash point.



$$H_2C=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_3$$

$$H_2C=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2CH_2CH_3$$

$$H_2C=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

$$H_2C=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

Figure 2 Reactive species (monomers) for acrylics.

Higher molecular weight members offer lower odor and higher flash point, and also impart greater flexibility in the finished adhesives. Additionally, the lower molecular variants tend to be lower in overall cost and result in somewhat better adhesion to some surfaces. Depending on which properties are of most importance in a particular application, the lower molecular weight, the higher molecular weight, or blends thereof can be employed.

The tendency of acrylic monomers to spontaneously and quickly polymerize makes it necessary for adhesive formulators to include various types of chemical stabilizers as part of the formulation to assure good shelf stability. These stabilizers are generally complex organic compounds that have a strong ability to react with free radicals (the cure chemistry most commonly employed with acrylics). These stabilizers stop unwanted side reactions and assure good shelf life of formulated adhesive products.

In addition to the methacrylate monomers that are responsible for adhesive hardening, and the initiators and stabilizers already mentioned, most acrylic adhesives also contain polymers of various types and molecular weight. These additional components are included by formulating chemists to control handling properties, cure rates, flexibility, strength, adhesion, and environmental resistance. The exact nature of specific components is held as a trade secret by companies. Some insight into the types of polymers used and their combinations and levels can be found by searching patent literature and various technical journals.

It should be noted that modifiers to improve flexibility are particularly important in systems based on the most common monomer, methyl methacrylate. Polymerized methyl methacrylate monomer is a hard brittle material, not very useful as an adhesive. Consequently, most companies have developed unique proprietary ways to add flexible polymers to acrylic adhesives to achieve desired flexibility.

In summary, in light of a broad spectrum of acrylic adhesive formulations, it can be assumed that any purchased acrylic adhesive on the market today will be a complex, highly formulated product having numerous ingredients to control cure, handling properties, shelf life, physical properties, and adhesion.

VI. CURE INITIATING CHEMISTRY

As has been noted above, in order for adhesive systems containing methacrylated monomers to cure, a free radical must be generated. A typical means of generating a free radical is shown in Fig. 3. This method of initiating the cure of acrylic adhesives is also known as a redox reaction. Redox reactions for acrylics typically involve the use of a chemical substance, often an aromatic amine (as shown in Fig. 3). These amines are present in one portion or component of the adhesive. They typically react with another chemical substance—typically a peroxide (also shown in Fig. 3). The result of the reaction of amine and peroxide is the formation of a free radical which is capable of reacting with methacrylated monomers to begin the polymerization process and subsequent cure.

The curing reaction will generally continue as long as there are unreacted monomer molecules present and there are no chemical or other factors present that could interfere with the reaction's completion. With some formulations, certain surfaces and certain contaminants can interfere with the reaction resulting in incomplete cure of the adhesive, and low bond strength. Surfaces and contaminants to avoid are usually mentioned in the manufacturer's literature. Barring any unwanted interfering reactions as mentioned above, the polymerization and curing process, once begun, will ultimately lead to the formation of the high molecular weight polymers useful as adhesives.

The complex details of properly initiating and appropriately controlling the chain reactions in acrylic adhesives have been carefully worked out by adhesive chemists (with the most effective ways of achieving this kept secret by companies that supply these adhesive materials). When accomplished skillfully, the final result is a tough high molecular weight complex polymer, useful as an adhesive. A full and complete review of even the published information on this cure chemistry is beyond the scope of this chapter. The reader can gain further insight by consulting the bibliography at the end of this chapter.

It should be noted that in addition to the use of amines and peroxides there have been other initiating reactions reported as methods to generate free radicals and cure acrylic adhesives. One example is shown in Fig. 4. In addition to this example, literature searches will reveal numerous other mechanisms to initiate cure. As seen in Fig. 4, organic compounds used to initiate the reaction can vary considerably; however, they all tend to result in the formation of critically important free radicals. These radicals are capable of

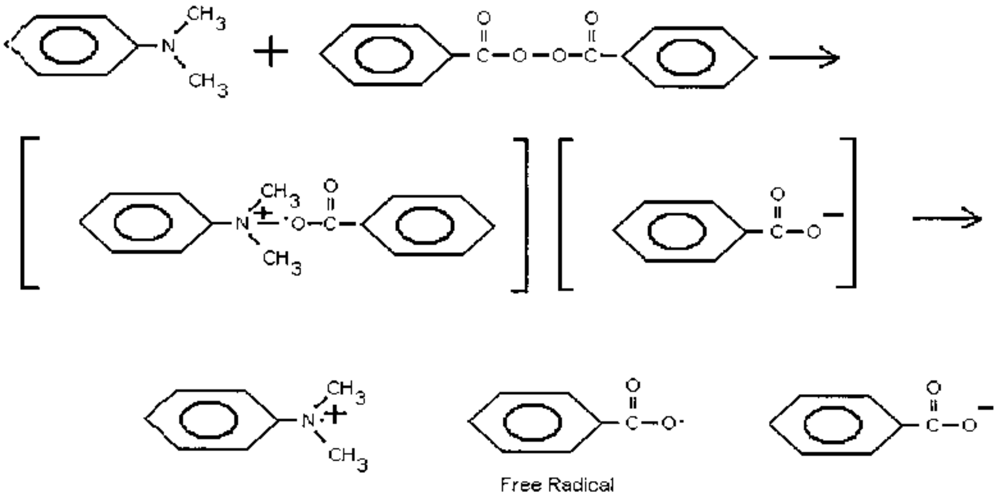


Figure 3 Redox reaction for acrylics.

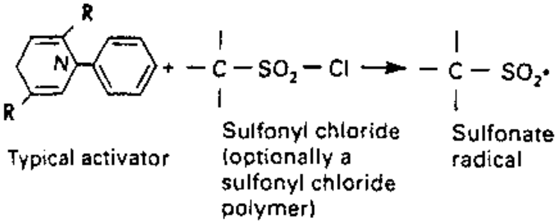


Figure 4 Amine plus sulfonyl chloride initiation of the cure of acrylic adhesives.

reacting with monomeric species found in the composition, ultimately resulting in polymerization and cured high molecular weight polymers.

VII. UNIQUE CHARACTERISTICS OF ACRYLICS

The polymerization of acrylic adhesives via free radicals (chain reaction) allows acrylic adhesives to be dispensed and cured using unique techniques. Other types of adhesive products often cure by condensation polymerization reactions which dictate certain cure characteristics and handling techniques.

Different curing possibilities for acrylics follow from the fact that the free radicals, once formed, during acrylic adhesive cure will continue to propagate throughout the curing adhesive. This means that cure, even if begun at a very localized region, can proceed throughout the adhesive glue line without additional mixing. This is in contrast to epoxy and urethane types which require intimate mixing for full cure.

As a consequence, two distinctly unique methods of handling and curing acrylic adhesives follow from their cure chemistry. These are the so-called "accelerator lacquer" cure and the "no-mix" or "honeymoon" cure. These methods of handling acrylics are depicted in Figs. 5 and 6.

Figure 5 depicts the use of a peroxide-containing accelerator lacquer to cure the acrylic adhesive. The accelerator lacquer is usually in the form of a low viscosity liquid that is brush or spray applied to one or both of the substrates being bonded. Figure 5 shows the use of a solvent-carried peroxide-containing lacquer film former. When this accelerator lacquer is applied to one of the surfaces and dried, it represents a source of free radicals due to the presence of the peroxide incorporated into it. The peroxide in the accelerator lacquer will remain unchanged chemically, until adhesive is applied over the lacquer. At this point, amines in the adhesive react with the peroxide-containing lacquer to disassociate the peroxide, forming free radicals. These free radicals are then transported into the bulk of the adhesive and continue to propagate through the polymerizing methacrylate monomers to give the final full cure.

The use of accelerator lacquers as a means to cure acrylics has been a very popular method since it allows the priming and storing of parts, the achievement of very rapid cures, and does not require expensive meter-mix-dispense equipment. It should be noted that this cure mechanism is not possible with condensation polymers, such as epoxies and urethanes, since they require full and intimate mixing of both components to achieve complete cures.

Figure 6 depicts another unique method of curing acrylics, the "honeymoon" or "no-mix" method. This technique also takes advantage of the ability of free radicals to

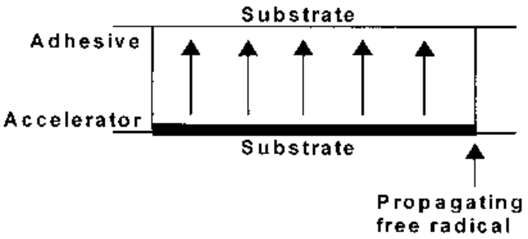


Figure 5 Accelerator lacquer cure.

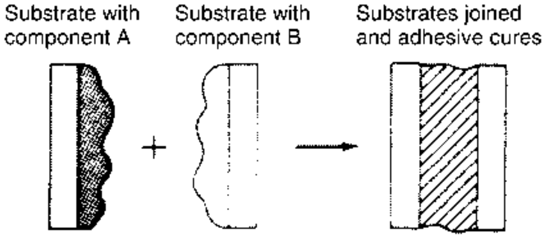


Figure 6 Honeymoon, or no-mix, cure for acrylic adhesives.

propagate throughout the adhesive to complete the cure without the need for intimate mixing. In this approach, a bead of component A is applied to one surface, while a bead of component B is applied to the other. As in the case of the accelerator lacquer, no reaction occurs until the two surfaces are mated. Once the two surfaces are joined, a rapid generation of free radicals occurs followed by monomer polymerization and full adhesive cure. As with the accelerator lacquer, this technique requires the use of only inexpensive dispensing equipment, but is not possible with adhesive types other than acrylics.

VIII. ACRYLIC ADHESIVE "FAMILIES"

Acrylic adhesives, like many other adhesive types on the market today, have had a series of technical improvements often referred to as "generations" or "families." These so-called "generations" of acrylic adhesives originally did represent fundamental changes in the formulations and significant improvement options to potential users. In recent years, these distinctions have been blurred considerably. Most products on the market today are advanced formulations offering performance, handling, and safety features well beyond products introduced decades earlier. Nevertheless, some of the early nomenclature is still used, and certainly is common in older literature. Consequently, they are reviewed here for historical purposes. In the following sections, each of the important acrylic types is covered separately in an attempt to clarify what they are and how they differ from one another.

A. Conventional Acrylic Adhesives

"Conventional" or "first generation" acrylic adhesives are the earliest examples of this technology. They contain methacrylated monomers, a variety of polymers, an

Table 1 Conventional, or First Generation, Acrylic Adhesives

Component	Parts by weight
Styrene–methyl methacrylate copolymer syrup	40
Methacrylic acid	9
Poly(methyl methacrylate) syrup	49
Accelerator–stabilizer package	2

Table 2 Bond Performance of First Generation Acrylic Adhesives

Substrate	Lap shear strength (MPa)[a]
Clean steel	26.2
Clean aluminum	21.4
Rigid poly(vinyl chloride)	17.9
Steel to nylon	20.5
Steel to polystyrene	16.7
Steel to ABS[b]	17.1
Galvanized steel	2.9

[a] ASTM D1002. 1000 psi ≈ 6.9 MPa.

[b] Acrylonitrile–butadiene–styrene.

initiator/stabilizer package, and methacrylic acid. Such formulations, a typical example of which is shown in Table 1, emerged in the early 1970s and found considerable utility in bonding thermoplastics.

Products classified as “first generation” are still on the market and are sold primarily for bonding thermoplastics. They provide excellent gap filling characteristics, rapid cure and adhesion, and are generally stronger than the substrates themselves.

Typical bond performance of adhesives of the first generation type is shown in Table 2. The adhesives have good adhesion to thermoplastics such as polystyrene, ABS, and poly(vinyl chloride), to wood and rubber, and to steel and aluminum provided the metals are clean. It can also be seen from this table that adhesion to galvanized steel is lower than to other metals. Bonding to galvanized steel was a problem with first generation acrylic adhesives but it has been overcome with more recent embodiments of this technology covered later in this chapter.

It should be noted that if adhesives of the type shown in Table 2 are applied and cured using an accelerator lacquer, bond strengths equivalent to those achieved with mix-in peroxide pastes are obtained. In bonding ABS to itself, for example, the literature reports stock breaks in the range of 5.9 MPa when either a mix-in accelerator or an accelerator lacquer are used.

Data have also been reported in company literature claiming first generation acrylic adhesives will resist aggressive environments such as exposure to alcohols and hot water immersion. The patent literature also reports that when using mix-in accelerators, good bond strengths are retained for at least 35 days in aggressive environments (e.g., in condensing humidity cabinets). The failure mode of substrate failure in plastic substrates, such as ABS, is also reported.

B. DH Acrylic Adhesives

The so-called ‘‘Dexter Hysol (DH) acrylic adhesives’’ are an example of one of the later generation products and are loosely an extension of the original technology. DH and other generations are often lumped together under a general term, ‘‘second generation’’ acrylic adhesives. These adhesives differ from the original offerings in the polymers used, the monomers used, and an increasing use of novel cure chemistry and specialty adhesion enhancing additives. In some cases the term ‘‘DH’’ is used interchangeably with ‘‘second generation,’’ although adhesive suppliers would argue that this is not accurate and the two terms represent quite different types of products.

Nevertheless, one obvious difference between these materials and earlier types is that the accelerator lacquers used with these newer systems often were oily, and peroxides other than benzoyl peroxide were often used. The oily accelerator lacquers that are available for curing DH acrylics are difficult to apply and once primed, parts are difficult to handle.

Second generation and DH acrylic adhesives were notably different from earlier systems in that they were the first type of acrylic adhesives that could be cured and good bonds to unprepared metals could be obtained. These systems showed the ability not only to bond to unprepared steel and aluminum surfaces, but also to aluminum and steel surfaces that still had varieties of different oils and drawing compounds on them. This ability marked a significant advancement in acrylic adhesives and established them as a unique family of adhesive materials for bonding oily and unprepared metals.

These types of acrylic adhesive systems enjoyed considerable popularity when they were first introduced. More recently, however, they have been replaced by other, more ‘‘user-friendly’’ adhesive formulations that do not require nondrying (oily) primers and accelerators. In addition, some of the key raw materials have been of limited availability, interfering with manufacturers’ ability to supply product consistently.

C. HP Second Generation Acrylic Adhesives

The emergence of the DH acrylic adhesives occurred concurrent with the introduction of the so-called ‘‘HP’’ or ‘‘high performance’’ acrylic adhesives. This type of system, as with the DH types, offered users the ability to bond through oily metals, but did not require the use of awkward oily primers. They also were based on formulations that contained specialty adhesion promoting components, often contained monomers that were less flammable than first generation products, and often were also considerably lower in odor.

Adhesives of HP type have been shown to bond bronze, lead, nickel, magnesium, copper, aluminum, steel, and stainless steel, in addition to most of the other substrates that earlier offerings were capable of bonding. They did, however, continue to show weaknesses when zinc surfaces were bonded. So these adhesives may not be well suited for certain applications in the automobile area where galvanized steel is being bonded (Note that later generations covered in this chapter do not necessarily have this shortcoming).

Table 3 gives the lap shear bond strength of typical substrates bonded with high performance acrylic adhesives. It can be seen from these data that bonds to oily metals are at least as strong, and often stronger, than bonds obtained with clean surfaces. When HP acrylics were used to bond oily metals, and the bonded parts were subjected to aggressive environments (e.g., condensing humidity, salt spray, water immersion, and gasoline immersion) for up to 1000 hours, little or no reduction in overall bond strength was reported.

Table 3 Bond Performance of "High Performance" Acrylic Adhesives on Oily Metals

Substrate	Lap shear strength (MPa)[a]
SAE 1010 steel (oily)	44.1
SAE 1010 steel (solvent wiped)	42.1
SAE 1010 steel (grit blasted)	41.0
6061-T6 aluminum (oily)	35.1
6061-T6 aluminum (solvent wiped)	33.6
6061-T6 aluminum (grit blasted)	34.7
2024-T3 aluminum (oily)	35.1
2024-T3 aluminum (solvent wiped)	32.5

[a] ASTM D1002. 1000 psi ≈ 6.9 MPa.

D. HI and Current Families of Acrylic Adhesives

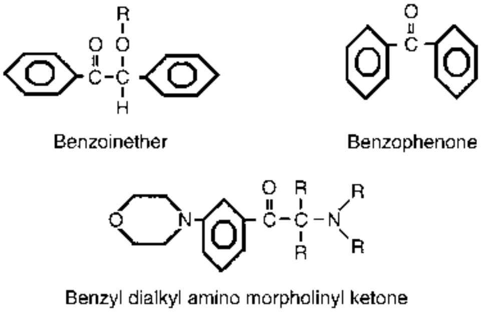
Another advancement in acrylic adhesives has been in the area of acrylics with improved low temperature properties, sometimes called "HI" or "high impact" acrylics. These variants of the technology not only offer outstanding low temperature properties, but also significant heat resistance makes them ideal for applications where product performance over a wide temperature range is required. Formulators have also further advanced the art in the use of ingredients that are nonflammable and have little or no odor.

These products represent additional advances made by polymer scientists and formulating chemists. They use unique molecular building blocks and polymers, sometimes of different families than strictly acrylic, leading to numerous "hybrids" involving other polymer and elastomer types emerging very recently. In addition to the properties noted above, HI products retain virtually all of the performance features of earlier variants.

E. Equal-Mix Acrylic Adhesives

A disadvantage of many acrylic adhesive products on the market today is that those that require mixing may require an awkward mix ratio. The first generation products, for instance, generally required a mix of 20 parts adhesive to 1 part curing agent, making highly automated production very difficult to achieve effectively. As the various generations of acrylics have emerged, more convenient mix combinations also have been introduced; first 10 to 1, then 4 to 1 variants, then 2 to 1, and even certain products with 1 to 1. Recently true equal-mix products have emerged, and even products that do not require significant mixing at all have come to the market.

The no-mix or honeymoon type acrylic adhesives are unique in that polymerization is adequately achieved after the A component of the adhesive is applied to one substrate to be bonded, and the B component is applied to the other substrate to be bonded. When these two halves are joined together, as shown in Fig. 6 previously, enough free radicals are generated to initiate and complete the cure. The no-mix technology is unique in that it has found extensive use in the electronics industry, and is a very useful technique in bonding magnets for electrical motors where the fast cure and easy application technique have found extensive utility.



Benzoinether

Benzophenone

Benzyl dialkyl amino morpholinyl ketone

Figure 7 Typical photoinitiators.

F. Photocurable (1-Part No-Mix) Acrylic Adhesives

A separate class of acrylic adhesives, not always listed with this family of materials, is the systems that will cure via exposure to light of various wavelengths. Of most interest are the ultraviolet (UV) radiation (below 300 nm wavelength) and, to some extent, the visible range (400 to 700 nm wavelength). These types of adhesives obviously are of utility in bonding substrates that are transparent in the UV and visible regions which is typical of many clear plastics and glass.

To achieve UV cure requires a specific type of initiator called a photoinitiator. These materials are added to the formulations and result in the formation of free radicals when exposed to UV or visible light. Representative compounds that are sensitive to UV light, particularly of 200–300 nm wavelength, are the benzoin ethers, benzophenones, and similar compounds. These and a compound that can activate in the visible region are shown in Fig. 7. When these photoinitiators are exposed to the correct wavelength of light they dissociate into smaller segments to form free radical-containing molecular fragments that ultimately result in a cure much like other acrylic adhesives.

Compositionally, photoinitiated acrylics are much like the formulations already reported in this chapter, but it should be noted that these use special photoinitiators in place of redox or other forms of generating free radicals. The only significant difference is found in the use of acrylate, rather than methacrylate, as the carrier monomer. The acrylates are much more prone to UV initiation and propagation than the methacrylates and are consequently the better choice for the formulators.

Company literature from several adhesive suppliers is currently available that lists UV curable and visible light curing acrylic adhesives as part of their product package. This type of acrylic adhesive is being used successfully in polycarbonate lens bonding.

IX. USES OF ACRYLIC ADHESIVE

Worldwide use and sales for acrylic adhesives of the types discussed here are difficult to determine, particularly since so many of the chemistries involved are nowadays hybrids of more than one type. Acrylics would, no doubt, not be considered the major chemical family of adhesives, when compared to epoxies and urethanes. Nevertheless, due to the need for the unique handling characteristics and performance properties achievable with acrylics, they maintain and will continue to maintain an important position among high performance structural adhesive types.

Acrylic adhesives' distinct ability to bond quickly to a variety of unprepared metals has meant that they are a significant factor in bonding certain electrical components, such as magnets for fractional horsepower motors. Acrylics have also been found to be the most effective way to bond aluminum, where fast room temperature bonding to unprepared aluminum is required. Their unique adhesion to aluminum has translated into their use in bonding aluminum for construction (windows and doors), recreation (boats), and military (repair and primary bonding) applications. They also offer potential in the automotive area where bonding metals used in primary structures is becoming a possibility. The use of acrylics for metal exterior structures has also been an area of active investigation.

Acrylics offer some unique capabilities to bond to plastics without surface priming. They are also very good gap filling materials which makes their use preferable to solvent welding in many cases. The markets served include the recreational and industrial areas. Uses in the area of plastic appliances and other plastic molded devices are also known to exist.

In the future the various families of acrylic adhesives are expected to grow as more and more design engineers specify bonded parts and as specialty substrates continue to emerge that are bondable only with acrylic adhesives. The development of formulations with lower overall odor, 1-part systems, and hybrid types will also have a positive effect on overall growth.

X. SUMMARY

Curing acrylic adhesives were introduced decades ago and have been a class of adhesive materials that have continued to be improved since their introduction. Significant advances have occurred in making these materials tougher, faster curing, more resistant to aggressive environments, and easier to handle. Current versions will no doubt be replaced by even more improved variants as this technology continues to be a rich area for research.

XI. ACRYLIC ADHESIVE SUPPLIERS

SUPPLIER	PRODUCT	COMMENT
Lord Corporation Erie, PA	Versilok®, Lord®, Fusor®	General purpose and most types
Loctite Hartford, CT	Depend®	"Modified" pastes
Permabond Englewood, NJ	Quickbond™	"Toughened" acrylics
Devcon Danvers, MA	MVP™	Acrylic adhesives
Hysol Pittsburgh, PA	Engineering Adhesive	"Modified" types
Beacon Chemical Mount Vernon, NY	Magnacryl®	Paste
Dymax Torrington, NJ		UV curable

SUPPLIER	PRODUCT	COMMENT
Ciba Geigy Madison Hts., MI	Aravite™	2-part general purpose
3M Minneapolis, MN	DP-810	General purpose
IPS Corp. Newark, DE	Weld-On®	2-part general purpose
Saf-T-Lok Lombard, IL	High Impact™	Syrup
Denka Japan	Hardloc™	Syrup
Dexter Hysol, CA	H4200 and H4400	High elongation

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Anaerobic Adhesives

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I. INTRODUCTION

Anaerobic adhesives are mixtures of acrylic esters that remain liquid when exposed to air but harden when confined between metal surfaces. These mixtures can be used for a large number of industrial purposes, such as locking threaded fasteners, sealing threaded pipe connections, retaining cylindrical machine components, sealing flange joints, bonding structural components, sealing porous metal castings, welds and powdered metal parts, and many other applications that are still being found more than 50 years after the initial invention [1]. Several reviews have been published that describe anaerobic adhesives and their applications [2–6].

The first anaerobic adhesives were made at the General Electric Company by aeration of a polyethylene glycol dimethacrylate. This "Anaerobic Permafil" required continuous aeration to prevent hardening [7]. Although a number of internal applications had been identified, the problems associated with shipping and storage made the product so impractical that the company decided to discontinue its manufacture.

Vernon Krieble, chairman of the Chemistry Department at Trinity College in Hartford, Connecticut, learned about the product through his son, Robert Krieble, who was employed at General Electric. Vernon Krieble found a chemical solution to the problem by using cumene hydroperoxide (I) (see Section XII for all structures) as the initiator and packaging in half-filled oxygen-permeable polyethylene bottles [8]. He licensed the GE patent and in 1954 founded the American Sealants Corporation, which later became Loctite Corporation [9]. At the present time anaerobic adhesives and sealants are manufactured or sold on every continent by more than a dozen companies. Applications in virtually every industry, and technological innovation, as measured by patent activity, continue unabated.

II. FORMULATION

A large number of variations are possible for anaerobic curing products, but all will consist of the following components:

1. *Monomer*. Methacrylate esters are used in almost all anaerobic products. Acrylates, acrylic and methacrylic acids, and few other vinyl polymerizable monomers may be used for special purposes.

2. *Initiator*. A hydroperoxide (typically, cumene hydroperoxide) is almost always used as an initiator, although there are some variations and it is also possible to take advantage of small amounts of "native" hydroperoxide present in the methacrylate monomers.

3. *Accelerator*. A large number of chemical accelerators have been developed which can catalyze the anaerobic cure and reduce the large differences in cure speed on different surfaces. The most commonly used accelerators are saccharin [benzoic sulfimide (II)] and aromatic amines such as *N*,*N*-dimethyl-*p*-toluidine (III) and 1,2,3,4-tetrahydroquinoline (IV).

4. *Stabilizers*. All methacrylate monomers must contain some free-radical inhibitor if they are to be shipped and stored safely. Hydroquinone and *p*-methoxyphenol are most commonly used for this purpose. Most formulations will also contain benzoquinone, naphthoquinone, and similar stabilizers. Since the anaerobic compositions are strongly catalyzed by traces of metals, many formulators have found it advantageous to add chelators such as tetrasodium ethylenediaminetetraacetic acid (EDTA) (V).

5. *Modifiers*. A very large number of modifications in the cured and uncured properties of anaerobic formulations can be brought about by the addition of components that have little or no effect on the fundamental anaerobic cure chemistry. These modifiers can increase the viscosity, control thixotropy, add color or fluorescence, increase sealing effectiveness, reduce strength, increase toughness, increase heat resistance, provide lubrication, and reduce settling of fillers.

6. *Surface activators*. In some applications anaerobic sealants will cure more rapidly if the surface is treated with a solution containing a metal salt or other chemical that will catalyze the polymerization. These substances will often be components that could not be added to the sealant without causing premature gellation.

III. REACTION MECHANISM

Anaerobic adhesives and sealants have been developed primarily in industrial laboratories, and most of the published literature are patents. A number of papers have been published within the last two decades which discuss the reaction mechanisms of anaerobic adhesive cure [10–20].

A. Oxygen Inhibition

The polymerization mechanism of anaerobic adhesives is similar to that of other free-radical initiation systems except for the special ways in which the inhibiting effect of oxygen is used to delay the polymerization, and in the chemical activation that occurs at the metal surface.

Initiation:	$\mathrm{I} \rightarrow \mathrm{I}\cdot$	
	$\mathrm{I}\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot$	
Inhibition:	$\mathrm{M}\cdot + \mathrm{O}_2 \rightarrow \mathrm{MOO}\cdot$	Weak free radical
Propagation:	$\mathrm{M}\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot$	
Termination:	$\mathrm{M}\cdot + \mathrm{M}\cdot \rightarrow \mathrm{M}_2$	Free radical lost
	$\mathrm{M}\cdot + \mathrm{I}\cdot \rightarrow \mathrm{MI}$	Free radical lost

The reaction rate of oxygen with free radicals is very high and the peroxy radical formed is a relatively poor initiator. When the supply of oxygen is used up within a thin bond line, the propagation step can provide rapid development of adhesive strength. Although there is little disagreement about the importance of oxygen in the propagation step, the greatest interest and study has been directed to the initiation step in the process described above. The role of the bonding surfaces and the effect of different types of accelerators account for most of the literature on the cure mechanism of anaerobic adhesives.

B. Transition Metals

An important factor in the initiation of anaerobic adhesive cure is the redox reaction between a hydroperoxide and transition metals with adjacent oxidation states [10].

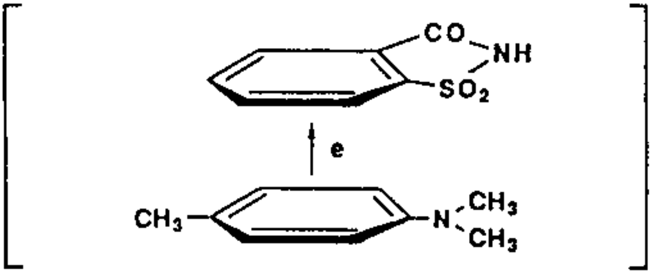
$$Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO\cdot + OH^-$$

$$Fe^{3+} + ROOH \rightarrow Fe^{2+} + ROO\cdot + H^+$$

In the reactions above, other transition metals will react similarly, and copper is particularly active. Where cumene hydroperoxide (CHP) is used, $R = C_6H_5C(CH_3)_2$.

C. Accelerators

The use of saccharin and *N*,*N*-dimethyl-*p*-toluidine (DMPT) results in a substantial acceleration of the initiating reaction. Although each of these components itself is an accelerator, their combination has a strong synergistic effect. It has been suggested that a charge-transfer complex is formed by these materials [11]. It is not clear whether this complex is itself an initiator or whether it acts on other components to generate initiating species.



This same study indicated that the rate of anaerobic polymerization was nearly independent of the concentration of CHP and proceeded at a significant but slower rate with no hydroperoxide. This does not indicate that the hydroperoxide is not essential to the anaerobic cure but that it does not participate in the rate-determining step.

The use of 1-acetyl-2-phenylhydrazine [APH (VI)] and saccharin resulted in a somewhat slower reaction rate than with DMPT unless a catalytic amount of copper was added. In this study the concentration of CHP was found to be very important where the molar ratio of CHP/APH was less than 1. Where the ratio was greater than 1, the rate was independent of CHP [12]. These papers [11,12] have been reviewed [13]. The accelerating effect of the salts of saccharin and 6-methyl-1,2,3,4-tetrahydroquinoline (VII), 1,2,3,4-tetrahydroquinoline (IV), or 1,2,3,4-tetrahydroquinaldine (VIII) on the anaerobic polymerization of methyl methacrylate were studied. No organic peroxides were required for these polymerizations [14].

The effect on initiation reactions of charge-transfer complexes of *o*-benzosulfanilide (IX) and tertiary aromatic amines with various substituents was studied. The rates increased with increasing electron donor and decreasing acceptor properties of the substituents on the amine [15]. Aromatic tertiary amines mixed with benzosulfimides formed charge-transfer complexes whose decay products were effective catalysts for polymerization of polyethylene glycol dimethacrylate. The most effective catalyst system was DMPT with dibenzenesulfonamide (X). The effectiveness of the system was increased by the addition of CHP [16].

A study using a model reaction system consisting of cumene hydroperoxide (CHP), *N*,*N*-dimethyl-*p*-toluidine (DMPT), and *o*-benzoic sulfimide (saccharin) in toluene (without reactive acrylic monomer) showed conclusively that the DMPT was depleted significantly during the initiation step of an anaerobic reaction. The saccharin concentration was unchanged during this process. The initiating species may be radical anions derived from DMPT rather than reactive free radicals derived from the CHP [17].

A dilatometric study was carried out on the polymerization of an anaerobic system containing diethylene glycol dimethacrylate, DMPT, CHP, saccharin, and iron filings. DMPT was more effective than *N*,*N*-dimethylaniline (XI), triethylamine, or tributylamine. Saccharin was more effective than benzoyl cyanamide (XII), phthalimide (XIII), or succinimide (XIV) [18].

D. Role of Saccharin

It has been suggested that one of the functions of the saccharin in anaerobic cure is to dissolve metal ions from the surfaces in order to catalyze the decomposition of CHP. X-ray photoelectron spectroscopy of a model anaerobic adhesive cured in contact with a metal surface indicates that trace amounts of metal or metal ions are found at the interface [19].

E. Oxygen Absorption

Studies of the oxygen absorption of triethylene glycol dimethacrylate indicate that the reaction is catalyzed by DMPT and by DMPT with saccharin. This oxygen absorption appears to be continuous, although the active oxygen content of the system appears to level off due to decomposition of the peroxide formed. Oxalic acid substantially inhibits the absorption of oxygen [20].

IV. MONOMERS

The first anaerobic patents mentioned only the polyglycol dimethacrylates with tetraethylene glycol dimethacrylate (XV) as the dominant example [7,8]. Neopentylglycol dimethacrylate (XVI) was first mentioned in a patent assigned to Borden [21]. The use of acrylic or methacrylic acids to improve adhesion to smooth surfaces was mentioned in a patent assigned to Loctite [22]. The use of diallylphthalate (XVII) and diallylphthalate prepolymer as comonomers with tetraethylene glycol dimethacrylate was claimed in a patent filed by Kalinowski [23].

A series of polyurethane polyacrylates were prepared by reaction of toluene diisocyanate (XVIII), other isocyanates, and isocyanate-terminated oligomers with hydroxyalkyl methacrylates [24]. These monomers could be tailored to provide the strength and toughness required for some structural adhesive applications. The incorporation of hard and soft segments into the polyurethane backbones provided significant improvements in toughness, cure-through-gap, and cryogenic strength properties [25].

The use of monomethacrylates in anaerobic formulations was disclosed in a patent assigned to Loctite. Specifically mentioned were hydroxyethyl (XIX), hydroxypropyl (XX), cyclohexyl (XXI), tetrahydrofurfuryl (XXII), dimethylaminoethyl (XXIII), and glycidyl methacrylates (XXIV), and cyanoethyl acrylate [26]. Methacrylate esters containing residual carboxylic acid groups were prepared by the reaction of hydroxyethyl methacrylate with phthalic anhydride (XXV), pyromellitic dianhydride (XXVI), and benzophenonetetracarboxylic acid dianhydride (XXVII). The residual acid provided improved adhesion [27,28]. The reaction product of hydroxyalkylmethacrylates with maleic anhydride (XXVIII) also produced monomers with residual acid as well as additional curable unsaturation [29]. The dimethacrylates of the bisglycol esters of dicarboxylic acids were used to formulate anaerobic adhesives. Among the dicarboxylic acids mentioned were phthalic (XXIX), maleic (XXX), fumaric (XXXI), and malonic (XXXII) [30].

Three Bond Company used trimethylolpropane trimethacrylate (XXXIII) [31] and ethoxylated bisphenol A dimethacrylate (XXXIV) [32] in anaerobic formulations. These monomers have some advantages in providing improved heat resistance. At Henkel & Cie. dicyclopentadienyl methacrylate (XXXV) was used in anaerobic formulations with high strength [33]. Rohm and Haas has disclosed the use of dicyclopentenyloxyethyl acrylate (XXXVI) and methacrylate in anaerobic formulations [34]. These monomers provide good cure strength on metal parts that have not been degreased and also have lower odor and volatility than do the corresponding dicyclopentadienyl esters. Silicone methacrylates have been formulated by Dow Corning [35] and Toshiba Silicones [36].

Methacrylate esters have been prepared by the reaction of methacrylic acid with epoxies such as the diglycidyl ethers of bisphenol A (XXXVII) [37]. Methacrylate esters suitable for anaerobic adhesives have also been prepared by the reaction of glycidyl methacrylate (XXXVIII) with a hydroxyl-terminated polyester [38]. The reaction of isocyanatoethyl methacrylate (XXXIX) with polyols resulted in monomers that could be formulated into anaerobic adhesives and sealants [39].

V. INITIATORS

The most commonly used initiator for anaerobic adhesives is cumene hydroperoxide. Many other hydroperoxides have been disclosed, such as *t*-butylhydroperoxide (XL), *p*-menthane hydroperoxide (XLI), diisopropylbenzene hydroperoxide (XLII), pinene hydroperoxide (XLIII), and methyl ethyl ketone hydroperoxide (XLIV) [40]. Some diperoxides, such as di-*t*-butylperoxide (XLV) and dicumylperoxide (XLVI), have been claimed, but these may function only because of hydroperoxide contamination [41].

Storage-stable anaerobic formulations can be prepared with no hydroperoxide if the methacrylate resin is aerated in the presence of an amide and a tertiary amine [42]. Anaerobic adhesives have been formulated with alkyl hydroxyethyl peroxides such as *t*-butyl-2-hydroxyethyl peroxide (XLVII) [43]. An adhesive formulated with *t*-butylperoxymaleic acid has improved surface adhesion (XLVIII) [44].

VI. ACCELERATORS

The first accelerator used in an anaerobic adhesive was tributylamine [45]. Saccharin was also found to be an effective accelerator [46] and the combination of saccharin and *N*,*N*-dimethyl-*p*-toluidine was particularly effective if properly stabilized [47]. A large number of patents have been issued on various accelerators and combinations thereof. *N*-Aminorhodanine (XLIX) [48], 1-acetyl-2-phenylhydrazine (VI) [49,50], benzenesulfonylhydrazide (L) [51], dibenzenesulfonamide (X) [52], and similar compounds have been disclosed.

The use of saccharin has been of particular interest and a number of compounds have been prepared that have a similar chemical structure and reactivity. The reaction of sulfuryldiisocyanate (LI) with acetic acid gives a disulfonamide that is an effective accelerator [53]. Similar reactions of *p*-toluenesulfonyl isocyanate (LII) and chlorosulfonyl isocyanate (LIII) can be used to prepare many different compounds which are active accelerators [54,55]. These methods allow the preparation of accelerators with improved solubility.

VII. STABILIZERS

The monomers used in anaerobic adhesives and sealants generally contain at least one free-radical stabilizer, such as hydroquinone or *p*-methoxyphenol. It was found that benzoquinone, naphthoquinone, and similar compounds provided improved shelf stability without retarding the anaerobic cure [56]. It was also found that anaerobic formulations could be stabilized with a stable nitroxide free radical such as di-*t*-butyl nitroxide (LIV) [57]. The use of a soluble metal chelating agent such as tetrasodium EDTA (V) was found to be an effective method of stabilizing an anaerobic formulation against small amounts of metal contamination [58].

VIII. MODIFIERS

The wide variety of applications of anaerobic adhesives and sealants is made possible by the modifications that make the viscosity appropriate to the application. An application that requires penetration into close-fitting parts should have very low viscosity, while a product used with large, loose-fitting parts should have a high viscosity. A styrene acrylate copolymer could be used to increase the viscosity [59]. Polymethacrylates, cellulose esters, butadiene–styrene copolymers, acrylonitrile–butadiene–styrene copolymers, poly(vinyl chloride), copolymers of vinyl chloride and vinyl acetate, poly(vinyl acetate), cellulose ethers, polyesters, polyurethanes, and other thermoplastic resins have also been used to control the flow characteristics of anaerobic sealants [60]. The flow characteristics of anaerobic formulations can also be controlled by the addition of fumed silica and other solid additives which can impart "thixotropic" properties [61].

Many anaerobic adhesives and sealants may require a relatively low strength so that the components can be disassembled for repair or replacement. Many liquid plasticizers have been used for this purpose [62], but the use of a low-molecular-weight polyester has been found to be advantageous [63]. The "toughness" properties of anaerobic adhesives can be enhanced by the addition of a reactive elastomer [64]. The heat resistance of anaerobic adhesives and sealants can be enhanced by the addition of a bismaleimide

(LV) [65]. These maleimide additives appear to be relatively unreactive during the initial anaerobic cure. As the adhesive is exposed to high temperatures the methacrylate backbone degrades and the methacrylates can then copolymerize with the maleimides, forming a more heat-resistant matrix [66].

The addition of dyes to anaerobic adhesives and sealants assists in identification and inspection of the products. Automated inspection procedures are made possible with dyes that fluoresce under ultraviolet light. Titanium dioxide pigments can make the sealants more visible.

Solid fillers are added to some anaerobic adhesives and sealants for various purposes. Mica, talc, and other mineral fillers can help to provide an instant seal capability to anaerobic pipe sealants. The sensitivity of the anaerobic cure system to metal contamination requires that these fillers be chosen very carefully.

Powdered graphite, polytetrafluoroethylene, and polyethylene can function as lubricants in pipe sealants and thread-locking compounds. This lubrication can prevent galling in close-fitting pipe threads [67]. Lubricating additives in thread-locking sealants can provide control of the clamping force exerted by a fastener at a given tightening torque [68].

IX. PRIMER/ACTIVATORS

The cure speed and adhesion of an anaerobic sealant can be increased by treatment of the surface with a solution containing activating chemicals. Early anaerobic thread lockers were strongly affected by part cleanliness, and degreasing the parts with a chlorinated solvent improved performance dramatically. The condensation product of an aldehyde and a primary or secondary amine, a sulfur-containing free-radical accelerator (LVI), or a compound of an oxidizable transition metal were some of the materials that could be added to activate the anaerobic cure [69–71]. Ferrocene (LVII), a derivative containing the ferrocene moiety, or a polymer incorporating ferrocene was an effective activator for anaerobic adhesives [72]. The copper, cobalt, manganese, or chromium salts of an acid phosphate acrylic monomer (LVIII) were found to be effective activators as well as adhesion promoters [73].

X. APPLICATIONS

1. *Thread locking*. The first applications for anaerobic adhesives were for locking threaded fasteners. Filling the “inner space” between a nut and bolt with a hard, dense material prevents self-loosening.
2. *Thread sealing*. The effect of filling the space between threaded parts or the space between inner and outer pipe threads provides a seal that can prevent the leakage of oil and other fluids in machinery as well as prevent corrosion of the threaded parts.
3. *Retaining*. Cylindrical press-fits and bearing assemblies can be retained with anaerobic adhesives, allowing accurate alignment and relaxed tolerances. Retaining and sealing of cup plugs and oil seals in castings is a major application.
4. *Impregnation*. Powdered metal parts, porous castings, and welds can be sealed against leakage of liquids or gases. This impregnation can also allow such parts to be plated and improves their machinability.

5. *Preapplied.* Thread lockers and sealants are made that can be coated on threaded parts in the form of a dry-to-the-touch film. These preapplied materials remain inert until assembly releases a quick-curing resin.

6. *Gasketing.* Anaerobic flange sealants can be applied manually or by automated methods such as tracing, stenciling, and screen printing. These products can eliminate a variety of preformed, precut gaskets and can also be used as a gasket dressing.

7. *Structural bonding.* Tough structural bonds can be achieved with some anaerobic adhesives for bonding components such as ferrite magnets, honing stones, identification tags, and decorative inserts.

Other applications include the fabrication of foundry molds [74,75] and the surface mounting of electronic components [76].

XI. STANDARDS AND SPECIFICATIONS

Testing standards and performance specifications for anaerobic adhesives and sealants have been established by government agencies and industrial organizations in several countries. In the United States there are military specifications for thread lockers, sealants, and retaining compounds. Mil-S-22473E, 12 April 1983, "Sealing, Locking and Retaining Compounds: (Single Component)" covers 15 of the earliest "letter grade" products. Specifications are set for color, viscosity, locking torque on $\frac{3}{8}$-24 steel nuts and bolts, and fluid tightness. The effects of immersion in a number of fluids, heat aging at 149°C, and hot strength at 149°C (or 93°C for some grades) are also measured. This specification calls for measurement of an "average locking torque" after 90, 180, 270, and 360 degrees of turn.

Mil-S-46163A, 12 July 1983, "Sealing, Lubricating and Wicking Compounds: Thread-Locking, Anaerobic, Single-Component" covers nine grades of product for sealing (type I), lubricating (type II), and wicking (type III). Specifications are set for color, viscosity, locking torque (break and prevailing torque) on $\frac{3}{8}$-16 steel, zinc- and cadmium-plated nuts and bolts, fluid tightness, lubricity, and "wicking" into preassembled fasteners. The immersion, heat aging, and hot strength tests are similar to those done in Mil-S-22473E.

Mil-R-46082B, 10 June 1983, "Retaining Compounds Single Component, Anaerobic" (Amendment 6, 9 January 1990) covers three types of retaining compounds, which are tested with a pin-and-collar compressive shear specimen. The three types vary primarily in viscosity, although there are also differences in heat resistance and strength. These products are subjected to immersion, heat aging, and hot strength tests similar to those described above.

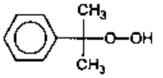
In the United Kingdom the Ministry of Defence (MOD) has issued specifications DTD 5628–5633, which cover test procedures and performance requirements for a range of products. Five strength bands and four viscosities, from penetrating to thixotropic, are defined. The torque strengths are tested on M8 nuts and bolts and the shear strength in 12-mm pins and collars. The development of these specifications and the test procedures have been described by C. L. Brett at the MOD. The "breakloose" torque on nuts and bolts requires particular attention to a transient measurement where the first torsional motion is detected. Other products show somewhat different behavior, with no distinct "breakloose," and the torque at which the sealant begins to yield is not easily detected [77]. British Standard BS 5292 relates to the use of anaerobic sealants on gas appliances.

In Germany, standards have been published describing the "Compression Shear Test" (DIN 54452), "Dynamic Viscosity Determination of Anaerobic Adhesives by Rotational Viscometer" (DIN 54453), "Initial Breakaway Test at Bonded Threads" (DIN 54454), and "Torsion Shear Test" (DIN 54455). DIN 54455 is particularly interesting since it is one of a very few tests in which a nut and bolt (M10) are seated to a measured torque before the anaerobic sealant is allowed to cure.

In the United States the Industrial Fastener Institute has published standards entitled "Test Procedure for Locking Ability Performance of Non-metallic Locking Element Type Prevailing Torque Lock Screws" and "Test Procedure for the Locking Ability Performance of Chemical Coated Lock Screws." The American Society for Testing and Materials (ASTM) has published a "Standard Test Method for Shear Strength of Adhesives Using Pin-and-Collar Specimen" (ASTM D4562-90, October 1990). A subcommittee of ASTM Committee D-14 on Adhesives has studied torque strength tests and performance standards for anaerobic adhesives.

The International Organization for Standardization (ISO) has finalized an International Standard (ISO/DIS 10964: 1993) "Adhesives—Anaerobic Adhesives—Determination of Torque Strength of Anaerobic Adhesives on Threaded Fasteners." This standard describes testing procedures for liquid and preapplied sealants using manual and graphical procedures.

XII. LIST OF STRUCTURES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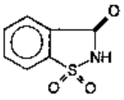
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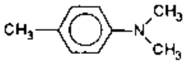
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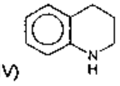
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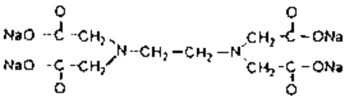
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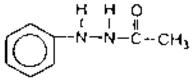
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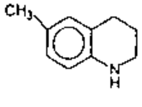
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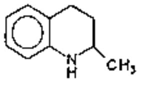
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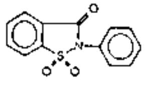
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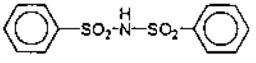
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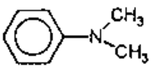
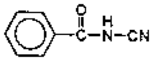
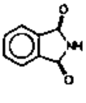
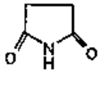
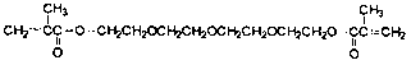

(XI)


(XII)

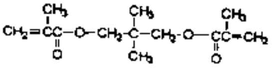

(XIII)


(XIV)


(XV)

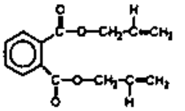
$CH_2{=}\overset{CH_3}{\underset{O}{CC}}{-}O{-}CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2O{-}\overset{CH_3}{\underset{O}{CC}}{=}CH_2$

(XVI)

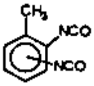


$CH_2{=}C(CH_3)-C(=O)-O-CH_2-C(CH_3)_2-CH_2-O-C(=O)-C(CH_3){=}CH_2$

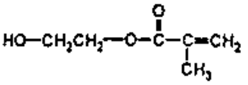
(XVII)



(XVIII)

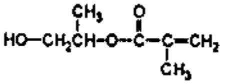


(XIX)



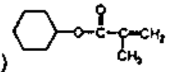
$HO-CH_2CH_2-O-C(=O)-C(CH_3){=}CH_2$

(XX)

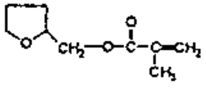


$HO-CH_2CH(CH_3)-O-C(=O)-C(CH_3){=}CH_2$

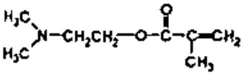
(XXI)



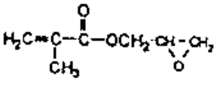
(XXII)



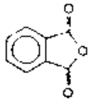
(XXIII)



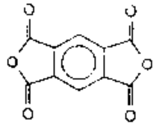
(XXIV)



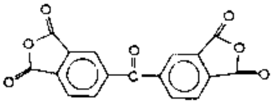
(XXV)



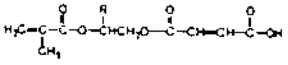
(XXVI)



(XXVII)

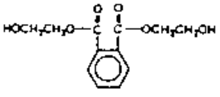


(XXVIII)

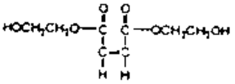


$H_2C{=}C(CH_3)-C(=O)-O-CH(R)CH_2O-C(=O)-CH{=}CH-C(=O)-OH$

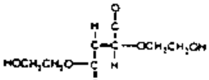
(XXIX)



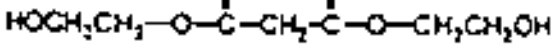
(XXX)



(XXXI)

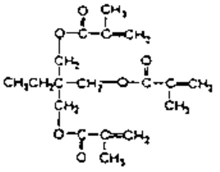


(XXXII)

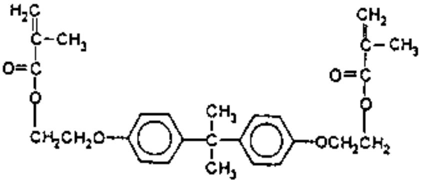


$HOCH_2CH_2-O-C(=O)-CH_2-C(=O)-O-CH_2CH_2OH$

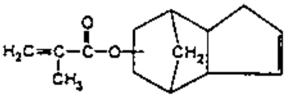
(XXXIII)



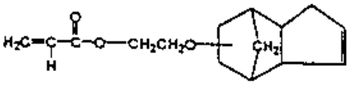
(XXXIV)



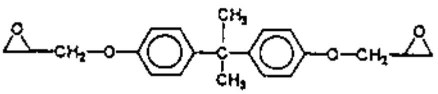
(XXXV)



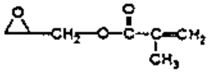
(XXXVI)



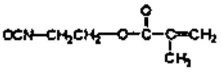
(XXXVII)



(XXXVIII)

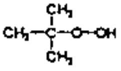


(XXXIX)



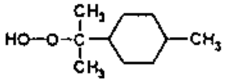
$\mathrm{OCN{-}CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2}$

(XL)

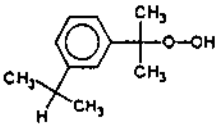


$\mathrm{CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}O{-}OH}$

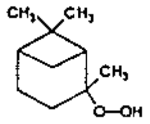
(XLI)



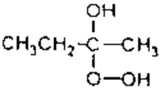
(XLII)



(XLIII)

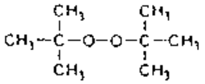


(XLIV)



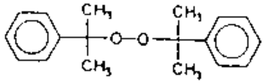
$\mathrm{CH_3CH_2{-}\overset{OH}{\overset{|}{\underset{O-OH}{\underset{|}{C}}}}{-}CH_3}$

(XLV)

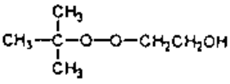


$\mathrm{CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}O{-}O{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_3}$

(XLVI)

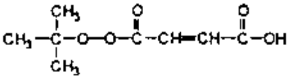


(XLVII)



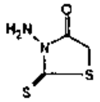
$\mathrm{CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}O{-}O{-}CH_2CH_2OH}$

(XLVIII)

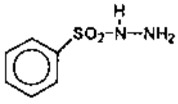


$\mathrm{CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OH}$

(XLIX)

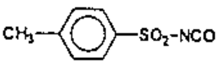


(L)



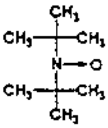
(LI) OCN—SO$_2$-NCO

(LII)

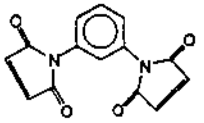


(LIII) Cl—SO$_2$-NCO

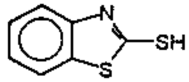
(LIV)



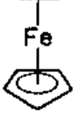
(LV)



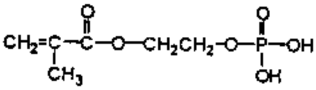
(LVI)



(LVII)



(LVIII)



$\mathrm{CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{\underset{OH}{\underset{|}{P}}}}{-}OH}$

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Aerobic Acrylics: Increasing Quality and Productivity with Customization and Adhesive/Process Integration

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I. INTRODUCTION

It is axiomatic that manufacturing productivity is increased and per unit cost is decreased by making assembly and automation processes more efficient. High-quality parts further lower costs by reducing rework and replacement liability costs. Environmental consciousness and regulatory compliance have become a permanent and increasing component of assembly costs.

Aerobic adhesives cure rapidly to form tough, durable bondlines with structural strength. They also produce highly adhesive protective coatings, sealants, and pottings *at the place and speed required by the assembly process*. Overall economic efficiency is improved because:

The complete lack of solvents allows easy compliance with environmental and worker safety regulations.
Aerobic adhesives improve productivity of automated assembly processes by curing "instantly," but only on demand.
Profitability is increased by substantially eliminating the time delay between assembly and quality control procedures.
Tough, durable bond lines reduce replacement and liability costs.

Defined in very broad terms, most manufactured items are assembled by using:

Press or snap fits
Mechanical fasteners (screws, rivets, welding)
Chemical fasteners (adhesives)

"Aerobic" adhesives were developed as an advance over anaerobic and cyanoacrylate adhesives. Anaerobic (threadblocking) adhesives are used to augment mechanical fasteners such as screws, bolts, or press-fits. Cyanoacrylates tend to be used for nondurable bonding on rigid surfaces and for durable rubber bonding.

Aerobic adhesives, on the other hand, were designed to be used as the sole attachment device. They are as fast as many "instant glues" yet durable enough to be considered a "chemical fastener," replacing the need for mechanical fasteners, in many instances.

Chemical fasteners must be designed to meet the requirements of the assembly, the process, and environmental protection and worker safety.

Adhesives and sealants designed to complement and enhance all three stand the best chance of offering equipment designers and manufacturers the highest quality at the lowest per unit cost.

In addition, the twin challenges of increasing global competition and heightened environmental quality awareness mandate that manufacturers replace the commonly used, but simplistic, price per pound decision calculation with an in-depth understanding of the factors associated with obtaining the highest-quality product, the most efficient process, and having the least environmental impact.

Aerobic acrylic ultraviolet (UV) and activator curing adhesives were developed with the idea of meeting the requirements of maintaining or increasing product and environmental quality while delivering the ultimate in process efficiency.

II. HISTORICAL PERSPECTIVE/TECHNOLOGY REVIEW

A. Aerobic Acrylic Curing Technology—Activator and Heat Cures

Chemical or heat curing structural strength aerobic adhesives technology was first introduced to the assembly industry in the early 1980s [1,2]. High-performance characteristics derived from combining urethane oligomers with (meth)acrylic monomers and "elastomeric domain" compounds. The meaning of the term "aerobic" and how it is different from anaerobic adhesives and 2nd-generation acrylic adhesives are explained in these and other articles [1–4].

Aerobic adhesives are composed of proprietary catalysts, elastomeric domain fillers, and low-vapor-pressure monomers. Formulations derived from this technology do not exhibit the severe sensitivity toward air inhibition shown by other acrylic adhesives. The result is that aerobic adhesives are usable on more porous surfaces and in wider gaps than was previously considered practical.

Of course, all vinyl polymerizations can be inhibited by air, hence the commonly seen "tacky" feel of many UV cured products. Therefore, those physical properties that are recognized as being affected by air inhibition mechanisms are compared in Appendix A.

One of the tests is maintaining strength through a gap. This can be affected by air inhibition, as well as by the diffusion of accelerators. In another test, air was beaten into several adhesive formulations. The aerobic adhesives were only marginally affected by air inclusion when cured between surfaces. Like anaerobics, fillets or adhesive squeezed outside of a bonded joint will remain uncured unless exposed to UV light.

In the last test, a porous material, pine wood, was chosen as a substrate because it assures that air is to remain in intimate contact with the curing adhesive. The ability to lock the threads of an iron nut and bolt without use of an activator is a recognized test for determining whether a formulation is capable of anaerobic cure.

B. Reactive Aerobic Acrylic Adhesives—Use and Cure Mechanism

1. *Chemical Cure*

Chemical bonding techniques for all acrylic adhesives are similar. First, the activator is applied to one of the surfaces to be joined as a thin film. While the permissible "ratio" of activator to adhesive is quite wide (10 : 1 to 50 : 1), too much activator will lower bond strengths. Activators are available in solvents to help assure thin film applications. Second, the adhesive is applied to the mating surface, and the two surfaces are brought together and held until handling strength is reached.

Application of activator to both substrates is recommended where one substrate is porous or where gaps of more than 20 mils are to be filled. Activator and adhesive may be applied to the same surface, but this initiates the bonding action so that the parts must be joined immediately.

Advantages of Activator Curing Aerobic Acrylics

Simple no-mix application
Multiple curing methods available
Broad applicability to a wide variety of substrates (metal, plastic, glass, ceramics) with minimal surface preparation
Tolerance for oil-contaminated surfaces
Rapid bonding at room temperature
Excellent bond flexibility
High peel strength, lap shear strength, and impact resistance
Excellent solvent resistance
Wide latitude in cure rate
Ability to bond heat-sensitive substrates
Low shrinkage during polymerization
Excellent reproducibility and reliability
Good low- and high-temperature properties
Wide formulating flexibility for specific end-use requirements

2. *Heat Cure*

Many aerobic formulations can be heat cured, *but only between two surfaces*. Table 1 shows the heat curing properties in an adhesive used to fix surface mount devices onto printed circuit boards compared to a typical epoxy and a typical anaerobic formulation used for the same purpose.

3. *Curing by Ultraviolet Light*

Aerobic adhesives are easily converted to UV curing formulations. This is not surprising as (meth) acrylics are commonly used as the base resin in UV inks and coatings. However, UV products usually have rather poor adhesion to hard, tough surfaces such as metal.

Table 1 Time for Complete Cure

Temperature (°C)	Aerobic adhesive	Epoxy	Anaerobic adhesive
110	5 min	Unknown	Unknown
120	45 s	39 min	30 min
150	20 s	2–5 min	1–3 min
175	10 s	1 min	20 s

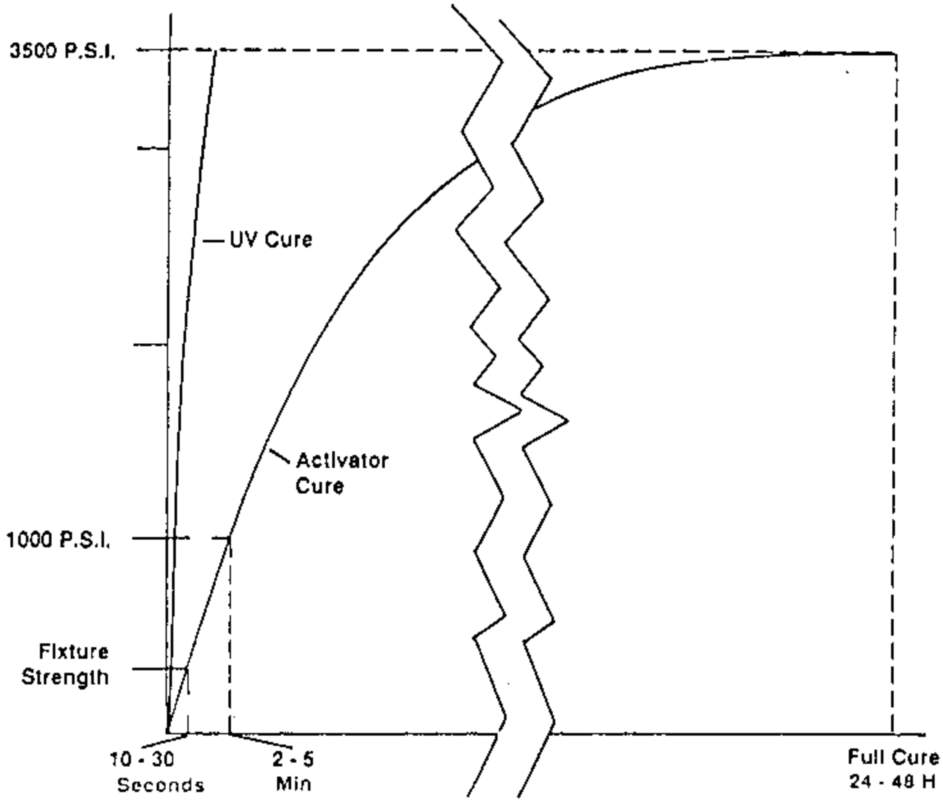


Figure 1 Typical adhesive tensile strength on cold-rolled steel.

Many UV curing aerobic adhesives show the unique property of having structural properties regardless of the cure mechanism used, as shown below. A more detailed discussion of UV curing aerobic acrylics can be found in Sec. IV.

Figure 1 shows that complete cure using a preapplied activator requires 24–48 hr. UV cure, however, is complete—reaching the same strength level in only seconds.

C. Increasing Product Quality Through Use of Aerobic Acrylic Adhesives

Aerobic acrylic UV and activator curing technology was developed with a view to maintaining the formulation flexibility necessary to meet a broad range of application requirements. Adhesives, sealants, and coatings providing improved product quality have been the result. In addition to increased formulation flexibility, improvements in resin characteristics possessing toughness and durability have resulted in assemblies of superior quality and performance [5–7].

D. Tough, Durable Bonds Yield Higher-Quality Assemblies

The essence of acceptable assembly quality is to eliminate production line rejects and failures over the life of the manufactured product. Aerobic acrylic activator curing

Table 2 Typical Torsional Impact[a]

Adhesive	Values (in.-lb)
Polyamide epoxy	7 ± 5
Cyanoacrylate	2 ± 2
Anaerobic	12 ± 5
2nd-generation acrylic	20 ± 7
General-purpose aerobic acrylic (metal deformation)	40 ± 10
High-impact aerobic acrylic	60 +

[a] On degreased, sandblasted steel, 1/2-in. overlap.

adhesives and sealants have been in use in demanding automotive, medical, electrical, and electronic applications for the past 20 years. Designed to resist vibration, shock, and impact, they have withstood the severe environmental stresses of thermal, as well as physical, shock. Excellent for bonding closely fitting metal, glass, ceramic, filled plastic, and thermoset plastic parts, aerobic adhesives improve durability by also acting as shock-absorbing cushions. High tensile/shear strength to 3000 psi, combined with flexibility and the ability to absorb shock, results in a toughness developed to increase the useful life of the bonded or sealed part. Table 2 compares the toughness as measured in impact strength of aerobic acrylics with other adhesive products offered to OEM (original equipment manufacturers). Appendix B tabulates a range of properties available from different aerobic adhesive formulations [1].

E. Adhesive Customization Improves End-Product Quality

Aerobic adhesives have a wider latitude in formulating for specific end-use requirements than other acrylic adhesives [1,2]. Flexibility, opacity, cure speed, and surface compatibility may be controlled over a wide range to produce adhesives for metal, glass, many plastics, ceramics, and hard woods. The cured properties of specific aerobic formulations are scarcely affected by efficient thickening agents such as fumed silica. As a consequence, it is possible for an end user to pick a set of cured properties and then have the adhesive's viscosity modified to specific requirements. The properties of three representative cured formulations are outlined in Appendix B.

Two of many excellent examples of how aerobic acrylic technology improves product quality are the following. A photocopier manufacturer uses an aerobic adhesive to attach large glass lenses to metal frames. The application requires an adhesive that can absorb the forces generated from the large differences in expansion characteristics between glass and metal. Type B formulated adhesives were shown to provide adequate bonds with tensile strength exceeding the deformation strength of the metal frames. However, when subjected to a 300°F temperature range, the glass lenses frequently broke. Increasing the bondline thickness to 10 mils and using a flexible type C formulation produced shock-absorbing bonds, and the lenses now pass the thermal cycle requirements.

An aerobic acrylic adhesive has also been used to increase both product performance and reliability while reducing assembly costs in the manufacture of motorcycle alternators. A major manufacturer of high-performance motorcycles had been holding ceramic

Table 3 Enhancing Quality and Processes Through Aerobic Adhesives and Coatings

Enhancing productivity	Productivity is increased by making assembly automation processes more efficient.
Enhancing quality	High-quality parts reduce replacement liability costs. Quality improvements due to toughness, durability, and structural strength of bondpottings and sealants and protective coatings lower liability exposure.
Bondline durability	Aerobic adhesives cure to form bonds with structural strength; produce highly adhesive practical coatings, sealants, and pottings at the speed required by an efficient assembly process
Customized curing	Aerobic acrylics improve productivity. They facilitate automation by curing "instantly," but only on demand.
Profitability	Profitability can be increased by lowering per unit labor content.
Worker safety and regulatory compliance	Low-volatile, 100% solids means minimal EPA and OSHA impact.

EPA, Environmental Protection Agency; OSHA, Occupational Safety and Health Administration.

magnets in place with a plastic retaining ring. The manufacturer had to increase the alternator's output from 17 to 22.5 amps to 3600 rpm without increasing the size of the alternator. It was known that replacing the retaining ring with a bonding process would permit more magnet mass in the same space.

F. Adhesive Customization Together with Rapid Fixture and/or Cure "On Demand" Improve Process Efficiency

On hundred percent solids, solvent-free-aerobic acrylic adhesives are often customized to the needs of the assembly and the process. They produce permanent, structural strength bonded assemblies, pottings, and (electronic) coatings within seconds. Productivity is increased; assembly automation processes are made more efficient because the curing technology can be customized to fit the requirements of the process. The several curing methodologies are completed in seconds and can be installed at the time and place most convenient to the manufacturing process. Table 3 summarizes the advantages of using aerobic acrylic adhesive technologies.

Examples of how aerobic acrylics' formulation flexibility allows tailoring the adhesive to the process to maximize efficiency include the following:

1. A manufacturer of high-speed printers also requires 5 min of assembly time before fixture occurs in a 10 mil shimmed bondline gap. In this application, a number of ferrite magnets are bonded to metal frames and assembled in the proper geometrical arrangement in one step. This adhesive process replaces a combination of mechanical clamps, spacers, and holding screws.
2. A manufacturer of restaurant appliances fastens a stainless steel top to a combined counter/refrigerator/stove unit. The standard attachment technique included both welding and the use of self-tapping screws. An aerobic acrylic adhesive has replaced these techniques resulting in a lower cost assembly requiring less skilled labor.

3. Aerobic acrylics also show enhanced cure speed, tensile strength, moisture resistance, and the ability to resist automotive bake cycles, which can be as high as 450°F. The operation also requires fixturing through a variable 10 to 20 mil gap in less than 30 s. Thixotropic adhesive is applied to the area to be bonded and activator sprayed directly on top of the adhesive. The metal is immediately folded to form a ‘‘hem’’ joint.
4. A fuse manufacturer replaced a 30 min epoxy used in a heat cure process to assemble stainless steel inserts into phenolic holders. By utilizing an aerobic adhesive bonding process, the assembly was complete in 30 s at room temperature. The resulting increase in productivity more than offset the higher adhesive cost. A cyanoacrylate bonding process was even faster, but did not resist aging in a moist atmospheric environment or pass a drop test for impact resistance.
5. Many kinds of adhesives are utilized in the bonding of loudspeaker magnets, DC motor assemblies, and other types of magnet bonding. Some manufacturers still prefer to use mechanical clamps. The factors that contribute to the choice of a joining process include the cost of the adhesive, labor rates, speed of adhesive fixture, acceptability of odor level, and energy costs. Aerobic acrylic adhesives have been used primarily for their rapid fixture (as little as 12 s) resulting in faster assembly rates. Table 4 compares cure speed and other simple considerations used when choosing an adhesive for attachment of ferrite. The above applications are illustrated in Fig. 2.

The most familiar automotive use of activator curing types of aerobic acrylics is in DC motor assembly. This end use is particularly illustrative of the process streamlining and cost savings opportunities offered by this unique technology. An epoxy method is shown in Fig. 3.

First used commercially in 1982, to bond ferrite magnets, cold bonding processes have increased in utility and sophistication, as indicated in Fig. 4. Productivity enhancing and quality improving uses are limited only by the imagination of the design engineer.

Table 4 Some Adhesives for Magnet Bonding

Adhesive	Cure conditions	Gap	Disadvantages
Heat curing epoxy	30 min at 300°F	Any	Clean surfaces critical; high energy cost; cool-down time
Nylon hot melt	Induction heating of preapplied patch	Any	Clean surfaces critical; high energy cost; cool-down time; parts breakage
Anaerobic acrylic	30–60 s	10–20 mils	Clean surfaces critical; two-step process; cost/lb
2nd-generation acrylic	30–120 s	10–30 mils	Flammable vapors; noxious odors; stringy two-step process; OSHA/EPA problems
Aerobic acrylic	10–20 s	10–40 mils	Two-step process; cost/lb

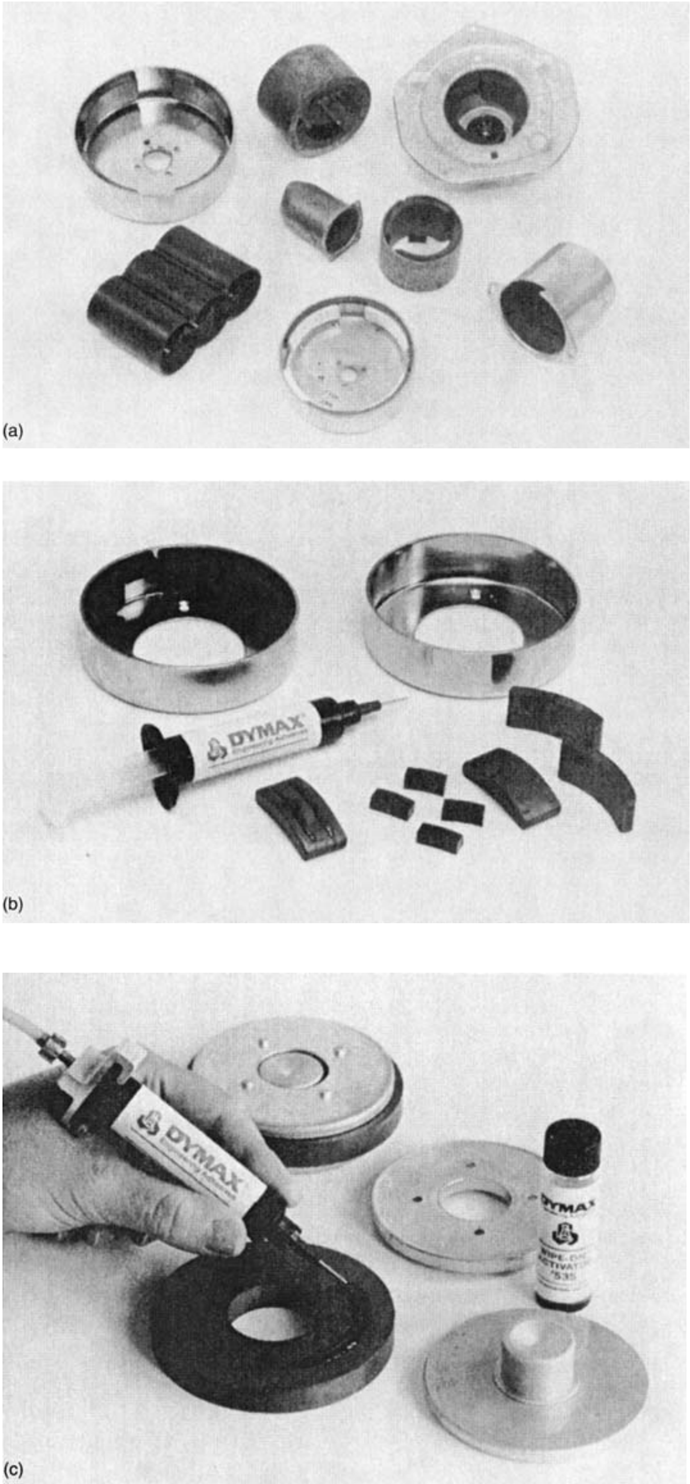


Figure 2 Ferrite assemblies bonded in 10–30 s with aerobic acrylics. (a) Automotive DC motors. (b) Alternators. (c) Loudspeaker. (d) Stepping motors.

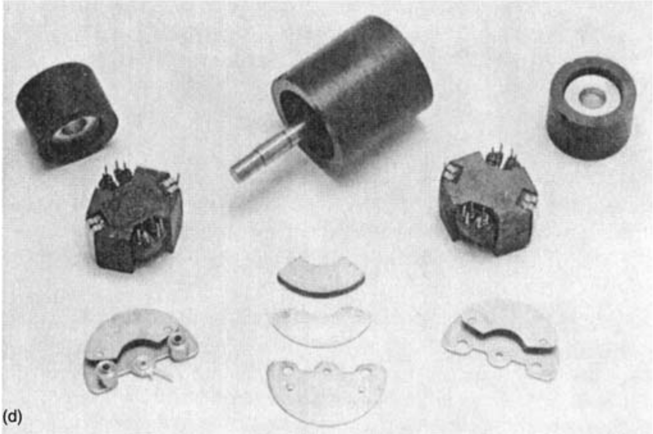


Figure 2 (Continued).

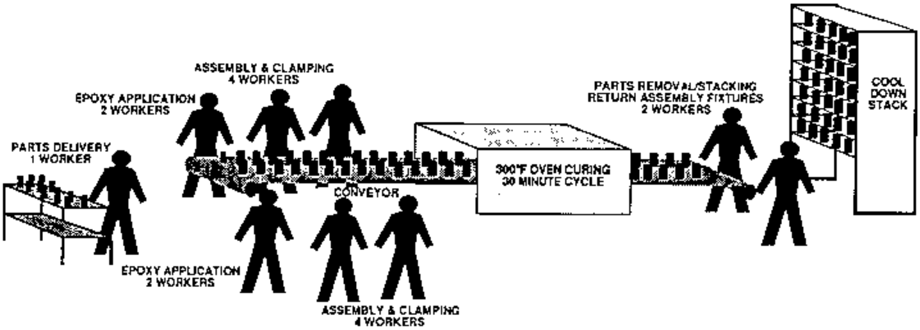


Figure 3 Heat-cured epoxy assembly method. Steps (nine workers): (1) one brings parts to conveyor belt. (2) Two apply epoxy adhesive. (3) Four assemble magnets into housing, attach stainless steel fixturing clamp, place on conveyor belt. (4) Parts are heated to 300°F for 30 min to cure the epoxy. (5) Two workers remove hot parts to cool down stack. Return fixtures to beginning of line. (6) After 24-hr cool down, parts go into the main assembly process.

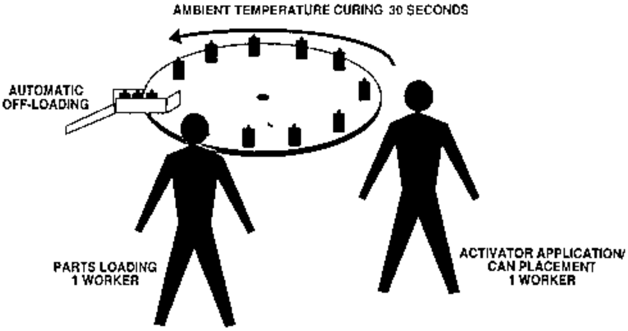


Figure 4 Dymax method. Steps: (1) Worker loads magnets to automatic feeder/adhesive dispenser; also brings motor cans to second worker station. (2) Second worker applies activator to can housing with a semiautomatic dispenser. (3) Second worker then places can over magnets that have been previously placed into fixtures robotically. (4) Turntable cycles, engaging fixture pressure mechanism. (5) Bonded parts are automatically off-loaded to continue in production.

Table 5 Process Comparison

	Epoxy method[a]	Dymax method
Workers	9	2
Adhesive cost	5 cents/part	20 cents/part
Scrap rate	5%	0.1%
Process	Off line (24-hr delay)	In line—large Q.C. and W.I.P. savings
Other	Oven and energy costs	Capital depreciation

[a] Another method to cure epoxies or preapplied (nylon) adhesive patches is induction heating.

Table 5 shows the difference in labor, time, and by extension, cost between using an epoxy and an aerobic acrylic adhesive.

III. AN EXAMPLE OF HIGH RELIABILITY BONDING WITH 100% QUALITY ASSURANCE TESTING

Figure 5 shows two ferrite magnets being held on a typical fixture prior to DC motor assembly. A special viscosity grade of rapid curing, moderate tensile, high-durability adhesive acrylic is depicted on the vertically held magnets. An easily dispensable viscosity was combined with a nondripping rheology as part of the customizing process for the manufacturer. After dispensing, the DC motor can be placed (usually robotically) over the ferrite fixture. A rotation of the timing table opens springs on the fixture and the magnets are pressed against the can with 20–50 lb pressure. Fixture strength occurs within 10–30 s, depending on the adhesive grade chosen, whereupon the bonded can may proceed to the next assembly step.

A 100% quality assurance check can be made within 2–5 min by pushing on the bonded ferrites at a predetermined force with a "go–no–go" gauge.

One vendor for DC motors experienced a rejected assembly about once in every 10,000 units. This simple go–no–go test finds this small number of rejects, which are then recycled.

Parts can be easily cleaned and rebonded, eliminating concerns of waste disposal.

Figure 6 illustrates high adhesive strength combined with UV cure, e.g., a sealant being applied to a zinc-plated DC motor flange. UV cure is obtained in about 30 s.

The plastic headlamp is structurally bonded together in the same time frame. Two adhesives are used; one adheres to the nylon reflector, the other to the lens.

A capacitor potting compound needs aggressive adhesion to the metal can edges, providing a positive seal despite stresses induced during thermal changes.

The cost savings realized from process improvement, quality improvement, and worker environment have resulted in aerobic adhesives being widely used in DC motor assembly. One motor, entirely constructed using a combination of aerobic adhesives, press bits, and swagging, is illustrated in Fig. 7. Both activator and UV curing methods are used where these cure technologies maximize productivity and durability.

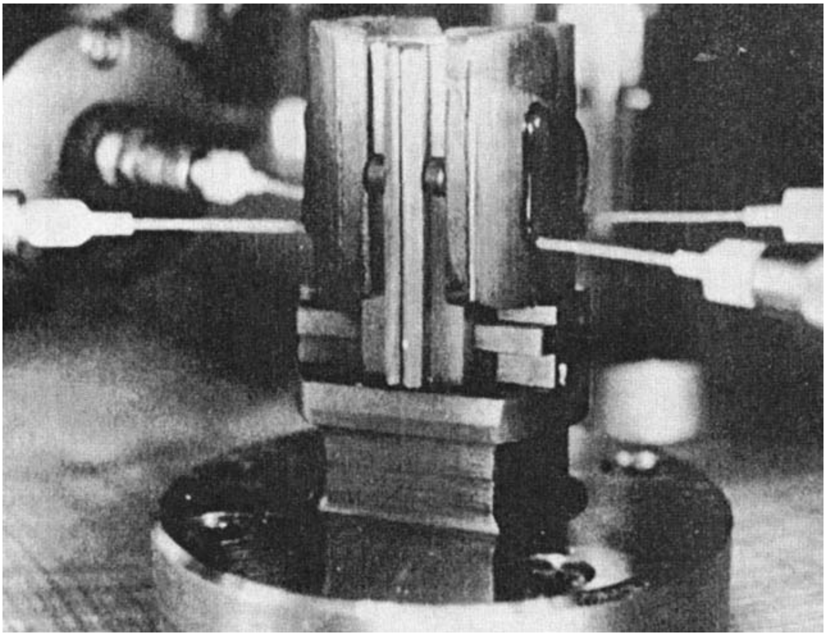


Figure 5 Two ferrite magnets being held on a typical fixture prior to DC motor assembly.

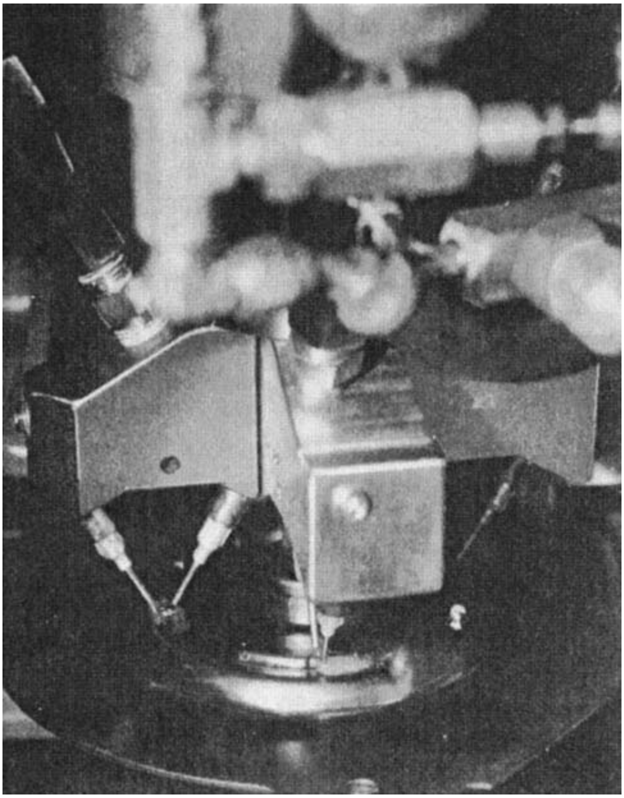


Figure 6 High adhesive strength combined with UV cure.

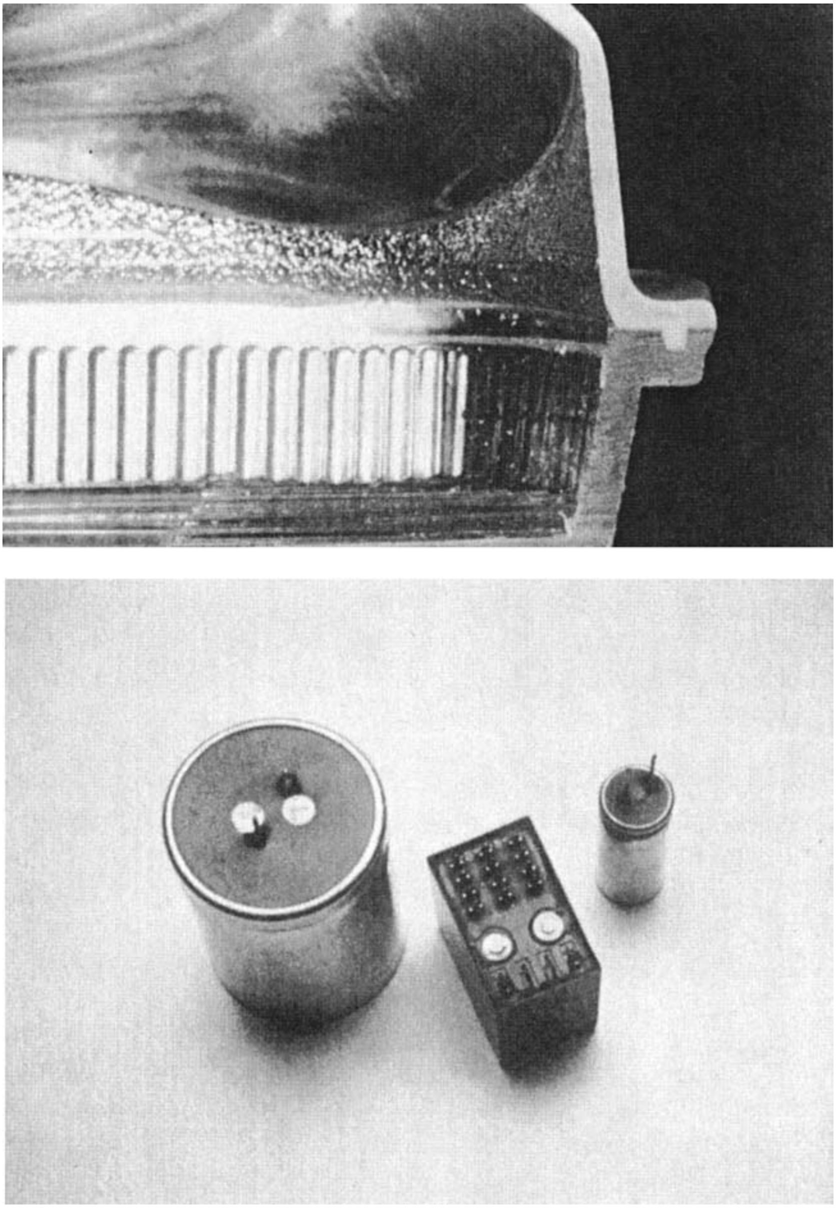


Figure 6 (Continued).

IV. UV CURING/A NEW TECHNOLOGY IN ACRYLIC ADHESIVES

A. Historical Perspective/Technology Review

The concept of cross-linking polymers with UV light attained full commercial acceptance in the coatings and ink industries in the late 1970s, extending UV technology to joining smooth, nonporous substrates. These initial efforts proved disappointing as resins tended to give low-strength bonds to surfaces that were difficult to adhere to, including metals and other nonporous surfaces. The presence of oils, dirt, and grease was particularly harmful,

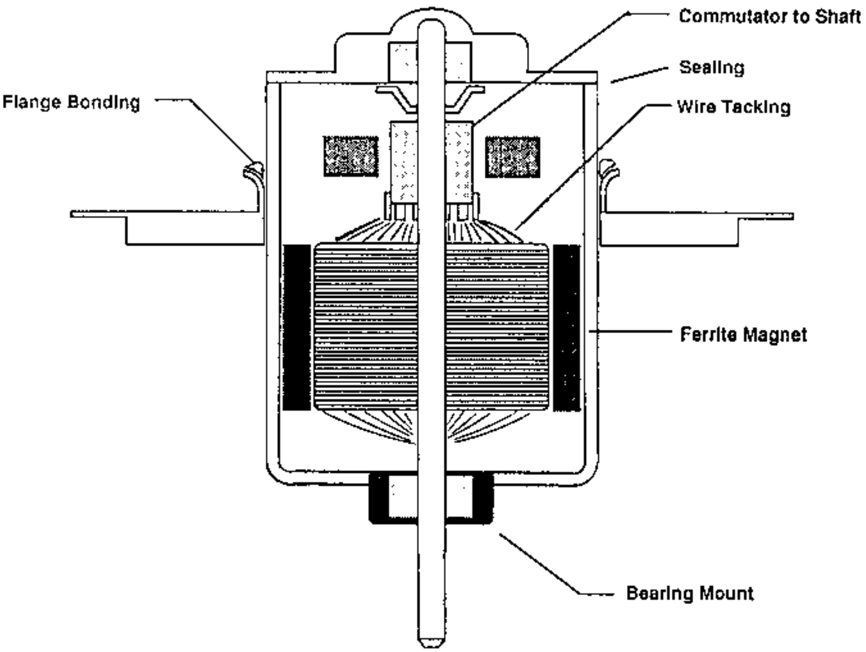


Figure 7 Motor constructed using a combination of aerobic adhesives, press bits, and swagging.

as well. Plastics, which have low-energy surfaces, and glass were also difficult to bond structurally. Early attempts at formulating structural adhesives reflected these limitations. Consequently, in the 1970s and early 1980s, the use of UV adhesives gained little acceptance.

In the early 1980s, UV curing grades of aerobic acrylic adhesives, however, were developed to provide structural bonds within seconds at room temperature on a wide variety of substrates. Parts may be precisely positioned and then structurally joined "on demand" at both a place and time convenient to the assembly process.

B. Advantages of UV Curing Aerobic Acrylics

Ultraviolet curing grades of aerobic acrylics yield tough, impact-resistant, structural adhesives with tensile strengths up to 3000 psi when joining metal, plastic, glass, ceramics, and other substrates. Adhesive potting to $\frac{1}{4}$ in. can be produced in a single exposure to high-intensity UV light. Transparent optical adhesives are also derived from this technology.

Figure 1 showed steel adhesion tensile strengths of a typical aerobic adhesive cured with either activator or UV light. The ability to use multitype curing technologies to achieve structural adhesion strength greatly expands design capabilities and helps design in a more optimum, a more productive, assembly process.

Surface dryness and depth of cure are dependent on both the lamp used and the individual formulation. High intensities are required for the most rapid and deepest cures. A potting grade UV aerobic will cure to $\frac{1}{4}$ in. in 30 s under a 100,000 microwave/cm^2 mercury vapor lamp. Table 6 shows curing times with various lights. The optical region of the electromagnetic spectrum is defined into UV, a narrow band of visible light, and a belt of infrared radiation, as shown in Fig. 8. An exploded view of the UV spectrum with

Table 6 Some Sources of Light

Source	Wavelength	Intensity at 350–400 nm (watts/cm^2)	Seconds to cure 1 (2-mil gap between glass slides)[a]	Seconds to cure 1 (1/8″ deep wire tack)[a]
Sunlight	Full spectrum	Very low	10–30	Not recommended
Mineral light	350–400 nm	100–7000	5–20	15–100 (higher intensities only)
Black light				
275-watt consumer style sunlamp[b]	Full spectrum + heat	5000–7000	1–10	5–30
Industrial-grade mercury arc lamp type I	300–400 nm + visible light	5000–10,000	1–15	5–30
Industrial-grade mercury arc lamp type II[c]	Full spectrum + heat	1,500,000	0.5–4	2–10
Pulsed xenon arc lamps; solar simulators[c]	Full spectrum + heat	Very high	Fast	1–5
Dymax "worker friendly" UV lamps	300–400 nm + visible light	50,000–150,000	Fast	1–5

[a] Speed of cure varies according to formulation.
[b] Shielding recommended.
[c] Shielding required.

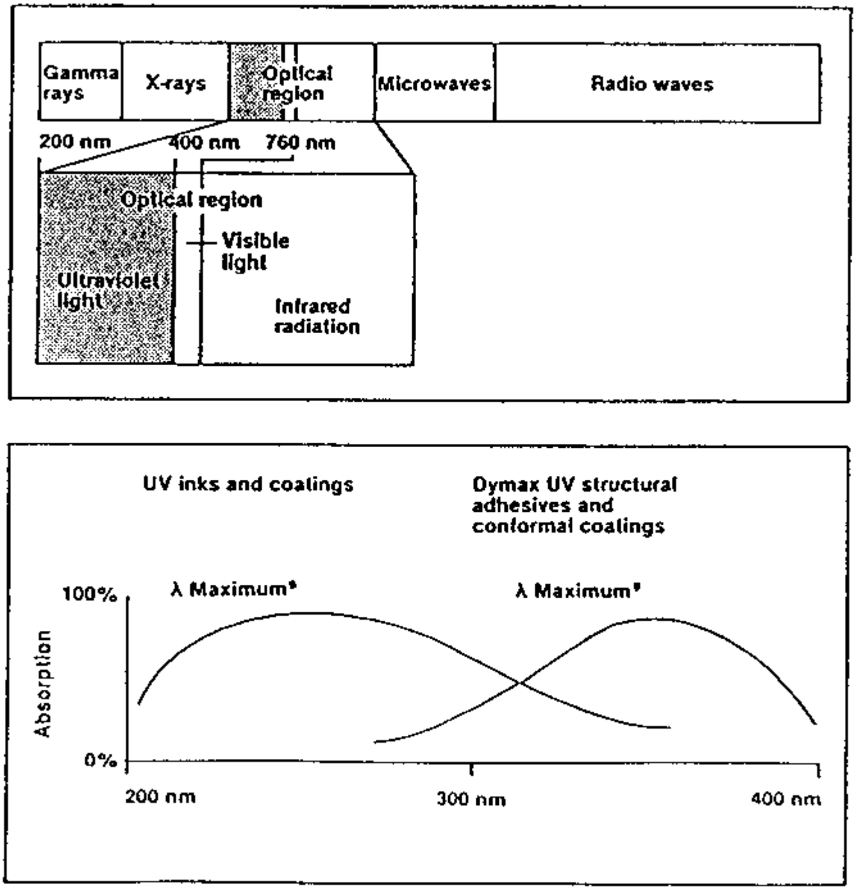


Figure 8 (Top) Optical region of the electromagnetic spectrum is defined into ultraviolet, a narrow band of visible light, and a belt of infrared radiation. (Bottom) An exploded view of the UV spectrum with absorbance curves for Dymax UV adhesives compared to typical UV inks and coatings. λ Maximum = that point at which maximum absorption of UV energy occurs.

absorbance curves for Dymax UV adhesives as compared to typical UV inks and coatings is also shown in Fig. 8.

C. Curing Lights and Mechanisms

Only initiators sensitive to long-wave UV light over 325 nm are used in UV aerobic acrylic adhesives. Long-wavelength UV light is sometimes referred to as "black light" and is generally considered harmless. Short-wavelength radiation, on the other hand, can produce burns. (Sunburn from overexposure is a familiar example.) The high-intensity lamps listed in Table 6 all require shielding to protect workers from the short wavelengths that they emit in addition to long-wave UV light.

Special long-wave light generators are available for curing aerobic adhesives utilizing fiber optics that will transmit UV light, and small "penlight" lamps have become available, too. These light sources are ideal for hand assembly of small parts such as electronic components. These light sources are illustrated in Fig. 9.

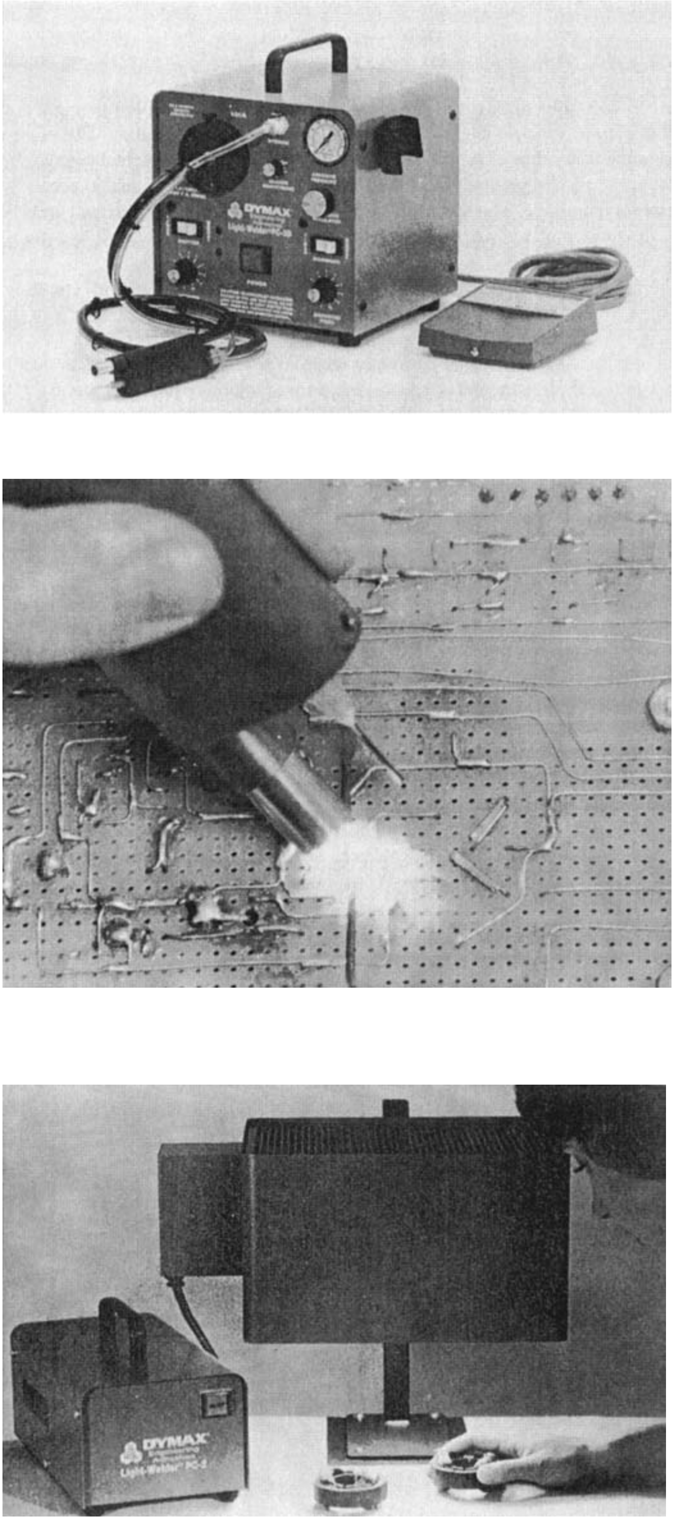
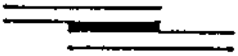
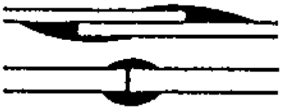


Figure 9 Long-wave light generators.

Figure 9 (Continued).

Table 7 Bonding Categories Using UV Aerobic Acrylic Adhesives

Bonding	Light welding	Potting/coating (other)
		
Glass window assembly	Chip bonding	Potting to 1/4-in. deep
Lens bonding	Speaker software assembly	Abrasion-resistant coatings
Polycarbonate shield assembly	Wire tacking	Solder mask
Plastic film laminations	Temporary bonding	Encapsulating
Costume jewelry	Ferrite magnet assembly	
Glass/plastic stemware	Electrical leads to lamp housing	
Lamp assembly	Sealing motor parts	
	Tamper proofing of mechanical fasteners	
	Cotume jewelry	

D. Bonding Categories

Categories of uses of UV aerobic acrylic adhesives are listed in Table 7. One category is the bonding and lamination of clear materials such as glass and plastics. Because UV aerobics exhibit high strength, toughness, and good structural properties, the second category has been designated "light welding": a process of joining parts by bridging the joint with cured adhesive, replacing long cure times or mechanical fasteners. A third category is adhesive potting and speciality coatings on smooth surfaces such as metal.

1. Light Welding

The ability to bridge bond many surfaces while retaining structural properties has led to a new concept for the joining of abutting surfaces. "Welding with light" is the process of laying a bead of liquid adhesive across the joint formed by abutting metal, glass, ceramic, thermoplastic, paper, and other surfaces and joining them by polymerizing (curing) the adhesive in a few seconds with exposure to long-wave UV light. Parts to be joined can be positioned to exacting tolerances. The adhesive may be applied either before or after positioning and then fixtured or "welded" on demand by exposure to UV light. The low shrinkage of UV aerobics helps assure nonmovement of parts due to the curing cycle. Small parts can be joined in 1–10 s at room temperature. Thick bondlines require longer times or more powerful light sources.

Some ferrite parts require bridge bonding because adhesive between the surfaces interferes with electrical properties. The common technique of using a paste epoxy requiring long time-cycles or heat-cures can be replaced by a fast-curing "light-welding" technique. The parts are held in position, and a bead of thixotropic UV aerobic adhesive is applied across the joint and cured with UV light. A 200 W in. industrial light requires 2 s, while a low-power "black light" effects cures in 30 s. Figure 10 illustrates various UV applications.

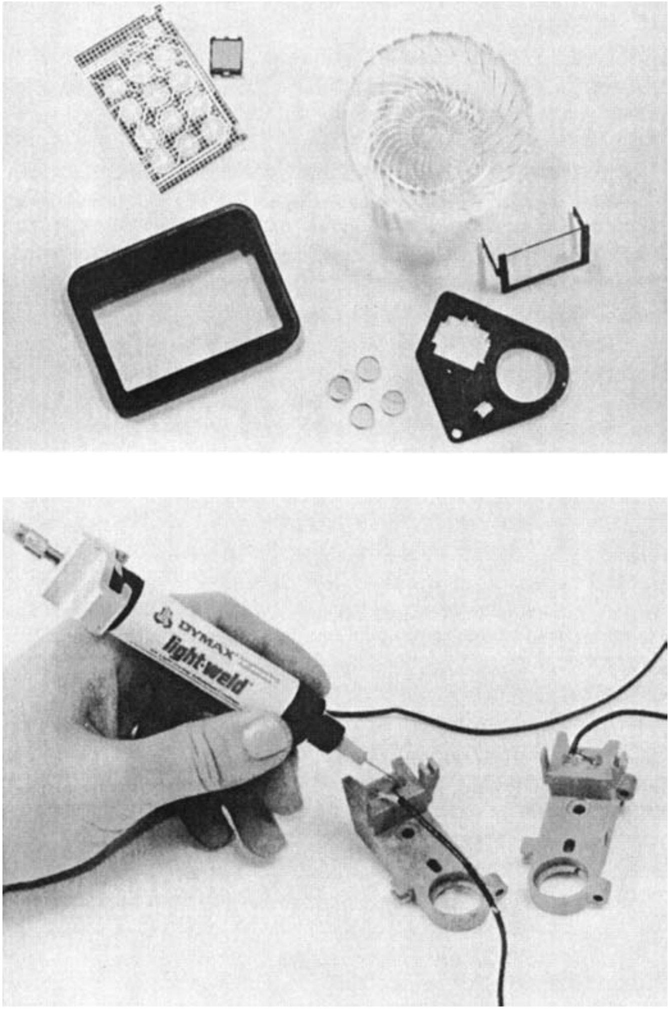
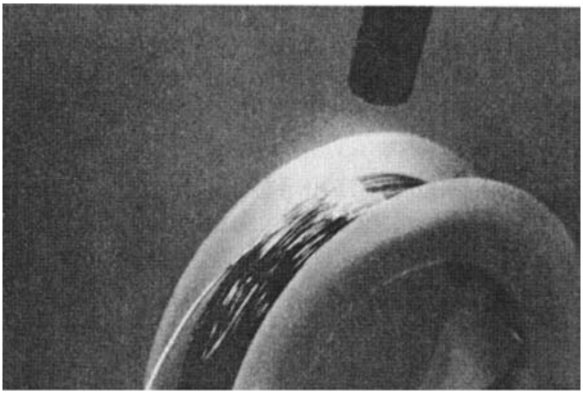


Figure 10 Various UV applications.



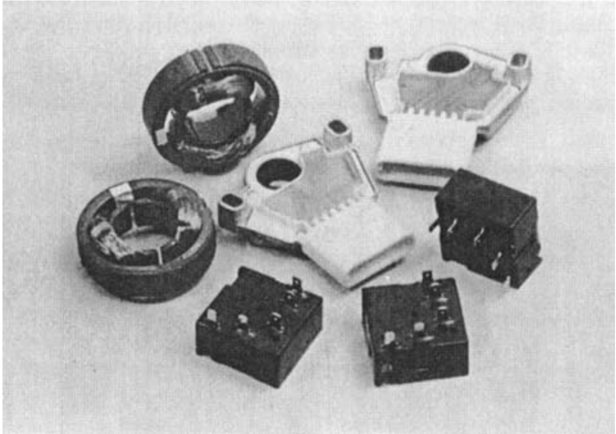


Figure 10 (Continued).

E. UV Aerobics—Improving Efficiency in the Assembly Process

Because of the relatively higher resin costs, process improvement evaluations are replacing unit or batch cost considerations. Many of the new coatings and adhesives provide downstream benefits, which, when factored into the overall cost of manufacturing, equal or reduce cost as compared to traditional coating technologies.

For example, a highly filled epoxy resin, for potting wires into a board connector, represents about one or two cents of the total component cost. The cost associated with mixing, heat curing, handling, and cooling hot pats adds about five cents to the assembly process cost. Finally, cost associated with downstream quality control and rejected parts adds, conservatively, another two or three cents.

Alternatively, the newest generation of structural adhesives adds up to four-six cents material cost per component. The material's high efficiency and quality, however, lower assembly and quality costs. A company saves as much as 30–50% in overall component manufacturing cost and achieves a dramatic reduction in rejects.

Similarly, a 70% solvent-based or water-based conformal coating solution might cost as little as half of a solvent-free curing alternative. The energy expense to remove water, however, is high. The economic and environmental penalties to remove solvents are even greater. New OSHA and EPA regulations are expected to further restrict solvent usage. The seemingly prime disadvantage of infrared and UV alternatives are further offset when one considers that up to 70% of the lower-priced coatings can be lost to evaporation.

The automotive industry leads the way in harsh environmental use of consumer electronics. Electronics represents over 10% of current costs to car makers. Much of the costs is for sensing and controlling components.

Because conventional UV resins cure only when exposed to UV light, resin underneath components will not cure and is unacceptable for automotive use. The aerobic UV coatings have a unique secondary heat curing ability (as low as 85°C), which makes them attractive. Simply raising the temperature of the boards for 5 min allows the uncured resin to "shadow cure."

One major automobile manufacturer was concerned about the use of urethane coatings with regard to solvent safety and emissions regulations. The cost and size of the complex coating supply and solvent evaporation equipment were other issues. Also, a 2 hr oven time limited the type of board it could coat and presented a severe handicap to short-run production and just-in-time delivery systems.

The company now sprays an aerobic coating onto the board. Because there are no solvents, boards move immediately beneath a high-intensity UV light for just 5 s. Short-run production is no longer a problem.

As we have suggested, aerobic adhesive technology has proven remarkably well suited to cures effected by UV light. Aerobic acrylics cured by UV light have the potential for vastly broadening the market for acrylic adhesives.

As previously discussed, UV potting compounds used to be limited by their inability to cure through more than several mils. For larger gaps (most potting projects), slower curing epoxies have been the sole option for many manufacturers. Now, however, fast curing UV aerobic acrylic adhesives can pot depths of several inches in areas accessible to UV light.

F. UV Aerobics—Improving End-Product Quality

Adhesive and coating advances allow electronics design and assembly engineers to meet new quality demands. They bring new cost considerations to electronics production, too. For example, conformal coatings, tacking adhesives, and potting compounds used in military electronics have stringent specifications because of the demanding environments in which they are used.

Protection from high vibration, G-force stresses, thermal shocks, and moist or abrasive atmospheres is mandated, along with adhesion, strain relief, and overall stronger component attachment. Consumer products, from computers to appliances, are moving from "safe" office and home areas to more demanding environments as well.

In one example, a UV aerobic acrylic replaced an epoxy adhesive in an aircraft application. Epoxy adhesives frequently have been used to bond through-hole hybrid components onto PC boards. This prevents breaking of the fragile leads under common aircraft stresses such as temperature changes and vibration.

The manufacturer encountered drawbacks with this method, however. Cured epoxy is labor intensive and difficult to remove when rework is required. It is rigid and does not allow adequate expansion/contraction during temperature cycling. Cracks can occur in the bond, weakening the strength up to 50% of pretemperature cycling values. One must measure and mix two components. Epoxy requires a minimum 15-min oven cure at 250°F, presenting the danger of circuit damage.

When a UV aerobic acrylic combining urethane and acrylic resins was substituted, the following characteristics were obtained: high strength before and after thermal shock testing, ease of rework, good bonding and processing, no stringing on application, and no runout during heating. The pattern spreads evenly and is cured with a single pass under a light. This application has been well documented in a paper given at the U.S. Navy Best Practices Production Workshop, September 1989 [7].

The same paper, authored by Dr. Olexander Hnojewyj and Mark Murdoch [7], documented how a flexible grade of UV aerobic acrylic provided a quick cost-effective solution for supporting 46-flex and 26-flex pins, which previously had exhibited a higher than expected breakage rate.

The aerobic acrylic had excellent adhesion to the polyimide-flex-and-epoxy-glass laminate and supplied visual clarity for inspection of the reinforced pins. Cure was less than 1 min, and the material flowed well into through-hold cavities and around pins.

The material proved easy to apply both manually and with a pneumatic dispenser. UV acrylic reworkability with isopropyl alcohol or heat was quick and easy as well. In this case, the acrylic was more expensive than epoxy or silicone, but proved more cost-effective because of its virtual elimination of flex failures.

The new generation of acrylic adhesives show their versatility in other electronic assembly applications.

A surface mount aerobic acrylic was chosen by an Asian PC board manufacturer because the adhesive could be applied and cured faster, yielding an overall reduction of per-unit costs and improved productivity. Additionally, the aerobic acrylic yielded better green strength and UV fixturing before heat cure held chips in place and prevented skewing. The fast cure at higher assembly line throughput also helped prevent damage to temperature-sensitive components. Overall quality was improved.

Wire and component tacking with UV curing aerobic acrylic adhesives has been adopted by a manufacturer of flight systems boards where the need was to tack numerous wires and components in place and reduce manufacturing costs at the same time. Two populated boards with fluorocarbon insulated wires, soldered in various configurations, were bonded in this test. Adhesives being compared were exposed to various mil-standard specifications for humidity, immersion, temperature, and Humiseal coating.

The cyanoacrylates failed because they separated from the board. Although epoxies exhibited the necessary resistance to harsh environments, their lengthy cure time and a need to hold the wires in place during cure make their use inconvenient and impractical. The UV acrylic proved economical and effective, maintained integrity, and met all military standards.

Aerobic acrylic conformal coatings have provided major advantages to PCB manufacturers. Currently, solvent-based products dominate conformal coating processes, but safety, EPA, and processing considerations indicate their eventual decline. Although most solvents evaporate in ovens within a few hours, smaller volume manufacturers use systems requiring several days to complete solvent evaporation and/or cure of the resin systems.

UV aerobic coatings offer a solvent-free component that is 100% solids and requires no mixing. It is applied by spray or dip and then cured in as few as 5 s using high-powered UV lights. For low-volume applications, low-cost desktop lamp systems are available. This rapid cure translates into line speeds up to 15 ft/min. Figure 11 illustrates application and curing for conformal coatings. Figure 12 portrays the actual bonding area for various applications.

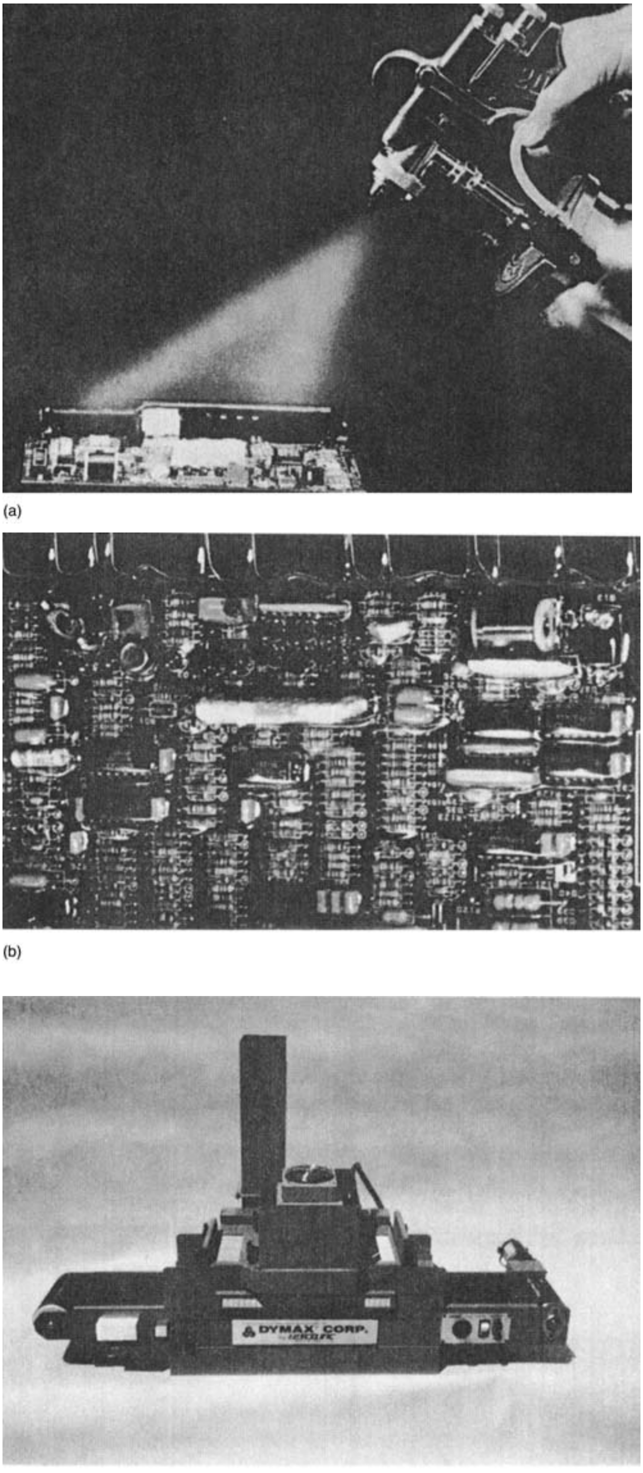


Figure 11 Application and curing of UV conformal coatings. (a) Spray coating. (b) Dip coating. (c) Table-top high conveyorized intensity UV lamp cures at 6–12 ft/min.

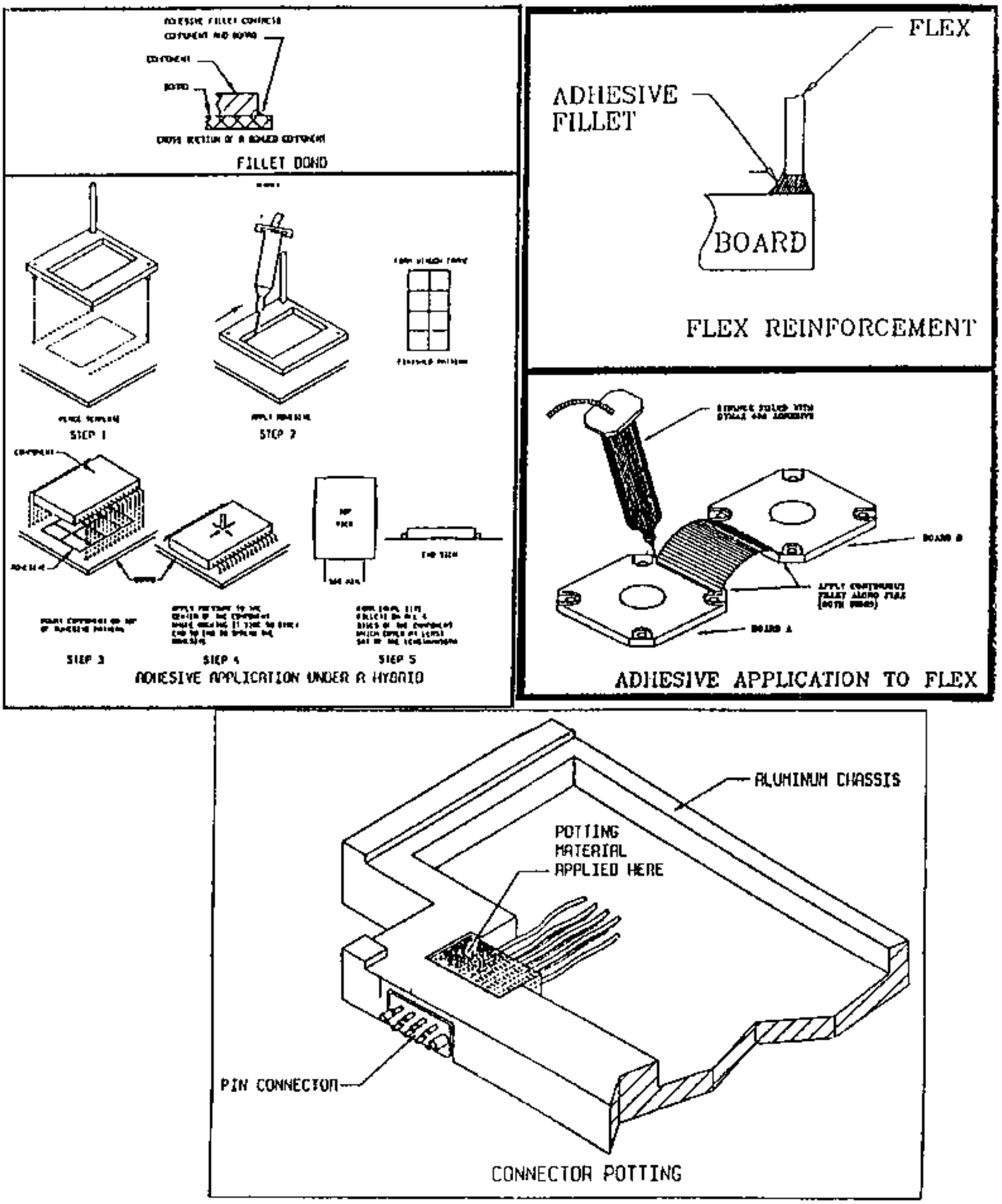


Figure 12 Bonding area for various applications.

V. SUMMARY

Acrylic adhesives provide substantial advantages for assembly operations such as fast, room-temperature fixtures, the ability to bond a wide variety of surfaces (even oily metal), bondline flexibility, and good environmental and solvent resistance. Aerobic acrylic adhesives, owing to their lack of noxious odors, low flammability, and lower toxicity parameters, overcome many of the disadvantages previously associated with acrylic adhesives. In addition, one-component UV light curing grades with superior structural properties and full cure in as little as 1 s, offer new opportunities in potting, bridge bonding, wire tacking, and glass plastic assemblies.

Because structural-strength aerobic adhesives and sealants cure at the speed and convenience of the assembly process, it is no longer necessary to pace assembly speed to an adhesives open time. The desired curing is effected in seconds. This ability to provide "instant cure" at the time and place demanded by the assembly process offers an attractive assembly and sealing alternative. The use of UV curable adhesives for sealing applications represents a new technology. With ever-increasing competition, cost savings due to automation have become the key to productivity. The potential of this new, easily adaptable technology is now being recognized by users in a variety of industries to lower costs and increase productivity while providing high-quality goods and incurring little environmental impact.

APPENDIX A: EFFECTS OF AIR INHIBITION

Tensile shear (steel) thickness (ASTM D-1002) 24-hr cure	Anaerobic Structural adhesive	2nd-generation acrylic	Aerobic acrylic
2 mils	4500 psi	5000 psi	4000 psi
20 mils	2500 psi	3200 psi	3500 psi
60 mils	0	1000 psi	2500 psi
20 mils (with air beaten into the adhesive)	1000 psi	2000 psi	3000 psi
Cure on pine wood 40 mil gap	500 psi	Partial substrate failure	Substrate failure
Time to fixture steel nut and bolt at 75°F; no accelerator used	2–6 hr	4–24 hr	No fixture after 30 days

APPENDIX B: EFFECT OF AEROBIC FORMULATION VARIATIONS

	A	B	C
Fixture rate[a]	5 min	25 s	12 s
Complete room-temperature cure[b]	24–72 hr	4–24 hr	2–8 hr
Bondline appearance	White, hazy	White, hazy	Transparent
Gap filling	30 mils	20 mils	20 mils
Shore D hardness	50	75	10
Texture	Tough, resilient	Rigid	Very flexible
Typical end uses	Ferrite, bonding, "Plexiglas" fibreglass, assembly	Sheet metal, galvanized steel, bonding, graphite, glass	Lens bonding, Kevlar, window mounts
Tensile, cold-rolled steel	2000 psi	3500 psi	1800 psi

[a] Fixture rates are defined as the time required for two microscope slides, bonded in a ½-in. overlap, to resist movement from light finger pressure. Gaps estimated at 1–3 mils.

[b] Varies with ambient temperature and condition of the substrate.

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Technology of Cyanoacrylate Adhesives for Industrial Assembly

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I. INTRODUCTION

Adhesives have been used since ancient times, but only since the advent of synthetic polymers (plastics) has their use become of major importance because manufacturers can now synthesize polymers and compound adhesive formulations to fit the requirements of the application. In other words, adhesives can be engineered for improved characteristics such as speed of cure, heat resistance, and impact resistance. Cyanoacrylates are just such an adhesive.

Cyanoacrylate adhesives can be defined as single-component chemically active liquids that react very rapidly with moisture or other weakly alkaline materials to form clear, hard solids. Their important characteristics are:

1. Very fast curing
2. Applied as liquids
3. Cured by a chemical reaction
4. Activated by alkaline materials
5. Form hard plastic materials after curing.

II. CHEMISTRY OF THE SYSTEM

The term *cyanoacrylate* comes from the chemical structure of these materials. Figure 1 depicts the general formula for cyanoacrylates. As the figure shows, cyanoacrylate adhesives are made up of carbon, hydrogen, oxygen, and nitrogen. The way these atoms are

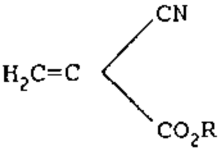

Figure 1 General formula for cyanoacrylate adhesives.

arranged in the molecule is important because the arrangement or configuration of the atoms affects the chemical properties of the molecule.

The CN group is called a nitrile or cyano group. In addition to giving these adhesives part of their name, the cyano group is highly polar and gives the molecule some of its strong adhesive character. The remainder of the molecule, the acrylate portion, is also polar and further enhances its adhesive character.

The letter "R" is used in organic chemistry to represent a part of a molecule that differs within a "family" of compounds. In the cyanoacrylate family, the R group is the alcohol that forms the ester with the acylic acid portion of the molecule. The type of alcohol used gives the cyanoacrylate adhesive its name. Thus methyl cyanoacrylate is the ester formed between methyl alcohol and cyanoacrylic acid. Figure 2 shows the configuration of some of the commercially available cyanoacrylate adhesives.

All of the molecules shown in Fig. 2 are thin, watery liquids at room temperature. In this low-viscosity state, these molecules are capable of flowing freely onto the surface of the parts to be bonded. However, such thin liquids would have little or no ability to bridge the gap between the mated parts. The carbon-to-carbon double bond shown in Fig. 2 to be common to all cyanoacrylates is capable of reacting such that adjacent molecules are linked together to form a large chain. The chains become so large that the adhesive changes from a liquid to a hard, tough solid. The chemical reaction involved, called polymerization, is depicted in Fig. 3.

The initiator that drives the polymerization or curing reaction of cyanoacrylate adhesives can be any of the chemicals that generate free radicals. Electromagnetic

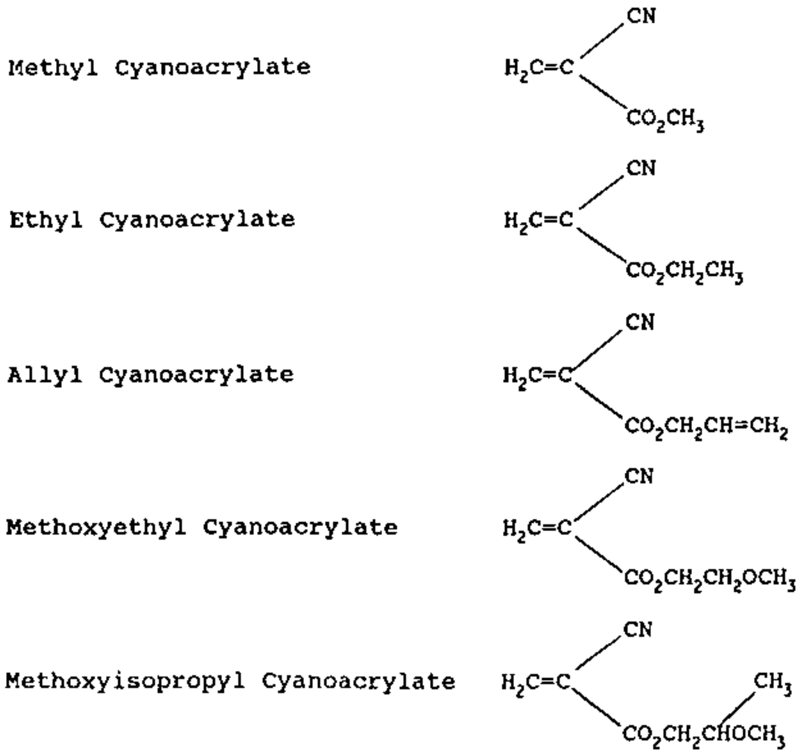

Figure 2 Configuration of common cyanoacrylate adhesives.

Figure 3 Polymerization of cyanoacrylate adhesives.

radiation in the form of heat or ultraviolet light can also trigger the reaction, but usually only enough to cause problems with product shelf life. The more likely route for cyanoacrylate polymerization is by an ionic initiation. Any molecule more alkaline than water can initiate the curing reaction. This type of polymerization is characteristically much faster than a free-radical type and is the reason that cyanoacrylates cure so rapidly. It is this cure speed more than any other property that makes these adhesives so popular on the production line. Many adhesives are stronger or more durable than cyanoacrylates, but none can cure as quickly and to such a wide variety of substrates as the cyanoacrylates.

Although it is not essential to understand the chemistry of cyanoacrylate polymerization to be able to use these adhesives, knowing that a chemical reaction is taking place helps the user to understand how application conditions affect their performance. Consider the fact that the common polymers, such as polyethylene, polystyrene, and poly(vinyl chloride) (PVC), are made in sophisticated reactors. Parameters such as temperature, monomer concentration, and amount of activator are carefully controlled.

With cyanoacrylate adhesives, the reactor used to convert the liquid monomer to the hard solid is the space between the parts being bonded. When conditions vary in this space, the performance of the adhesive will vary. Such parameters as temperature, humidity, space between the parts, and the type of surface being bonded can vary considerably in a given application.

Figure 2 shows a number of different types of cyanoacrylic esters. There are subtle differences between them that can be utilized in specific applications. Methyl cyanoacrylate is a more polar compound than any of the others. This gives the cured adhesive a higher cohesive, or internal, strength. As a result, it has a higher shear strength which can be utilized on metal parts and other parts that are rigid enough themselves to benefit from the strength of this hard, brittle polymer.

Ethyl cyanoacrylate is a little less polar than methyl cyanoacrylate, and has the ability to wet plastic surfaces more readily, and is a better solvent for plastics. With this added ability to make intimate contact with the surface, the bonds on plastic are stronger with ethyl cyanoacrylate than with the methyl ester. This difference in performance gives rise to the adage that *m*ethyl is for *m*etal and *e*thyl is for *e*verything else. Sometimes this difference can be utilized in reverse to good advantage to avoid stress cracking on such sensitive plastics as polycarbonate and polyacrylate.

Also shown in Fig. 2 is an allyl cyanoacrylate. This molecule contains a second double bond that can be made to react after the initial polymer chain is formed. This secondary bonding can occur between adjacent polymer chains, causing cross-linking of the chains. Such cross-linked polymer chains are more heat resistant than is the uncross-linked polymer.

The data presented in Table 1 compare the heat resistance of allyl cyanoacrylate and methyl cyanoacrylate determined by heating a steel lap shear specimen for 1 week

Table 1 High-Temperature Resistance of Allyl Cyanoacrylate

	Shear strength[a]	
Temperature (°C)	Allyl	Methyl
25	3000	3600
100	3900	250
120	900	0
150	1500	0
250	1700	0

[a] Steel/steel per ASTM D1002. Aged 1 week at temperature indicated, cooled and measured at 25°C.

at various temperatures. At room temperature the two types are essentially equal in strength. The slightly higher strength of the methyl cyanoacrylate caused by its higher polarity can be seen clearly in the higher value obtained in the test cured and aged at room temperature.

The effect of exposure to 100°C shows up in the loss of strength for the uncross-linked methyl cyanoacrylate and a higher strength for the allyl cyanoacrylate because of the extra strength contributed by the reaction of the double bond in the allyl cyanoacrylate. After exposure to 120°C, all the strength of the straight-polymer-chain methyl cyanoacrylate is lost. The strength of the cross-linkable allyl cyanoacrylate is also reduced, suggesting the loss of the contribution to its strength by intermolecular association. Only the contribution from the allyl group survives.

Higher temperature causes the allyl double bonds to react faster. As a result, more cross-linking can take place and more of the strength is retained. Resistance to temperature above 120°C is possible provided that the parts are clamped during the curing process. Because of the extensive cross-linking, the resultant polymer is very brittle and it is recommended only for metal and other rigid, higher-temperature-resistant substrates.

The fourth type of cyanoacrylates presented in Fig. 2 are the alkoxyalkyl esters. Methoxyethyl cyanoacrylate and methoxyisopropyl cyanoacrylate esters have all the desirable properties of the methyl, ethyl, and allyl cyanoacrylates, with the added advantage of low vapor pressure. As a result, these monomers have little or no odor, which makes them popular for use in environments where ventilation is a problem. The low vapor pressure also reduces the fogging of adjacent parts so often seen with "regular" cyanoacrylates on damp days, a problem discussed in more detail below.

In addition to the benefits of low odor and reduced fogging, these adhesives form stronger bonds to low-energy substrates such as EPDM rubber, natural rubber, and other difficult-to-bond plastics. This property seems to be a function of the solvent action of the uncured adhesive, so care must be taken to avoid stress cracking when the adhesive is used on sensitive substrates such as polycarbonates and polyacrylates.

While the alkoxy cyanoacrylates cure by the same mechanism as regular cyanoacrylates, the cure speed is a bit slower and the overall strength is about 20% lower than that of ethyl cyanoacrylates. The strength is well in excess of the strength of more plastic substrates, however; the 20% reduction in strength is not significant.

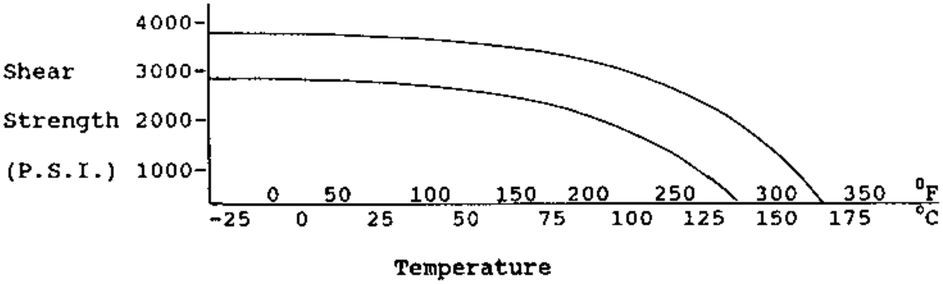

Figure 4 Hot strength of allyl cyanoacrylate, 100 cP Brookfield, bond cured at room temperature for 24 h, heated for 2 h at temperature and tested hot.

Table 2 Temperature Performance of Allyl Cyanoacrylates

	Lap shear strength (psi) (steel)
Room temperature	3112
100°C (212°F)	3353
250°C (480°F)	1493

III. HOT STRENGTH

In general, standard industrial cyanoacrylates do not operate effectively above 180°F (see Fig. 4). However, the new allyl types of cyanoacrylates can operate as high as 480°F before the bond loses sufficient strength to be operationally effective (see Table 2). Allyl cyanoacrylates for metal-bonding applications have proven effective in wave solder and under-hood (automotive) applications. In Fig. 4, bonded assemblies are cured at room temperature for 24 h. The assemblies are heated for 2 h and tested hot.

IV. SPEED OF CURE

A typical cure curve for 100-cP methyl cyanoacrylate is shown in Fig. 5. The speed of cure is influenced by the thickness of the bond, the activity of the surface, and the designed speed of the adhesive.

1. *Versatile*. There are few materials to which cyanoacrylate will not bond/adhere, even dissimilar materials (polyethylene, polypropylene, and Teflon are some materials that require pretreatment).
2. One-component without solvent, therefore easily dispensed.
3. *Economical*. A small drop goes a long way. It is important to apply the least amount for maximum strength (see Table 3).

The following equivalents are for application of the adhesive to actual parts.

1 lb = 30,000 bonds 1 in. square and 1 mil thick
1 oz = 1,875 bonds 1 in. square and 1 mil thick
2 g = 132 bonds 1 in. square and 1 mil thick

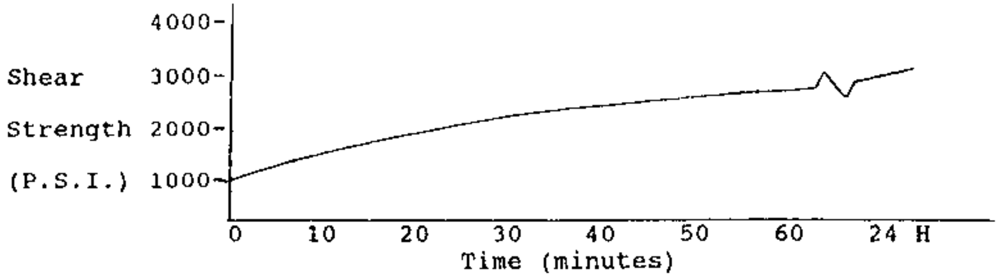

Figure 5 Typical cure curve for 100- cP methyl cyanoacrylate.

Table 3 Approximate Conversion Chart for Estimating Use[a]

1 drop =	0.006 g
2 drops =	0.012 g
5 drops =	0.030 g
10 drops =	0.060 g
50 drops =	0.300 g ($\frac{1}{3}$ g)
167 drops =	1.00 g
330 drops =	2.00 g
4,666 drops =	1 oz
75,500 drops =	1 lb

[a] Based on the assumption that 1 drop = 0.006 g.

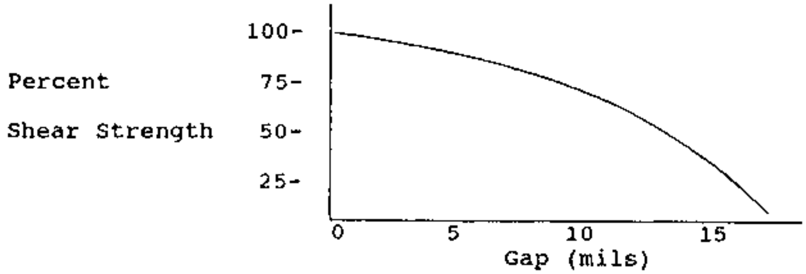

Figure 6 Gap-filling capability of cyanoacrylate.

Cyanoacrylate adhesives have limited gap-filling capability (see Fig. 6). Low-viscosity grades can fill gaps to approximately 2 mils, medium viscosity up to 10 mils, and high viscosity up to 15 to 20 mils. However, note that the speed of cure will be slower and the ultimate strength lower as the gap increases. For example, when the gap is 15 mils it requires 1 h for sufficient handling strength, but with a gap of 1 mil it takes only 10 s. Cure speed can be increased by the use of a chemical accelerator. Moisture and water resistance is limited. Resistance against water, although poor when two rigid parts are bonded, is markedly improved when at least one of the two parts is flexible.

Table 4 Typical Fixture Time with Activator[a]

Gap (in.)	With activator	Without activator
0.000	1 s	10 s
0.005	50 s	600 s

[a] Steel/steel, 25°C, ethyl cyanoacrylate.

V. ACTIVATORS

Since bases are catalysts for the curing reaction and acids are stabilizers for the cyanoacrylates, the pH value of the surface will control the cure speed. Surfaces that tend to be acidic will cure slowly compared to a neutral surface, which in turn will cure more slowly than an alkaline surface. In most applications the objective is to speed the cure; therefore, all the commercially available activators are weak bases dissolved in a volatile carrier. Applying an activator to a surface places a layer of the weak base in position to initiate the cure. Since they are stronger bases than moisture, they are able to neutralize the stabilizer systems in the adhesive more effectively, and thus they can tolerate larger gaps than would be possible with moisture alone. In general, the fixturing time is 10 times faster with activator than without it. Even with activator, the effect of the gap is clear (see Table 4).

Another advantage of the activator is the ability to cure a film or drop of the adhesive on a surface. The activator can be applied either to the surface being coated or to the top surface of the adhesive. The adhesive cures to a clear, hard, dry plastic that can be used to locate parts in position or to form a protective coating. Because the curing reaction is ionic, it is not sensitive to oxygen as are free-radical reactions, and it will cure through to the surface without the tackiness associated with free-radical curing systems.

VI. IMPROVED COMMERCIAL CYANOACRYLATE COMPOUNDS

A. New Flexible Cyanoacrylates

New cyanoacrylate compounds exhibit good adhesion to various plastics and elastomeric surfaces, such as Mylar, copper foil, and vinyl films. These products show better impact resistance and good flexibility compared to standard cyanoacrylates, good resistance to cracking under flexing or bending, and a longer open time than that of standard products.

B. New Cure-Through-Gap Cyanoacrylates

Through changes in the manufacturing process, cyanoacrylates can now be highly purified. This added purification step has led to the development of a group of materials that can cure through a gap without the typical reduction in shear strength and overall performance. More traditional formulations show a dramatic reduction in shear strength as the gap increases (see Fig. 6). Table 5 shows cure through a gap and the corresponding shear strength for these new, highly purified cyanoacrylates.

Table 5 Percent Cure Through 0.008-in. Gap

Time (h)	Gap-filling cyanoacrylate	Regular cyanoacrylate
2	25	13
24	100	40
72	100	100

Table 6 Set Time Across a 0.004-in. Gap

	Time (s)	
Product viscosity (cP)	Surface-insensitive cyanoacrylate	Ethyl cyanoacrylate
100	6–8	55
500	7–12	> 60
1500	8–12	> 60
8000	8–12	n.a.[a]

[a] Not applicable.

C. New Ultrafast-Cure Surface-Insensitive Cyanoacrylates

The new range of surface-insensitive cyanoacrylates provides ultrafast cures independent of gap. In addition, these cyanoacrylates will rapidly bond acidic and low-energy surfaces. The fast cure also minimizes the occurrence of frosting and fogging. Table 6 shows a comparison of these new surface-insensitive materials compared to a standard ethyl-grade cyanoacrylate. These products are also suited to bonding various wood substrates and porous surfaces without the use of activators.

D. New Low-Odor Cyanoacrylates

Owing to unique manufacturing processes and chemical reformulations, cyanoacrylates can now be completely odor free. These products, which have almost no detectable odor, improve worker comfort and acceptance. Also, there is no unsightly fogging (chlorosis) of expensive parts adjacent to the bond line as can be seen with other types of cyanoacrylate adhesives on hot, humid days. This improves production rates of acceptable parts.

VII. SIGNIFICANT CYANOACRYLATE CHARACTERISTICS

A. Polypropylene and Polyethylene Bonding

Polyolefin bonding has been advanced using cyanoacrylates through the use of surface primers. These primers promote adhesion to untreated polyethylene (PE), polypropylene (PP), and EPDM rubber. Table 7 shows comparison bonds using standard industrial-grade cyanoacrylates.

Table 7 Comparison Bonds Using Standard Industrial-Grade Cyanoacrylates

	PE/PE		PP/PP	
Lap shear (psi)	Primed	Unprimed	Primed	Unprimed
After 15 min, room temperature	90	50	185	52
After 24 h, room temperature	108	50	200	52

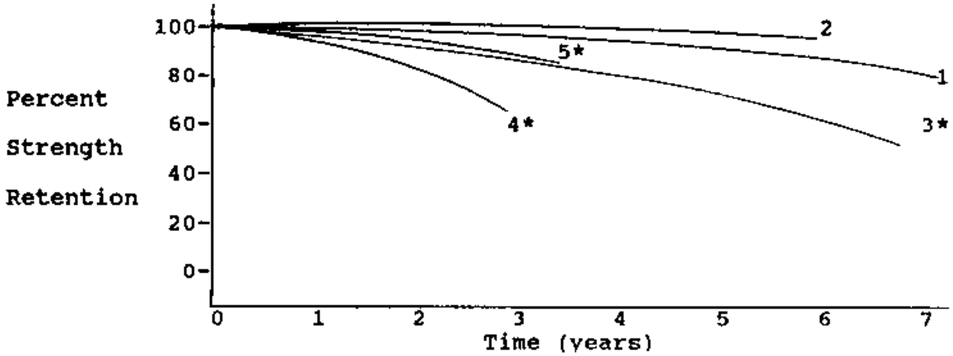

Figure 7 Durability of cyanoacrylate adhesives. Asterisk denotes substrate failure.

B. Medical-Grade Materials

When fully cured, cyanoacrylates will meet class VI standards for plastics, the highest class of safety and biocompatibility as defined by the *United States Pharmacopoeia* (USP).

C. Thermal Conductivity

Cyanoacrylates are essentially thermally nonconductive materials. The value for a typical methyl-grade cyanoacrylate is 2.1 (Btu-in.)/(hr-ft^2-°F).

D. Durability

Assemblies joined with cyanoacrylate adhesives exhibit good long-term durability, particularly when the materials are somewhat flexible, such as rubbers and most plastics (see Fig. 7). Bonded lap shear specimens have been aged outdoors for 7 years with good retention of strength (see Table 8).

When impact resistance and/or strength is required, it can be improved dramatically by the "rubber sandwich" technique. In this case, a rubber sheet bonded between the rigid plastic or metal substrates will absorb all peel and impact forces. It is also useful in absorbing stresses when thermal expansion and contraction occur.

VIII. CHLOROSIS

There are times when various environmental factors can affect bonding results. One such phenomenon is *chlorosis*, in which white particles appear on the bonded parts. Chlorosis

Table 8 Strength Retention of Cyanoacrylate Bonds After Outdoor Weathering

	Percentage strength retention when stored at 73°F and 50% relative humidity for (yr):						
Material bonded	1	1.5	2	3	4	5	7
Neoprene to neoprene	100		80				60
Neoprene to acrylic	93		87			93	
Butyl rubber to aluminum	65[a]	92[a]			55[a]		55[a]
Polystyrene to polystyrene		80[a]		83[a]			
Rigid PVC to rigid PVC		93[a]		100[a]			

[a] Substrate failure.

may occur with the use of cyanoacrylate, depending on the bonding method, bonding conditions, atmospheric influences, and other factors. The usual reaction received from users when chlorosis does occur is concern over the possible effect on the strength of the bond and the unsightly external appearance. The phenomenon of chlorosis is nothing more than an adhesion of particles to the surface of the part and has no effect on the quality of the bond.

Chlorosis develops when a portion of liquid evaporates in the air without being solidified (polymerized). It becomes a powdery resin through a polymerization reaction with moisture in the air. The powdered resin falls back to the surface of the bonded parts. Chlorosis can develop under the following conditions:

1. Excessive amounts of adhesive.
2. Bonding under conditions of high room moisture content (relative humidity), as may be the case during a rainy period.
3. Subjecting the bonded portion to airtight or almost airtight conditions immediately after bonding.

Chlorosis can be avoided by taking the following actions:

1. Avoid the use of adhesive in excessive amounts.
2. Perform the bonding operation under appropriate moisture conditions (avoid excessive accumulation of water on the material surface); 50% relative humidity is ideal.
    a. Allow several minutes after removal of grease from the object being bonded.
    b. Thoroughly dry the object to be bonded before actual bonding.
    c. Wear polyethylene gloves during the bonding operation.
3. Attempt as much as possible to scatter vaporizing monomer.
    a. Avoid subjecting bonded material to airtight or nearly airtight conditions immediately after the bonding operation.
    b. Ventilate the bonded object immediately after the bonding operation by use of an electric hot-air blower or other appropriate means.
    c. Perform the bonding operation under conditions of free air circulation.
4. Promote the polymerization reaction (resinification).
    a. Assure appropriate heat conditions for the bonded object [up to about 158°F (70°C)].
    b. Blow heated air over the bonded area immediately after the bonding operation.

5. Form a protective shield on the surface where chlorosis is likely to develop by applying oil to the area surrounding the material surface immediately before or after the bonding operation.

Chlorosis can be eliminated by the following:

1. Wipe the particles carefully with a dry cloth.
2. Wipe off the particles with solvent.

The particles can readily be wiped off by the use of a cloth containing a solvent such as dimethylformamide, nitromethane, acetone, or chlorinated or fluorinated solvents. In this case, however, if the bonded object is plastic, caution must be exercised because plastics can be affected adversely by solvents.

Poor bonding arises from problems associated with the adhesive itself: for example, its decreased adhesive power. The simplest method of checking on the spot for any decrease in adhesive power is to test with Bakelite samples. If the adhesive is found to have decreased adhesive power, it has probably been stored improperly.

Material kept in the work environment up to 6 months will not suffer deterioration. For periods over 6 months, storage in 40°F or below can triple the useful shelf life.

IX. SUMMARY

Cyanoacrylates have shown themselves well in permanent outdoor assemblies as well as in temporary manufacturing aids. They are safe, convenient materials to incorporate in plant operations. New developments in technology have improved moisture resistance, setting times, gap filling, clarity, high-temperature resistance, and flexibility, and most recently, cyanoacrylates have become less surface sensitive.

As always, thorough testing of a specific application should precede specification. New research has led to improved commercially available models that are finding use in applications previously thought unsuitable for cyanoacrylates. Where appropriate, cyanoacrylates can increase productivity dramatically and reduce fundamental costs, to produce high-integrity parts for aircraft, industrial, agricultural equipment, electronic, automotive, and maintenance applications.

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Silicone Adhesives and Sealants

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I. INTRODUCTION

Silicone adhesives and sealants were introduced approximately 40 years ago and many of the silicones used in the early days are still performing. Products are available in a variety of forms, from pastelike materials to flowable adhesives. Both single- and multicomponent versions are available, with several different cure chemistries. Most of the silicones of commerce are based on polydimethylsiloxane (PDMS) polymers. Other siloxane polymers may be used when resistance to ultrahigh temperature, ultralow temperature, or solvents is required.

Applications are extremely broad. A partial list includes construction, highway, automotive, appliance assembly, original-equipment manufacture, maintenance, electronics, aerospace, and consumer uses. In some cases, silicones compete with other materials, such as polyurethanes, polysulfides, and acrylics, whereas in applications requiring long-term durability, silicones alone are specified. Silicones are often chosen for their excellent resistance to weathering and temperature extremes, their adhesion, and their ability to accommodate substrate movement. When silicone sealants and adhesives are mentioned, the thought of excellent durability comes to most readers' minds. Silicones [named for the similarity of the $(CH_3)_2SiO$ polymer repeat unit to the analogous organic ketones, $R_2C{=}O$] occupy a unique position between inorganic and organic materials. The saturated inorganic Si—O—Si polymer backbone provides flexibility and stability to sunlight, while the methyl groups ensure low intermolecular forces. Some of the key attributes of silicones, which are responsible for their unique properties and durability are [1]:

Low surface tension
High water repellence
Partially ionic backbone
Large free volume
Low apparent energy of activation for viscous flow
Low glass transition temperature
Freedom of rotation around bonds
Small temperature variations of physical constants
High gas permeability
High thermal and oxidative resistance
Low reactivity

Insolubility in water
High silicon–oxygen bond energy

Selected properties of PDMS are as follows:

Critical surface tension of wetting	24 mN/m
Water contact angle	110°
Glass transition temperature	150 K
Energy of rotation	0 kJ/mol
Activation energy for viscous flow	14.7 kJ/mol
Si–O bond energy	445 kJ/mol
Percent polar contribution	41%

The saturated backbone and high Si—O bond energy result in products that perform very well in applications involving exposure to sunlight. Since the silicone polymer does not absorb energy in the ultraviolet (UV) region of the light spectrum, one must be cautious with the use of clear silicones. The silicones need no UV absorbers to be stable (and contain none); thus the UV light from the sun can pass through clear silicones to the surface below the sealant. If the surface is sensitive to UV light, deterioration of the substrate may occur. Except for light-protected areas and unsensitive substrates (such as glass), the most judicious choice is a pigmented silicone. The pigment acts as a UV blocker and protects the substrate beneath the silicone. Because of the unparalleled stability to UV radiation, silicones are the sealants of choice for wet glazing techniques and the only generic class of sealants allowed for structural glazing (the adhering of glass and other building materials to structures with no attachment other than the silicone). Structural glazing is used in all-glass buildings and skyscrapers.

Other types of sealants often contain large amounts of filler and UV stabilizers to afford some degree of longevity in sunlight. This makes the nonsilicones satisfactory for some applications, but not in applications in which the sun shines directly on the bond line. This application is reserved for silicones. A specialty application for silicones, which further illustrates their UV-light durability, is in the sealing of accelerated UV-weathering test machines. The excellent stability to UV light is true only for pure silicones and is not true of "siliconized" organics or "modified silicones." These contain very little silicone and thus have durability characteristics determined primarily by their base polymer systems.

Silicones have low intermolecular forces that result in relatively flat physical property response with temperature change. An example of this flat response is shown in Fig. 1, in which the viscosity of silicone polymers and a hydrocarbon oil are plotted as a function of temperature [2,3]. The relatively low response of silicone properties to temperature is important during sealant application (e.g., no heating needed in cold weather and no flow in hot weather). Even more important, however, is the fact that the performance of the cured sealant or adhesive will be less temperature dependent than will most organic-based products. This has practical implications: in building joints, for example. In cold weather, the building components shrink, and joint sealants must maintain elasticity to accommodate this movement. This is also fundamental to their use as a structural glazing sealant/adhesive. The sides of all-glass buildings can get very warm in the summer sun, and the silicone must not lose strength at these temperatures. While this rather constant performance is critical in some construction applications, it is also important in many industrial and appliance applications, such as steam irons, where the sealant simultaneously prevents water leakage and acts as an assembly adhesive.

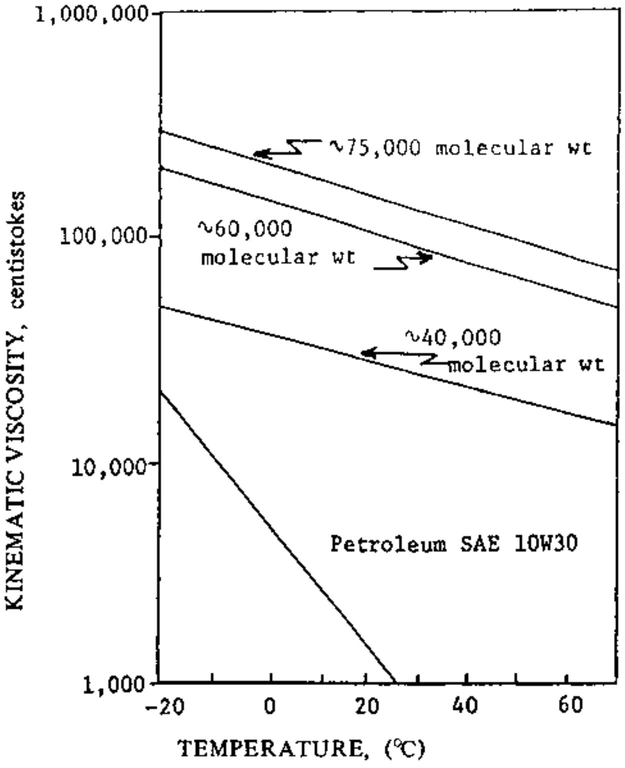

Figure 1 Viscosity versus temperature.

Silicone sealants are rated for their movement capability, with classes at ± 12.5%, ± 25%, ± 50%, and even higher joint movement capability. This too is quite unique, since high-movement nonsilicone sealants rarely perform for long periods of time above ± 25% joint movement.

II. CURE CHEMISTRY

Silicones are available in one- and multicomponent forms. The one-component types are commercially the most important and will be the focus of most of this discussion. These products, which generally cure by reaction with atmospheric moisture, are called RTV (room-temperature vulcanizing) sealants or adhesives. The surface cure rate of these products is a function of the cure system, but the rate of cure in depth depends on the ability to transmit water vapor through the mass of sealant. Silicones are highly permeable to moisture vapor, and generally the one-component types cure at a rate of about 0.3 cm/day. Due to this high vapor permeability, the one-component silicones typically cure faster than do their nonsilicone counterparts.

The multicomponent products generally do not rely on moisture penetration for cure. Their chief attribute is fast cure in very deep sections. Thus many industrial production lines that demand fast cure use a two-component sealant (including the use of silicone encapsulants for electrical components). Cure of these two-part systems can be accelerated further by additional catalyst or exposure to elevated temperatures.

One of the more common two-part cure chemistries is based on the addition reaction of Si—H cross-links with vinyl functional polymers using platinum catalysts. This chemistry is shown below. One advantage of this addition chemistry is that it produces no cure by-products. Another common two-part chemistry involves condensation cure with alkoxysilane cross-linkers using Sn(IV) catalysts.

$$-Si(Me)_2OSi(Me)_2CH = CH_2 + HSi- \rightarrow -Si(Me)_2OSi(Me)_2CH_2CH_2Si-$$

A simplified cure mechanism for the one-component silicone RTV sealants or adhesives is shown below.

Reaction of cross-linker with polymer ends:

$$2RSiX_3 + HOSi(Me)_2O[(Me)_2SiO]_nSi(Me)_2OH \rightarrow$$
$$X_2(R)SiO[(Me)_2SiO]_nSi(R)X_2 + 2HX$$

Reaction of cross-linker with polymer ends:

$$\underset{(A)}{X_2(R)SiO[(Me)_2SiO]_nSi(R)X_2} + H_2O \rightarrow \underset{(B)}{OH(X)(R)SiO[(Me)_2SiO]_nSi(R)X_2} + HX$$

Reaction of resultant polymer end with another polymer:

$$A + B \rightarrow X_2(R)SiO[(Me)_2SiO]_nSi(R)(X) - O - Si(X)(R)O[(Me)_2SiO]_nSi(R)X_2 + HX$$

As indicated, the X groups above are hydrolyzable. Repeated hydrolysis and reaction of resultant polymer end groups leads to full cure, with elimination of HX as the leaving group. Examples of leaving groups, cross-linkers, and the common cure system names are given in Table 1.

Numerous other cross-linkers may be used. For the trifunctional cross-linkers, the R group may be methyl, ethyl, vinyl, and several other groups, with methyl the most common. In some cases tetrafunctional and higher-functionality cross-linkers or polymeric cross-linkers may also be employed. The acetic acid cure system should be avoided where substrates are subject to acid corrosion.

Two other classes of silicones deserve mention. These are the water-based silicones that are used in sealant and coating applications and the silicone pressure-sensitive adhesives. Water-based silicones can be prepared by anionic polymerization of siloxanes in water using a surface-active catalyst such as dodecylbenzenesulfonic acid [4]. The resulting emulsion can then be cross-linked in several ways, including the use of alkoxysilane copolymerization or tin catalysts in conjunction with colloidal silica. The result is essentially an emulsion of cured PDMS in water. Various fillers and other components are added, resulting in a sealant composition. Upon evaporation of water,

Table 1 Examples of Leaving Groups, Cross-Linkers, and Cure Systems

Leaving group (HX)	Cross-linker	Cure system
$HOC(O)CH_3$	$CH_3Si[OC(O)CH_3]_3$	Acetic acid
$HOCH_3$	$CH_3Si(OCH_3)_3$	Alcohol
$HONC(CH_3)(C_2H_5)$	$CH_3Si[ONC(CH_3)C_2H_5]_3$	Oxime
$CH_3C(O)CH_3$	$CH_3Si[OC(CH_2)CH_3]_3$	Acetone
$HN(CH_3)C(O)C_6H_5$	$CH_3Si[N(CH_3)C(O)C_6H_5]_3$	Benzamide

a silicone elastomer results. These sealants have the advantages of low odor, ease of installation, and easy cleanup. Their properties are rather close to those of their conventional silicone counterparts.

The components of the silicone pressure-sensitive adhesives (PSAs) are analogous to their organic counterparts [5]. Generally, a silicate resin and a silicone polymer or gum are dissolved in solvent. Both the resin and the polymer typically contain silanol (Si—OH) groups that are reacted during processing of the PSA, leading to a cross-linked network. Additional reactions can be accomplished through the use of free-radical catalysts. The extent to which these cross-linking reactions occur, the resin/polymer ratio, as well as the respective molecular weights of these components, are important in setting the properties of the PSA.

Silicone PSA products are used in a number of medical and industrial applications, ranging from a variety of PSA tapes and transfer films to automotive bonding. Advantages for the silicone PSA products include resistance to temperature extremes, chemical resistance, conformity to irregular surfaces, and electrical properties. They are also unique to most PSAs in their ability to adhere to difficult low-energy substrates, such as polytetrafluoroethylene and other silicones.

III. PROCESSING CONSIDERATIONS

Silicone adhesives and sealants typically contain polymer, fillers, cross-linker, catalyst, and other additives. The most common fillers are the reinforcing fumed silicas or the less reinforcing grades of calcium carbonate. Other fillers and pigments, such as carbon black and titanium dioxide, are also used. Silicones are typically made in high shear, vertical change can mixers, but continuous processing equipment may also be employed. Processing details are generally held proprietary, but some general guidelines are in order.

Since most silicones cure through reaction with water, it is important that the moisture content of fillers and other additives be controlled. The moisture content of fumed silica, for example, can vary from 0.2 to over 2%, depending on the humidity conditions during storage. It is also critical that introduction of moist air be kept to a minimum during mixing. Air incorporated during processing must generally be removed to reduce the tendency toward cured gels and related appearance problems in the final product.

The dispersion of the filler particles is also important to final sealant appearance. With increasing costs of fillers, it is also important to optimize dispersion to maximize the rheological and reinforcement benefits provided by the fillers. Manufacturers must balance the mixing time and energy required for complete dispersion with resultant product appearance and physical properties.

IV. PROPERTY DETERMINATIONS

Since most silicone adhesives and sealants are elastomeric in nature, their physical property testing often parallels classical rubber testing approaches. Common tests include durometer, tensile strength, elongation, and modulus. Several methods are available for the measurement of rubber properties, but the most commonly used are the American Society for Testing and Materials (ASTM) D-412, Test Method for Rubber Properties in Tension, and the ASTM C-661, Standard Test for Indentation Hardness of Elastomeric-Type Sealants by Means of a Durometer. These properties vary widely with the product and its intended application. Durometer measurements can range from Shore A less than 20 to over 50. Tensile strength ranges from less than 0.2 to greater than 5 MPa, and elongation varies from about 100 to 2000%.

Cure time testing tends to be somewhat subjective, but again there are methods available, such as ASTM C-679, Tack-Free Time of Elastomeric Sealants. Tack-free time is the curing time required for the product to develop a skin that is not damaged when subjected to application and removal of a plastic film. It is important in all cases to determine the cure characteristics of the product in actual working conditions. Since most silicones cure by reaction with moisture in the air, the sensitivity of cure time to humidity should be determined. Surface cure rates can usually be tailored to meet application requirements.

The rheological properties of adhesives and sealants are important in many applications. When these products must be pumped or applied through automated equipment, the flow characteristics at pertinent shear rates are critical. Sophisticated rheological measurements can be performed to predict performance. The rheology of silicone adhesives and sealants can be tailored through adjustment of polymer viscosity, filler loading, and incorporation of various additives.

Often, only the extrusion rates of adhesives and sealants are measured, which is accomplished by subjecting the product to a given pressure and measuring its flow rate through a nozzle of known diameter (see ASTM C-1183, Extrusion Rate of Elastomeric Sealants). For many sealant applications, the sealant must not flow under its own weight in conditions of low shear rate. In this case, some measurement of "slump" is generally made. Several methods are available for measuring slump [see ASTM D-2202, Standard Test for Slump of Sealants, and ASTM C-639, Standard Test for Rheological (Flow) Properties of Elastomeric Sealants]. Again, it is important to determine the rheological performance of the product in the actual application.

Adhesion testing is a matter of some controversy. There is, however, a growing trend among manufacturers, specifiers, and standards organizations to move toward tests that better predict performance in application. The 180° peel adhesion test is often used as an internal quality control tool by manufacturers. This test allows for measurement of lot-to-lot consistency of products. The methodology for this test can be found in ASTM C-794, Test Method for Adhesion In-Peel of Elastomeric Joint Sealants. In its typical form this test involves placing a bead of the product onto the substrate, with a flexible member embedded in the product. The product is allowed to cure, and the member is then pulled away from the substrate. The force required for peel is noted, along with the mode of failure. The advantages of this test are that it is fast and lends itself well to subjecting the adhesive bond to environmental stresses such as hot-water exposure.

A series of tests that are better predictors of performance of sealants involves the preparation of tensile-adhesion joints or H pieces. In this case, the sealant bead is placed between blocks of the two substrates of interest and allowed to cure. This joint can then be pulled to destruction, with measurement of strength and failure mode. In addition, various environmental stresses may be applied, such as UV light exposure (weatherometry), water exposure, and cyclic movement. Testing in this way allows for improved prediction of movement capability and long-term performance. The methodology involved in this testing is included in the following methods: ASTM C-1135, Determining Tensile Adhesion Properties of Structural Sealants, and ASTM C-719, Test for Adhesion and Cohesion of Elastomeric Joint Sealants Under Cyclic Movement.

Any sealant or adhesive that is expected to perform in outdoor applications should be tested after exposure to light, heat, and water. For most forms of weatherometry, 500 to

1000 h is considered approximately the equivalent of 1 year outside in most climates (United States). If a minimum of 5 years of service is expected from the sealant, no less than 2500 h, and probably 5000 h in a UV fluorescent accelerated weathering machine should be used (as the conditioning cycle for rubber property testing). This is true for silicones and all other sealants that are expected to perform in such applications. This is a startling contrast to the 250 to 500 h used in most present standards (see Refs. 6 and 7).

V. BASIC FORMULATIONS

As mentioned in the processing section, silicone sealants and adhesives generally contain polydimethylsiloxane (PDMS) polymer, cross-linkers, fillers, catalysts, and other additives. These additives may be pigments, plasticizers (often unreactive PDMS polymers), and adhesion additives (such as silane coupling agents). Given below are simple formulations and properties (Table 2) for oxime-cured silicone sealants [8]. In these examples, the use of a nonreactive silicone plasticizer and a nonreinforcing carbonate filler results in substantial modulus reduction. This approach can also be used to modify the physical properties of silicones based on other cure chemistries. Low-modulus sealants are often used in sealant applications requiring high movement capability. High-modulus sealants are used more in structural and adhesive applications.

A. High-Modulus Oxime Sealant

	Percent by weight
Hydroxyl-ended PDMS polymer	80–85
Fumed silica	5–10
Oxime cross-linker	5–7
Sn(IV) catalyst	0.05–0.10

B. Medium-Modulus Oxime Sealant

	Percent by weight
Hydroxyl-ended PDMS polymer	60–80
Silicone plasticizer	5–20
Fumed silica	2–6
Calcium carbonate	20–30
Oxime cross-linker	5–7
Sn(IV) catalyst	0.05–0.10

Table 2 Properties of Oxime-Cured Silicone Sealants

	Sealant	
Property	High modulus	Medium Modulus
Tack-free time (min)	20–30	30–60
Durometer (Shore A)	25–35	20–30
Tensile strength (MPa)	1.2–2.1	0.9–1.4
Elongation (%)	200–400	400–700
100% Modulus (MPa)	0.5–0.9	0.35–0.5

VI. SUBSTRATE BONDING

Applications for silicones in bonding are numerous. Generally, one sealant will not bond to all substrates and it is common practice to develop new formulations to meet the ever-increasing list of requirements. In some instances primers are used for certain substrates, but silicones are usually self-priming. This self-priming feature is important from the standpoints of reducing installation costs and in reducing dependency on high-solvent primers, which are sometimes subject to environmental regulations. The surface characteristics for a given type of substrate can vary considerably between substrate manufacturers. For this reason it is always advisable to check adhesion before specifying a particular sealant. In addition, the importance of proper substrate cleaning and preparation should not be overlooked. Most adhesive and sealant producers will recommend the proper procedures for surface preparation. Some of the more common substrates and related applications for silicones are given in Table 3.

Table 3 Applications of Substrates

Substrate	Examples	Typical applications
Masonry	Concrete Mortar Brick	Construction Highway Consumer
Natural stone	Marble Granite Sandstone	Construction
Wood	Unpainted Painted	Construction Glazing Consumer Maintenance
Glass	Float Reflective	Construction Glazing Maintenance Original-equipment manufacturing Consumer
Metals	Aluminum Steel Copper Stainless steel Galvanized steel	Construction Glazing Electronics Maintenance Original-equipment manufacturing Consumer
Coated metals	Paints Fluorocarbon Polyester	Construction Glazing Maintenance Original-equipment manufacturing
Plastics	PVC PMMA Polyester Engineering plastics	Construction Glazing Maintenance Automotive Sanitary Original-equipment manufacturing Consumer

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Epoxy Resin Adhesives

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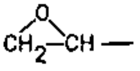
I. INTRODUCTION

Epoxy or epoxide resins are a group of reactive compounds that are characterized by the presence of the oxirane group

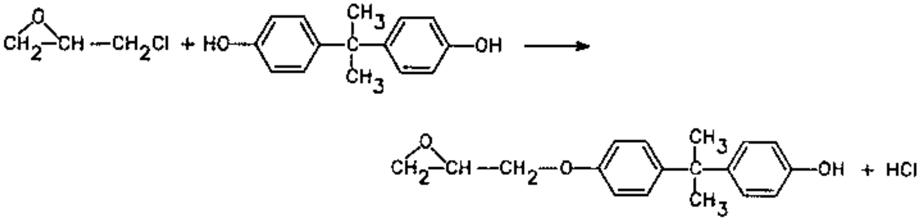


They are capable of reacting with suitable hardeners to form cross-linked matrices of great strength and with excellent adhesion to a wide range of substrates. This makes them ideally suited to adhesive applications in which high strength under adverse conditions is a prerequisite. Their unique characteristics include negligible shrinkage during cure, an open time equal to the usable life, excellent chemical resistance, ability to bond nonporous substrates, and great versatility. Although they were hailed as wonder products when first introduced, it has now been accepted that they will not do everything. They have, however, clearly established niches, especially in high-technology applications, and have shown steady growth, generally ahead of the industry average. Sales of epoxy resins in Europe, for example, totaled 101,000 metric tons in 1980, 150,000 metric tons in 1985, and 205,000 metric tons in 1990.

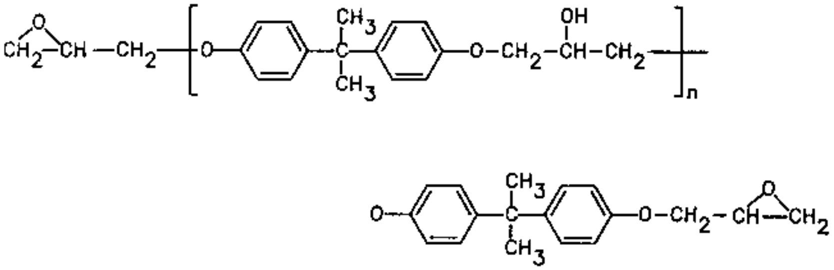
Although work on epoxy resins started in the mid-1920s, the first commercially useful epoxy resins appeared during World War II. These were based on the diglycidyl ether of bisphenol A (usually referred to as DGEBA resins), and today these resins, in a range of molecular weights, constitute the majority of all epoxy resins used. By contrast, however, hardeners come in a variety of shapes and sizes, including amines and amides, mercaptans, anhydrides, and Lewis acids and bases. Choice of hardener depends on the application requirements, and the wide range of hardeners available increases the versatility of adhesives based on epoxy resins.

II. CHEMISTRY OF EPOXY RESINS

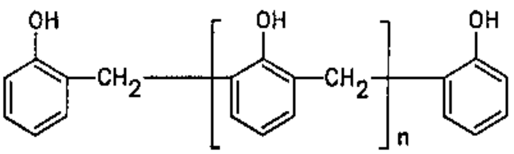
Epichlorhydrin is capable of reacting with hydroxyl groups, with the elimination of hydrochloric acid. The most widely used epoxy resins are the family of products produced by the reaction between epichlorhydrin and bisphenol A.

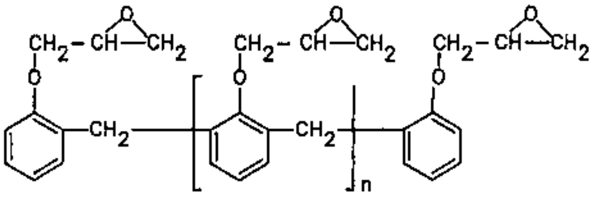


This reacts with additional epichlorhydrin to produce a molecule of general structure



Commercially useful grades are relatively low-molecular-weight products in which *n* ranges from 0 to about 4. When *n* is between 0 and 1, the product is a liquid, and this is the most useful product for adhesive applications. As *n* increases, the product moves toward a brittle solid. Solid grades find application principally in paints. Regardless of molecular weight, the resulting resin has two epoxy groups per molecule. Resins of greater functionality can be produced from polyols having more than two hydroxyl groups per molecule. Thus phenol novolac resins, having the general structure can be reacted with epichlorhydrin to produce epoxy novolac resins.





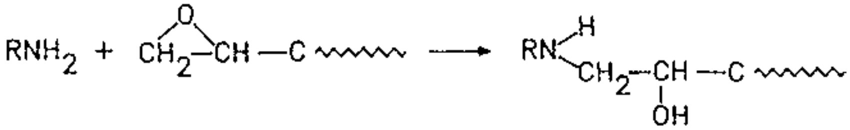
These products may have much greater functionality, although stearic considerations limit the useful size of the molecule. Because of their higher functionality, epoxy novolacs have greater cross-link density, generally yielding better temperature resistance at the expense of increased brittleness. They are thus seldom used on their own, but make useful modifiers of the properties of DGEBA resins.

Other products that may be epoxidized in this way include dihydric and trihydric phenols, aliphatic polyols such as glycerol, and simple alcohols such as butanol or allyl alcohol. These products, especially the monofunctional glycidyl ethers, are used at relatively low percentages to modify properties of DGEBA resins, particularly to achieve lower viscosities.

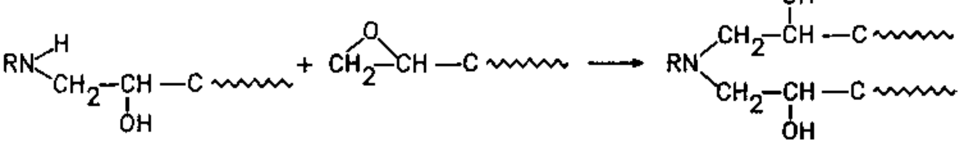
Epoxy groups may also be produced by oxidation of olefinic unsaturation within animal and vegetable oils. The resulting products have too low a functionality for use as resins in their own right, but are added to DGEBA resins to introduce a measure of flexibility. Major manufacturers of epoxy resins include Shell, Dow and CIBA-GEIGY.

The resulting epoxy resin is capable of reacting with various products, or itself, to form a solid, infusible product of considerable strength. The fact that these reactions generally occur without the production of low-molecular-weight by-products means that shrinkage during cure is negligible. This reduces stresses in the cured structure, contributing to the strength of the cross-linked matrix and eliminating the need for sophisticated clamping techniques.

The two cross-linking reactions are external, by reaction of the oxirane group with active hydrogen, and internal, by homopolymerization through the oxirane oxygen. The former is typical of cross-linking by hardeners and the latter of catalyzed cross-linking. Both hardeners and catalysts are referred to as curing agents. The classic epoxy curing mechanism is illustrated by the reaction between a primary amine and an epoxy group:

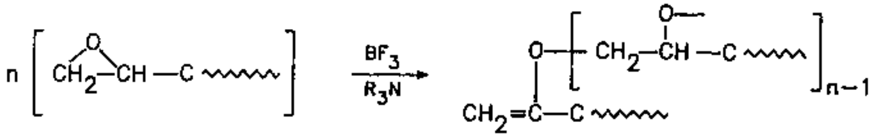


This product can react with an additional epoxy group to continue the cross-linking process.



This reaction is characteristic of hardeners having active hydrogens available, including amines, amides, and mercaptans. The reaction is catalyzed by hydroxyl groups, especially phenolic hydroxyls and tertiary amines. Because of the bulk of the substituent groups involved, steric factors have a major influence on the reaction rate. Thus low-molecular-weight hardeners tend to react more vigorously and produce more cross-linked structures, while hardeners of high molecular weight tend to react more sluggishly. Hardeners may thus be selected to produce highly exothermic reactions or reactions that take place only under the influence of external heat. Similarly, DGEBA resins having both epoxy groups at the ends of the molecule will react more readily with hardeners than will epoxy novolacs or other types of epoxies in which one or more of the functional groups may be hindered by the rest of the molecule.

Homopolymerization occurs readily in the presence of catalysts, especially at elevated temperatures.



Again this reaction is accelerated by hydroxyl groups or tertiary amines. This is also the predominant reaction with anhydrides. In fact, reactions with resin and hardener or catalyst are very much more complex than these idealized reactions, and both reactions as well as a number of side reactions probably occur to varying extents in any cross-linking mechanism. Major suppliers of curing agents include Anchor Chemicals, Dow, Shell, and Cray Valley Products.

III. PROPERTIES OF EPOXIES

A. Resins

Epoxy resins react with hardeners in stoichiometric quantities. Thus a knowledge of the number of reactive sites is needed in order to calculate correct ratios. For the resin this is given by the epoxide equivalent weight (EEW), which is the quantity of resin required to yield one epoxy group. For a DGEBA type in which $n = 0$, the molecular weight is 340. Since there are two epoxy groups per molecule, the EEW is thus 170. Typically, the pure liquid DGEBA resins commercially available for adhesive applications have EEW in the range 180 to 310, usually 190 to 210, while for paints or special applications, EEW may reach 2000 or more. The epoxy novolacs usually have EEW in the range 150 to 250, usually around 180.

The viscosity of a DGEBA resin is dependent primarily on molecular weight. Even at low molecular weight, viscosity is typically in excess of 6,000 cP, while at EEW 190 viscosity is usually around 12,000 cP. For applications requiring low viscosity it is thus necessary to include other types of epoxy resin or to use reactive or nonreactive diluents to achieve the desired viscosity.

B. Hardeners

Stoichiometric ratios can be calculated similarly for hardeners. In principle, each active hydrogen will react with one epoxy group. Thus a low-molecular-weight aliphatic polyamine such as diethylene triamine (DETA) has a molecular weight of 103 and five active hydrogens. The hydrogen equivalent is thus 20.6. The stoichiometrically correct ratio with an epoxy resin of EEW 200 would thus be 100 parts resin to 10.3 parts of DETA. In practice there is always a percentage of homopolymerization, especially at the temperature of reaction, and smaller amounts of DETA will still cause a complete cure, at the expense of increasing brittleness.

In general, suppliers of proprietary hardeners do not furnish detailed chemical descriptions. Instead, they supply data on recommended mix ratios, and from this the formulator can calculate the correct quantities. With catalysts, stoichiometry is not critical, in theory. In practice, however, the quantity used will affect both the rate of cure and the cured properties. Thus with catalysts, in practice, the mix ratio is sometimes more critical than is the case with hardeners.

C. Mixed Product

During cure of epoxies, especially systems with a short pot life or large mixes, considerable heat is evolved. This accelerates the cure, leading to even greater heat evolution. Mixes larger than 5 kg can reach excessive temperatures even with systems that have relatively long pot lives in quantities of 100 g. In addition to shortening the pot life dramatically, exothermic reactions can push the peak temperature to the point where thermal degradation occurs, or at least to a level that creates excessive stresses in the curing matrix, causing it to crack on cooling. Except in certain circumstances, peak exotherm temperature should be limited by formulation to 150°C or preferably less in the mix quantities used. Cured epoxy resins may be formulated to be extremely hard, with Shore D hardeners of 80 or more, or soft, flexible products that barely produce a reading on the Shore A scale. When cured at approximately stoichiometric ratios and unmodified with diluents or plasticizers, however, they are generally hard and tough to brittle, especially DGEBA and epoxy novolac types.

Heat distortion temperature (HDT) or deflection temperature (DT) is a measure of the tendency of cured product to soften when heated. It is a feature of the inherent thermoplasticity in cured epoxy compounds as a result of the relatively low cross-linking density, and may be any value from below 50°C to about 250°C, depending on formulation and cure cycle. Resins and hardeners of high functionality tend to have higher HDT. Postcuring at elevated temperature can increase HDT significantly.

IV. FORMULATING EPOXY ADHESIVES

Epoxy resins offer a unique combination of properties for adhesive applications. These include the ability to formulate liquid systems without solvents or carriers, the ability to convert these systems to cured products without the production of low-molecular-weight by-products, the ability to bond dissimilar or nonporous surfaces, and the ability to produce thick sections without subsequent stress cracking due to shrinkage.

Although epoxy resin and hardener may be used in unmodified form in adhesive systems, most systems will consist of components that have been modified by incorporation of various additives to achieve specific effects. Formulators will add catalysts or blend hardeners to obtain a specific usable life of the mix and to control the curing temperature. Reactive diluents may be added to modify viscosity or flexibility. Fillers impart improved compression strength and reduce shrinkage and cost. Solvents may be used to reduce viscosity or improve adhesion. Various additives may be added, usually at a low percentage, to reduce aeration, improve adhesion to difficult surfaces, or minimize settlement of fillers. Depending on the application, particular properties such as flame retardency, electrical insulation or conductivity, or chemical resistance may be improved by formulating.

A. Resins

Although DGEBA resins provide the backbone of most epoxy formulations, they may be blended with other types to achieve modifications. Epoxy novolacs, having higher functionality, increase the cross-linking density, which improves heat resistance but decreases impact resistance. Incorporation of epoxidized oils increases flexibility at the expense of heat and chemical resistance. Low-viscosity polyfunctional epoxies based on polyols or polyhydric phenols reduce viscosity and can increase functionality without impairing cured properties. Monofunctional reactive diluents will also decrease viscosity and form part of the polymer backbone, to impart a measure of flexibility without the possibility of migration. Properties of commercially available epoxy resins and diluents from various suppliers are listed in Table 1.

B. Curing Agents

Use of mixed hardener systems is common. Hardeners may be blended to achieve properties intermediate to the individual components, to reduce exotherm or accelerate cure, to modify the cured properties, or simply to arrive at a more convenient mix ratio. Several classes of curing agents each having distinctive characteristics may be used.

1. *Aliphatic primary amines*. Common examples are diethylene triamine (DETA), tetraethylene pentamine (TEPA), *n*-aminoethyl piperazine, and isophorone diamine. They give good room-temperature cure at stoichiometric ratios, but have poor HDT, inconvenient mix ratios, high peak exotherm, and are strongly irritant. Isophorone diamine produces very light colored mixes with good color stability.

2. *Aromatic primary amines*. These offer improved heat and chemical resistance and longer pot life with reduced exotherm, but poor color stability and sluggish cure. They are generally solids and require some formulating to produce easily handleable products. Reactions proceed best at elevated temperatures, where their irritancy can be a problem. For room-temperature cures they should be used with catalysts, of which phenols, BF_3 complexes, and anhydrides are the best. *m*-Phenylene diamine (MPDA) and methylene dianiline (MDA) are the best examples.

3. *Amine adducts*. Both aliphatic and aromatic amines can be adducted with small amounts of mono- or diglycidyl epoxies to produce amine adducts of medium to high viscosity that have decreased volatility and irritancy, more convenient mix ratios, and often, better reactivity.

4. *Tertiary amines*. Although their primary use is as catalysts with other hardeners, tris(dimethylaminomethyl) phenol (DMP 30) is an effective curing agent on its own, at both room and elevated temperatures.

5. *Amides*. Although amides on their own are too unreactive, reaction products of polyamines with fatty acids to produce amidopolyamines provide the largest group of commercial hardeners for adhesive applications. Reduced volatility and irritancy and a convenient mix ratio offer the compounder ease of handling. The mix ratio is relatively noncritical; increasing hardener levels yield increased flexibility and adhesion but reduced HDT and chemical resistance. Initially, amidoamines have poor compatibility and an induction period is necessary to allow the reaction to start. Pot lives are relatively long

Table 1 Epoxy Resins

Resin[a]	Chemical type	EEW	Viscosity (cP at 25°C)	Supplier
Low viscosity				
Araldite DY026	1:4 Butanediol diglycidyl ether	110–115	10	CIBA GEIGY
DER 732	Propylene glycol diglycidyl ether	305–335	55–100	Dow
DER 736	Propylene glycol diglycidyl ether	175–205	30–60	Dow
Epikote 812	Glycerol triglycidyl ether	140–160	100–170	Shell
Epikote 871	Linoleic acid diglycidyl ether	390–470	400–900	Shell
Medium viscosity				
Araldite GY260	DGEBA	185–196	12,000–16,000	CIBA GEIGY
DER 331	DGEBA	182–192	11,000–14,000	Dow
Epikote 880	DGEBA	185–192	10,000–16,000	Shell
Beckopox EP 140	DGEBA	180–192	9,000–12,000	Hoechst
High viscosity				
Epikote 834	DGEBA	230–280	(Softens at 35–40°C)	Shell
DER 337	DGEBA	230–250	Not given	Dow
Beckopox EP 151	DGEBA	400–500	20,000–30,000	Hoechst
Araldite EPN 1139	Epoxy novolac	170–180	50,000	CIBA GEIGY
Epikote 154	Epoxy novolac	176–181	3,500–7,000 at 52°C	Shell
DEN 438	Epoxy novolac	176–181	20,000–50,000 at 52°C	Dow
Monofunctional				
Allyl Glycidyl Ether	Allyl glycidyl ether	114	1	Shell
Dow BGE	Butyl glycidyl ether	143	3	Dow
Cardura E	Versatic acid glycidyl ether	240–250	7–8	Shell
Beckopox EP 080	2-Ethylhexyl glycidyl ether	190–205	2–3	Hoechst

[a] Note that trade names and grade designations may vary from country to country.

and exotherms low, but low-temperature cure is poor. Small quantities of imadazoline improve adhesion to metal. Dicyandiamide is a special example of an amide that can be used on its own. Its low reactivity yields a usable life in excess of 6 months, but at elevated temperatures it reacts quickly.

6. *Mercaptans*. Most mercaptans on their own are unreactive, but with catalysts produce flexible cures. Certain mercaptans in conjunction with DMP 30 provide extremely rapid cure, with low exotherm, making them ideally suited to retail applications.

7. *Acids and anhydrides*. This group of curing agents provides the best high-temperature performance. Boron trifluoride monoethylamine, oxalic acid, and maleic and phthalic anhydride are used for electrical or high-temperature applications, often with catalysts such as benzyldimethyl amine (BDMA) or DMP 30. Table 2 lists properties and characteristics of various curing agents.

C. Reactive Diluents

In addition to the monofunctional epoxies described under resins, products with active hydrogens, such as furfuryl alcohol, coal tars, or phenols, will react with the epoxy resins

Table 2 Epoxy Curing Agents

Curing agent	Usage (phr)[a]	Uncatalyzed cure (°C)	HDT (°C)	Applications
Aliphatic primary amines				
Diethylene triamine	10–12	Ambient	80–100	Short pot life
Tetraethylene pentamine	13–15	Ambient		Ambient curing systems
Diethylamine propylamine	5–8	40–80		
n-Aminoethyl piperazine	22–25	Ambient		
Aromatic primary amines				
m-Phenylene diamine	12–15	60–100	150–180	Longer-pot-life general-purpose expoxies
Methylene dianiline	25–28	60–100		
Tertiary amines				
Benzyl dimethylamine	6–10	60–100	80–100	Catalysts, especially with polysulfide
Tris (dimethylaminomethyl) phenol	3–6	20–60		
Amides				
Dicyandiamide	3–5	120–160	120	Latent catalysts for one-pack epoxies
Acids				
Boron trifluoride monoethylamine	2–4	120–150	175	Heat-resistant epoxies
Oxalic acid	5–10	120–160	60–120	Catalyst for anhydrides
Anhydrides				
Phthalic anhydride	60–80	120–140	120–150	Encapsulation
Maleic anhydride	50–80	80–120		

[a] DGEBA epoxy of EEW 200.

to form part of the cured structure. Triphenyl phosphite both reacts and accelerates. Lactams also react with the hardeners. Since all these products tend to degrade the performance of the cured product, it is preferable to use difunctional low-viscosity epoxies to reduce viscosity. Where applicable, functionality of reactive diluents must be allowed for when calculating ratios.

D. Plasticizers

Conventional plasticizers may be used in formulated products. Phthlate esters are the preferred plasticizers. They exhibit little tendency to migrate and have good compatibility with both resins and hardeners. Addition rates are typically 5 to 20%. Chlorinated plasticizers may be used to reduce flammability, especially in conjunction with antimony trioxide. The effect of plasticizer additions is generally to degrade most physical properties, although at low additions the effect is usually small. The effect of plasticizer additions on various important properties is as follows:

Pot life: lengthened
Impact resistance: increased
Peak exotherm, *tensile strength*, *chemical resistance*, *HDT*: decreased

It should be noted that plasticizers do not introduce marked flexibility into epoxy resin systems. Nor is this generally a desirable attribute in adhesive applications, where epoxies are usually selected because of their great strength.

E. Fillers

Two types of fillers may be incorporated into formulated epoxy systems. Powder fillers are added to increase viscosity, improve abrasion resistance and gap-filling properties, impart specific electrical or mechanical properties, or reduce cost and shrinkage. Addition levels may be 50 to 300 parts by weight of resin (phr). Although most fillers will increase the density of the cured product, certain lightweight fillers will decrease density. Viscosity increases depend on surface area, oil absorption, and filler type. Chemical resistance may be improved or made worse, depending on fillers selected. Highly alkali fillers should be avoided, especially with acid-cured systems, as they may retard setting.

Fibrous fillers may be added to impart specific rheological properties or to reinforce the system. They will usually improve both tensile strength and impact resistance. Addition levels are much lower at 10 to 50 phr, as they usually cause much more rapid thickening. Table 3 lists common fillers.

Settlement of fillers during storage depends primarily on the particle size of the filler and its density, and the viscosity of the formulated product. Settlement can be reduced or eliminated by proper formulation. Fine particle fillers with relatively low specific gravity in high-viscosity products will settle much less, especially if the product is at all thixotropic. Where coarse fillers must be used, an approach toward a fully filled voidless system where the volume of liquid is such as just to fill the voids will solve the problem. Incorporation of fine fillers, use of a pigment-dispersing aid, and where application permits, use of a thixotroping agent will help to reduce or eliminate settlement.

Depending on addition levels, fillers will generally increase the usable life and extend the cure time of the mix. Tensile and compressive strength usually increase maximally then decrease on further additions. Most fillers have relatively little effect on HDT. Chemical resistance will vary from filler to filler. Shrinkage is usually reduced.

Table 3 Fillers and Extenders

Filler	Specific gravity	Oil absorption (%)	Relative cost	Usage level	Purpose
Silica	2.5–2.7	20–30	Low	50–500	Bulk, price reduction, stability, and reduced exotherm
Quartz	2.5–2.7	15–30	Low	50–300	
Calcium carbonate	2.6–2.8	15–25	Low	50–300	
China clay	2.3–2.6	30–60	Low	20–100	
Carbon	2.0–2.2	—	Medium	5–50	Thermal and electrical conductivity
Aluminum powder	2.5–2.7	—	High	20–100	
Copper powder	8.8–9.0	—	High	20–100	
Silica carbide	3.2	—	Medium	50–200	Abrasion resistance
Microballoons	—	—	High	10–50	Low-density
Asbestos		—	Low	5–20	Reinforcement
Glass fiber	2.4–2.6	—	Medium	10–50	Reinforcement

F. Solvents

Although a major advantage of epoxy adhesives is their ability to be formulated without solvents, under certain circumstances solvents may be included. On porous substrates solvents may be added to reduce viscosity and assist penetration. On certain nonporous substrates, particularly some plastics, addition of a small percentage (1 to 3%) of a suitable solvent will improve adhesion. Common solvents are low-boiling aromatic solvents, ketones, or esters.

G. Additives

Additives are typically products added at levels of 0.1 to 0.5% to modify specific properties. Most commonly used additives are defoamers, antisettling or wetting agents, thixotropes, and adhesion promoters. Use of antioxidants or preservatives is rare. Because of their minimal shrinkage, compressive strength of cured epoxies is very high. Since aeration will reduce this substantially, use of defoamers, especially in heavily filled systems, is quite common. Many defoamers are suitable, but silicone-based defoamers should be avoided on surfaces where adhesion in critical. Addition levels of 0.05 to 0.2% usually suffice.

Antisettling agents, pigment dispersers, or wetting agents may be included in filled formulations. Depending on the formula, particularly the selection of fillers, such products may reduce or eliminate settlement. Usuage will generally be at a level of 0.1 to 0.3% of formulation. These agents are best added prior to incorporation of the fillers. Various thixotropes are used in epoxy formulations to reduce or eliminate flow in products designed for use on vertical surfaces, to improve gap-filling properties, or to reduce settlement of fillers. Fumed silica is widely used at levels of 0.1 to 3%. At low levels, the effect on viscosity is small except in high-viscosity systems, but settlement will be reduced. At higher addition levels, even low-viscosity products can be converted to firm pastes. To improve the efficiency of fumed silica, especially in the resin component, small quantities of polar liquids may be added.

Other thixotroping agents include Bentones and Tixogels, of which a number of grades are available, and China clay or kaolin, usually added as a filler, but which imparts thixotropy to the formulated product. Organofunctional silanes are extremely effective adhesion promoters. Added at levels of 0.05 to 0.2%, they can improve adhesion to certain nonporous substrates, such as glass, metals, and certain plastics. Formulators can select from a number of different functional groups, but generally epoxy functional types will be used in the resin component and amine functional grades in the hardener.

H. Elastomers

Occasionally, elastomers may be included in solvent-based formulations. Poly(vinyl butyral) improves adhesion to metal, as does nitrile rubber, while natural and synthetic rubbers may be incorporated to improve flexibility.

V. APPLICATIONS

Epoxy resin adhesives are used mainly in niche applications rather than as general-purpose adhesives. Due to the high strengths that can be achieved and the relatively high costs, they are generally used in structural applications in both concrete and metal bonding. Their good electrical properties allied to low shrinkage and good durability suit them for potting and encapsulating. Low shrinkage and good gap filling make epoxies ideal for applications where clamping is difficult, while the fact that both components are generally liquid up to the moment of cure means that they can be used where applications constraints require long open or assembly times. Conversely, systems with very short cure times are perfect for consumer applications. Good adhesion to nonporous surfaces allows them to be used in demanding situations. They find major outlets in the construction, automotive, and electronics industries.

A. Building and Construction

Water-based epoxy primers are ideal for damp porous substrates, as such primers will penetrate to an adequate depth to ensure good adhesion and produce a sound surface for bonding. Emulsifiable resins and hardeners are available, and the better systems deactivate the emulsifier system during cure to ensure that the cured system is not unduly water sensitive (Section VI.A). Solventless epoxy primers are used for bonding new concrete to existing concrete. Polyamide hardeners are preferred because of their ability to cure satisfactorily in the presence of water. Accelerators and diluents may be added, but fillers are generally omitted. The primer is applied to the existing concrete, and the fresh concrete cast before the resin has set (Section VI.B).

Epoxy adhesives are suitable for tiling, both for floor tiles in applications requiring acid or chemical resistance and in high-hygiene areas and also for tiling on vertical surfaces, where it is essential that tiles should not delaminate. Epoxy tiling systems are suitable for glazed tiles, clay and ceramic tiles, and decorative marble or granite tiles, where priming is recommended. Adhesives will usually be filled and thixotropic, especially for vertical tiling. Epoxies are also used for decorative paving in commercial and residential properties. Flooring made of small pebbles of different colors and textures bonded with relatively small proportions of epoxy are attractive and provide good drainage of water in areas such as swimming pool surrounds. Light-colored systems with good ultraviolet (UV) resistance are required. Hardeners should be based on isophorone diamine because of its good color stability, and UV stabilizers may be included.

Self-leveling floors are produced from low-viscosity epoxy systems. Low-exotherm, unfilled systems are preferred. The entire floor should be cast in one operation, and thickness should preferably be at least 5 mm over the entire area. Because of their excellent chemical resistance to a wide range of chemicals, epoxies are often selected for flooring in chemical plants. Systems vary from trowelable to pourable or brushable and are usually filled. Choice of hardener and filler will depend on the specific chemicals encountered. Although tables of chemical resistance from suppliers will aid in selection of a suitable system, this system should always be tested using the chemicals that the floor is expected to withstand.

B. Metal Bonding

While construction applications usually require reactive hardener systems to give good room-temperature cure, many metal bonding applications require strength at elevated temperatures. Usually, however, they also permit heat curing and postcuring. Surface preparation is crucial to achieving high bond strength and will always involve at least degreasing and abrading. Because of the high strength of the substrates, joint design is also very important and should always aim to provide the largest practicable bonded areas. Since high-strength epoxies are generally hard, joint design should aim to produce bonds that are in tension or compression rather than shear or peel.

Solvent-free systems may include adhesion promoters such as silicones, flexibilizers such as liquid polysulfide rubbers, and reinforcing fillers, either fibrous or micronized. Room-temperature to mildly elevated-temperature systems will be cured with amidopolyamine hardeners, often at ratios considerably in excess of stoichiometric requirements. This increase in hardener quantity improves flexibility and adhesion at the expense of tensile strength and heat distortion temperature. For applications at higher temperatures, use is made of more reactive polyamine hardeners, often with metal powder as filler. These will have postcuring cycles of several hours at temperatures that are increased in steps up to 150 to 180°C. Alternatively, solvent-based hybrid systems can be formulated, incorporating phenolic resins, nitrile rubbers, and poly(vinyl acetals). These solvent-based systems are typically single-component, applied to both mating surfaces. After the solvent has flashed off, the assembly is clamped and cured at elevated temperature. This type of system is particularly suited to applications such as bonding of brake linings to their backing pads (Section VI.C).

C. Road Making

Epoxy adhesives find applications in various aspects of road making. Two major areas are bullnosing and fixing of reflective road studs. Bullnosing requires a system with good impact and compressive strengths and a pot-life time of 1 to 4 h. Cast masses are on the order of 5 to 25 kg, so low-exotherm systems should be used. Fillers and flexibilizers may be included. Fixing of road studs is often performed on roads that are in use, so cure time should be as short as is practicable. Again, good impact and compressive strengths are required.

D. Wood Bonding

Although PVA adhesives for nonstructural applications and formaldehyde-based resins for structural applications have price advantages over epoxies and offer excellent performance, epoxies have advantages in certain applications. First, the open time may be as long as required. Second, with suitable primers they give more reliable bonds on difficult species, such as very dense or oily timbers. Third, they may be used to bond wood to other surfaces, such as metal or concrete, although in this case the formulator will concentrate more on the other substrate, as wood is not a difficult surface for epoxy adhesives. Primers may be emulsions in water or, particularly on oily surfaces, a conventional epoxy reduced to low viscosity with suitable solvents. The adhesive may also contain solvents to reduce viscosity and allow high filler loadings.

E. Engineering Applications

Epoxies find many applications in industry, especially on the engineering side. Grouting of bolts into concrete or rock surfaces, either to strengthen a rock face or for fixing of heavy machinery, is a common application. Such adhesives are usually filled systems, often using reactive hardeners to achieve rapid setting. Epoxy systems for horizontal grouting will usually be thixotropic to prevent the adhesive from slumping or flowing out (Section VI.D).

Crusher backing epoxies are used to fill the gap between the replaceable liners and the outer housing in industrial crushers. These products have conflicting requirements: fast setting but with low exotherm even in large volumes, low viscosity for easy pouring but with minimal settlement of fillers. In addition, they must have good impact resistance, negligible shrinkage, and be easy to remove when the liners are replaced.

F. Electrical Applications

Excellent electrical insulation makes epoxy systems suitable for potting and encapsulation of electrical and electronic components. Here use is made of one-pack epoxies employing latent curing agents such as dicyandiamide. At the curing temperature the system will have very low initial viscosity, ensuring good wetting and bubble release. The low residual stresses protect components from mechanical damage. Fillers or pigments may be added to render the cured article opaque.

The low shrinkage and good durability of epoxies also fits them for capable jointing compounds. Here a measure of flexibility is desirable. The cured article may need to be worked on from time to time, so systems that can be cut or peeled off may be required. Usable lives of 15 min to 1 h are the norm. Components should be selected for good water resistance (Section VI.E).

G. Film Adhesives

Latent catalysts used in conjunction with either liquid or solid resins are cast in thin films on plastic or release paper for unsupported films or onto absorbent papers or cloths for supported films and then cured to B stage. These films can subsequently be cut to shape and placed between mating surfaces for subsequent heat curing (Section VI.F).

H. Miscellaneous Applications

Epoxy adhesives are popular for retail or consumer applications. They may be supplied as liquids, pastes, putties, or as one-pack systems in stick form. Considerable ingenuity has been employed in the packaging to ensure that stoichiometric ratios are roughly correct. They are usually available as 5 min systems using mercaptan accelerators or standard setting systems where amidopolyamine hardeners are preferred because their mix ratios are relatively noncritical, and they lend themselves to formulating 1:1 mix ratios (Section VI.G).

Mercaptan accelerators are also used for systems with very short pot life, in automatic dispensing machines which meter the components, mix, and dispense in seconds. Systems with pot lives of 40 s can be handled in automated production lines. Epoxy resins are employed in a number of other niche applications, including adhesives to control static buildup in computer installations, carveable epoxies for pattern making and tooling, and acid-resistant adhesives for fastening tops to automotive batteries and for laminating and repair of glass-reinforced plastics. A selection of guide formulations for various applications follows.

VI. GUIDE FORMULATIONS

Parenthetical numbers that follow the components listed in the formulations below correspond to these suppliers:

1. Hoechst AG
2. Cray Valley Products
3. Dow Chemicals
4. Anchor Chemicals
5. Degussa
6. Thiokol Corp.
7. Shell Chemicals
8. Union Carbide
9. Sud Chemie AG
10. CIBA GEIGY
11. SKW Trostberg
12. Diamond Henkel

A. Water-Based Epoxy Primer

Beckopox EP 140 (1)	20.0
Versaduct 429 (2)	20.0
n-Butanol	5.0–10.0
Water	55.0–50.0

B. Epoxy Adhesive for Bonding New Concrete to Old

Base:	DER 331 (3)	80.0	Hardener:	Ancamine MCA (4)	30.0
	Epodil L (3)	15.0		Ancamide 500 (4)	24.0
	Aerosil 200 (5)	4.5		Anchor K54 (4)	6.0
	Water	0.5		Thiokol LP 3 (6)	40.0
		100.0			100.0

C. Metal-to-Metal Adhesives

1. *Ambient Cure*

Base:	Epikote 880 (7)	80.0	Beckopox EP 151 (1)	16.0
	Epikote 834 (7)	19.8	Beckopox EP 140 (1)	16.0
	Silane A 187 (8)	0.2	Quartz powder	50.4
		100.0	Beckopox EH 610 (1)	7.2
			Beckopoz EH 652 (1)	10.4
				100.0
Hardener:	Versamid 125 (2)	100.0		

2. *Elevated Cure*

Base:	Beckopox EP 140 (1)	100.0	DER 331 (3)	5.0
			DEN 438 (3)	20.0
Hardener:	Amicure CG 1200 (4)	7.0	Phenodur PR 263 (1)	25.0
	Ancamine 2014 AS (4)	2.0	Mowital B30H (1)	5.0
	Amicure UR (4)	3.0	Nitrile rubber	5.0
		12.0	Methyl ethyl ketone	10.0
			Toluene	30.0
				100.0
Cure schedule: 60 min/130°C			Cure schedule: 15 min/180°C	

D. Grouting Adhesive

Base:	DER 331 (3)	45.0	Hardener:	MDA	15.0
	DER 732 (3)	5.0		Thiokol LP 3 (6)	15.0
	Silica 150 mesh	46.0		m-Cresol	15.0
	Tixogel VZ (9)	4.0		Silica 150 mesh	50.0
		100.0		Tixogel VZ (9)	5.0
					100.0

E. Cable Jointing Epoxy

Base:	Araldite GY 260 (10)	100.0	Hardener:	Ancamine LV (4)	60.0
	Epodil L (4)	20.0		Quartz flour	72.0
	Quartz flour	15.0		Magnesium silicate	3.0
		135.0			135.0

F. Film Adhesives for Preimpregnation

Hot-melt type		Solvent type	
Epikote 880 (7)	100.0	DER 652 (3)	133.0
Epiclon B570 (4)	86.0	Dyhard 100 S (11)	4.0
Amicure DB/U (4)	3.0	Dimethyl formamide	15.0
	189.0	Dowanol PM (3)	15.0
		BDMA	0.3
			167.3

G. Fast-Setting Retail Epoxy Liquid

Base:	DER 331 (3)	100.0	Hardener:	Capcure 3-800 (12)	90.0
				Capcure EH-30 (12)	10.0
					100.0

VII. SUMMARY

Advantages of epoxy resin adhesives may be summerized as follows:

1. Ability to bind a wide range of substrates.
2. Negligible shrinkage during cure, which minimizes stresses.
3. Elimination of galvanic corrosion when bonding dissimilar metals.
4. Solvent-free liquids with open times similar to pot life.
5. Minimal clamping requirements.
6. High strength, good durability, and resistance to a wide range of environments.
7. Flexible formulating, permitting a wide range of pot lives, application conditions, and cured properties.
8. Stoichiometrically cured epoxies generally inert and physiologically harmless.

Disadvantages are:

1. Two-component systems require mixing in correct ratios, with attendant pot-life problems.
2. Many components toxic or irritants.
3. Relatively poor heat resistance of many cured systems.
4. Inherent brittleness, requiring careful joint design.
5. Poor cure at low temperatures.
6. Careful surface preparation required.
7. Need for skilled applicators.
8. High cost.

ACKNOWLEDGMENTS

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Pressure-Sensitive Adhesives

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I. INTRODUCTION

Pressure-sensitive or permanent-tack adhesives are, as their name implies, adhesives that remain sticky even when dried or cured. This means that they are capable of bonding to surfaces simply by the application of light pressure. This makes them arguably the most convenient products available today from the end user's viewpoint and undoubtedly, accounts for the success they enjoy. Although figures are hard to come by, a survey by Business Trend Analysts quoted in the June 1990 issue of *Adhesives Age* shows that pressure-sensitive adhesives grew from 38% of total adhesive sales in the United States in 1980 to 44.6% in 1988, at an annual rate of 12%, to reach a sales value of $4.9 billion in 1989.

Tack is a word used to describe various phenomena, including *wet tack*, which is the ability of an adhesive to form a bond while still wet; *green tack*, which is the ability of certain polymers, specifically rubbers, to bond to themselves for several hours after drying, even though the surfaces do not feel sticky; and *pressure-sensitive tack*, which is the phenomenon of importance to this section. This relates to the ability of a dried film to bond tenaciously to most surfaces under light pressure. As pressure is increased, the bond improves. The classic theory of tack is that it arises from the presence of a two-phase system in which an elastic continuous phase provides the strength while a disperse phase acts as a viscous liquid that wets and adheres to the surface. Although this appears to be the dominant mechanism in the older rubber–resin systems, however, many modern systems do not rely on this apparently incompatible two-phase system. Acrylics, for example, can produce aggressive tack from a single component. Thus tack is also believed to stem from the viscoelasticity of many polymers, allowing them to conform to the substrate to be adhered and "wet" it even in the dry state. It follows that a fundamental requirement for tack is a glass transition temperature substantially below the application temperature to permit the necessary degree of flow.

Pressure-sensitive adhesives fall into three broad product categories: water based, solvent based, and hot melt. Application areas tend to overlap, and all three types can be used in most of the application areas. Despite this overlap, tapes tend to be produced from solvent-based adhesives, while water-based adhesives are preferred for label stock. Hot melts are used in both applications. Pressure-sensitive tapes for a variety of uses, such as masking, packaging, and insulation, are the largest application area, followed by self-adhesive labels. Although these applications appear outwardly similar, in fact there are fundamental differences. With tapes the adhesive fills the major role, ensuring adequate adhesion and requiring special properties, which may include high dielectric strength, heat resistance, or low toxicity. In labeling applications the major demands are on the backing, which needs the right lay-flat or curl properties and ease of cutting and printing, with relatively few demands on the adhesive. For certain applications, the adhesive may have to retain flexibility and tack at temperatures down to −20°C, or be easily removable. With tapes the adhesive is usually applied directly to the backing, while label adhesives are usually applied to the release paper and subsequently transferred to the backing. Other pressure-sensitive applications include self-adhesive floor tiles, adhesives for decor papers and flypapers, gloss lamination, disposable diapers and other personal hygiene products, and temporary assemblies.

II. PRODUCT TYPES

Traditional pressure-sensitive adhesives were solutions of rubber and resin in solvent, and these dominated the market until well after World War II. From that time, as an increasing array of elastomers became available, as the price of solvents soared, and as environmental opposition to the use of solvents increased, water-based and hot-melt types made substantial inroads into the solvent-based market. This trend is likely to continue, although solvent-borne adhesives will probably always retain niches in areas where drying speed or ability to key into specific surfaces will outweigh environmental, handling, or price considerations.

A. Solvent-Based Adhesives

The three major components are an elastomer, which provides the elastic phase, the tackifier, and the carrier. The earliest pressure-sensitive adhesives used natural rubber tackified with wood rosins, or later, zinc oxide. With the advent of synthetic rubbers and other polymers, formulators have a very much larger range of elastomers at their disposal, including butyl rubber, styrene–butadiene rubber (SBR), polyisoprene, and the more recent thermoplastic rubbers, which are block copolymers of styrene with butadiene or isoprene, as well as acrylic polymers. Silicone elastomers are available for specialty applications, especially for use at elevated temperatures. Vinyl ethers and polyisobutylene can be used as both elastomer and tackifier, depending on the grade. Many of these types are not compatible, and where intermediate properties are required, they are generally achieved by blending homologs from the same or related families.

Tackifying resins fall mainly into two classes: wood rosin derivatives and hydrocarbon resins. Gum rosin is no longer widely used, as heat or aging lead to loss of tack through oxidation. Stable derivatives are produced by hydrogenation or esterification, and these are used extensively as tackifiers. Modern hydrocarbon resins are usually aliphatic, aromatic, or terpenes, although blends of these or certain specialty types may be suitable. There is no universal guide to selection, and a good deal of trial and error may be necessary to arrive at the ideal elastomer–tackifier combination and proportions. In addition, these may differ from one application to another, depending on whether the end use has tack, peel, or shear as the dominant criterion.

B. Hot-Melt Adhesives

The fundamentals of pressure-sensitive hot-melt adhesives are similar to those of solvent-based systems. Most elastomers and tackifiers are suitable, although ethylene–vinyl acetate copolymers are also used and the conventional rubber types are not. Pressure-sensitive hot melts are dominated by thermoplastic rubbers, which are ideal for use in these applications. Their unique properties arise from their essentially two-phase structure, in which thermoplastic regions of styrene end blocks lock the elastomeric midsections of butadiene or isoprene at room temperature but allow the elastomer to move freely at elevated temperatures or in solvent. This gives the polymer properties that are akin to those of vulcanized rubbers at room temperature, while allowinig it to behave as a thermoplastic when heated or dissolved. This structure is illustrated in Fig. 1.

Early pressure-sensitive hot-melt adhesives used ethylene–vinyl acetate copolymers as elastomers, but they are seldom used now. Atactic polypropylene is sometimes used on its own or in admixtures. More recently, vinyl ethers and acrylic resins have become available and will probably play an increasingly important role as the technology is developed, especially on polar surfaces.

The major differences between solvent-based and hot-melt pressure-sensitive adhesives is that with hot melts the viscosity can no longer be controlled with solvents, and must, instead, be controlled either by temperature or by formulating. A further limitation is that waxes cannot, in general, be used for reducing viscosity as is the case with conventional hot melts, as waxes tend to reduce tack drastically. Hence the major influence on viscosity in the formulation must come from the choice and quantity of tackifier resin.

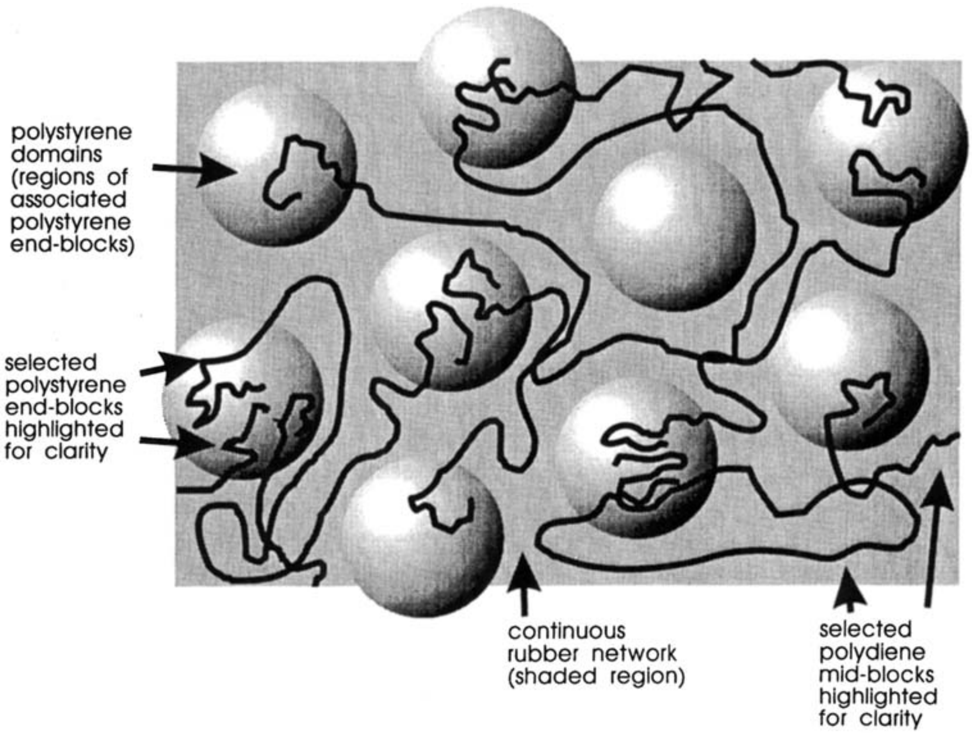

Figure 1 Structure of thermoplastic rubber.

Table 1 T_g Values of Monomers in Common Use

Soft monomers	T_g (°C)	Hard monomers	T_g (°C)
Butyl acrylate	– 54	Methyl methacrylate	105
Isobutyl acrylate	– 40	Vinyl acetate	29
2-Ethyl hexyl acrylate	– 85	Styrene	100
Ethyl acrylate	– 22	Acrylonitrile	100

Low-melting-point resins or even liquid resins may be used to keep application temperatures as low as practicable.

Because pressure-sensitive hot melts will be applied typically at temperatures between 120 and 160°C, heat resistance is a critical factor. Double bonds accelerate oxidative degradation, leading to a loss of tack, while cleavage will usually result in increased tack, but a drop in viscosity. Use of antioxidants is essential, and trials should always be undertaken to ensure that enough of the right antioxidant has been incorporated to protect the hot melt adequately at the application temperature even if a machine stoppage leads to the molten adhesive being kept in a heated bath for much longer than usual.

C. Water-Based Adhesives

Various dispersions are available which even in unmodified form exhibit aggressive tack and good adhesion, especially to polar substrates. Produced by conventional emulsion polymerization techniques, the tack, peel, and shear properties of these dispersions can be varied within wide limits by the choice of monomers. A dispersion will usually consist of at least two monomers, one of high glass transition temperature (T_g) and the other with a low T_g value, and the ratio of the two will determine the final properties of the film. Table 1 lists the T_g values of monomers in common use.

Cross-linkable monomers may be included to make the formulated adhesive curable by catalysis, heat, or radiation, thereby improving the performance of the film, especially at higher temperatures. Since the dispersion has both toughness and tack built in, no further compounding is necessary, making pressure-sensitive acrylic dispersions the easiest products to work with. In most applications, however, the formulator will prefer to modify the properties to order, and use of tackifying resins added either in solution or as a dispersion is common. Vinyl ethers can again be used either as sole binders or as tackifiers to modify the properties of the base dispersion.

Water-based systems have good aging characteristics, resisting the effects of heat, ultraviolet (UV) light, and oxidation. Thus use of antioxidants is not normally necessary. Table 2 lists the major advantages and disadvantages of the various types of pressure-sensitive adhesives.

III. FORMULATING

As mentioned earlier, the critical characteristic is the correct tackifier and components ratio. Although no rules exist for tackifier selection, there are certain shortcuts, based on chemical compatibility and melt point. Certain classes of tackifiers work well with specific types of elastomers. For example, aliphatic hydrocarbons generally work better with

Table 2 Advantages and Disadvantages of Pressure-Sensitive Adhesives

Solvent based	Water based	Hot melt
	Advantages	
Quick drying	Easy cleaning	Very fast setting
Good adhesion to nonpolar substrates	Good adhesion to polar substrates	No solvent waste
Good key on certain plastics	Good heat and aging resistance	Environmentally acceptable
Versatile	Environmentally acceptable	100% active
	High solids	
	Ready to use	
	Disadvantages	
Flammability	Slow drying	High equipment cost
Toxicity	Requires heat to dry	Requires heat
Relatively low solids	Poor on nonpolar surfaces	Thermal degradation
Less easy to clean		Difficult to clean
		Can melt substrate
		Difficult to package

natural rubbers, and, aromatic types are preferred for SBR. With block copolymers, aliphatic resins of low melt point improve tack and low-temperature flexibility, while high-melting aromatic resins in small quantities stiffen the product, giving improved heat and shock resistance. Rosin derivatives and terpene resins offer good performance with most elastomers, generally at higher cost. In general, resins with solubility parameters close to those of the elastomer selected are most likely to offer good performance.

Tackifiers with melt points substantially above the T_g value of the elastomer can be expected to improve the strength of the adhesive at elevated temperatures but reduce the tack, while low-melting resins will impact greater tack and low-temperature flexibility at the expense of creep resistance and shear strength. The tackifier is responsible primarily for the balance of tack, peel, and shear properties in the finished adhesive. Usually, some of these properties must be traded off to optimize one property. For any given system, increasing tack is generally related to decreasing peel and shear strengths, and similarly, any modification intended to improve shear strength is likely to be at the expense of tack. High peel and shear strengths both require high cohesive strength within the film, but peel strength is dependent on adhesion to a much greater extent than is shear.

Thus most formulations are compromises which will favor the property that is most critical in the application intended. Figure 2 illustrates typical dependence of tack, peel, and shear performance in a given system as the resin/elastomer ratio is increased. The maxima occur at different tackifier percentages. Silicon elastomers for pressure-sensitive adhesives are invariably used in conjunction with silicon gums as tackifiers. Table 3 displays the uses of various elastomers, and Table 4 contains information on tackifiers and plasticizers.

Solvents are selected primarily on the basis of solubility parameters and evaporation rate. Where mixed solvent systems are used to achieve the desired balance at the best cost, the selection should be such that the slowest solvent remains an effective solvent for the system on its own. In addition, consideration should be given to the effect of the solvent on the substrate: too strong a solvent could degrade the substrate, but the right choice can assist in keying the adhesive to the surface.

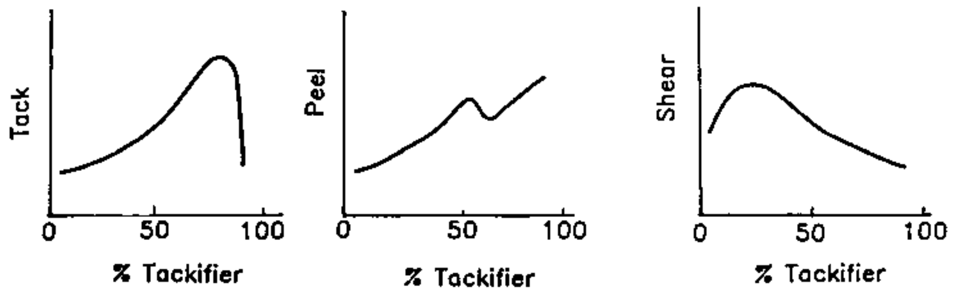

Figure 2 Dependence of tack, peel, and shear on resin/elastomer ratio.

Table 3 Elastomers in Common Use

Elastomer	Used in
Rubbers	
Natural rubber	Solvent-based and water-based glues
Butyl rubber	Solvent-based glues
Styrene–butadiene rubber	Solvent-based and water-based glues
Block copolymers	
Styrene–butadiene–styrene	Solvent-based and hot-melt glues
Styrene–isoprene–styrene	Solvent-based and hot-melt glues
Other polymers	
Polybutene	Solvent-based and hot-melt glues
Poly(vinyl ether)	Solvent-based and water-based glues
Acrylic	Solvent-based and water-based glues
Ethylene–vinyl acetate	Hot-melt glues
Atactic polypropylene	Hot-melt glues
Silicon	Solvent-based glues

The use of plasticizers is relatively uncommon in solvent-based pressure-sensitive adhesives, especially for use on tapes. Where plasticizers are included, their compatibility with the substrate should be considered, to ensure that plasticizer migration will not lead to transfer of the adhesive. Where plasticizing of block copolymers is intended, plasticizers should be selected that are compatible with the diene midblocks rather than with the polystyrene domains.

Additives used should include stabilizers or antioxidants, especially in products containing ethylenic unsaturation. Thickeners or thixotropes may be used to modify rheology. Fillers may be used in certain applications, in which case pigment-dispersing aids may be included to reduce settlement. Silane coupling agents may be used to improve adhesion to specific substrates. UV absorbers may be added to improve exterior durability, and pigments or dyes may be added to highlight the adhesive film.

Elastomers used in water-based systems include various rubber latices, especially natural rubber and SBR, and occasionally, polychloroprene. The bulk of the market in water-based adhesives is now held by acrylic dispersions. Although these are designed for use without modification, it is normal to formulate, especially by addition of tackifiers. Commonly used tackifying resins include soft resins, or hard resins in solution, which may

Table 4 Tackifying Resins and Plasticizers

Type and name	Melting point (°C)	Supplier
Aliphatic hydrocarbons		
Adtac LV	5	Hercules
Piccopale 100	100	Hercules
Quintone A 100	100	Nippon Zeon
Mixed hydrocarbons		
Hercotac 1148	94	Hercules
Quintone N 180	80	Nippon Zeon
Aromatic hydrocarbons		
Picco 6100	100	Hercules
Piccodiene 2215	103	Hercules
Necires RF 85	85	Neville
Nevchem NL 100	100	Neville
Terpenes		
Piccolyte S25	25	Hercules
Zonarez B 115	100	Arizona
Alresen PT 191	70	Hoechst
Rosin esters		
Staybelite Ester 10	84	Hercules
Floral 105	105	Hercules
Zonester 65	65	Arizona
Oulupale XB 100	96	Veitsiluoto
Alresat KE 300	Liquid	Hoechst
Resin dispersions		
Dresinol 205	75	Hercules
Aquatac 6085	85	Arizona
Oulutac 80 D	80	Veitsiluoto
Plasticizers		
Shellflex 451	Liquid	Shell

often be emulsified directly into the dispersion, and aqueous resin dispersions, which may be prepared separately and added or may be purchased from resin suppliers.

When using dispersions of tackifying resins, stability tests must be performed to ensure that there are no undesirable reactions between the emulsifier systems used in the resin dispersion and the elastomer dispersion. Resin dispersions often produce lower shear than resin solutions, thus necessitating reduced levels which result in lower tack. Additives used in water-based systems will include defoamers and preservatives as well as UV absorbers if necessary. Antioxidants are normally included only if service conditions require them. Catalysts may be added to cross-linkable grades to improve performance at elevated temperature, or self-cross-linking grades may be selected. Small quantities of solvents may be included to improve adhesion or penetration. Fillers are not generally used, although in applications on vinyl or carpet floor tiles fillers may be included at levels up to 30% to reduce the glue-line shrinkage and the price. Rheology modifiers, including polyacrylates or inorganic thixotropes such as fumed silica, may be added. Table 5 shows are characteristics of some common dispersions.

Table 5 Polymer Dispersions[a]

Name	Solid content (%)	Viscosity (cP)	T_g (°C)	Application area	Supplier
Acronol 81D	60	1400	-55	General	BASF
Arconal V205	69	1200	-40	Permanent labels	BASF
Lutanol I 65D	55	1700	N/S[b]	Tackifier	BASF
Mowiton DM758	60	5000	-65	Flooring adhesives	Hoechst
Revacryl A390	50	100	-55	Permanent labels	Harco
Revacryl 622	59	2000	-70	Deep-freeze labels	Harco
Vantac 300	58	1500	N/S[b]	Removable labels	Bevaloid

[a] Note that these are indicative values, not specifications.
[b] N/S, not stated in data sheets.

IV. APPLICATIONS

The major application area for all pressure-sensitive adhesives is in tapes. Self-stick labels provide a second large area, while a range of miscellaneous applications make up the balance of pressure-sensitive adhesive use.

A. Tapes

Tapes may be classified according to application areas, such as electrical, packaging, or medical, or in terms of the type of tape, usually defined by the backing, which may be paper, fiber, film, foil, or foam. Figures drawn from various tables produced by the Fredonia Group Inc. and published in *Adhesives Age* in June 1991 and the Frost and Sullivan Report, “The USA Market for Pressure Sensitive Adhesives,” in *Adhesives Age* in August 1991 showed that of a total U.S. pressure-sensitive adhesives market in 1989 of \$4.9 billion, \$2.6 billion was for sales of pressure-sensitive tapes. Table 6 illustrates the relative importance of the various backings and application areas.

An apparently simple tape may comprise a number of elements, including a release coating, the backing, a primer, and the adhesive layer. The release coating ensures that the adhesive layer does not transfer partially or completely to the back of the tape from the coated side. With certain types of backing a release layer may not be necessary, and in some instances a separate release film may be necessary. The release coating should allow the tape to unwind easily but not spontaneously. The need for priming also depends on the nature of the backing and may take the form of an applied coating or layer, a chemical treatment such as corona treatment, or a physical treatment such as exposure to heat. Priming may sometimes be necessary to inhibit movement of plasticizer from backing to adhesive layer, or vice versa, but the usual purpose of priming is to obtain adequate adhesion to the substrate. The earlier backings used were cloth, mainly for first-aid dressing. Cloth backings allow the skin to breathe and offer good flexibility and tensile strength while permitting easy tear. Generally, no priming or release coating is needed. Fabrics used include cotton, nylon, and polyester. Paper backing is the cheapest type of backing available. Saturated paper backings have better physical properties than unsaturated paper, particularly for tensile and tear strengths, water resistance and permeability, and generally do not require release backings, while unsaturated papers usually require some aid to release. Saturated papers are predominant for general-purpose creped masking tapes.

Table 6 Pressure-Sensitive Tape Market

Backing	Share (%)	Application area	Share (%)
Plastic and film	60.3	Packaging	38
Paper	23.1	Hospital and first aid	20
Cloth	11.9	Office and graphic art	17
Rubber	1.0	Construction	7.5
Other	3.7	Automotive	6.5
		Other	11

Plastic films comprise more than 60% of all tape backings. Originally based on cellophane, a wide range of plastics is now available for various applications. Polyester, unplasticized poly(vinyl chloride) (PVC), and biaxially oriented polypropylene (BOPP) are used for packaging tapes, while PVC is still preferred for electrically insulating tapes. Cellulose acetate is used for "invisible" tapes, and poly(tetrafluoroethylene) (PTFE), particularly in conjunction with silicon-based pressure-sensitive adhesives, is used where resistance to elevated temperatures, chemical inertness, or low friction are the main requirements. Plastic films are impermeable, thin, uniform, and smooth and are generally inert with good dielectric properties. Reinforced with glass fibers or rayon embedded in the tape to distribute the load over greater areas, they are suitable for heavy-duty packaging applications.

Other backings used include foams, typically PVC or polyurethane, rubber, and metal foils. Foams are used for sealing and gasketing or thermal or acoustic insulation. They work particularly well on uneven surfaces. Adhesive may be applied to both surfaces, allowing their use as assembly adhesives. A double-sided, release-coated interlayer is necessary for double-sided tapes. With foams, care must be taken to select an adhesive that does not cause the foam to collapse, either through solvent action or as a result of excessive heat. Rubber backings are used where flexibility is a primary requirement, although they also offer excellent electrical insulation. Aluminum foils are used mainly in the construction industry, to act as a moisture seal, to reflect heat or for insulation, or to offer a controlled leakage path for static electricity. Lead foils are occasionally used to screen harmful radiation.

Pressure-sensitive adhesives may also be coated directly onto release paper in order to produce transfer tapes, in which, as the name implies, the adhesive film will transfer from the release coating onto a substrate with which it is brought into contact. This permits exact placement of accurately controlled quantities of adhesive. Great care must be exercised in the choice of release paper to ensure successful application.

Packaging tapes represent the largest end use. Packaging, which includes closing of cartons, sealing containers, bundling, and protection of surfaces is based primarily on paper or plastic film backings, but other types may be used as well. Film-backed paper is replacing saturated paper for packaging applications, especially for masking and protection, while reinforced tapes are used for strapping large containers or bundling articles.

Hospital tapes and first-aid dressings still constitute an important area for pressure-sensitive tapes. Because of their ability to breathe, cloth tapes are still widely used, but other backings are now making their appearance for special applications, including invisible dressings and rigid or elastic support tapes. Choice of ingredients for adhesives is controlled by the need to produce a system that will not irritate the skin or inhibit healing.

In addition, it must not lose adhesion as a result of perspiration, but must permit easy and clean removal. Traditional adhesives were based on natural rubber and zinc oxide, but water-based acrylic systems now dominate.

Office and graphic art applications require a diversity of tapes and backings. Block-out tapes are often multilayer constructions incorporating colored films. Printed films are used for graphics displays, while clear protective sheets may be used to protect printed graphics against smudging or erasure. Dye-cut lettering is available. A variety of clear-film backings is used for temporary fixing tapes.

Electrical tapes or insulating tapes require adhesives that will not corrode wiring, joints, or components. They should resist deterioration resulting from age and exposure to heat. Occasionally, chemical resistance may also be required. PVC is still the most widely used backing, but other films, especially polyester, are increasing in use. Rubber- or elastomer-based adhesives are suitable for service up to 130°C, acrylics to 155°C, while silicones, preferably on PTFE, can be used up to 180°C.

Other applications include thermal and acoustic insulation and tinted films for glass in the construction industry, wood-grained or other decorative vinyls for the automotive and furniture industries, double-sided tapes for mounting or splicing, and foams for gaskets and seals in the appliance industry.

B. Labels

Peel-and-stick labels provide a quick and easy way to apply labels to almost any surface. Die cut and supplied on release papers, they can be printed in computers for addresses, while preprinted labels for an enormous range of applications, particularly difficult substrates such as polyolefins or cold, moist containers make labeling a pleasure compared with traditional wet-applied systems such as dextrines or caseins. Pressure-sensitive label stock provides reliable bonding, is easy to use and virtually instantaneous, and offers a choice of properties, including permanence or easy removal, high-temperature resistance, or low-temperature flexibility. Large or small labels can be easily stored and handled, and applied by hand, hand-held applicators, or semiautomatic or fully automatic industrial labelers.

Labels are generally regarded as falling into three classes: permanent label stock, removable labels, and labels for use at low temperatures. In addition, specialty applications include delayed-action labels, high-temperature applications, and decals. Permanent label stock is the mainstay of the label market. Label stock is invariably paper, and the labels, which are usually preprinted, are supplied on a release paper backing, leading to their popular name, "peel-and-stick" labels. Adhesives for permanent stock have high shear strength, and attempts to remove them will usually damage the label. Applications range from price stickers and address labels to inventory labels, shipping labels, warning signs, and labels for bottles, buckets, or drums.

By contrast, peelable or removable labels use adhesives with relatively low tack and shear strengths. On removal, no residue must remain on the surface from which the label was removed. Some removable labels use a water-soluble adhesive, permitting easy cleaning of the surface. These labels are used for temporary labeling or where they will frequently be replaced. Freezer labels use adhesives that have very good low-temperature flexibility to allow labels to be applied and remain adhered at temperatures down to −20°C or lower. They are characterized by very low glass temperatures, typically in the range −60 to −80°C.

Label adhesives are seldom solvent based. The majority are prepared using water-based adhesives, although hot melts are taking an increasing segment of this market. Important adhesive characteristics include the ability to be dye cut cleanly, low tendency to make the paper curl, coupled with ability to conform to the surface to which they are applied, very quick grab and good resistance to yellowing, and loss of tack with age. Acrylic dispersions, either with or without additional tackifiers, are the most widely used adhesives.

Production of label stock makes severe demands on the release paper. Since transfer coating is a common application method, the adhesive must wet the release paper adequately and yet transfer cleanly to the label when label and backing are united. The release paper must remove quickly and easily in use, but must remain firmly adhered during storage. Use of silicone releases is virtually universal, invariably requiring the use of wetting agents in the formulation to ensure that the adhesive wets the surface. There must be no transfer of the release coating to the adhesive surface, however, as this will destroy the tack of the adhesive.

C. Other Applications

The largest market outside tapes and labels is for adhesives for floor tiles. Peel-and-stick floor tiles are available from hardware stores for use by homeowners. These tiles usually have a hot-melt pressure-sensitive adhesive applied to the back so that laying to clean, prepared floors only needs the removal of a backing paper and pressing the tile into place. The adhesive layer in this application is substantially thicker than for tapes or labels, to ensure good contact over the entire area. Alternatively, vinyl flooring or carpets, either as tiles or in roll form, may be laid into water-based acrylic adhesives, although here the move is away from such adhesives in favor of more permanent adhesives typically based on vinyl acetate–ethylene copolymer dispersions. Acrylic dispersions are often used, however, usually in unmodified form, for application of vinyl tiles or sheeting over an existing impervious floor covering, where it is necessary to allow complete flash-off of the carrier prior to laying the new floor covering.

Personal hygiene products such as disposable diapers make use of self-adhesive strips, covered with a release tape that is removed at the point of use. Again unmodified acrylic dispersions as well as hot melts dominate this application. The same considerations apply here as in first-aid dressings, and in particular the adhesive must not cause skin irritation.

Gloss lamination, the application of thin films of polyester or polyolefin over printed paper to enhance gloss and protect the print, is an additional application area. Traditionally, this has been the preserve of solvent-based adhesives, which offer rapid drying, thus allowing high machine speeds, but water-based systems are increasing in popularity as the ability to formulate at very high solids reduces the drying time to acceptable limits.

V. COATING METHODS

Most of the popular coating methods are suitable for pressure-sensitive adhesives. Solvent-based adhesives are usually applied by roller coaters or occasionally by spray applicators. Water-based adhesives also use roller coaters predominantly, with nozzle feed machines the exception. Hot melts may be extruded, applied from slot orifice coaters, or calendared.

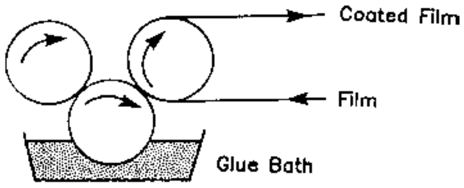

Figure 3 Reverse roll coater.

Although virtually any type of roll coater may be used, reverse roll coating is the most common. This may incorporate a doctor roll, doctor blade, or Mayer bar to meter the spread rate. With tapes, adhesive is usually applied directly to the tape, which then passes through a drying station incorporating countercurrent air, usually warm. The dried tape is then rolled and slit. With label stock, adhesive is normally applied to the release paper, dried, and then transferred to the label when the label stock is united with the release paper in a nip roll.

Adhesives for reverse roll application will typically have viscosities in the range of 1000 to 10,000 cP. While coating speeds in excess of 200 m/min are possible, machine speeds are normally limited by the speed at which the film can be dried. A simple reverse roll coater is shown in Fig. 3.

For low application weights of hot-melt adhesives, slot-orifice coaters are preferred. Variation of slot width and temperature allow a wide range of viscosities and coating weights to be handled. Calendaring is used for high-viscosity adhesives and high coating weights. Extrusion is used for very high viscosity systems and permits both mixing and coating to be performed in a single operation.

VI. TESTING

Because of the unique properties of pressure-sensitive adhesives, special tests not applicable to other types have been developed. While standard physical tests such as nonvolatile content, viscosity, and specific gravity are performed to ensure consistency of application, these tests do not predict adhesive performance. For pressure-sensitive adhesives, three critical performance characteristics are usually measured: tack, peel, and shear strength.

A. Tack

The classic test for tack of a pressure-sensitive adhesive film is the rolling ball tack test. Here a ball is rolled down an inclined plane onto a film of the adhesive. The length the ball travels across the film before stopping is a measure of the tack of the film. This test gives a good indication of tack with elastomer adhesives but is unreliable with water-based systems.

A more universal test is the probe test, in which the end of a cylinder of standard diameter is brought lightly into contact with the film for a very short time and the force required to separate it from the surface is measured. Similar in principle is the loop tack test, in which a loop of coated film is lowered onto a steel plate, making contact under its own weight, and the force required to withdraw the plate is then measured. All of these tests are markedly affected by the cleanliness of the ball, probe, or plate. Figure 4 illustrates the loop tack test.

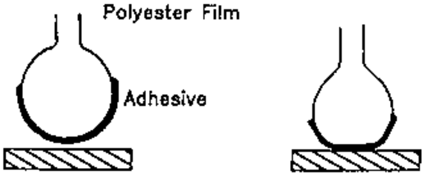

Figure 4 Loop tack test.

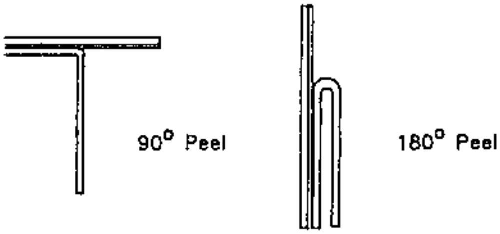

Figure 5 Geometry of 90- and 180-degree peel tests.

B. Peel

Peel strength is usually tested by laminating a coated film either to itself or to a specified substrate. The film is then peeled off the substrate at a steady speed at 90 or 180 degrees to the bond axis, and the force required for removal is measured. The result is always quoted as the force per unit width of film at a given rate of peel. Figure 5 shows the geometry of a 90- or 180-degree peel test.

C. Shear Strength

This test is a measure of the ability of a pressure-sensitive adhesive to withstand creep. A standard area of coated film is bonded to a steel plate and a weight suspended from it. The assembly is placed in an oven. In some shear tests the time for the assembly to delaminate at a fixed temperature is recorded, while in other tests the temperature at which failure occurs when the oven temperature is increased at a certain rate is the shear value quoted.

VII. GUIDE FORMULATIONS

Several guide formulations for various applications follow. It must be remembered that they should merely be used as a starting point to develop a satisfactory product. Not all materials will be available in all countries, and the nature and quality may vary from country to country. To simplify formulations, trade names have been used, and these may also differ. In most cases substitutes are available.

Parenthetical numbers that follow the components listed in the formulations below correspond to these suppliers:

1. Shell Chemicals
2. Hercules Inc.

3. Anchor Chemicals
4. Nippon Zeon
5. Hoechst
6. Firestone
7. Arizona
8. Harlow Chemicals
9. EKA Nobel
10. U.S. Cyanamid
11. Dow Chemicals
12. BASF

A. Solvent-Based Adhesives

1. *General Purpose Adhesives for Tapes*

	High shear	High tack
Cariflex TR 1101 (1)	100	—
Cariflex TR 1107 (1)	—	100
Piccolyte A 115 (2)	80	—
Abitol (2)	10	—
Foral 85 (2)	—	80
Piccolyte S 40 (2)	—	10
Ancazate BU (3)	1	1
SBP 62/82 (1)	250	300
Toluene	50	—

2. *Paper-Splicing Adhesive*

Natural rubber: pale crepe	7.5
Quintone D100 (4)	7.5
Antioxidant	0.2
Hexane	70.0
Toluene	14.8

3. *Self-Stick Carpet Tiles*

Synthacryl VSC 2291 (5)	20.0
Alresen PT 214 (5)	5.0
Methyl ethyl ketone	10.0
Toluene	30.0
Aerosil 200	0.0–5.0
Calcium carbonate, 10 μm	35.0–30.0

B. Hot-Melt Adhesives

1. *Label and Tape Adhesives*

	Soft, high tack	High strength
Cariflex TR 1102 (1)	—	100
Cariflex TR 1107 (1)	100	—
Floral 85 (2)	150	—
Shellflex 451 HP (1)	75	—

	Soft, high tack	High strength
Piccolyte S 85 (2)	—	100
Abitol (2)	—	50
Ancazate BU (3)	5	5

2. *Self-Adhesive Carpet Tiles*

Cariflex TR 1102 (1)	75
Cariflex TR 1107 (1)	25
Piccolyte A 115 (2)	100
Abitol (2)	50
Calcium carbonate	100
Antioxidant	5

3. *Disposable Industry Adhesive*

Stereon 840 A (6)	25
Zonatac 105 Lite (7)	58
Shellflex 371 (1)	16
Antioxidant	1

C. Water-Based Adhesives

1. *Adhesive for Permanent Label Stock*

Revacryl 630 (8)	60.0
Snowtack 301 CF (9)	35.0
Aerosol OT (10)	0.3
Dowfax 2A1 (11)	0.1
Ammonia solution	0.3
Foamstopper 101 (8)	0.1
Water	4.2

2. *Deep-Freeze Label Stock*

Revacryl 622 (8)	94.5
Hercolyn D (2)	4.5
Aerosol OT (10)	0.5
Dowfax 2A1 (11)	0.1
Water	0.4

3. *Removable Labels*

Revarcryl DP 3560 (8)	99.0
Aerosol OT (10)	0.5
Dowfax 2A1 (11)	0.1
Water	0.4

4. *PVC Floor Tile Adhesive*

Mowiton DM 758 (5)	40.0
Alresat KE 300 (5)	8.0
Calcium carbonate, 10 μm	32.0
Water	15.0
Collacryl D (12)	1.5–3.0
10% caustic soda solution	2.0–3.0

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Electrically Conductive Adhesives

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I. INTRODUCTION

Electrically conductive adhesives perform two primary functions. Like other types of adhesives, these materials provide a physical bond between two surfaces. In addition, an electrical interconnection between the two bonded surfaces is formed. This dual functionality is usually achieved by composite materials composed of metallic particles dispersed in an adhesive matrix. The electrical resistivity of conductive adhesives is compared to values of pure metals and polymers in Table 1.

There are two types of conductive adhesives: conventional materials that conduct electricity equally in all directions (isotropic conductors) and those materials that conduct in only one direction (anisotropic conductors). Isotropically conductive materials are typically formulated by adding silver particles to an adhesive matrix such that the percolation threshold is exceeded. Electrical currents are conducted throughout the composite via an extensive network of particle–particle contacts. Anisotropically conductive adhesives are prepared by randomly dispersing electrically conductive particles in an adhesive matrix at a concentration far below the percolation threshold. A schematic illustration of an anisotropically conductive adhesive interconnection is shown in Fig. 1. The concentration of particles is controlled such that enough particles are present to assure reliable electrical contacts between the substrate and the device (Z direction), while too few particles are present to achieve conduction in the X–Y plane. The materials become conductive in one direction only after they have been processed under pressure; they do not inherently conduct in a preferred direction. Applications, electrical conduction mechanisms, and formulation of both isotropic and anisotropic conductive adhesives are discussed in detail in this chapter.

II. APPLICATIONS

In this section we discuss three applications of electrically conductive adhesives: die attach adhesives, anisotropically conductive adhesives for liquid crystal display (LCD) assembly, and conductive adhesives for surface-mounted assembly of packaged components on printed wiring boards (PWBs). These applications were selected based on overall

Table 1 Bulk Electrical Resistivity Values for Selected Metals, Polymers, and Composites

Material	Resistivity (Ω cm)
Silver	1.6×10^{-6}
Copper	1.7×10^{-6}
Aluminum	2.7×10^{-6}
Pb/Sn solder	15×10^{-6}
Conductive epoxy	ca. 500×10^{-6}
Carbon	3000×10^{-6}
Antistatic composites	ca. 10^{4}
Epoxy resin	ca. 10^{15}

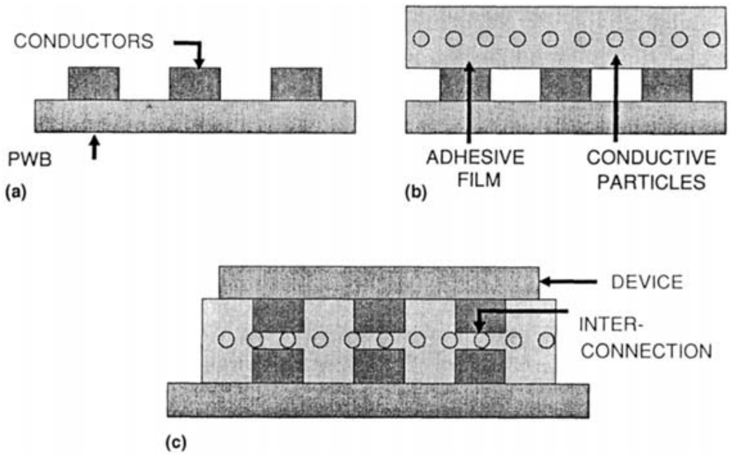

Figure 1 Anisotropically conductive adhesive assembly process: (a) bare substrate; (b) apply anisotropically conductive adhesive; (c) align device, cure under pressure.

volume usage, importance to the industry, and future technological as well as political impact.

Numerous other types of electrically conductive polymer composites are commercially available but are beyond the scope of this chapter. These materials are used in such applications as conductive inks [1], thermoplastic molded monolithic objects for electrostatic dissipation (ESD) [2] and electromagnetic interference (EMI) shielding applications [3], and a wide variety of other applications, including heating elements, switches, transducers, and batteries [2]. Similarly, the fabrication of conductive polymer materials via metal vapor deposition or electrodeposition onto polymer surfaces will not be discussed here.

A. Die Attach Adhesives

The most significant application for conductive adhesives in the manufacture of microelectronics is the attachment of silicon chips to lead frames. Of the 40 billion integrated circuits (ICs) manufactured each year, approximately 90% are encapsulated in plastic-molded packages, and most of these are assembled with conductive adhesives [4]. A schematic illustration of a plastic-molded IC package is shown in Fig. 2. The conductive

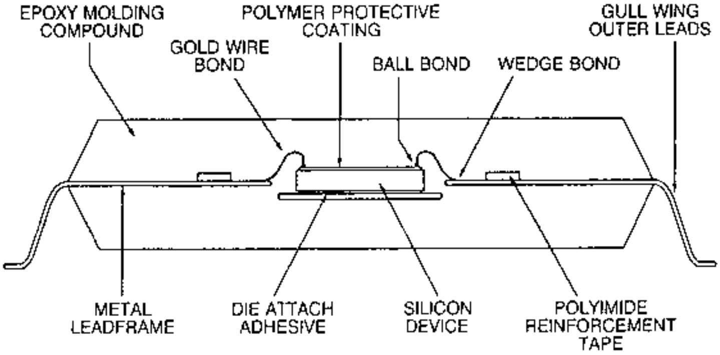

Figure 2 Cross section of a plastic-molded integrated circuit package.

adhesive forms the mechanical as well as electrical interconnection between the back side (ground plane) of the die and the plated copper lead frame. Initially, gold eutectic bonding was used for this die attach application. Several disadvantages to this process were encountered, however, including elevated assembly temperatures, cost of materials, and especially the stresses induced by coefficient of thermal expansion (CTE) mismatches [5]. Alternative interconnection materials were later developed, including silver glass materials for hermetic packages and conductive adhesives for nonhermetic applications. A review of these three die attach technologies has been published [6].

Adhesives gained acceptance rapidly, despite the industry's reluctance to incorporate organic materials in microelectronic packages, due to the following advantages:

Low cost
Low assembly temperatures
Low-stress joints
High thermal conductivity
High purity
Excellent reliability
Easy integration into the manufacturing line

Conductive adhesives also form sufficiently robust joints that withstand the temperatures and pressures experienced during wirebonding and over molding. The formulation of die attach materials is discussed in Section IV.

B. Interconnections to Liquid Crystal Displays

A relatively new application for conductive adhesives, and a very important one in terms of technological advance and future manufacturing techniques, is the assembly of liquid crystal displays (LCDs). Interconnecting flexible circuit connectors, tape automated bonding packages, and bare IC chips to glass panels have been the principal technology drivers for the development of anisotropically conductive adhesives. A brief history of LCD interconnection technology [7] as well as an analysis of current manufacturing techniques for display-based consumer electronics equipment [8] have been reported that illuminate material requirements for this rapidly evolving type of product. The principal reasons for developing anisotropic adhesive systems for interconnections to glass panel displays are:

1. Low assembly temperatures to prevent glass fracture
2. Very fine pitch (repeat distance between adjacent conductors) of 2 to 20 mils
3. Low cost

Neither isotropic conductive adhesives nor conventional solder interconnections, can easily satisfy these requirements.

Early LCDs contained the electronic drivers on a rigid circuit board, whereas the glass panel contained only the active display area. The two substrates were connected by an adhesively bonded flex circuit or heat seal connector (HSC). HSCs are the most primitive type of anisotropically conductive adhesive material. They are in wide use in Japan and are commercially available in United States.* HSCs are manufactured by screen printing conductive traces onto a flexible substrate (usually polyester) using either a graphite, silver, or silver–graphite ink. Alternatively, the conductor patterns may be formed by etching copper foils laminated to flex substrates. The conductive traces may be coated with a second layer of ink containing metallized spheres. A hot-melt adhesive, such as neoprene/ethylene–vinyl acetate [9], is applied over the entire top surface. The HSC is tacked into position at low temperatures onto one substrate, tested for accurate alignment, then fully cured at elevated temperatures (thermosets only). This process is repeated to join the second substrate. Thermoset hot melts offer improved reliability over thermoplastic adhesives [9,10]; however, the thermoplastics offer processing advantages, as they can easily be removed and repositioned if the HSC is not properly aligned to either the glass panel or rigid PWB. Interconnection pitch as fine as 11 mils can be achieved.

Most current LCDs are assembled using tape automated bonding (TAB) to package the driver chips. The TAB packages can also act as connectors between the PWB and the glass display. Connections are made to the glass panel by use of anisotropically conducting polymer films and to the PWB by solder reflow [9,11]. Anisotropically conductive adhesives for attaching TAB packages to low-cost polymer thick film (PTF) flex circuits were first used for the assembly of low-cost calculators [12,13]. Principles of anisotropically conductive adhesive formulation are described in (Section VB, pages 867–870).

Flip-chip interconnection of silicon ICs to glass displays, as well as to multichip module substrates, is the focus of current research efforts. Although most of the flip-chip effort is directed toward solder bumping for multichip modules [14], adhesive interconnections dominate the emerging display assembly technologies. Technologies that employ anisotropically conductive films [15,16], isotropically conductive adhesive bumps [17,18], and nonconductive adhesives [19] have been reported. An especially novel system that ensures isolaton in the X–Y plane, even at 2-mil pitch, has also been reported [7]. An ultraviolet (UV)-curable adhesive is applied to a large-scale integration (LSI) wafer and exposed through a mask such that only the material above the metallic contact pads on the die remains tacky. The surface is then coated with metallized polymer spheres, 10 μm in diameter; the spheres adhere only to the tacky regions above the 1-mil^2 pads. The chips are diced, assembled to glass substrates, and cured under pressure with an additional adhesive. Deformation of the elastomeric spheres, and flow of the adhesive during cure, ensures good electrical contact.

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*For example, two US distributors of Japanese heat seal connectors are Nippon Graphite Industries, and Nitto Denko America, Inc.

C. Surface-Mounted Assembly of Printed Wiring Boards

The future use of lead in the manufacture of electronic products is problematic. Lead is toxic, and although current worker exposure is low (and consumer exposure is negligible), regulatory and/or consumer forces may make the cost of using lead in electronics manufacturing prohibitive. A thorough assessment of lead use, as well as an evaluation of alternative joining technologies, has been published [20]. In addition, editorials have endorsed the elimination of lead from electronic products as a means of attracting consumers and increasing global market share in the next decades [21].

Conductive adhesives are one of the feasible alternatives to lead for electronics assembly. Isotropically conductive adhesives are suitable for standard pitch (50- to 100-mil) surface-mounted components and numerous commercial materials are available (see commercial supplier listing, Section VI.E). Anisotropically conductive adhesives are more suited to flex to rigid connections, fine pitch components (15- to 20-mil pitch), and flip-chip assembly (4- to 12-mil pitch) [22]. Adhesives are not ready to replace solder throughout the electronics industry, however, due to questions that remain concerning the reliability of electrical interconnections. Their implementation is currently limited to low-cost applications using polyester substrates and specialty applications where solder cannot be used. Additionally, the lack of equipment for large-volume assembly with anisotropically conductive adhesives, which require the simultaneous application of heat and pressure, impedes the acceptance of these promising materials.

III. CONDUCTION MECHANISMS IN METAL–POLYMER COMPOSITES

Increasing the concentration of metal particles in an insulating adhesive matrix changes the electrical properties of the composite in a discontinuous way. Assuming a random dispersion of the metal filler, as the concentration increases no significant change occurs until a critical concentration, p_c, is reached. This point, where the electrical resistivity decreases dramatically, called the *percolation threshold*, has been attributed to the formation of a network of chains of conductive particles than span the composite. A two-dimensional cartoon of a conductive adhesive below p_c and just above p_c is shown in Fig. 3. A typical plot showing the relationship between particle concentration and electrical resistivity is shown in Fig. 4.

Experimental [23] as well as theoretical [24–26] studies of percolation phenomena have been reported. In random and macroscopically homogeneous materials it has been demonstrated [27–29] that at concentrations of metal particles below the percolation threshold ($p < p_c$) a short-range percolation coherence length, ξ, exists. Electrical conductivity is probable for length scales less than ξ. Thus even if the metal-filled composite exhibits no bulk electrical conductivity, conduction can occur within domains that are smaller than ξ. As the concentration of metal particles approaches p_c, $\xi \rightarrow \infty$ and the composite becomes isotropically conductive.

The concentration of metal particles required to achieve p_c has been reported over a wide range, from less than 1 to more than 40 vol %. This range of values occurs due to several factors, including processing techniques [3,30,31], particle size in relatively monodisperse systems [32], particle size distribution [27], and particle aspect ratio. In many of the systems reported [23,25,33,34] random dispersions were assumed even when dense metal particles were employed. Recent work has demonstrated, however, that dense metal particles can settle, especially when the viscosity of the polymer matrix is low [27].

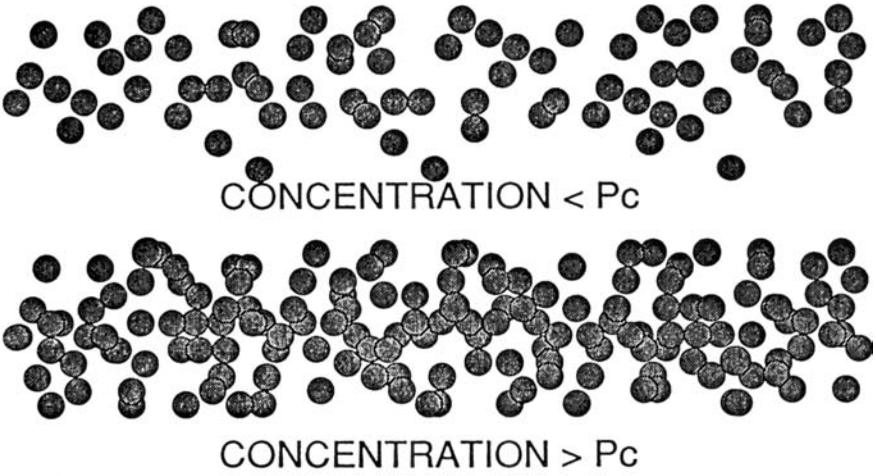

Figure 3 Electrical percolation threshold for conductive particles in an insulating matrix.

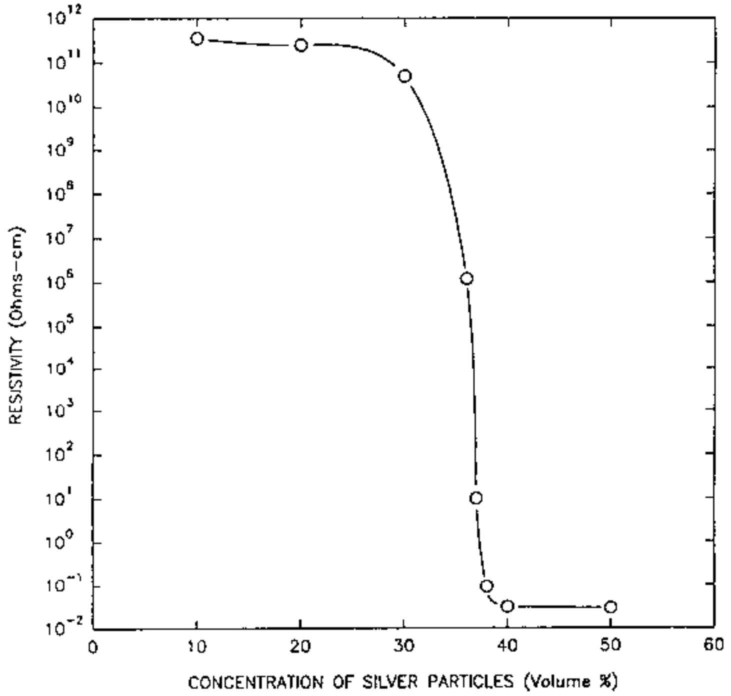

Figure 4 Resistivity of silver–phenolic composites. (From Ref. 23.)

Particle settling is another factor that may influence the observed onset of percolation. Depending on how the electrical properties of the sample are measured, the observed value for p_c may be either higher or lower than the value of p_c in a truly random system.

The size of the metal particles relative to any structure present in the polymer matrix can also affect the value of p_c. Segregated composites have been prepared by compression molding a mixture of metal and polymer particles [35]. When the radius of the polymer particle (R_p) is significantly larger than the metal particle size (R_m), the metal is confined to the regions between polymer domains [36]. Values of p_c as low as 6 vol % were achieved when $R_p/R_m = 16$. Metal-plated polymer spheres have been prepared where the effective $R_p/R_m \to \infty$ [37].

Another factor that influences the value of p_c is the aspect ratios of the metallic filler. Metal fibres, metal-plated glass fibers, and metal flakes can significantly lower the concentration required to achieve isotropic conduction as compared to spherical powders [3]. Values of p_c as low as 1 vol % have been reported with stainless steel fibers having an aspect ratio of 750 [37].

After mixing, some conductive epoxies do not always exhibit electrical conductivity. The electrical properties develop only after cure and the final resistance may be a function of the amount of time between mixing and cure [38–40]. This effect has been attributed to a fatty acid coating applied to the surface of the silver during manufacture of the flake. The coating is removed at elevated temperatures during cure. Solvents such as polypropylene glycol may dissolve the coating before cure, rendering the pastes conductive [39]. Growth of insulating coatings about the silver flake particles is postulated as the cause for the increase in electrical resistivity of some conductive adhesives upon standing at room temperature before cure [40].

A. Anisotropic Conduction Mechanisms

Several processing techniques have been developed to achieve anisotropic conductivity. One method aligns the conductive metal particles in a magnetic field [41–43]. Alternatively, anisotropy can be achieved in materials with random dispersions of metal particles. Using an adhesive composite where the concentration of metal particles is below but close to p_c results in a material with a short-range percolation length ξ. If the separation distance between substrate and device is less than ξ, whereas the pitch is much greater than ξ, anisotropic conduction is achieved. This approach is difficult to implement, as shorts between adjacent conductors, as well as opens between the substrate and device, are statistically possible.

Most commercially available anisotropically conductive adhesives are formulated on the bridging concept, as illustrated in Fig. 1. A concentration of conductive particles far below the percolation threshold is dispersed in an adhesive. The composite is applied to the surface either by screen printing a paste or laminating a film. When a device is attached to a PWB, the placement force displaces the adhesive composite such that a layer the thickness of a single particle remains. Individual particles span the gap between device and PWB and form an electrical interconnection. For successful implementation of anisotropically conductive adhesives, the concentration of metal particles must be carefully controlled such that a sufficient number of particles is present to assure reliable electrical conductivity between the PWB and the device (Z direction) while electrical isolation is maintained between adjacent pads (X, Y directions).

IV. FORMULATION OF ISOTROPICALLY CONDUCTIVE ADHESIVES

A. Requirements and Performance

A U.S. military hybrid specification (MIL-A-87172 of MIL-STD-883) established the selection and qualification requirements for polymeric adhesives used in military hybrid circuits and is used as a guide for die attach materials for nonmilitary applications as well.

Table 2 lists the requirements for a type I (electrically conductive) adhesive and test results of a typical current generation isotropically conductive adhesive as reported by Estes [44]. These requirements specify test ranges for characteristics that will establish processing, performance, and reliability.

In the process category, viscosity and pot life determine the suitability of a material for a specific application technique (e.g., stencil and screen printing, syringe dispensing, and pin transfer printing) and the length of time the material can be used. Shelf life is important from an inventory control point of view as well as a cost factor. Cure schedule will govern the product flow during the manufacturing process and also the compatibility

Table 2 Requirements for MIL-A-87172 and Typical Test Results

Test or condition	Requirement	Typical formulation
Material uniformity (3.4.1)	Inspect at 30 ×	Pass
Viscosity, cP (3.4.2)	Report for each batch	25,000–35,000
Pot life (3.4.3)	> 1 h/25°C	3 months
Shelf life (3.4.4)	> 12 months	> 12 months
Cure schedule (3.5.1)	Per supplier data sheet	180°C/1 h 150°C/1.5 h
Thermogravimetric analysis		
Wt. loss, 300°C, ASTM D-3850	$< 1\%$	0.45%
Filler content (3.5.2.2)	$\pm 2\%$ of reference lot	
Outgassed materials (3.5.3)	$H_2O < 3000$ ppm by RGA	User
Ionic impurities (3.5.4)	Total ionic (ppm)	
Hydrogen ion	$4.0 < pH < 9.0$	6.4
Extractable Cl^-	< 300 ppm	< 10
Na^+	< 50 ppm	< 10
K^+	< 50 ppm	< 10
$NH_4{}^+$	Report for information	< 20
Other ions if present > 5 ppm	Report for information	< 20
Total ionic	< 4.5 mS/m	3.3
Corrosivity (3.5.5)	No change, 48 h	Pass
Bond strength (3.5.6)		
Initial at 25°C	6.0 MN/m^2	12.4
Initial at 150°C	6.0 MN/m^2	7.8
At 25°C after 1000 h/150°C	6.0 MN/m^2	7.5
Coefficient of linear thermal expansion (3.5.7)	Below $T_g < 65 \times 10^{-6}$/°C Above $T_g < 300 \times 10^{-6}$/°C	45×10^{-6} 170×10^{-6}
T_g (glass transition temp.)	Information only	95°C
Second T_g		150°C
Thermal conductivity (3.5.8) measured at 121°C	Type I > 1.5 W/m K	> 2.0
Volume resistivity (3.5.9)		
For type I adhesive at 25°C	$< 5 \times 10^{-4}\ \Omega$ cm	0.0002
60°C	$< 5 \times 10^{-4}\ \Omega$ cm	0.00025
125°C	$< 5 \times 10^{-4}\ \Omega$ cm	0.00025
Measured after 1000 h/150°C	$< 5 \times 10^{-4}\ \Omega$ cm	0.00027
Solvent		No

Source: After Ref. 44.

with temperature-sensitive components. The thermogravimetric analysis specification is an attempt to limit volatile evolution during cure. This can be very important in preventing voids in the conductive adhesive which will adversely affect electrical and thermal conductivity, joint strength, and die cracking [5]. In addition, the evolution of volatiles has been correlated to surface contamination of the die bonding pads and poor wirebonding yields [45].

The other test requirements shown in Table 2 deal with performance and reliability. The outgassed materials test in part is concerned with residual solvent and moisture in the starting adhesive, as well as by-products of thermal degradation. Ionic impurities and corrosivity have been associated with damage to the active die and thus poor reliability where found in excess. Bond-strength requirements are necessary to ensure processibility during subsequent manufacturing steps such as wirebonding and overmolding (plastic packages). The aged bond strength is intended to be another measure of thermal degradation resistance. Coefficient of linear thermal expansion and T_g relate to stresses in a bonded assembly; however, the significance of the value is not indicated by the requirements. Thermal conductivity is another check on void formation, while volume resistivity, especially after aging, is a measure of adequate particulate content, sufficient particle to particle contact, and a stable particle–matrix–particle structure in the adhesive.

B. Formulations

1. *Epoxy*

Some of the first commercial conductive epoxy adhesives were simply based on silver powder dispersed in a liquid epoxy resin [e.g., diglycidyl ether of bisphenol A (DGEBA)] with an aliphatic amine [e.g., triethylene tetramine (TETA)] as a curing agent. Although capable of room-temperature cure, commercialization of this type of system was hampered by severe mix ratio disparity (typically, 50:1 by weight), problematic mixing due to viscosity differences, short pot life, and safety concerns. See Table 3 for typical properties of this type of formulation.

Solvents were often used to help disperse the silver particles, to lower viscosity, or to enhance conductivity. The presence of solvent can accomplish several objectives: first, by lowering the resin viscosity, additional silver can be added to the mix, increasing the likelihood of exceeding the percolation limit; and second, certain solvents can dissolve or displace lubricants on the surface of the silver flake (necessary for manufacturing the fine particles) that may interfere with the electrical contact between particles. The selection of a solvent involves consideration of its effect on both the epoxy cure reaction and the long-term performance of the adhesive. Most solvents reduce the cure reactivity of epoxy adhesives and some can prevent the development of a complete cure (lower alcohols are known to act in this fashion). The suitability of a particular solvent will also depend on its ability to leave or remain in the cured adhesive as intended. Low-boiling solvents may evaporate from a curing adhesive without void formation if the cure temperature is mild and the bond area (die) is small. Conversely, a high-boiling solvent may be retained in the cured adhesive to act as a plasticizer.

With improved formulations, organic-based conductive adhesives became feasible replacements for eutectic solders. Table 4 shows typical one- and two-part conductive adhesives from the 1970s. The one-part adhesive system employed a latent catalyst for long pot life but required a high-temperature cure cycle. The two-part system, formulated

Table 3 Early (ca. 1960) Conductive Adhesive Formulation and Properties

	Parts by weight	
	Part A	Part B
Ingredient		
Epoxy resin (Epon 828)	20	
Silver flake (10–20 μm)	75–80	
Solvent (glycol ether)	0.5	
Curing agent triethylene tetramine (TETA)		2.4
Total	100	2.4
Viscosity	50,000–100,000 cP	2 cP
Mixed properties		
Viscosity	10,000–100,000 cP	
Pot life	30–60 min	
Cure cycles	5–7 days RT 4 h 50°C 2 h 75°C 1 h 100°C	
Cured properties		
Glass transition	50–100°C	
Volume resistivity	0.01–1 Ω cm[a]	

[a] Value depends on amount of solvent and cure cycle.

Table 4 Die Attach Conductive Adhesives

	Parts by weight		
		Two-part adhesive	
Ingredient	One-part adhesive	Part A	Part B
Liquid DBEBA	100	100	
Latent catalyst (DICY[a])	8		
Liquid anhydride (HHPA[b])			80
Tertiary amine (BDMA[c])			1
Silver flake	100–250	140	159
Properties			
Mix ratio W/W	—	1	1
Mixed pot life	3–6 months	16–24 h	
Cure temperature	175°C	100°C	
Cure time	1 h	2 h	

[a] Dicyandiamide.
[b] Hexahydrophthalic anyhydride.
[c] Benzyl dimethylamine.

for a 1:1 by weight mix ratio could be cured at a lower temperature but had a shorter pot life. Formulations similar to the two-part system are still commercial today and are used where the low-temperature cure is critical. Some suppliers now offer this type of conductive adhesive is premixed, frozen syringes for added convenience.

The one-part formulation of Table 4 was improved over the years with respect to the curing temperature by the development of cure accelerators for DICY. However, concerns over residual outgassing of potentially corrosive cure by-products (e.g., ammonia) have resulted in the substitution of newer latent curing agents in modern formulations. An example of this type of curing agent is 1-cyanoethyl-2-ethyl-4-methylimidazole (sold as 2E4MZ-CN by Shikoku Chemicals Corporation), used at a level of 4 to 8 parts by weight of resin (phr), where the resin could be a liquid epoxy novolac [46].

As the die attach business became more competitive, adhesive suppliers refined their formulations to take advantage of small improvements in rheology, high-temperature performance, electrical conductivity, cure cycle, and ionic purity to satisfy customers' real or perceived needs. As a result, the current generation of conductive adhesive formulations may include new resins with lower viscosity, lower levels of ionic contamination, higher functionality, particulates with specific shapes, or combinations of shapes (e.g., flake and spheres); additives to control flow properties for better application techniques; conductivity enhancers to allow better particle-to-particle contact or higher concentrations of particles for improved conductivity; and adhesion promoters. Flow control additives are used in very low concentration and can be based on silicone oils, fluorocarbon or hydrocarbon surfactants, low-molecular-weight acrylic polymers, and so on. Some materials that provide conductivity enhancement include low-molecular-weight polypropylene glycols, select solvents, and some reactive diluents (low-molecular-weight mono- and difunctional epoxy resins). Organosilanes are the most commonly used adhesion promoters, but organotitanates can also be used. The use of additives with low boiling points that cannot be incorporated into the polymer structure should be minimized, however, to reduce void formation.

Residual stress in the die after assembly remains a concern when using epoxy die attach adhesives, especially with a large die. Various formulation techniques to reduce stress have been reported that include lowering the T_g of the matrix [47,48], formulating the matrix to exhibit two T_g values [49], reducing the modulus of the adhesive by minimizing silver content, and lowering cure temperature [47].

2. *Polyimides*

The development of polyimide-based conductive die attach adhesives resulted from the attractive properties exhibited by this generic class of materials. The high T_g value (typically, 100°C higher than epoxies) offers superior performance during high-temperature processing, such as wirebonding, overmolding, soldering, and lid sealing. Other properties of interest include low ionic contamination levels and a low CTE.

There are several disadvantages to using polyimides that limit their usefulness and increase manufacturing costs. In general, polyimide adhesives are formed by the thermally induced imidization of a polyamic acid precursor. The polyimide precursors are dissolved in a solvent such as *n*-methyl pyrrolidinone that must be removed before curing can begin. Most cure reactions generate water as a by-product which must also be removed carefully to prevent void formation. Finally, very high temperatures (>250°C) are required to cure the material fully. High residual stresses can result from a combination of the elevated process temperature, T_g, shrinkage during cure, and high modulus of the imidized resin.

Several major advances in polyimide chemistry have reduced some of the process difficulties. By end capping the polyimide precursor with acetylenic unsaturation, by-product free addition cures can be achieved. The development of a thermoplastic polyimide eliminates the high-temperature cure requirement [50]. Both of these modifications alter other characteristics, such as lowering of the high-temperature resistance over a traditional polyimide. The incorporation of dimethylsiloxane block segments into the polyimide backbone has also been reported [49]. This type of modification leads to an adhesive matrix with a lower modulus of elasticity and lower T_g value than those of unmodified polyimides and has been associated with lower-stress die attach assemblies.

3. *Silicones*

Silicone-based polymers have characteristics that make them desirable as the matrix of a conductive adhesive system. Their excellent thermal stability, low ionic impurity content, and especially, low modulus make silicones desirable for bonding very large die. A typical formulation would include linear polydiorganosiloxane oligomers with both vinyl and silicon hydride functionality, a platinum catalyst, an electrically conductive particulate, an adhesion promoter, reinforcing agents, and rheology modifiers [51]. The incorporation of sufficient silver flake to provide electrical conductivity will certainly increase the base polymer modulus and lower its elongation; however, from a mechanical property point of view, the silicones remain the primary choice for a low-stress die attach adhesive.

Reliability of the electrical properties of silicone-based isotropic adhesives has been the major difficulty to overcome and has essentially prevented commercialization. Another problem associated with silicones is that the addition polymerization reaction of silicones must be carefully controlled to prevent cure inhibition from various common chemical contaminants such as amines and sulfides. Other concerns include low-molecular-weight silicone polymer migration onto wirebond pads and very high CTE. There has been some activity in the development of hybrid resins that contain silicone blocks as comonomer with epoxies such that the epoxy processing can be maintained with the added stress reduction property of the silicones [52].

V. FORMULATION OF ANISOTROPICALLY CONDUCTIVE ADHESIVES

A. Requirements and Performance

Materials for use as anisotropically conductive adhesives must satisfy requirements even more stringent than those defined previously for isotropically conductive adhesives. No specifications, however, have been defined specifically for these materials. When used for flip-chip applications, the adhesive not only serves as a physical and electrical interconnection between the device and the substrate, but also serves as the environmental protection and passivation layer. This fact, combined with high adhesive concentrations, makes the ionic contamination levels of these materials more critical than for isotropic conductive adhesives. In addition, the processing of these materials has a greater influence on joint reliability as the anisotropic electrical properties develop only after heat and pressure are applied to the joint.

Numerous geometrical factors of the specific interconnection will also influence anisotropic adhesive formulation and processing, including lead planarity, IC pad metallization, and IC test patterns. The planarity of the leads on the substrate and/or device and the compliance of the conductive particles will determine if anisotropically conductive adhesives can be used in a particular application. For systems with large disparities between lead height, no electrical interconnection will be formed, as shown in Fig. 5. Fine-pitch IC packages for surface-mounted applications, such as the plastic quad flat pack (PQFP), often use gullwing leads that offer much compliance to the joint. Even if the

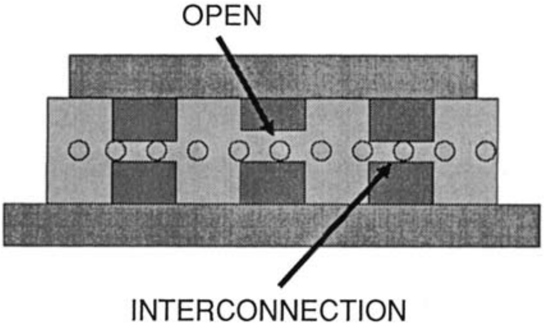

Figure 5 Effect of lead nonplanarity on anisotropically conductive adhesive interconnections.

leads are not initially coplanar, sufficient force can be exerted during assembly and cure to achieve electrical interconnection for all leads. Interconnecting flexible circuits and TAB packages to glass or rigid PWBs is relatively straightforward, whereas interconnecting bare silicon ICs to rigid substrates poses the greatest challenge.

Some of the requirements imposed on an anisotropically conductive interconnection used for flip-chip applications arise from the IC chip design. The metallization of the IC chip is usually aluminum or gold. Gold is preferred for the formation of reliable interconnections because an aluminum surface is coated with an insulating oxide that can be difficult for the conductive particles to penetrate (especially metal-plated polymer spheres). Most features on an IC, except for the bond pads, are passivated with an inorganic film such as Si_3N_4. However, some test patterns and grids located in the "streets" between chips are not electrically insulated. These metal features can cause electrical shorts between adjacent conductors via metal particle bridging. To prevent these problems, an additional insulating layer can be applied to the chip, or the bond pads can be bumped, raising the level of chip surface.

Data describing the reliability of joints assembled with anisotropically conductive adhesives are incomplete. Several papers have been published, but usually the sample size investigated is small, the accelerated stress tests are not standardized, and the results are highly dependent on device type (e.g., flexible circuit to rigid PWB, surface-mounted components, and flip-chip assembles). Further work is required in this area.

B. Formulation

1. *Particle Specifications*

The goal in formulating anisotropically conductive adhesives is to maximize particle concentration without compromising electrical isolation in the X–Y plane. Higher particle loadings increase the probability that an electrical interconnection will be made (especially for relatively small contact areas) and decrease contact resistance. Typical concentrations range from 5 to 15 vol % (30 to 60 wt % based on pure silver particles). The size of the particles usually ranges from 10 to 20 μm in diameter. Smaller particles offer the best results for very fine pitch applications.

To lower the probability of conduction in the X–Y plane (i.e., reduce the short-range percolation coherence length ξ), particles are used with an aspect ratio as close to 1 as possible. In contrast, isotropically conductive systems use flakes with high aspect ratios as fillers. Particle size distributions are minimized so that each particle can potentially serve as an electrical bridge between substrate and device.

Table 5 Current-Carrying Capability of Some Anisotropically Conductive Adhesives

Particle type	Current (mA)
Solid metal	200
Metal-plated glass	20
Gold-plated polymer	5

Numerous types of particles are used in anisotropic adhesive formulations. Silver has high electrical conductivity and good resistance to corrosion; however, electromigration may cause problems in some applications. Nickel is a lower-cost alternative, but corrosion has been reported during accelerated aging tests. Solder particles offer the opportunity to form fusible linkages [53]. Gold offers the best properties, but the cost may be prohibitive for large-volume applications. Plated glass or polymer particles provide a lower-cost solution. Using a particle with a polymer core offers additional advantages, including low aspect ratio, good particle size uniformity, and compliance, that can help accommodate nonplanar surfaces.

The current-carrying capabilities of different particles will influence particle selection and concentration for a particular application. Measurements of several different materials have been reported [16] that exhibit a range of almost two orders of magnitude, as shown in Table 5.

2. *Adhesive Matrix*

Both thermoplastic and thermosetting adhesives are used to formulate anisotropically conductive adhesives. During assembly, thermoplastics must be heated above their glass transition temperature (T_g) to achieve good adhesion and electrical interconnection. The T_g value must be sufficiently high to avoid polymer flow during use but sufficiently low to prevent thermal degradation of the substrate and device. The ease with which joints can be assembled and repaired are the primary advantages of thermoplastic matrices. Typically, the electrical interconnections are characterized by moderate reliability and their use is restricted to consumer products.

Thermosetting matrices, such as epoxies and thermosetting hot-melt adhesives, are used where increased reliability is required. Repair of anisotropically conductive interconnections assembled with thermoset adhesives is problematic, however, as the adhesive matrix must be removed completely from the substrate and device prior to reassembly.

An additional consideration for the selection of an adhesive system is that robust bonds must be formed to all surfaces involved in the interconnection. Materials commonly found include metallizations on the substrate and components (e.g., gold, solder, copper, aluminum, and indium tin oxide), polymer substrates and coatings (e.g., polyimide, polyester, epoxy, and acrylic adhesives), and chip passivation layers (e.g., SiO_2 and SI_3N_4). Adhesion promoters may be required.

The thickness of the adhesive applied to the substrate should be considered in the early stages of formulation. The required thickness is a function of the geometry of the substrate and device to be interconnected. If a film adhesive is used, the film thickness must be sufficient to fill the gap between substrate and device to prevent void formation, as illustrated in Fig. 6a. The film thickness cannot be arbitrarily large, however, as the bonding temperatures, pressure, and time must be sufficient to displace the excess

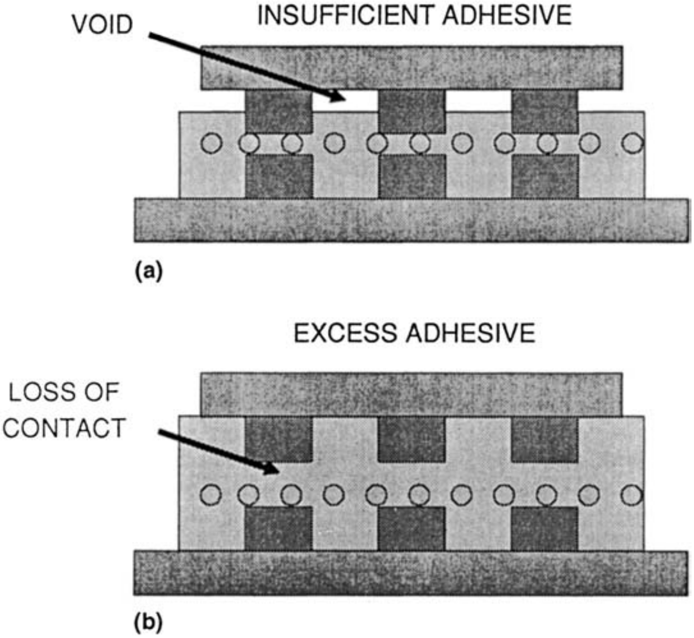

Figure 6 Effect of adhesive thickness on anisotropically conductive adhesive interconnections.

adhesive. Loss of electrical contact can result when the final bond line is greater than the diameter of the fillter particles, as shown in Fig. 6b.

Paste adhesives are less sensitive to height variations due to their lower viscosities. Particles in a low-viscosity matrix, however, are more susceptible to settling and agglomeration. This may lead to loss of isolation if the paste thickness applied is too great.

VI. MANUFACTURING WITH CONDUCTIVE ADHESIVES

A. Dispensing

Conductive adhesives are applied to the substrates using a wide range of standard techniques. For die attach applications, the isotropically conductive adhesive is applied using either a stamping tool or a syringe dispenser. To ensure complete void-free coverage, sophisticated multineedle syringe dispensers have been developed. Stencil and screen printing are used for the placement of isotropically and anisotropically conductive adhesive pastes on PWBs for the assembly of surface-mounted components. The development of ink-jet technology may prove to be another economical means of dispensing precise quantities of conductive adhesive paste [54]. Placement of anisotropically conductive films is accomplished by hand or by pick-and-place equipment.

B. Assembly

When using isotropically conductive adhesives, placement of components is performed by the same equipment as used for nonadhesive attachment techniques. Die bonders are similar to those used for eutectic bonding except for the type of adhesive dispenser. Surface-mounted placement machines developed for solder paste assembly can also be used with conductive adhesive pastes. After placement, the adhesives are cured in either batch or conveyorized ovens.

Assembly with anisotropically conductive adhesives is more complex, as the electrical interconnections require the simultaneous application of heat and pressure. For assembly of flex to rigid substrate interconnections, thermal compression bonders are used with either metal or ceramic hot bars. Pressures are typically in the range 25 to 100 kg/cm^2 [9]. Surface mounting of components with anisotropically conductive adhesives is usually accomplished by serial processes. Equipment similar to solder rework stations is used, where a device is aligned, placed into the adhesive, and cured under pressure with the application of heat by hot gas jets. This process is slow and difficult to control. Equipment costs are high due to low throughput resulting from curing each device in the placement machine. The pressure required to achieve interconnection will depend on the number and type of leads. A reliable batch processing technique, where all components on a PWB are cured simultaneously under pressure, is required before anisotropically conductive adhesives can be used for large-volume manufacturing of surface-mounted components.

Assembly of silicon chips onto substrates with anisotropically conductive adhesives uses specialized equipment, initially developed for flip-chip solder and TAB inner lead bonding. Heat and pressure are transmitted to the adhesive through a thermode attached to a robotic arm or a high-precision linear translator. Equipment requirements are more demanding than for solder assembly, as no self-alignment can occur. A minimum placement accuracy of ± 0.0005 in. is required. Coplanarity between the substrate and die is critical; one study reports maintaining coplanarity to within 0.00004 in. [19]. The pressure required to achieve interconnection depends on the size of the die, the type of conductive particle used, and the viscosity of the adhesive at the bonding temperature.

C. Reliability of Electrical Interconnections

The reliability of conductive adhesive electrical interconnections depends on the individual formulation and process employed [55]. In addition, the test vehicle configuration will strongly influence results. No comprehensive studies have been published, however, and no attempts to correlate chemical composition or a specific process variable to reliability performance have been reported.

Most conductive adhesive failures are accelerated by elevated temperature and humidity. In a study of 12 commercially available isotropically conductive adhesives, joint resistance increased between 160 and 35,000% when exposed to 65°C and 85% relative humidity (65/85) [56]. However, some adhesive manufacturers claim resistance change of less than 10% after 1000 h at 60°C and 90% relative humidity [57] and less than 4% after 1000 h at 85/85 [58]. Anisotropically conductive adhesive joints are even more susceptible to early failures under accelerated test conditions due to process variations [16]. Reliability screening tests can be used effectively to iteratively optimize process parameters.

D. Repair

Isotropically conductive adhesive interconnections can be repaired using techniques similar to those used for solder rework. By application of heat locally at a temperature above the T_g value, a section of adhesive can be softened and the device can be removed mechanically. Adhesive residue on the substrate can be removed, if desired, by a mild scraping action. Clean components can be reassembled with the addition of fresh adhesive and the assembly can be cured either by additional application of local heat or by repeating the original cure cycle [59]. Anisotropically conductive adhesive interconnections are more difficult to repair, due to the need to remove previously cured adhesive from all affected surfaces prior to reassembly. Thermoplastic matrices greatly facilitate the repair process.

E. Suppliers of Commercial Conductive Adhesives

The following list includes several commercial manufacturers of conductive adhesives commonly used for die attach as well as other interconnection applications. Many manufacturers sell both isotropically as well as anisotropically conductive materials. The list is not intended to be inclusive but merely to provide initial guidance.

Ablestik Laboratories
AI Technology
Chromerics, Inc.
Emerson & Cumings, Inc.
Epoxy Technology
Furane Products Company
Hitachi
Master Bond
Nippon Graphite
Polyflex Circuits
Quantum Materials
Tra-Con, Inc.
Zymet, Inc.

VII. CURRENT OUTLOOK

Conductive adhesive use should grow in the future. Die attach adhesive manufacturers are continually improving their formulations and developing new products in response to changing requirements (e.g., low stress and “snap cure” formulations). Anisotropically conductive adhesive use will become more widespread, as glass displays become an increasingly significant portion of the electronics market. Widespread replacement of solder paste as an interconnection material for surface-mounted assembly is more difficult to forecast. Isotropically conductive adhesives will probably prove inadequate for very fine pitch components. The use of anisotropics will be contingent on the development of a continuous process technology, as well as the demonstration of robust reliability.

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Adhesives in the Electronics Industry

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I. INTRODUCTION

Although the application of adhesives in the electronics industry is widespread, the production of printed circuit boards (PCBs) creates a demand for a wide spectrum of properties. Technical progress by research and development leads to more miniaturization of components and circuits, to a higher level of integration of printed circuits, and therefore to higher electrical power evolved per square unit. This trend continues. A lot of problems arising from this development could be solved by using special adhesives, sealants, or laminating resins only.

The aim of this short overview is to define the requirements of the electronics industry for adhesives, to derive their profile of properties, and to describe the state of the art. Additionally, encapsulating and sealing materials as well as binders for laminates are treated if there are analogous requirements regarding their properties. One well-known example of this situation is FR4-based material for PCBs, where the epoxy resin acts simultaneously as an adhesive for the copper foil and as a binder for the laminate. The primary fields for application of adhesives in the production of electronic circuits are adhesives for surface-mounted devices (SMDs), binders for laminates and/or adhesives for PCB base material, encapsulating and sealing materials for separate electronic components or complete circuits, and adhesive tapes used, for example, for flexible keyboards, feeding tapes, and covering materials. A variety of products are commercially available for all these applications.

II. REQUIREMENTS OF THE ELECTRONICS INDUSTRY ON ADHESIVES

As stated earlier, the main requirements for adhesives in the electronics industry result from the increasing miniaturization of the electronic devices, which is manifested in an increasing number of pins with decreasing distance between them. Therefore, both the number of leads per square unit of the circuit board increases and the conductor width decreases. Additionally, the "concentration" of devices on the board increases. Further requirements on the adhesives arise from the necessity of reaching high production rates using a simple technology with low energy consumption and of dealing with substances that are harmless for health and environment. From all these facts the following primary requirements result:

1. Precise casting and dosing of the polymeric material is necessary to ensure electrical insulation between the conducting tracks on a PCB. Additionally, the adhesive should not shrink or creep irreversibly during manufacture of electric circuits (e.g., heating by soldering or curing processes, mechanical stresses by automatic insertion). For these reasons, the thermal expansion coefficients of the adhesives should be in the same range as those of the devices and the PCB.
2. The increasing quantity of power dissipation per square unit as a result of the rising density of devices on PCBs leads to higher operating temperatures. Therefore, the thermal resistance of the applied adhesives has to correspond with the operating temperatures. Furthermore, a low dielectrical constant is essential for the adhesives and/or binders used for laminates because the heat dissipation is a result of dielectrical losses.
3. Up to now the electrical connection of devices and conducting tracks is made by solder processes, and therefore the adhesives have to withstand temperatures of about 260°C for a short time without remarkable losses in their performance. Up to now, conducting adhesives for electrical connections as an alternative have been used in special applications only.
4. The adhesives have to show adjusted rheological behavior. Depending on the application, materials with both high and low viscosity, with and without thixotropy, and with and without yield point are needed.
5. Since electronic circuitries have a filigree structure, they are sensitive against corrosive media. For this reason they must be covered with coatings or sealants of high purity. Alkaline and chloride ions and residual solvents especially have to be avoided.

III. CHEMICAL BASE OF ADHESIVES FOR THE ELECTRONICS INDUSTRY

The chemistry of polymeric materials used for adhesives in the electronics industry does not differ from that of polymers for other applications. Taking into account the requirements mentioned in Section II, it becomes clear that reactive resins evolving no volatile substances during the curing process are of special interest. The following polymeric materials are of particular importance:

1. *Expoxies* [unmodified types of bisphenol A, higher functionalized resins, novolac epoxies, cycloaliphatic resins, heterocyclic resins; one- and two-component systems; curing at room temperature, at elevated temperatures, or by ultraviolet (UV) irradiation], used as mounting adhesives, coverings, and binders for laminates [1,2]
2. *Acrylics* (cyanoacrylates; anaerobic, by heating or UV-irradiation cross-linking acrylates) for mounting adhesives, sealants, and for adhesive tapes [2,3]
3. *Silicone resins* (at room temperature or by heating and by UV-irradiation curing products) mainly for sealings and coverings [4]
4. *Polyimides* as mounting adhesives [1]

Since epoxies and acrylics are the most important base resins for adhesives in the electronics industry, they will be described in more detail.

A. Epoxy Resins

Examples of the resin components of expoxies are listed in Table 1. Several chemical substances can be used as hardeners for epoxies [5,6]. The two main groups of cross-linking agents used in industry are two or more functionalized amines and anhydrides of carboxylic acids. Cross-linking with amines is possible at room temperature as well as at elevated temperatures, depending on the chemical structure of the amines (Table 2). Anhydrides of carboxylic acids react at elevated temperatures only.

The cross-linking of epoxies by amines follows the addition of a primary amine with two epoxy groups, resulting in a tetrafunctional branching point, as one can see in Fig. 1. For the reaction of anhydrides with epoxy groups, the presence of a small fraction of hydroxyl groups (e.g., secondary hydroxyl groups of oligomeric epoxies) is necessary.

Table 1 Examples of Resin Components of Epoxies

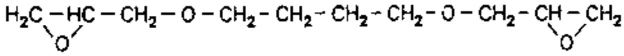
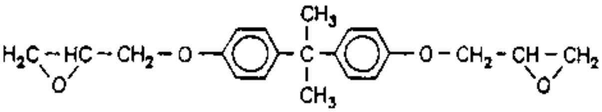
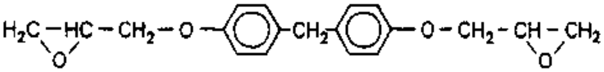
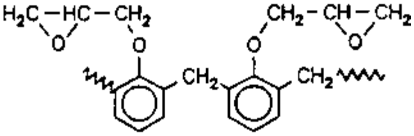
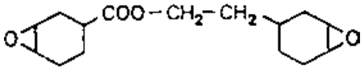
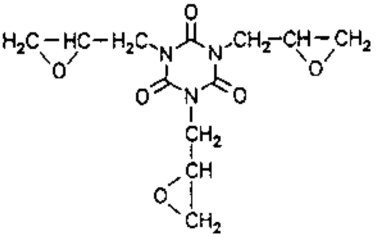
Structural formula	Name
	Butandiol–diglycidyl ether
	Bisphenol A–diglycidyl ether
	Bisphenol F–diglycidyl ether
	Novolac–epoxy–resin
	Cycloaliphatic epoxy resin
	Triglycidyl isocyanurate

Table 2 Reaction Temperatures of Amine-Based Hardeners

Amine	Cross-linking temperature (°C)
Aliphatic	Room temperature
Cycloaliphatic	50–100
Aromatic	80–150

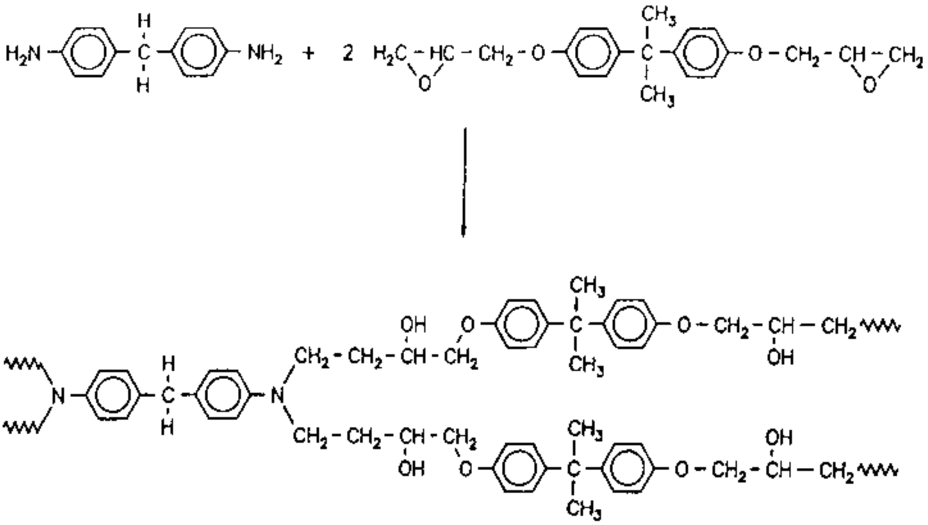


Figure 1 Cross-linking of epoxies by amines (simplified scheme).

At elevated temperatures a hydroxyl group reacts with an anhydride and then the carboxylic group of the resulting half-ester reacts with an epoxy group to get an adduct, as one can see from Fig. 2. Epoxies may be polymerized through cationic polymerization, initiated by UV radiation (Fig. 3).

B. Acrylic Resins

Acrylic resins used as adhesives are formed through radical or anionic polymerization [6]. Radical polymerization can be initiated by UV radiation as well as heat. The two reaction schemes are identical in principle (Fig. 4). Cyanoacrylates are of special interest for systems with very high reaction rates. Their reaction follows an anionic polymerization mechanism. Since the polarity of the cyanoacrylates is very high, water is able to act as an initiator (Fig. 5).

IV. MOUNTING ADHESIVES

Mounting adhesives are needed for the fixation of components in circuit boards during the loading process using surface-mounting technology (SMT) prior to soldering. As an alternative method, electrical-conducting adhesives can be used for the fixation of components. The advantage of this technique is that the soldering process can be avoided. Using SMD components for loading of PCBs, either an adhesive or a solder paste is needed to fix the devices. Which variant is selected for a particular application depends primarily on the board design. If a mixed loading of SMD components together with leaded devices must be used, fixation by an adhesive is the only applicable variant, but by using pure SMD loading, both adhesive and solder paste can be applied. It must be noted that the strength of fixation achievable by adhesives is higher than that achievable by solder pastes. On the other hand, an additional technological process, complete curing of the adhesive, is necessary. This disadvantage can be mitigated by using electrical-conducting adhesives, thus avoiding soldering altogether.

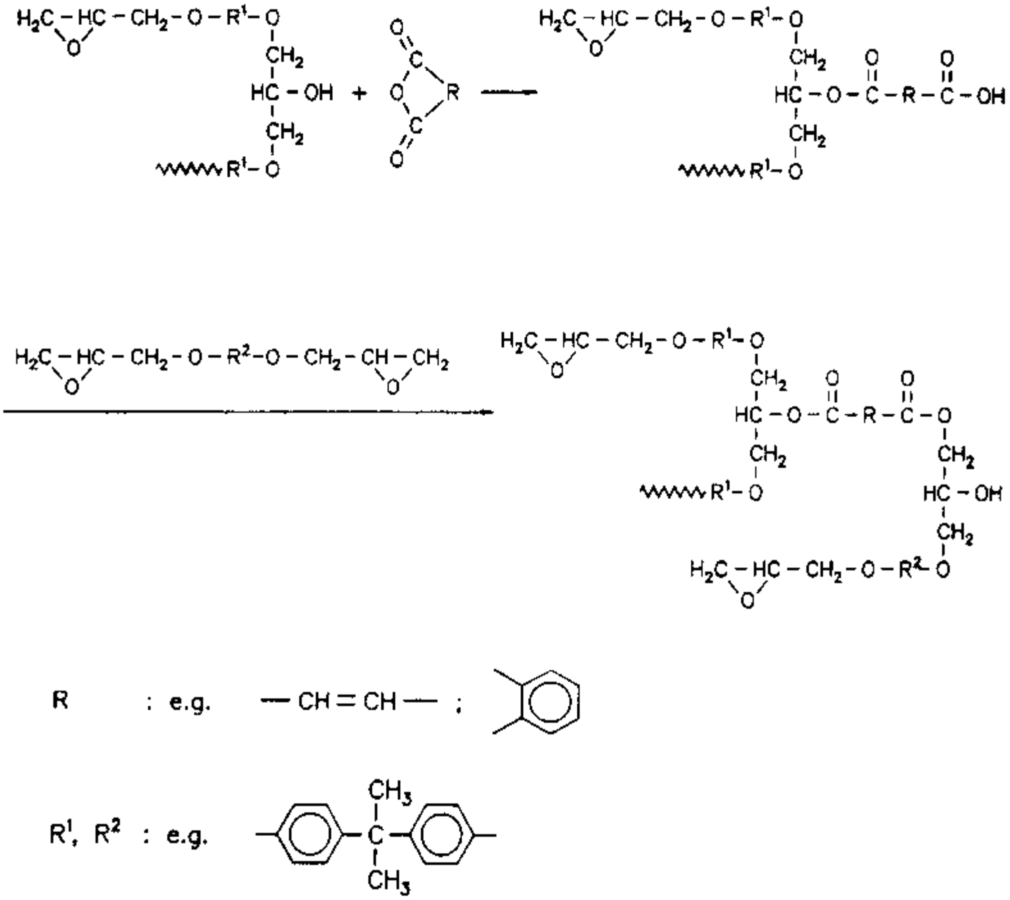


Figure 2 Cross-linking of epoxies by anhydrides (simplified scheme).

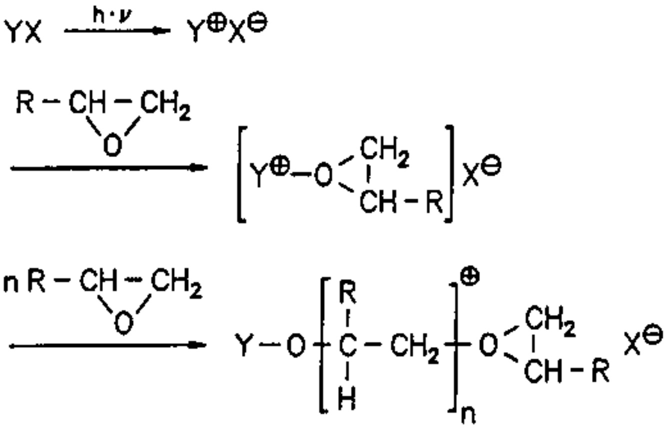


Figure 3 UV-initiated polymerization of epoxies.

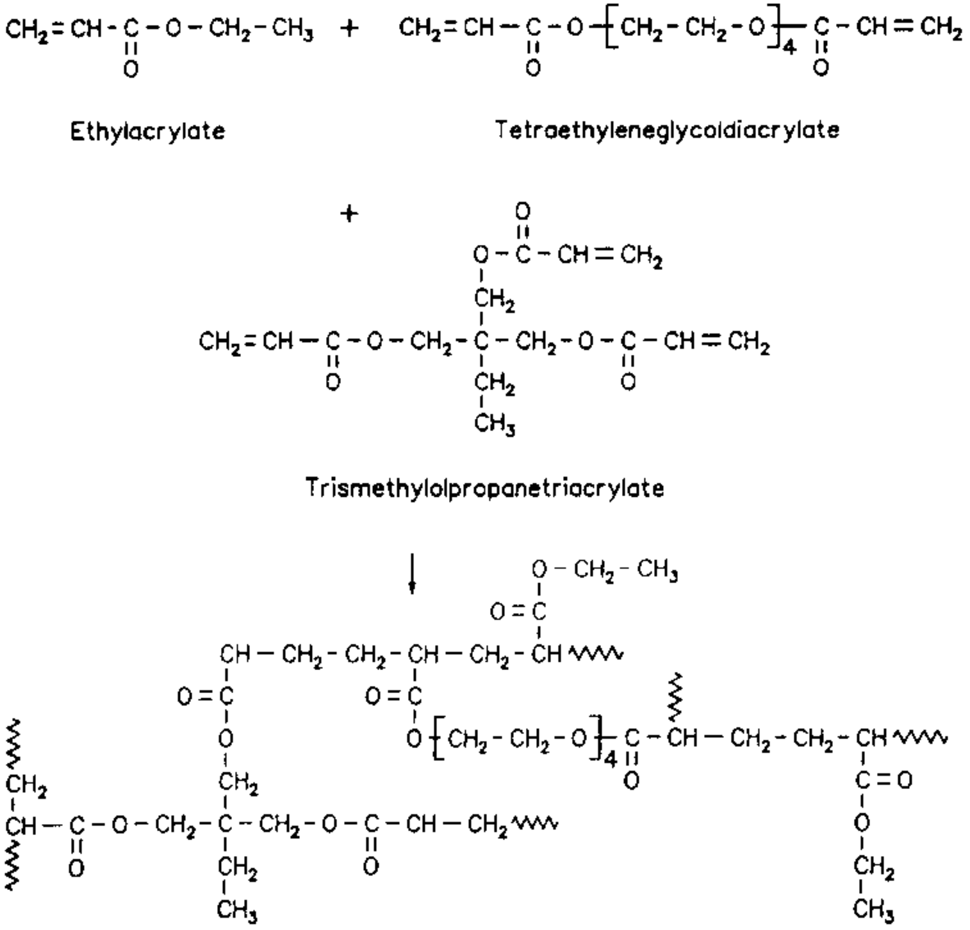


Figure 4 Cross-linking of acrylate resins through radical polymerization (simplified scheme).

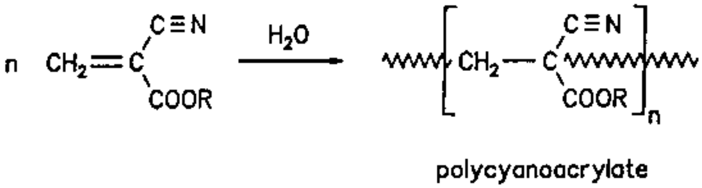


Figure 5 Polymerization of cyanoacrylates.

Requirements of SMD adhesives:

1. High adhesive strength of the uncured resins (wet adhesion) to get exact fixation of the components
2. Sufficient final strength after curing to guarantee the mechanical stability of the PCB
3. High curing rates at low temperatures to minimize the thermal stresses of thermally sensitive components
4. Low dielectrical losses

5. Processing behavior that meets such technological requirements as:
    a. One-component systems to avoid mixing failures
    b. Homogeneous systems, especially if filled adhesives are used
    c. Sufficiently long pot life
    d. Rheological behavior adjusted to the dosing process used

A. State of the Art

1. *Adhesives*

The most commonly used adhesives in the electronics industry are thermosetting one-component epoxy resins and UV-irradiation cross-linking acrylates [7].

Thermosetting epoxy resins. Generally, thermosetting epoxy resins are mixtures of the following:

Resins	50–80 wt %
Hardeners	20–50 wt %
Accelerators	0–3 wt %
Fillers, dyes, modifiers	0–20 wt %

At this time, thermosetting epoxy resins are the most important adhesive systems used for mounting [2]. One reason for their successful use for a long period is due to the great variability of their properties, which can be adjusted to a lot of requirements. Other advantages are simple processibility and good thermal stability. Furthermore, using modern efficient accelerator systems, the curing temperature of epoxies could be decreased to temperatures lower than 100°C and times shorter than 15 min. In this way, the thermal stressing of temperature-sensitive components can be minimized.

UV-cross-linking acrylate resins. Generally, UV-curing acrylate resins contain [8]:

Reactive oligomers/prepolymers	50–80 wt %
Monomers/reactive thinners	10–40 wt %
Photoinitiators/stabilizers/accelerators	1–5 wt %
Inhibitors/dyes	1–5 wt %

The advantages of UV-curing acrylates are curing times under UV irradiation of only a few seconds and the low energy consumption of UV lamps compared to the thermal energy needed for thermosetting systems. On the other hand, these adhesives cannot be cured completely by UV irradiation. Therefore, postcuring is necessary. Commercially available adhesives (e.g., epoxy acrylates, urethane acrylates, polyester acrylates, silicon acrylates, and methacrylates) contain functional groups, which allow complete hardening. It must be noted that due to the lower glass transition temperature of these polymers than of thermosetting epoxy resins, their maximum operating temperature is limited.

Electrical-and/or thermal-conducting adhesives [1,9]. The epoxies and acrylates described above are filled with metal powders to get electrical-conducting adhesives. For special applications polyimide and silicone adhesives are used also. Since the metallic particles must touch each other inside the resins to reach a sufficient level of conductivity, a metal content of 70 to 80 wt % is necessary. Silver is the metal generally used, since specific resistances of the filled adhesives down to about $10^{-4}\ \Omega\,\mathrm{cm}$ can be achieved (metallic silver has a specific resistance of $1.6 \times 10^{-6}\ \Omega\,\mathrm{cm}$). Using other metals, such as copper or nickel, the accessible electrical conductivity is too small. On the other side, copper-filled resins show good thermal conductivity and are therefore used for such applications where heat dissipation is of importance. To reach high heat dissipation levels, ceramic fillers such as aluminum oxide or boron nitride in a quantity of about 60 to 75 wt % are used. The resulting adhesives reach thermal resistances of 5 to 7 K/W. The main advantages of electrical conducting adhesives are (1) better resistance against mechanical stresses, resulting from large temperature variations compared with solder connections, and (2) electrical connections obtained at low temperatures since soldering is not required.

2. Deposition Processes

Adhesives of various rheological properties are available for the usual deposition processes: screen printing, pin transfer, and dispensing [7]. The adhesive droplet must have a definite height and size, which depend on the board design and the type of component, to bridge the distance between the surface of the circuit board and the electronical component. This can be achieved by a specific adjustment of the adhesive rheology, especially thixotropy and yield point. Usually, the adhesive is deposited on the board. If higher distances between board and device have to be bridged, an additional deposition of the adhesive on the underside of the component may be favorable to ensure wetting of both parts to bond and to counteract the drain-away of adhesive by gravitation. Some examples of distances between circuit board and various components are shown in Fig. 6. The usual diameter/height ratio of an adhesive droplet is about 10:1. Commercially available SMD adhesives may have ratios of up to 1:1 (Fig. 7).

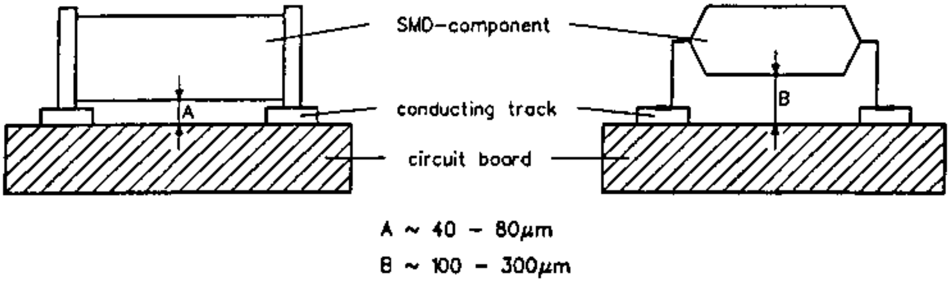


Figure 6 Droplet heights of SMD adhesives.

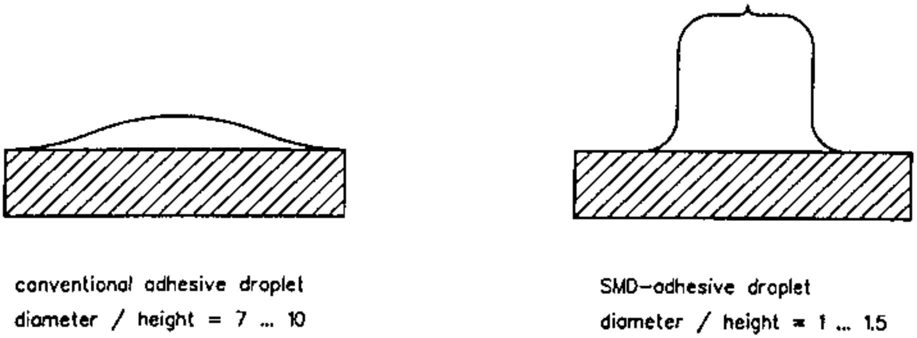


Figure 7 Comparison of droplet heights for conventional and SMD adhesives.

V. ENCAPSULANTS AND SEALINGS

Protection of components or of the entire circuit board against environmental influences is necessary in many fields of application to ensure proper operation. For this purpose special sealants and encapsulants based on curable epoxies, acrylates, and silicons were developed. Polyurethanes and polyimides are also used as encapsulants and sealings but have only limited importance. Requirements for sealings and encapsulants are:

1. Good wetting of the substrate and sufficient adhesion
2. Resistance against high and low temperatures, moisture, and corrosive media
3. Good processibility
4. Adjusted rheological behavior
5. Good elasticity to withstand mechanical stresses

A. State of the Art

A lot of problems arising from the requirements for encapsulants and sealings can be solved using modified epoxy and acrylate resins [2,10]. Furthermore, silicones became important, which is due to their high heat resistance, good elasticity, maintenance of their electrical properties over a wide range of temperatures and frequencies, and nonflammability [4]. A special type of application of silicones are the silicone gels, which are weakly cross-linked silicone rubbers and behave like elastic liquids. Owing to their good mechanical damping properties, silicon gels are used for encapsulating such components that must be protected against vibrations. On the other hand, encapsulated components are easy to repair since the polymer molecules of these silicones have sufficient mobility for ‘‘self-healing.’’

VI. ADHESIVE TAPES

Two types of tapes are discussed: carrierless adhesive foils (also called transfer adhesives) used, for example, in mounting or laminating processes, and tapes consisting of an adhesive on a carrier tape, used for contact and distance films in foil keypads, covering tapes in galvanizing and solder processes (Fig. 8), and as component supply in insertion installations (Fig. 9). The tape properties required depend, of course, on the type of application. Therefore, the following properties are important for component supply tapes [12]:

1. Constant width of tapes to avoid malfunctions of the handler
2. Sufficient adherence of the components on the tape
3. Stability of the adhesive against aging

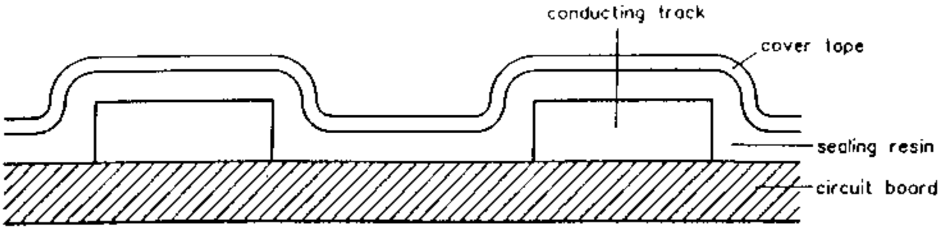


Figure 8 Covering tape with plastic sealing mass. (From Ref. 11.)

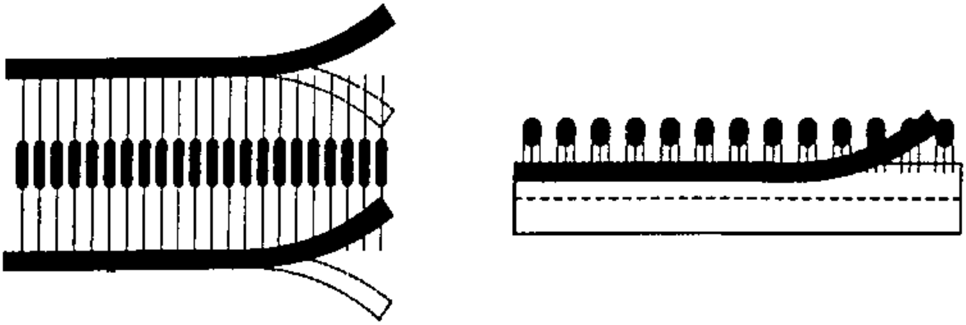


Figure 9 Two examples of adhesive tapes for component supply. (From Ref. 3.)

4. Possible tape lengths up to 5000 m on a spool for effective production
5. Well-defined strength–elongation behavior

It must be noted that the adhesion properties and aging behavior of the supply tapes are determined by the corresponding properties of the adhesives used, whereas the mechanical strength depends primarily on the carrier tape.

A. State of the Art

Tapes for component supply in loading installations usually consist of an acrylate- or rubber-based adhesive (also thermosetting) on a paper or polyester foil carrier (dependent on the mass of the components). Depending on the type of application, different materials are used for the adhesive and the carrier for covering tapes. Most important carrier materials are foils (PVC, polypropylene, cellulose, polyester, polyimide), papers, and woven and nonwoven fabrics (cotton, glass). Adhesives frequently used are based on rubbers, silicones, and acrylates. Carrierless adhesive foils are used, for example, for the bonding of copper foils and polyimide films to get special base materials for circuit boards.

VII. ADHESIVES FOR BASE MATERIALS FOR CIRCUIT BOARDS

The majority of base materials for circuit boards are combinations of a copper foil with a laminate, where the laminate itself consists of a carrier material and a resin. Thus properties of the base material such as mechanical strength, dimensional stability, and processibility are determined primarily by the carrier material. On the other hand, the resin materials are responsible for the thermomechanical and electrical properties as well as for its resistance against chemicals and moisture. Frequently used carrier materials are based on glass and carbon fibers, papers, and polyamide, whereas the majority of the laminating resins are thermosets such as epoxies, phenolics, cyanates, bismaleimide triazine (BT) resins, maleimides, and various combinations of these [13].

Furthermore, the overall properties of the base materials for circuit boards are determined essentially by the joint between the copper foil and the laminate. This joint can be realized by both an added adhesive and by the laminating resin itself, which additionally, acts as adhesive. An additional adhesive is needed in the manufacture of flexible circuit boards (e.g., polyimide/copper) or of paper-based rigid circuit boards. During this process the adhesive is deposited on the bottom side of the copper foil after it is joined to the laminate by heating under pressure. The primary requirements for such adhesives are:

1. Adjustable processing behavior
2. Systems without or with low organic solvent contents
3. Sufficient bonding strength at elevated temperatures (250 to 320°C for short times)
4. Dielectrical stability, low dielectric constant
5. Resistance against etching and galvanic processes

For the production of base materials for circuit boards with higher performance (e.g., glass/epoxy or graphite/cyanate ester combinations) and of multilayer boards, the laminating resin acts as adhesive or special bonding prepregs must be used. The requirements for the resins, which act as adhesive, depend on both the processing conditions and the desired properties of the final circuit board and are similar to those described above.

A. State of the Art

Base materials for circuit boards based on phenolic resin/paper laminates are used primarily for low-performance materials, which are needed, for example, in consumer electronics. The actual properties standard of these materials meets the requirements of the market. The laminating adhesives used for the manufacture of base materials are organic solutions or aqueous dispersions of thermosetting resins such as poly(vinyl butyral)–phenolic resin or acrylate–phenolic resin.

Flexible circuit boards consist primarily of polyimide-based carriers. The problem of bonding the copper foil on the polyimide carrier has not yet been solved satisfactorily. Due especially to their low bonding strength at elevated temperatures, the production of such materials is very limited. Nevertheless, adhesives for copper–polyimide systems were developed, where one-component epoxy resins (e.g., epoxy–polyester mixtures) and reactive hot melts (e.g., phenolic resin–nitrile rubbers) reached importance.

A wide range of high-performance materials for circuit boards is available for such systems, where the laminating resin acts simultaneously as adhesive for the copper foil. The majority of the systems consist of resins, which are based on epoxies, bismaleimides, cyanates, BT resins, and carrier materials, made from glass and carbon fibers and polyamides. Since the properties of the resins are adjustable over a wide range using combinations and modifications of the resins, the bonding strengths desired for the resulting circuit board base materials can be achieved for almost all kinds of applications. On the other hand, further developments are needed to get base materials having, for example, high thermal and moisture resistance.

VIII. OUTLOOK

The future development of electronical circuitries will be characterized by miniaturizing of components and circuits as well as a more and more dense packing of components on the printed circuit board. For this reason, the surface-mounting technology of electronical components will become more and more important. Additionally, using SMD techniques, a higher level of production of electronical circuitries can be reached. The preparation of special adhesives in one important precondition for the success of SMD techniques. In this connection it is essential to look for new reaction principles for one-component adhesives having higher curing rates at lower temperatures to increase the production rates and reduce the energy consumption and to replace the solder process by electrical- and/or thermal-conducting adhesion bondings.

The next era in loading technology has already begun. This technology is characterized by conducting tracks made in thin-layer technology by metal-sputtering processes and by electronical functions realized in thick-layer technology by structurated deposition of inorganic or organic pastes with well-defined electrical properties. Concerning this matter, the development of organic pastes with well-defined and adjustable electrical properties and rheological behavior is necessary.

In the future, environmental protection will become more and more a matter of concern. Harmless technologies and recycling processes for both the adhesives and the entire circuits will have to be developed. In this connection, the following requirements must be met by the polymeric materials: nontoxicity, low, or no, volatile-product content during use, suited for repairing and disassembling processes of components and recycling.

ACKNOWLEDGMENT

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Adhesives in the Wood Industry

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I. INTRODUCTION

Progress in research and development within the wood-based industry and within the adhesive industry has shown many successes during the past few decades. Notwithstanding this, the industrial requirements of the wood industry still induce technical improvement in the adhesives and their application in this area. What drives this technical development is the search for "cheaper," "faster-curing," and "more complex" adhesives. The first two requirements are caused by the heightened competition within the wood industry and efforts to minimize costs at a certain level of product quality and performance. The requirement "more complex" stands for new and specialized products and process. Adhesives play a central role within wood-based panels production. The quality of bonding and hence the properties of the wood-based panels are determined mainly by the type and quality of the adhesives. Development in wood-based panels, therefore, is always linked to development in adhesives and resins.

Both the wood-based panels industry and the adhesive industry shown a high commitment to and great capability towards innovation. The best evidence for this is the considerable diversity of types of adhesives used for the production of wood-based panels. Well known basic chemicals have been used for a long time for the production of adhesives and their resins, the most important ones being formaldehyde, urea, melamine, phenol, resorcinol, and isocyanate. The greater part of the adhesive resins and adhesives currently used for wood-based panels is produced with these few raw materials. The "how to cook the resins" and the "how to formulate the adhesive" therefore become more and more complicated and sophisticated and are key factors to meet today's requirements of the wood-based panels industry.

The quality of bonding and hence the properties and performance of the wood-based panels and beams are determined by three main parameters:

the wood, especially the wood surface, including the interface between the wood surface and the bondline
the applied adhesive
the working conditions and process parameters.

Good quality bonding and adequate properties of the wood-based panels can be attained only if each of these three parameters contributes to the necessary extent to the bonding and production process.

In this chapter are then covered the types of adhesives used in the wood industry and their characteristics. The influences on their performance of the adhesives' physicochemical characteristics, of their application parameters, of the wood itself, and of the wood composite process parameters are also described. In wood adhesives the application parameters other than the characteristics of the adhesive itself account for around 50% of performance.

II. TYPES OF WOOD ADHESIVES

In the wood-based panels industry a great variety of adhesives are currently is use. Condensation resins based on formaldehyde represent the biggest volume within the wood adhesives field. They are prepared by the reaction of formaldehyde with various chemicals such as urea, melamine, phenol, resorcinol, or combinations thereof. At delivery these adhesive resins are mainly liquid and consist of linear or branched oligomers and polymers in aqueous solution or dispersion. During hardening and gelling they convert to three-dimensionally crosslinked and, therefore, insoluble and nonmeltable networks. The hardening conditions used can be acidic (for aminoplastic resins), highly alkaline (for phenolic resins), or neutral to lightly alkaline (for resorcinol resins). Isocyanates [especially polymeric 4,4′-diphenyl methane diisocyanate (PMDI)] are another important chemical group used for various applications in the wood industry, especially for water resistant bonds. In Table 1 are reported the main wood adhesives in use today with their main applications.

III. OVERVIEW ON REQUIREMENTS CONCERNING WOOD ADHESIVES

Table 2 summarizes the general parameters of importance for wood adhesives. Research and development in adhesives and resins are mainly driven by the requirements of the bonding and production processes and by the intended properties of the wood-based panels. These requirements are summarized in Table 3.

The necessity to achieve shorter press times is omnipresent within the woodworking industry, to keep production costs low. An increased production rate gives the chance to reduce production costs. This is only valid when the market is able to absorb such a high level of production. Shorter press times within a given production line and for certain types of wood-based panels can be achieved by, among others:

highly reactive adhesive resins possessing rapid gelling and hardening and steep increase in bonding strength even at a low degree of chemical curing

highly reactive adhesive glue mixes obtained by the addition of accelerators, special hardeners, crosslinkers, and others

the optimization of the pressing process, e.g., by increasing the effect of the steam shock by (i) increased press temperatures, (ii) a more marked difference in the moisture content between the surface and the core layer of the panel before hot pressing, or (iii) an additional steam injection step.

constancy of as many parameters of the production process as possible.

Table 1 Fields of Application for Various Wood Adhesives

Adhesive type	V20	V100	V313	FP	MDF	PLW	HLB	MH	ven.	furn.
UF	x				x	x	x	x	x[a]	x[a]
MUF	x[b]				x					
MF/MUF		x	x		x	x	x	x		
MUPF		x			x	x				
PF/PUF		x		x	x	x	x			
RF							x			
PMDI	x	x			x					
PVAc								x	x	x
old nat.adhesives										x
nat.adhesives	x	x	x		x	x				
inorg.adhesives	x			x[c]						
activation				x						

UF, urea–formaldehyde resin; MUF, melamine fortified UF resin; MF/MUF, melamine and melamine–urea resins (MF resins are only used mixed/coreacted with UF resins; MUPF, melamine–urea–phenol–formaldehyde resin; PF/PUF, phenol and phenol–urea–formaldehyde resin; (P)RF, resorcinol–(phenol–)formaldehyde resin; PMDI, polymeric methylenediisocyanate; PVAc, polyvinylacetate adhesive; old nat.adhesives, old (historic) natural adhesives (e.g., starch, glutin, casein adhesives); nat.adhesives, natural adhesives (e.g., tannins, lignins, carbohydrates); inorg.adhesives, inorganic adhesives (e.g., cement, gypsum); activation: activation constituents of wood to function as adhesives (i.e., lignin).

V20, particleboard according to DIN 68761 (parts 1 and 4, FPY, FPO), DIN 68763 (V20) and EN 312-2 to 4 and 312-6; V100, particleboard according to DIN 68763 and EN 312-5 and 312-7, option 2 (internal bond after boil test according to EN 1087-1); V313, particleboard according to EN 312-5 and 312-7, option 1 (cycle test according to EN 321); FP, hardboard (wet process) according to EN 622-2; MDF, medium density fiberboard according to EN 622-5; PLW, plywood according to EN 636 with various resistance against influence of moisture and water; HLB, laminated beams; MH, solid wood panels according to OeNORM B 3021 to B 3023 (prEN 12775, prEN 13353 part 1 to 3, prEN 13017-1 and 2, prEN 13354); ven., veneering and covering with foils; furn., production of furniture.

[a] Partly powder resins.

[b] Boards with reduced thickness swelling, e.g., for laminate flooring.

[c] Special production method.

Table 2 General Requirements for Wood Adhesives

Composition, solids content, viscosity, purity
Color and smell
Sufficient storage stability for given transport and storage conditions
Easy application
Low transport and application risks
Proper gluing quality
Climate resistance
Hardening characteristic: reactivity, hardening, crosslinking
Compatibility for additives
Cold tack behavior
Ecological behavior: Life cycle analysis (LCA), waste water, disposal, etc.
Emission of monomers, Volatile organic compounds (VOC), formaldehyde during production of the wood-based panels and during their use

Table 3 Actual Requirements in the Production and in the Development of Wood Adhesives

Shorter press times, shorter cycle times
Better hygroscopic behavior of boards (e.g., lower thickness swelling, higher resistance against the influence of humidity and water, better outdoor performance)
Cheaper raw materials and alternative products
Modification of the wood surface
Life cycle assessment, energy and raw material balances, recycling and reuse
Reduction of emissions during the production and the use of wood-based panels

Cheaper raw materials are another way to reduce production costs. This includes, for example, the minimization of the melamine content in a MUF resin, to produce boards with reduced thickness swelling or increased resistance against the influence of water and high humidity of the surrounding air. Impeding factors (often temporary) can be the shortage of raw materials for the adhesives, as was the case with methanol and melamine during the 1990s.

Life cycle analysis and recycling of bonded wood boards also concerns the adhesive resins used, since adhesives and resins are one of the major raw materials in the production of wood-based panels. This includes, for example, the impact of the adhesives on various environmental issues such as waste water and effluent management, noxious gas emission during panel production and from the finished boards, or the reuse of panels to burn for energy generation. Furthermore, for certain recycling processes the type of resin has also a crucial influence on their feasibility and efficiency.

Gas emission from wood-based panels during their production can be caused by chemicals inherent to wood itself, such as terpenes or free acids, as well as by volatile compounds and residual monomers coming from the adhesive. The emission of formaldehyde especially is a matter of concern, but so are possible emissions and discharges of free phenols or other materials. The formaldehyde emission noted only after panel manufacture and adhesive resin hardening is due, on the one hand, to the residual, unreacted formaldehyde present in urea–formaldehyde (UF)-bonded boards, or as gas trapped in the wood or dissolved in the moisture still present in the panel. On the other hand, in aminoplastic resins the hydrolysis of weakly bonded formaldehyde from *N*-methylol groups, acetals, and hemiacetals as well as in more severe cases of hydrolysis (e.g., at high relative humidity) from methylene ether bridges, increases again the content of emittable formaldehyde after resin hardening. In contrast to phenolic resins, a permanent reservoir of potentially emittable formaldehyde is the consequence of the presence of these weakly bonded structures. This explains the continuous, yet low, release of formaldehyde from UF-bonded wood-based panels even over long periods. However, the level of emission depends on the environmental conditions, a fact which may be described by the resin hydrolysis rate which indicates if this formaldehyde reservoir will or will not lead to unpleasantly high emission values [1–4]. The higher this hydrolysis rate is, the higher is the potential reservoir of formaldehyde which contributes to subsequent formaldehyde emission. The problem of formaldehyde emission after adhesive hardening in panel manufacture can fortunately be regarded today as solved, due to clear and stringent emission regulations in many European and other countries and to successful long term R&D investement by the chemical industry and the wood working industry.

The so-called E1-emission class regulations shown in Table 4 for different panel products describe the level of formaldehyde emission which is low enough to prevent

Table 4 Actual Regulations Concerning Formaldehyde Emission from Wood-Based Panels According to the German Regulation of Prohibition of Chemicals (formerly Regulation of Hazardous Substances) for E1 Emission Class (the Lowest Emission Types panels)

(a) Maximum steady state concentration in a climate chamber:
  0.1 ppm (prEN 717-1; 1995)
(b) Laboratory test methods (based on experimental correlation experiences):
  Particleboard: 6.5 mg/100 g dry board as perforator value (EN 120; 1992)
  MDF: 7.0 mg/100 g dry board as perforator value (EN 120; 1992)
  Plywood: 2.5 mg/h-m^2 with gas analysis method (EN 717-2)
  Particleboard and MDF: correction of the perforator value to 6.5% board moisture content

any danger, irritation, or inflammation of the mucous membranes in the eyes, nose, and mouth. However, it is important that not only the boards themselves, but also veneering and carpenters' adhesives, lacquers, varnishes, and other sources of formaldehyde be controlled, since they also might contribute to a close environment formaldehyde steady-state concentration [1–4].

IV. AMINOPLASTIC ADHESIVE RESINS (UREA RESINS, MELAMINE RESINS)

The various aminoplastic resins are the most important class of adhesives in the wood-based panels industry, especially for the production of particleboards and medium density fibreboard (MDF), and partly also for oriented strandboard (OSB), plywood, blockboards, and some other types of wood panels. They are also used in the furniture industry as well as in carpenters' shops.

Aminoplastic adhesive resins are formed by the reaction of urea and/or melamine with formaldehyde. Based on the raw materials that are used various types of resins can be prepared, namely:

UF	urea–formaldehyde resin
MF	melamine–formaldehyde resin
MUF	melamine–urea–formaldehyde cocondensation resin
mUF	melamine fortified UF resins
MF + UF	mixture of an MF and a UF resin
MUPF, PMUF	melamine–urea–phenol–formaldehyde cocondensation resin.

The most important parameters for the aminoplastic resins are:

(a) The type of monomers used.
(b) The relative molar ratio of the various monomers in the resin:

F/U	molar ratio of formaldedhyde to urea
F/M	molar ratio of formaldehyde to melamine
$F/(NH_2)_2$	molar ratio of formaldehyde to amide or amine groups, whereby urea counts for two NH_2 groups, and melamine for three NH_2 groups.

(c) The purity of the different raw materials, e.g., the level of residual methanol or formic acid in formaldehyde, biuret in urea, or ammeline and ammelide in melamine.

(d) The reaction procedures used, e.g.

the pH variation sequence
the temperature variation sequence
the types and amount of alkaline and acidic catalysts
the sequence of addition of the different raw materials
the duration of the different reaction steps in the cooking procedures.

The production of aminoplastic adhesive resins is usually a multistep procedure where both alkaline and acidic steps occur. Aminoplastic resins can be prepared in a variety of different types for all the different needs in wood bonding. This can be achieved by just using the three main monomers mentioned above and varying the preparation procedure.

A. UF Resins

Urea–formaldehyde resins [1–9] are based on a series of consecutive reactions of urea and formaldehyde. Using different conditions of reaction and preparation a practically endless variety of condensed UF chemical structures is possible. UF resins are thermosetting resins and consist of linear or branched oligomers and polymers always admixed with some amounts of monomers. The presence of some unreacted urea is often helpful to achieve specific effects, e.g., a better storage stability of the resin. The presence of free formaldehyde has, however, both positive and negative effects. On the one hand, it is necessary to induce the subsequent hardening reaction while, on the other hand, it causes a certain level of formaldehyde emission during the hot press, resin hardening cycle. Even in the hardened state, low levels of residual formaldehyde can lead to the displeasing odor of formaldehyde emission from the boards while in service. This fact has changed significantly the composition and formulation of UF resins during the past 20 years.

After hardening, UF resins consist of insoluble, three-dimensional networks which cannot be melted or thermoformed again. In their application stage UF resins are used as water solutions or dispersions or even in the form of still soluble spray dried powders. These, however, in most cases have to be redissolved and redispersed in water for application.

Despite the fact that UF resins consist of only the two main components, namely urea and formaldehyde, a broad variety of possible reactions and resin structures can be achieved. The basic characteristics of UF resins can be ascribed at a molecular level to:

their high reactivity
their waterborne state, which renders these resins ideal for use in the woodworking industry
the reversibility of their aminomethylene bridge, which also explains the low resistance of UF resins to water and moisture attack, especially at higher temperatures; this is also one of the reasons for the hydrolysis leading to subsequent formaldehyde emission.

The reaction of urea and formaldehyde is basically a two-step process, usually consisting of an alkaline methylolation (hydroxymethylation) step and an acid condensation step. The methylolation reaction, which usually is performed at a high molar ratio ($F/U = 1.8$ to 2.5), is the addition of up to three (four in theory) molecules of bifunctional formaldehyde to one molecule of urea to give methylolureas; the types and the proportions of the formed methylol groups depend on the molar ratio F/U. Each methylolation step has its own rate constant k_i, with different values for the forward and the backward reactions. The formation of these methylol groups mostly depends on the molar ratio F/U. The higher the molar ratio used, the higher the molecular weight the methylolated species formed tends to be. The UF resin itself is formed in the acid condensation step, where still the same high molar ratios as in the alkaline methylolation step is used ($F/U = 1.8$ to 2.5): the methylol groups, urea and the free formaldehyde react with linear and partly branched molecules with medium and even higher molar masses, forming the polydisperse molar mass distribution pattern characteristic of UF resins. Molar ratios lower than approximately 1.8 during this acid condensation step tend to cause resin precipitation.

The final UF resin has a low F/U molar ratio obtained by the addition of the so-called second urea, which might also be added in several steps [8,9]. The second urea process step needs particular care. It is important for the production of resins with good performance, especially at the very low molar ratios usually in use now in the production of particleboards and MDFs. This last step also includes the distillation of the resin solution to usually 66% resin solids content, which is performed by vacuum distillation in the reactor itself or in a thin layer evaporator. Industrial manufacturing procedures usually are proprietary and are described in depth in the literature only in rare cases [7–11].

The type of bonding between the urea molecules depends on the conditions used: low temperatures and slightly acid pHs favor the formation of methylene ether bridges ($–CH_2–O–CH_2–$) and higher temperatures and lower pHs lead preferentially to the formation of more stable methylene bridges ($–CH_2–$). Ether bridges can be rearranged to methylene bridges by splitting off formaldehyde. One ether bridge needs two formaldehyde molecules and additionally it is not as stable as a methylene bridge, hence it is highly recommended to follow procedures that minimize the formation of such ether groups in UF resins. In the literature other types of resin preparation procedures are also described. Some of these yield uron structures in high proportion [12–15] or triazinone rings in the resins [15–17]. The latter are formed by the reaction of ammonia or an amine, respectively, with urea and an excess of formaldehyde under alkaline conditions. These resins are used, e.g., to enhance the wet strength of paper.

The following chemical species are present in UF resins:

free formaldehyde, which is in steady state with the remaining methylol groups and the post-added urea

monomeric methylol groups, which have been formed mainly by the reaction of the post-added urea with the high content of free formaldehyde at the still high molar ratio of the acid condensation step

oligomeric methylol groups, which have not reacted further in the acid condensation reaction or which have been formed by the above-mentioned reaction of post-added urea

molecules with higher molar masses, which constitute the real polymer portion of the resin.

The condensation reaction as well as the increase in the molar mass can also be monitored by gel permeation chromatography (GPC) [18,19]. At longer acid condensation steps, molecules with higher molar mass form and the GPC peaks shift to lower elution volumes.

Because of the necessity to limit the subsequent formaldehyde emission, the molar ratio F/U has been decreased constantly over the years [20]. The main differences between the UF resins with high and low formaldehyde content are the reactivity of the resin due to the different contents of free formaldehyde and the degree of crosslinking in the cured network. The main challenge has been to reduce the content of formaldehyde in the UF resins and to achieve this without any major changes in the performance of the resins. In theory this is not possible, because formaldehyde is the reactive partner in the reaction of urea and formaldehyde during the condensation reaction as well as curing. Decreasing the molar ratio F/U means lowering the degree of branching and crosslinking in the hardened network, which unavoidably leads to a lower cohesive bonding strength. The degree of crosslinking is directly related to the molar ratio of the two components.

The UF resin formulators have revolutionized UF resin chemistry in the past 30 years. For example, in a straight UF resin for wood particleboard the above mentioned molar ratio F/U was approximately 1.6 at the end of the 1970s. It is now 1.02–1.08, but the requirements for the boards (e.g., internal bond strength or percent thickness swelling in water) as given in the quality standards are still unaltered. Also the reactivity of the resin during hardening, besides the degree of crosslinking of the cured resins, depends on the availability of free formaldehyde in the system.

It has, however, to be considered that it is neither the content of free formaldehyde itself nor the molar ratio which should be taken as the decisive and only criterion for the classification of a resin concerning its subsequent level of formaldehyde emission. In reality the composition of the glue mix as well as the various process parameters during board production also determine the level of formaldehyde emission. Depending on the type of board and the process of application, it is sometimes recommended to use a UF resin with a low molar ration F/U (e.g., F/U = 1.03), hence presenting a low content of free formaldehyde; while sometimes the use of a resin with higher molar ratio (e.g., F/U = 1.10) to which a formaldehyde catcher has been added in the glue mix will give better results. Which of these two possible ways is the better one in practice can only be decided by trial and error in each case.

The higher the molar ratio F/U, the higher is the content of free formaldehyde in the resin. Assuming stable conditions in the resins, which means that, e.g., post-added urea has had enough time to react with the resin, the content of free formaldehyde is very similar even for different manufacturing procedures. The content of formaldehyde in a straight UF resin is approximately 0.1% at F/U = 1.1 and 1% at F/U = 1.8 [19–21]. It also decreases with time due to aging reactions where this formaldehyde reacts further. Table 5 summarizes the various influences of the molar ratio F/U on various properties of wood-based panels. Table 6 summerizes the influence of the molar rations F/U and $F/(NH_2)_2$,

Table 5 Influence of the Molar Ratio on Various Properties of UF-Bonded Wood-Based Panels

Decreasing the molar ratio leads to	
a decrease of	the formaldehyde emission during the production of the wood-based panels
	the subsequent formaldehyde emission
	the mechanical properties
	the degree of hardening
an increase of	the thickness swelling and the water absorption
	the susceptibility of hydrolysis

Table 6 Molar Ratios F/U and F/$(NH_2)_2$, Respectively, of Pure and Melamine Fortified UF Resins Currently in Use in the Wood-Based Panels Industry

F/U or F/$(NH_2)_2$ molar ratio	Resin type
1.55 to 1.85	Classical plywood UF resin, also cold setting; use is only possible with special hardeners and additives, e.g., melamine containing glue mixes for an enhanced water resistance
1.30 to 1.60	UF plywood resin; use for interior boards without special requirements concerning water resistance; to produce panels with low subsequent formaldehyde emission, the addition of formaldehyde catchers is necessary
1.20 to 1.30	Plywood or furniture resin with low content of formaldehyde; also without addition of catchers, products with a low subsequent formaldehyde emission can be produced
1.00 to 1.10	E1 particleboard and E1 MDF resins; especially in MDF production further addition of catchers is necessary. Modification or fortification with melamine can be done
below 1.00	MDF resins and special glue resins for boards with a very low formaldehyde emission; in most cases modified or fortified with melamine

respectively, of pure and melamine fortified UF resins currently in use in the wood-based panels industry.

The molar mass distribution of UF resins is determined

by the degree of condensation and
by the addition of urea (and sometimes also other components) after the condensation step; this again shifts the resin mass distribution towards lower average molar masses.

For this reason the molar mass distribution is much broader than for other polymers: it starts at the low molar mass monomers (the molecular weight of formaldehyde is 30, for urea it is 60) and goes up to more polymerized structures. It is not clearly known, however, what are really the highest molar masses in a UF resin. Molar masses of up to 500,000, determined by light scattering, have been reported [18,22]. The conditions of molecular level shear within the chromatographic columns [23] should guarantee that all physically bonded clusters, caused by the interaction of the polar groups present in the resins and which might simulate too high a molar mass, are separated and that these high numbers between 100,000 and 500,000, measured using low angle laser light scattering (LALLS) coupled to GPC, really do describe the macromolecular structure of a UF resin in the right manner. A second important argument for this statement is the fact that up to such a high molar mass the on-line calibration curve determined in the GPC–LALLS run is stable and more or less linear. It does not show any sudden transition as would be the case of a too sharp increase in apparent molar mass if molecular clustering occurred again after the material has passed through the column.

The molar mass distribution (and the degree of condensation) is one of the most important characteristics of the resin and it determines several properties of the resin. Consequence of highly condensed resin structures (high molar masses) are:

the viscosity at a given solids content increases [19,24]
the flowing ability is reduced

the wetting behavior of a wood surface becomes worse [24]
the penetration into the wood surface is reduced [25,26]
the distribution of the resin on the furnish (particles, fibers) worsens
the water dilutability of the resin becomes lower
the portion of the resin that remains soluble in water decreases [22]

Diluting the resin with a surplus of water causes precipitation of parts of the resin. These parts preferably contain the higher molar mass molecules of the resin and their relative proportion increases at higher degrees of condensation [22]. Information on correlations between the molar mass distribution (degree of condensation) and mechanical and hygroscopic properties of the boards produced, however, is rather rare and often equivocal [7,19,27–29].

The influence of the degree of condensation is mostly felt during the application and the hardening reaction (wetting behavior and penetration into the wood surface which depend on the degree of condensation). At higher temperatures, during the curing hot press cycle, the viscosity of the resin drops, before the onset of hardening again leads to an increase of viscosity. With this temporary lowering of the viscosity the adhesive wetting behavior improves significantly, but its substrate penetration behavior also changes. The reactivity of an aminoplastic resin seems to be independent of its viscosity (degrees of condensation), at parity of molar ratio. Ferg [30] mentioned that the bonding strength increased with the degree of condensation of the applied UF resin. The higher molar masses (higher viscosity resin fractions) give a more stable glue line and determine the cohesive properties of the hardened resin [7]. Also Rice [29] and Narkarai and Wantanabe [28] reported that the resistance of a bondline against water attack and redrying increased with the viscosity of the resin. The reason again might be that resins with an advanced degree of condensation remain to a greater extent in the glue line, avoiding resin over-absorption by the substrate and hence avoiding starving of the bondline. Rice [29] found an increase of the thickness of the glue line with an increased viscosity of the resin, obviously due to its lower penetration into the wood substrate. However, it must be taken into consideration that the strength and stability of a glue line decrease with increased glue-line thickness [31]. According to the findings of Sodhi [32] the bonding strength decreases the longer is the waiting time before application of the glue mix. Once the hardening reaction has started and, therefore, the average molar mass has started to increase, the worse the resin wetting behavior and its penetration in the wood surface appears to be.

1. *Cold Tack Properties of UF Resins*

Cold tack means that the particle mat has attained some strength already after the prepress at ambient temperature, without any hardening reaction having occurred. This “green” strength is necessary for better handling of the particle mat during transfer on the production line. This can well be the case in multiopening presses, in special forming presses, or in plywood mills, where the glued veneer layers are prepressed to fit into the openings of the presses. At least a low level of cold tack is also necessary to avoid blowing out and loss of the fine wood particles from the surface when panels enter a continuous press at high belt speeds. On the other hand, cold tack can lead to agglomeration of fine wood particles and fibers in the forming station.

Cold tack is generated during the dry out of glue line, and reaches a maximum after a certain period of time. After this point the cold tack decreases again, when the glue line starts to dry out. Both the intensity of the cold tack as well as the optimum length of time in which it develops after application of the adhesive can be adjusted by the degree of condensation of the resin as well as by using special resin preparation procedures [33–35]. Also various additives can increase the cold tack of the adhesive resins, e.g., some thermoplastic polymers such as poly(vinyl alcohol).

2. *Isocyanate (PMDI) as Accelerator and Fortifier for UF Resins*

Polymeric methylenediisocyanate (PMDI) can be used as an accelerator and as a special crosslinker for UF resins. UF resins and PMDI can be sprayed separately without prior mixing onto the particles [36,37] or for improved performance the two resins can be premixed and then applied [8,38,39]. In the usual mixing procedure PMDI is pumped under high pressure into the UF resin [40,41]. Usually 0.5 to 1.0% PMDI based on dry particles is used, whereas at the same time the UF gluing factor might be reduced slightly. The specific press time is said to be reduced by up to 1 s/mm.

Addition of PMDI to UF resins with a very low molar ratio was also recommended to achieve low formaldehyde emission. The poor properties of the UF resin due to its very low molar ratio can then be improved by the addition of PMDI [42–45].

B. Improvement of the Hygroscopic Behavior of Boards by Melamine Fortified UF Resins (MUF, MUPF and PMUF Resins)

The resin used has a crucial influence on the properties of wood-based panels. Depending on the requirements, different resin types are selected for use. Whereas UF resins are mainly used for interior boards (for use in dry conditions, e.g., in furniture manufacturing), a higher water resistance can be achieved by incoroporating melamine and also some phenol into the resin (melamine fortified UF resins, MUF, MUPF, PMUF). The level of melamine addition and especially the resin manufacturing sequence used in relation to how melamine is incorporated in the resin can be very different. The different types of these resins which exist today are given in Table 7. The different resistances of these resins against hydrolysis are based on their differences at the molecular level. The methylene bridge linking the nitrogens of amido groups can be split rather easily by water attack in UF resins. The same is not so easy in the case of M(U)F resins, mainly due to the much lower water solubility of melamine itself which is a consequence of the water repellency

Table 7 Molar Ratios $F/(NH_2)_2$ of MUF/MUPF Resins Currently in Use in the Wood-Based Panels Industry

$F/(NH_2)_2$ molar ratio	Resin type
1.20 to 1.35	Resins for water resistant plywood, in the case of the addition of a formaldehyde catcher
0.98 to 1.15	E1 particleboard resin and E1 MDF resin for water resistant boards (PB: EN 312-5 and 312-7; MDF: EN 622-5). For particleboards according to option 1 (V313 cycle test) MUF resins can be used; for boards according to option 2 (V100 2 h boiling test, tested wet) MUPF or MUF with a special approval is necessary. In this case, especially for the MDF production, formaldehyde catchers are added
$\ll 1.00$	Special resins for boards with very low formaldehyde emission during board service [81,82]

characteristic of the triazine ring of melamine. The equivalent methylene bridge is instead very stable to hydrolytic attack in phenolic resins. The melamine fortified products, however, are much more expensive due to the much higher price of melamine compared to urea. Therefore, the content of melamine in these resins is as high as strictly necessary but always as low as possible.

A MUF resin, at parity of all other conditions, yields a lower pH drop after addition of the hardener than a UF resin [46]. This lower drop of the pH due to the buffer capacity of the triazine ring of melamine, however, also causes a decrease of the hardening rate of the resin and, therefore, a lengthening of its gel time [1], hence a lengthening of the hot press time is necessary. This is also seen in the shifts of the exothermic differential scanning calorimetry (DSC) peak of hardening which are observed in thermal experiments [47].

The deterioration of a bondline and hence its durability under conditions of weathering is determined essentially by:

The failure of the resin (low hydrolysis resistance, degradation of the hardened resin causing loss of bonding strength).

The failure of the interface between the resin and the wood surface (replacement of physical bondings between resin and reactive wood surface sites by water or other nonresin chemicals). The adhesion of UF resins to cellulose is sensitive to water not only due to the already mentioned lability to hydrolysis of the methylene bridge and of its partial reversibility, but also because theoretical calculations have shown that on most cellulose sites the average adhesion of water to cellulose is stronger than that of UF oligomers [8,48]. Thus, water can displace hardened UF resins from the surface of a wood joint. The inverse effect is valid for PF resins [8,49].

The breaking of bondings due to mechanical forces and stresses: water causes swelling and, therefore, movement of the structural components of the wood-based panels (cyclic stresses due to swelling and shrinking, including stress rupture).

The durability of a glue line can be enhanced by the incorporation of hydrophobic chains into the hardened network. This was done by introducing urea-capped di- and trifunctional amines containing aliphatic chains into the resin structure or by using the hydrochloride salts of some of these amines as a curing agent [50–54]. By this approach some flexibility is introduced into the hardened network, which should decrease internal stresses.

In UF resins the aminomethylene link is susceptible to hydrolysis and, therefore, it is unstable at higher relative humidity, especially at elevated temperatures [55,56]. Water also causes degradation of the UF resin with greater devastating effect the higher is the temperature of the water in which the boards are immersed. This different behavior of boards at different temperatures also is the basis for standard tests on which is based the classification of bondlines, resins, and bonded wood products. These classes include the lowest requirements (interior use) for the normal production of UF-bonded boards up to water and weather resistant boards (V100 boiling test, V313 cycle test, water and boil proof (WBP), and others) according to various national and international standard specifications.

Hardened UF resins can also be hydrolyzed by moisture or water, due to the relative weakness of the bond between the nitrogen of the urea and the carbon of the methylene bridge, and this is especially so at higher temperatures. During this reaction the methylene bridge is eliminated as formaldehyde [57,58]. The amount of liberated formaldehyde can be taken under certain circumstances as a measure of the resistance of the resin against hydrolysis. The main parameters influencing the rate and extent of the hydrolysis are temperature, pH, and degree of hardening of the resin [59]. The acid which has induced the hardening of the resin can also and especially induce such a hydrolysis and hence loss of bonding strength.

Another approach to increase the resistance of UF resins against hydrolysis is therefore, based on the fact that the resin acid hardening causes acid residues in the glue line. Myers [60] pointed out that in the case of such an acid hardening system the decrease in the durability of adhesive bonds could be initiated both by the hydrolysis of the wood cell wall polymers adjacent to the glue line as well as in the case of UF-bonded products by acid-catalyzed resin degradation. A neutral pH glue line, therefore, should show a distinctly higher hydrolysis resistance. The amount of hardener (acids, acidic substances, latent hardeners) therefore should always be adjusted to the desired hardening conditions (press temperature, press time, and other parameters) and never follow "the more the better." Thus, too high an addition of hardener can cause brittleness of the cured resin and a very high acid residue in the glue line. However, glue-line neutralization must not take place as long as the hardening reaction is ongoing, otherwise this would delay or even prevent curing. This aspect is quite a challenge which in practice has not yet really been solved. Higuchi and Sakata [61] found that a complete removal of acidic substances by soaking plywood test specimens in an aqueous sodium bicarbonate solution resulted in considerable increase in water resistance of UF glue lines. Another attempt was made by these authors [62,63] using glass powder as an acid scavenger, which reacts only slowly with the remaining acid of the glue line and, therefore, does not interfere with acid hardening of the resin. Dutkiewicz [64] obtained some good results in the neutralization of the inherent acidity of a hardened UF-bonded glue line by the addition of polymers containing amino or amido groups. All these solutions, however, are not used as yet in broader industrial applications.

Laminate floorings require a very low, long term (24 h) thickness swelling of the MDF/high density fiberboard (HDF) or particleboard cores of which they are composed. Requirements usually are a maximum value of 8 or 10%, sometimes a maximum value of 6% or even lower, all figures based on the original thickness of the board. Such low percentage thickness swelling results cannot usually be obtained by just using straight UF resins, whereas the incorporation of melamine in the resin is a suitable way to achieve the desired results. Other possibilities could be a pretreatment of the particles or the fibers (e.g., acetylation) or a special posttreatment of the board. The necessary melamine content in the resin depends on various parameters, e.g., the type of wood furnish, the pressing parameters (pressure profile, density profile), and on resin consumption which can vary between a few percent up to more than 30%, based on liquid adhesive resin. Due to the considerable cost of melamine itself the content of melamine must always be only as high as necessary but as low as possible. Other important parameters are the resin manufacturing procedure, which considerably influences the thickness swelling of the boards even at the same adhesive solids content and at the same content of melamine.

Melamine fortified UF resins and MUF resins can be manufactured in a variety of ways, for example:

(i) By cocondensation of melamine, urea, and formaldehyde in a multistep reaction [65–69]. In this regard a comprehensive study of the various reaction types was done by Mercer and Pizzi [70]. They especially compared the sequence of the additions of melamine and urea.

(ii) By mixing of an MF resin with a UF resin according to the desired composition of the resin [71–73].

(iii) By addition of melamine in various forms (pure melamine, MF/MUF powder resin) to a UF resin during the application of the glue mix. In the case of the addition of pure melamine, a UF resin of a higher molar ratio must be used, otherwise there is not enough formaldehyde available to react with the melamine in order to incorporate it into the resin.

(iv) Melamine also can be added in the form of melamine salts such as acetates, formates, or oxalates [74–78], which decompose in the aqueous resin mix only at higher temperatures and enable some savings of melamine for the same degree of water resistance compared to original MUF resins. Additionally they act as a hardener. Some of the reasons why melamine salts yield a saving in melamine content have also been identified [74].

The higher the content of melamine, the higher is the stability of the hardened resin towards the influence of humidity and water (hydrolysis resistance) [79,80]. Resins containing melamine can be characterized by the molar ratio $F/(NH_2)_2$ (Table 7) or by the triple molar ratio F:U:M. The mass portion of melamine in the resin can be described based on (i) the liquid resin, (ii) the resin solids content, or (iii) the sum of urea and melamine in the resin.

One of the most interesting tasks is to clarify if there is a real cocondensation within MUF resins or if two independent networks are formed, which only penetrate each other. The application of MUF resins is very similar to the UF resins, with the difference that the level of hardener addition is usually much higher.

MUPF resins are mainly used for the production of so-called V100 exterior grade boards according to DIN 68763 and EN 312-5 and 312-7, option 2. They contain small amounts of phenol. Production procedures are described in patents and in the literature [83–87] and a coreaction has been demonstrated here, although often not contributing to resin effectiveness [83,84,88,89].

PMF/PMUF resins, in which the amount of phenol is much higher than in MUPF resins, usually contain only little or no urea at all. The analysis of the molecular structure of these resins has shown that either there is no cocondensation between the phenol and the melamine, but that there exist two distinct networks [90–93], or that cocondensation can indeed occur [88]. The reason for this is the different reactivities of the phenol methylols and the melamine methylols, depending under which pH conditions the reaction is carried out.

C. Reactivity and Hardening Reactions

During the curing process a three-dimensional network is built up. This leads to an insoluble resin which is no longer thermoformable. The hardening reaction is the continuation of the acid condensation process during resin production. The acid hardening conditions can be adjusted (i) by the addition of a hardener (usually ammonium salts such as ammonium sulfate or ammonium nitrate) or (ii) by the direct addition of acids (maleic acid, formic acid, phosphoric acid, and others) or of acidic substances, which dissociate in water (e.g., aluminum sulfate). Ammonium chloride has not been in use in the particleboard and MDF industry for several years because of the generation of hydrochloric acid during combustion of wood-based panels causing corrosion problems and because of the suspected formation of dioxins [94].

Ammonium sulfate reacts with the free formaldehyde in the resin to generate sulfuric acid, which decreases the pH; this low pH and hence the acid conditions enable the condensation reaction to restart and finally the gelling and hardening of the resin takes place. The pH decrease takes place with a rate depending on the relative amounts of available free formaldehyde and hardener and is greatly accelerated by heat [46,61].

UF resins differ from other formaldehyde resins (e.g., MF, MUF, and PF) due to their high reactivity, and hence the short hot-press times which are achievable. Hot press times shorter than 4 s/mm board thickness are possible in the production of particleboards with modern, long continuous press lines. This requires highly reactive UF resins, an adequate amount of hardener, as high a press temperature as possible, and a marked difference in moisture content of the glued wood particles in the surface and the core of the mat before hot pressing. This moisture gradient induces the so-called steam shock effect even without the additional steam injection often used in North American plants. The optimal moisture content of the glued particles is 6 to 7% in the core and 11 to 13% in the surface. The lower the moisture content in the core, the higher the surface moisture content can be. However, a critical total moisture content in the mat must not be exceeded as this might cause problems with steam ventilation and even steam blisters in the panel. For this it is necessary to have low moisture content of the glued core particles and it is necessary to be thrifty with any extra addition of water in the mat core. The lower the resin solids content on the wood, the lower is the amount of water applied to the wood furnish and hence the lower is the moisture content of the glued core particles. For the surface layers, on the other hand, additional water is necessary in the glue mix to increase the moisture content of the glued particles. This additional water, however, cannot be replaced by a higher moisture content of the dried particles themselves before blending, because this water must be available quickly for a strong steam shock effect. This would not be the case if the water would still be present in the wood furnish as the internal wood cell wall moisture content.

The mechanism of the hardening reaction of a MUPF/PMUF resin is not really clear. MUF resins harden is the acid range, whereas phenolic resins have their minimum of reactivity under these conditions. There is then the possibility that the phenolic portion of the resin might not really be incorporated into the aminoplastic portion of the resin during hardening. Different opinions and confusing reports have been advanced as regards PMF resin hardening. During the hardening of PMF resins either no cocondensation occurs [95] and in the hardened state two independent interpenetrating networks exist, or some cocondensation is reported to occur [88]. Only in model reactions between phenolmethylols and melamine have indications for a cocondensation via methylene bridges between the phenolic nucleus and the amino group of the melamine been found by ^{1}H nuclear magnetic resonance (NMR).

In order to increase the capacity of a production line, especially by shortening the panel hot press times, adhesive resins with a reactivity as high as possible should be used. This includes two parameters: a short gel time and a rapid and instantaneous bond strength development, even at a low degree of chemical curing.

The reactivity of a resin at a certain molar ratio F/U or $F/(NH_2)_2$ is determined mainly by its preparation procedure and the quality of the raw materials used. Figure 1 shows the comparison of two straight low formaldehyde emission (E1) UF resins with the same molar ratio, but prepared according to different manufacturing procedures. The differences between the two resins are clearly evident by their different rates of strength increase obtained in the so-called ABES (Automatic Bonding Evaluation System) test [96]. Resin A shows a distinctly quicker increase in bond strength than resin B, a fact which also has been verified in the industrial scale production of boards.

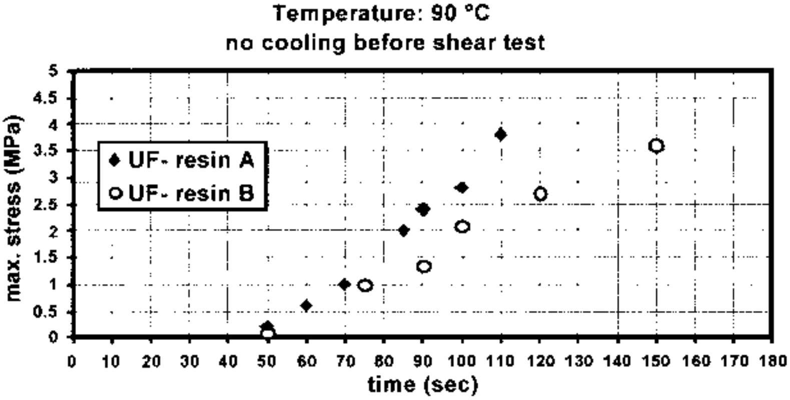


Figure 1 Comparison of two UF resins with the same molar ratio F/U, but with different reactivities, due to different preparation procedures, tested by means of the Automatic Bonding Evaluation System (ABES) according to Humphrey [96,97]. UF-resin A, UF resin with F/U = 1.08 and special preparation procedure for higher reactivity; UF-resin B, traditional UF resin with F/U = 1.08.

Table 8 Acceleration of Aminoplastic Resins by Addition of an Accelerator [98]

	Standard glue mix (parts by weight)	Glue mix with accelerator (parts by weight)
Component		
liquid UF resin (F/U = 1.05)	100	100
accelerator	—	2.5
hardener solution (ammonium sulfate 20%)	10	10
formaldehyde catcher (urea)	—	2
Property		
calculated molar ratio F/U of the glue mix	1.05	1.05
gelation time at 100°C (s)	44	36

1. *Glue Mixes with Enhanced Reactivity*

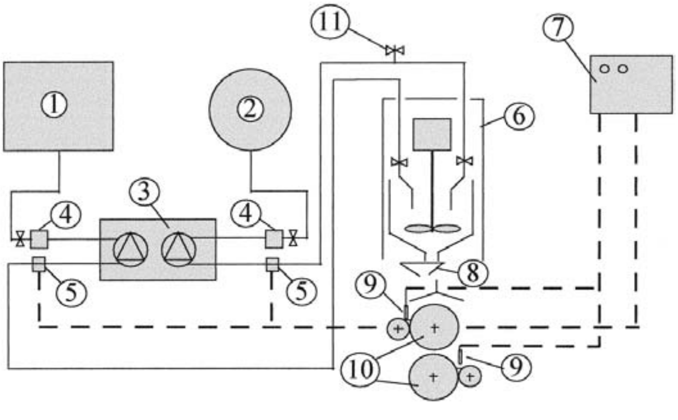
Table 8 describes an example of the use of an accelerator which distinctly increases the gelling rate of a core layer glue mix, hence enabling a significant shortening of the necessary press time. The quick reaction of the accelerator with the hardener salt generates the acid for the acid-induced hardening reaction of the resin. The accelerator is mixed with the resin just prior to use. Since it does not contain any hardener or acid, there is no limiting pot life of this premix. To compensate for the additional formaldehyde, small amounts of formaldehyde catchers are recommended for addition to the glue mix.

2. *Highly Reactive Adhesive Resins in Plywood, Parquet Flooring, and Door Production*

Plywood, parquet flooring, and doors are usually produced using aminoplastic adhesives. The press time necessary for these applications depends on the press temperature, the total thickness of the wood layers which have to be heated through, and the reactivity of the resin glue mix. Traditional adhesive resin systems need rather long press times due to their low reactivity, causing a low capacity of the production line. In these systems the hardener is premixed in greater proportion with the adhesive resin. The limitation of these is the too short pot life obtained after hardener addition, causing early gelling of the glue mix in the storage vessel. Using smaller glue mixes increases the chances of improving the resin reactivity. With this presupposition very reactive hardeners can be used. They decrease the gel time of the glue mix and hence the necessary press times. Special aminoplastic resin systems with distinctly higher reactivity have therefore been developed to fulfill the requirements of each customer in terms of saving time, energy, and costs. The higher the reactivity, the higher is the capacity of the production line, or the lower is the necessary press temperature at a given press time. Lower temperatures are beneficial for the quality of the wood itself as well as for saving energy costs.

It has been shown that such very reactive hardeners perform favorably also when in liquid form. This enables the use of various acids or acidic substances in the formulations of these hardeners. Such reactive adhesive systems usually consist of two liquid components, one being a high viscosity resin and the other a high viscosity liquid hardener. The hardener contains some inorganic fillers or organic thickeners. The mixing of these two components is performed just prior to the application of the resin mix to the roll coater. The liquid–liquid two-component mixer is installed preferably above the roll coater, in order to reduce considerably the amount of each batch of prepared glue mix. If a long stop of the production occurs the lost amount of the ready-to-use glue mix is rather small. Another advantage of this system is that both components can be pumped directly from the storage vessels to the mixer, without the use of any powder. The disadvantage of these two-component systems is the fixed ratio between the extender and the hardener. If the amount of extender should be changed, the amount of the hardener itself is also changed and hence the glue mix reactivity and pot life are changed too.

Because of the well known marked influence of the temperature on the pot life, cooling of the whole system is necessary using a chilled water cooler. The raw adhesive resin should have a temperature not higher than 15°C prior to use, which is especially important in summer due to the higher room temperature. Cooling of the adhesive resin can be performed in a small vessel with cooling coils, which is installed between the storage tank and the mixer. Additionally the roll coater itself also needs cooled cylinders in order to stabilize the temperature at approximately 15°C. Figure 2 shows the scheme of a liquid–liquid two-component mixing station.



1. glue resin tank
2. hardener tank
3. twin pumps
4. filter unit
5. flow sensor
6. mixer
7. switchbox
8. distributor
9. level sensor
10. roll coater
11. ventilation valve

Figure 2 Scheme of a liquid–liquid two-component glue mixing station.

D. Correlations Between the Composition of Aminoplastic Resins and the Properties of the Wood-Based Panels

Not much work has been done up to now concerning the prediction of bond strengths and other board properties based on the results of the analysis of the adhesive resin in its liquid state. What has been investigated and derived up to now are correlation equations that correlate the chemical structures in various UF resins having different molar ratios F/U and different types of preparations with the achievable internal bond strengths of the boards as well as the formaldehyde emission measured after resin hardening.

The basic aim of such experiments is the prediction of the properties of the wood-based panels, hence of the adhesive resin in its hardened state, based on the composition and the properties of the liquid resins used before their hardening. For this purpose various structural components were determined by means of NMR spectroscopy and the ratios of the amounts of the various structural components were calculated, for example:

- (i) for UF resins:
  - free urea related to total urea
  - methylene bridges with crosslinking related to total sum of methylene bridges
  - sum of methylene bridges in relation to sum of methylols
- (ii) for MF resins:
  - unreacted melamine to monosubstituted melamine
  - unreacted melamine to total melamine
  - number of methylene bridges in relation to the number of methylol groups
  - degree of branching: number of branching sites at methylene bridges in relation to total number of methylene bridges
- (iii) for MUF resins:
  - sum of unreacted melamine and urea to sum of substituted melamine and urea
  - number of methylene bridges in relation to number of methylol groups or to the sum of methylene bridges and methylol groups

These ratios then are correlated to various properties of the wood-based panels, e.g., internal bond strength or subsequent formaldehyde emission. Various papers in the literature describe examples of such correlations and present workable predictive equations. For UF resins: Ferg [30], Ferg et al. [99,100]; for MF resins: Mercer and Pizzi [101]; for MUF resins: Mercer and Pizzi [102], Panamgama and Pizzi [103].

For certain boards, some good correlations exist. Even these equations, however, cannot predict all properties for all types of UF resins. This is because it must be assumed that a general correlation for various resins and various panels cannot exist. Other correlation equations might have to be used sometime. However, the types of equations that have already been published describe how a universal equation for this task might look. Only the coefficient need to be changed from case to case. These results are of some importance, because they show that at least for a certain combination of resin type and board type, correlations do indeed exist. It will be the task for chemists and technologists to evaluate in further detail all possible parameters as well as their influence on the performance of the resins and the wood-based panels. It can also be assumed that the various parameters mentioned above will also be decisive for other combinations, even if the numerical values of the coefficients within individual equations might differ. The range of the molar ratio under investigation in the papers mentioned above was rather broad.

Table 9 UF Resin Glue Mixes for the Production of Particleboard and MDF, Parts by Weight

Components/resin mixes	PB-CL[a]	PB-FL[a]	PB-CL[b]	PB-FL[b]	MDF[a]
PB–UF resin[a,c]	100	100	—	—	—
MDF–UF resin[d]	—	—	—	—	100
MUF resin[e]	—	—	100	100	—
Water	—	10–20	—	10–20	30–80
Hardener solution[f]	8	2	15	6	2
Urea solution[g]	up to 5	up to 5	up to 5	up to 5	15

PB, particleboard; CL, core layer; FL, face layer.

[a] For use in dry conditions.

[b] For use in moist conditions.

[c] UF resin with molar $F/U = 1.03$ to 1.08.

[d] UF resin with molar $F/U \approx 0.98$ to 1.02.

[e] MUF resin with molar $F/(NH_2)_2 \approx 1.03$ to 1.08.

[f] Ammonium sulfate solution (20%).

[g] Urea solution (40%).

It would not appear to be possible to use these equations for predictions within narrow ranges of molar ratio, e.g., the usual range of an E1 UF resin with approximate $F/U = 1.03$ to 1.10. A method showing how different resin preparation procedures, for equal molar ratio resins, can be included in these correlation equations also needs to be developed.

E. Glue Resin Mixes

Table 9 summarizes some resin glue mixes for different applications in the production of particleboard and MDF. Table 10 summarizes various resin glue mixes for different applications in the production of plywood, parquet flooring, and furniture.

V. PHENOLIC RESINS

Phenolic resins [phenol–formaldehyde (PF) resins] show complete resistance to hydrolysis of the C–C bond between the aromatic nucleus and the methylene bridge and, therefore, are used for water and weather resistant glue lines and boards such as water and weather proof particleboards, OSB, MDF, or plywood for use under exterior weather conditions. Another advantage of phenolic resins is the very low formaldehyde emission in service, after hardening, also due to the stability of the methylene bridges between aromatic nuclei. The disadvantages of phenolic resins are the distinctly longer press times necessary for hardening when compared to UF resins, the dark color of the glue line and of the board surface as well as a higher equilibrium moisture content of the boards due to the hygroscopicity of the high alkali content of the board.

The preparation procedure of a phenolic resin is a multistage process, characterized by the time, sequence, and amount (in the case of several steps) of the additions of phenol, formaldehyde, and alkali as the most important raw materials. Similarly to all other formaldehyde condensation resins two main reactions predominate:

Methylolation: there is no special preference for ortho or para substitution, preference which, however, could be achieved using special catalysts [104–106].

Table 10 UF Resin Glue Mixes for the Production of Plywood, Parquet Flooring, and Furniture, Parts by Weight

Components/resin mixes	A	B	C	D	E
UF resin[a]	100	100	100	—	—
UF resin[b]	—	—	—	100	—
UF resin[c]	—	—	—	—	100
Extender[d]	20	40	10	—	—
Water	—	10–20	—	—	—
Hardener solution[e]	10	—	—	—	—
Hardener solution[f]	—	20	—	—	—
Powder hardener[g]	—	—	3	—	—
Powder hardener[h]	—	—	—	25	—
Liquid hardener[i]	—	—	—	—	10–20

Glue mix A: standard glue mix. Glue mix B: containing higher proportion of fillers than in A. Glue mix C: high solids content, gives an enhanced water resistance to the glue line. Glue mix D: two-component glue mix: liquid resin + ready-to-use hardener in powder form, no addition of other components necessary. Glue mix E: two-component glue mix: high viscosity liquid resin + high viscosity liquid hardener.

[a] UF resin with molar F/U ≈ 1.3.

[b] UF resin with molar F/U ≈ 1.5 to 1.6.

[c] High viscosity UF resin with molar F/U ≈ 1.3 to 1.4.

[d] Extender: rye- or wheat-flour. In some cases some inorganic fillers are also included.

[e] For example, ammonium sulfate solution (20%).

[f] For example, ammonium sulfate–urea solution (20%/20%).

[g] For example, ammonium sulfate in powder form.

[h] Ready-to-use powder hardener, containing powdered hardener, formaldehyde catcher, extenders, and other additives.

[i] High viscosity filled hardener, containing inorganic fillers or organic thickeners, hardener, and sometimes some formaldehyde catcher and other additives.

Methylolation is strongly exothermic and includes the risk of an uncontrolled reaction [107].

Condensation methylene and methylene ether linkages are formed; the latter do not exist at high alkaline conditions. During this stage chains are formed, still carrying free methylol groups. The reaction is stopped just by cooling down the preparation reactor thus preventing resin gelling.

Phenolic resins contain oligomeric and polymeric chains as well as monomeric methylolphenols, free formaldehyde, and unreacted phenol. The contents of both monomers have to be minimized by the proper preparation procedure. Various preparation procedures are described in the literature and in patents [108–117].

Special PF resins consisting of a two-phase system of a highly condensed and insoluble PF resin and a lower condensation standard PF resin have also been prepared [118] and used industrially. Another two-phase resin consists of a highly condensed PF resin still in an aqueous solution and a PF dispersion [119]. The purpose of such special resins is the gluing of panel products of higher moisture content wood, where the danger of overpenetration of the resin into the wood surface would cause a starved glue line and other serious problems.

The properties of the resins are determined mainly by the F/P molar ratio, the concentration of phenol and formaldehyde in the resin, the type and amount of the preparation catalyst (in most cases alkaline), and the reaction conditions. The reaction itself is performed in an aqueous system without addition of organic solvents. The higher the F/P molar ratio, the higher is the reactivity of the resin hence the higher its hardening rate [120], the degree of branching, and the three-dimensional crosslinking. At lower F/P molar ratios linear molecules are formed preferably. Chow et al. [121] found an increase in the bonding strength of plywood with increasing F/P molar ratio; however, the bonding strength remained constant for molar ratios higher than 1.4. This value is still distinctly lower than the common industrial molar ratios of PF resins for wood adhesives.

Usually sodium hydroxide is used as a catalyst, in an amount up to one mole per mole phenol (molar ratio NaOH/P), which corresponds to a portion of alkali in the liquid resin of approximately 10% by weight. The pH of a phenolic resin is in the range of 10 to 13. The preponderant part of the alkali is free NaOH, and a smaller part is present as sodium phenate. The alkali is necessary to keep the resin water soluble via the phenate ion formation in order to achieve a degree of condensation as high as possible at a viscosity that still can be used in practice. Additionally the alkali content significantly lowers the viscosity of the reaction mixture. Thus, the higher the alkali content of the resin, the higher is its possible degree of condensation, hence the greater is the reactivity of the resin and the higher its hardening rate and, therefore, the shorter is the necessary press time.

High alkali contents have also some disadvantages. The equilibrium moisture content in humid climates increases with the alkaline content as do some hygroscopic-dependent properties (longitudinal stability, thickness swelling, water absorption), and some mechanical properties (creep behavior) become worse. The alkali content also causes a cleavage of the acetyl groups of the hemicelluloses. This leads to an enhanced emission of acetic acid compared to UF-bonded boards. The higher the alkali content, the higher is the emission of acetic acid. In European Norms EN 312-5 and 312-7 the content of alkali is limited to 2.0% for the whole board and 1.7% for the face layer, both figures being based on oven-dried mass of the board.

Besides NaOH, other basic catalysts can be and are used, such as $Ba(OH)_2$, LiOH, Na_2CO_3, ammonia, or hexamine. However, with some notable exceptions, these are not used in practice. The type of catalyst significantly determines the properties of the resins [122–124]. Replacing alkali in PF-bonded boards could give some advantages. Ammonia being a gas evaporates during the hot press process and does not therefore contribute to the alkali content and the hygroscopicity of the boards. It is important to hold a fairly high pH as long as possible during hot pressing in order to guarantee a high reactivity and hence a short press time [125,126].

The condensation process of PF resins can be followed by monitoring the increase in viscosity and by gel permeation chromatography (GPC) to measure the molar mass distribution. Chromatograms have been obtained by Duval et al. [122], Ellis and Steiner [127], Gobec et al. [128], Kim et al. [129], and Nieh and Sellers [130].

The penetration behavior strongly depends on the molar masses present in the resin: the higher the molar masses (approximately equivalent to the viscosity of the resin at the same solid content), the worse is the wettability and the lower is the penetration into the wood surface [131,132]. The lower molar masses are responsible for the good wettability, however, too low a molar mass can cause overpenetration and hence starved glue lines. Contact angles of phenolic resins on wood increase strongly with the viscosity of the resin, which increases with the molar masses [133]. The higher molar masses remain at the wood surface and form the glue line, but they will not anchor as well in the wood surface. Depending on the porosity of the wood surface, a certain portion with higher molar masses must be present to avoid an overpenetration into the wood, causing a starved glue line; this means a certain ratio between low and high molar masses is necessary

Table 11 Properties of PF Adhesive Resins

	Particleboard CL	Particleboard FL	AW100-Plywood
Solids content (%)	46–48	ca. 45	46–48
Total alkali (%)	7–9	3–4	7–10
Free alkali (%)	6–8	2–3	6–9
Viscosity (mPa s)	300–700	300–500	500–800
Density (g/ml)	ca. 1.23	ca. 1.18	ca. 1.23

CL, core layer; FL, face layer; AW100-plywood according to DIN 68705.

[127,130,134–141]. Gollob and co-workers [109,142] found a decrease in the wood failure with increased molar mass averages of PF resins.

The penetration behavior of resins into the wood surface also is influenced by various other parameters, such as wood species, amount of glue spread, press temperature, and pressure and hardening time. The temperature of the wood surface and of the glue line and hence the viscosity of the resin (which itself also depends on the degree of advancement of the resin at the time of measuring) influences the penetration behavior of the resin [143]. Table 11 summarizes the properties of various PF resins.

The contents of free monomers (formaldehyde, phenol) depend on the type of the resin and the preparation procedure. Usual values are <0.3 mass% for the free formaldehyde and <0.1 mass% for free phenol.

The storage stability of liquid PF resins ranges from a few weeks up to several months, depending on the degree of condensation, the content of alkali, and the viscosity. An important parameter for the length of the possible storage time is the viscosity of the resin, with regards to both the proper application onto the wood surface during blending as well as the danger that the resin might gel in its storage tank. The lower the alkali content, the lower the storage stability. The aging behavior can also be monitored using GPC [144].

The molecular characterization of PF adhesive resins is done in similar way to that of all the other condensation resins by determining:

the molar ratios of the main components: F/P/NaOH; F/P; NaOH/P
the composition of the resins, based on liquid form of delivery
the degree of condensation and molar mass distribution, molar mass averages
the content of reactive sites and functional groups and their distribution in the resin, type of bridges between the aromatic rings of the phenol molecule, branching sites and others.

Due to the hydrolysis-resistant C–C bonding between the aromatic ring and the methylene group it is not possible to determine the molar ratio in the usual chemical way. This is only possible by ^{13}C-NMR. The F/P molar ratio of PF resins is usually between 1.8 and 2.5, depending on the type of resin. The higher the molar ratio, the higher its reactivity as well as its storage stability. However, the hardened resin is more brittle due to its higher level of crosslinking.

A. Reactivity and Hardening Reactions

Phenol–formaldehyde core layer resins usually have the highest molar masses and hence show a high reactivity and quick gelation. They contain higher amounts of alkali than face layer resins in order to keep the resin soluble even at higher degrees of condensation. The higher the degree of condensation during the production process (the higher the viscosity), the shorter the gel time [145]. The upper limit of the degree of condensation of the resin during its production process is given by (i) the viscosity of the resin (the resin must be able to be pumped, and a certain storage stability as well as a proper distribution of the resin on the particles during blending is required) and (ii) the flow behavior of the resin under heat, guaranteeing wetting of the unglued matching second wood surface and a sufficient penetration into the wood surface. Too high a moisture content of the glued particles limits the level to which it is possible to dilute the resin and its solids content.

The hardening of a phenolic resin can be seen as the transformation of molecules of different sizes via chains lengthening, branching, and crosslinking to a three-dimensional network with theoretically an endlessly high molar mass. The hardening rate depends on various parameters, such as molar mass, molecular structure of the resin, the portions of various structural elements as well as possible catalysts and additives.

Alkaline PF resins contain free reactive methylol groups in sufficient number and can harden even without any further addition of formaldehyde, a formaldehyde source, or catalysts. The hardening reaction is initiated by heat only. The methylol groups react to form methylene and methylene ether bridges. Under high temperatures methylene ether bridges can rearrange to methylene bridges. The lowest possible temperature for a sufficiently fast gel rate is approximately 100°C. In some cases to improve this, potash in the form of a 50 mass% solution is added in the core layer resin mix in an amount of about 3 to 5% potash solid based on resin solids content.

Pizzi and Stephanou investigated the dependence of the gel time on the pH of an alkaline PF resin [146]. Surprisingly they found an increase in the gel time in the region of very high pH values (above 10). Standard commercial PF adhesive resins with a content of NaOH of 5 to 10 mass% have exactly such pHs. A decrease of the pH in order to accelerate the hardening process is not possible, because a spontaneous precipitation would occur with such standard PF resins. A change in pH of the resin, however, might occur when the resin comes into contact with a wood surface. Wood is generally acidic in character, and especially with rather acidic wood species, the pH of the resin could significantly drop when in contact with the wood surface [147].

Lu and Pizzi [148] showed that lignocellulosic substrates had a distinct influence on the hardening behavior of PF resins, whereby the activation energy of the hardening process was much lower than for the resin alone [149] and the hardening rate much faster [149]. The reason is a catalytic activation of the PF condensation by carbohydrates such as crystalline and amorphous cellulose and hemicellulose. Covalent bondings between the PF resin and the wood, especially lignin, play only a minor role, however.

The gelling process can be monitored via DSC, ABES, or dynamic mechanical analysis (DMA). The chemical hardening can be followed also by solid state NMR, looking (i) at the increase of the amount of methylene bridges based on the amount of aromatic rings [123,150,151], (ii) at the portion of 2, 4, 6-three-substituted phenols [151], or (iii) at the ratio between methylol groups and methylene bridges [152,153]. This degree of hardening, however, is not equal to the degree of hardening as monitored by DSC. Plotting one of these degrees of chemical hardening versus the degree of mechanical hardening, as measured, e.g., via ABES or DMA, reveals the hardening pattern of a resin [151,154,155].

An acid- rather than alkali-induced gelling reaction of PF adhesive resins can cause severe deterioration of the wood substrate at the interface and, therefore, its use has lost its significance in the application of PF resins to bond wood. Pizzi et al. [156] describe, however, an effective procedure for the self-neutralization of acid hardened PF glue lines. The system is based on a mixture of a complex formed by morpholine and a weak acid in the presence of para-toluene sulfonic acid. The complex decomposes with heat and reforms on cooling to a complex in which the weak acid has been exchanged with the weak base, yeilding an almost neutral glue line. The system prevents, to a considerable extent, the acid deterioration of the wood substrate. Several other attempts based instead on incorporating the acid chemically into the resin or fixing the hardeners physically in the glue line have failed [157].

The acceleration of the hardening reaction is possible by using as high a degree of condensation as possible. Another approach is the addition of accelerating esters [146,158], among which, for example, is propylene carbonate [158,159]. The mechanism of this acceleration is not yet completely clear; it might be due to the hydrogen carbonate ion after hydrolysis of propylene carbonate [160] although this has been shown to be unlikely [146,159] or due to the formation of hydroxybenzy alcohols and temporary aromatic carbonyl groups in the reaction of the propylene carbonate with the aromatic ring of the phenol as in the Kolbe–Schmidt reaction of CO_2 with phenol to give salicylic acid [146]. The higher the addition of esters such as propylene carbonate, the shorter the gel time of the PF resin [146]. Other accelerators for PF resins are potash (potassium carbonate), sodium carbonate [95,161], guanidines, or sodium and potassium hydrogen carbonate. Also chemicals inherent to wood might have an accelerating influence on the hardening reactivity of PF resins [161].

Since phenolic resins for wood bonding harden only thermally, postcuring during hot stacking is very important. In contrast to UF-bonded boards, PF-bonded boards should be stacked as hot as possible to guarantee a maximum postcuring effect. The strength of the panel improves during hot stacking due to continuous slow curing of the PF resin. On the other hand, very high temperatures during stacking might cause partial deterioration of the wood, seen as discoloration.

B. Modification of Phenolic Resins

1. *Post-Addition of Urea*

The addition of urea to a phenolic resin causes several effects:

decrease of the content of free formaldehyde
decrease of the viscosity of the adhesive resin
acceleration of the hardening reaction via the possible higher degree of condensation of the resin
reduction of the costs of the resin.

The urea can be added to the finished PF resin or during its manufacture. The distinct decrease of viscosity observed when urea is added to the finished PF resin is caused by the cleavage of hydrogen bonds [162] and by the dilution effect. There is obviously no cocondensation of this postadded urea with the phenolic resin. Urea reacts only with the free formaldehyde of the resin to form methylols which, however, do not react further due to the high pH [163]. Only at high temperatures did Scopelitis and Pizzi [164] suppose some phenol–urea cocondensation occurs, but in their case the phenol used was the much more reactive resorcinol.

The higher the amount of postadded urea, the worse the properties of the boards. A reason for this might be urea's diluting effect on the PF resin. Surprisingly Oldoerp and

Marutzky [165] found enhanced board properties at higher degrees of addition of uncondensed urea. Since, however, in these experiments the postadded urea could be extracted completely from the boards, no significant cocondensation between the urea and the phenolic resin could have occurred. Using such PUF resins, the adhesive solids content should be calculated based only on the PF resin solids content in the PUF resin.

2. *Cocondensation Between Phenol and Urea*

A real concondensation between phenol and urea can be performed in three ways:

Reaction of methylolphenols with urea [166–169].

Acidic reaction of urea–formaldehyde concentrate (UFC) with phenol followed by an alkaline reaction [170,171].

Reaction exclusively under alkaline conditions of urea and phenol in competition with each other leading to reaction of methylol ureas with phenol and PF oligomers, and to reactions of methylolphenols with each other, as well as reactions of methylolphenols with urea [117,172]

The kinetics of the cocondensation of monomethylolphenol model compounds and urea under alkaline conditions is reported by Pizzi et al. [173] and Yoshida et al. [174]. The same kinetics but under acidic conditions is described by Tomita and Hse [166,170,175]. The interaction of esters and copolymerized urea on the fast advancement and hardening acceleration of low condensation alkaline PUF resins is reported by Zhao et al. [117,172].

3. *Addition of Tannins*

The purposes of the addition of tannins are to accelerate the hardening reaction [110,116,176–178] and to replace phenol or a part of the PF resin [179–185].

4. *Addition of Lignins*

Lignins can be added to phenolic resins (i) as an extender, e.g., in order to increase the cold tack or to reduce costs, or (ii) to achieve a chemical modification of the resin, whereby the lignin is chemically incorporated into the phenolic resin [186–190]. The idea behind this is based on the chemical similarity between the phenolic resin and lignin or between phenol and the phenylpropane unit of the lignin. The lignin can be added at the beginning, during the cooking procedure, or at the end of the condensation reaction. It is not clear whether the lignin is really always incorporated into the phenolic resin or not. In practice lignin is used at present in just a few North American mills, only as a neutral filler/extender in adhesive resins.

5. *Addition of Isocyanates*

Isocyanates [polymeric MDI (PMDI)] as a fortifier for phenolic resins have only been used in the past in rare cases. Deppe and Ernst [41] reported a precuring reaction between the isocyanate and the phenolic resin, even if both components had been applied separately to the particles. Hse et al. [36] also found good results with an isocyanate and a PF resin added separately to wood particles. Pizzi and Walton [191] reported on the reactions and their mechanisms of PF resins premixed in the glue mix with nonemulsifiable water-based diisocyanate adhesives for exterior plywood. Pizzi et al. [192] reported on the industrial applications of such systems (PF + PMDI + sometimes tannin accelerator; UF + PMDI)

[192–194], on the marked curing acceleration of the PF resin by the isocyanate, and on the excellent results which were obtained industrially with these systems. Very recently this approach, due to its excellent performance, lower cost, and ease of preparation has received intense attention, and several other studies on the subject have been recently published [195–198].

C. Correlation Between the Composition of a Resin and the Properties of Wood-Based Panels Bonded with the Resin

Similar to the investigations described above for the aminoplastic resins, NMR results of the liquid phenolic resins can be correlated with certain board properties [199]. For this purpose various structural components are determined by means of ^{13}C-NMR and the ratios of the amounts of the various structural components are calculated, e.g.:

methylol groups to methylene bridges
ratio of free ortho and para sites in relation to all possible reaction sites
methylol groups in relation to all possible reaction sites
methylene bridges in relation to all possible reaction sites
ether bridges in relation to all reaction sites

These ratios are then correlated to various properties of the wood-based panels, e.g., internal bond strength after boiling or after boiling + redrying, and subsequent formaldehyde emission.

Also for phenolic resins it is not clear whether universally valid correlation equations will exist or if they will differ for different types of resins and boards, although the correlations obtained appear to have a lower coefficient of variability than for the aminoplastic resins. Nevertheless, it can be safely assumed that the various parameters used with at least be the same in most cases, even if the actual numerical values of the coefficients within the individual equations might differ.

D. Adhesive Resin Glue Mixes

Table 12 summarizes the various glue mixes for different applications.

Table 12 Examples of PF Glue Mixes for Particleboard, Oriented Strandboard, and Plywood Parts by Weight

Components	Particleboard core layer	Particleboard face layer	OSB	OSB	AW100-Plywood
PF-resin A	100	—	100	—	—
PF-resin B	—	100	—	—	—
PF-resin C	—	—	—	—	100
PF-powder resin	—	—	—	100	—
Water	—	—	—	—	—
Potash 50%	6	—	6	—	6
Extender	—	—	—	—	10–15

PF-resin A, medium alkali content (8–10%); PF-resin B, low alkali content (3–5%); PF-resin C, medium alkali content (6–8%); PF-powder resin, no addition of water, no dissolving of the powder before blending the strands; Extender: e.g., coconut shell flour.

VI. ISOCYANATES

A. Adhesives for Wood-Based Panels (Polyisocyanates)

Adhesives based on isocyanates (especially PMDI) have been used for more than 25 years in the wood-based panel industry [40,41,200–203], but still have a relatively low consumption volume compared to systems based on UF, MUF, or PF resins. The main application is the production of waterproof panels, but there is also the production of panels from raw materials that are difficult to glue, such as straw, bagasse, rice shells, or sugar cane bagasse. PMDI can be used as an adhesive for wood-based products such as exterior particleboard, exterior OSB, laminated strand lumber (LSL), MDF, or other specially engineered composites. During hot pressing the viscosity of PMDI is lowered, allowing it to flow across and penetrate below the surface, locking in the wood subsurface as has been shown by Roll [204]. The low wetting angle of PMDI compared to water-based condensation resins allows a rapid penetration into the wood surface; however, this also might result in starved bondlines [205].

PMDI is produced during the manufacturing of monomeric MDI. The PMDI produced industrially by phosgenation of di-, tri-, and higher amines contains a mixture of the three different MDI isomers, triisocyanates, and different polyisocyanates, and thus the structure and the molar mass depend on the number of phenyl groups. This distribution influences to a great extent the reactivity, but also the usual characteristics such as viscosity, flow, and wetting behavior as well as the penetration behavior into the wood surface. The structure and the molar mass depend on the number of aromatic rings [206]. For PMDI the distribution of the three monomeric isomers has a great influence on the quality, because the reactivities of the various isomers (4,4′-, 2,4′-, and 2,2′-MDI) differ significantly [207]. The greater the portion of the 2,2′- and 2,4′-isomers, the lower the reactivity. This can lead to different bonding strengths as well as to residual low reactive isomers in the wood-based panels produced. In the monomeric form (MDI) the functionality is 2 and the NCO content is 33.5%, while PMDI has an average functionality of 2.7 with an NCO content of approximately 30.5%. The HCl content is usually below 200 ppm. PMDI is cheaper than pure MDI and has a lower melting point (liquid at room temperature) due to the increased asymmetry. It is less prone to dimerization and, as a consequence, it is more stable during storage than pure MDI. PMDI is used whenever the color of the finished adhesive is not of concern [208].

The excellent application properties of PMDI and of the wood-based panels produced with it are based on the special properties of PMDI, especially the excellent wetting behavior of a wood surface when compared to waterborne polycondensation resins. Due to this fact surfaces with poor wetting behavior such as straw can also be bonded. According to Larimer [209] the wetting angles for PMDI on various surfaces are much lower than for UF resins. Additionally, these resins show a good penetration behavior into the wood surface, which seems to be determined by the small molar mass of PMDI when compared with polycondensation resins. Marcinko et al. [210] found in their measurements, using solid state ^{13}C-NMR, DSC, fluorescence microscopy, and DMA, that PMDI could penetrate 5–10 times further into wood than PF resins. PMDI not only penetrates the macroscopic hollows of the wood substance, but even penetrates the polymer structure of the wood. This enables good mechanical anchoring. The good wetting and penetration behavior of PMDI can sometimes cause starved glue lines. Due to PMDI's high reactivity and its low molar mass, a special interfacial layer between the wood surface and the adhesive appears to form. If hardening is quicker than the thermodynamically induced desorption during the hardening reaction, then a polyurea/biuret network might form interpenetrating the wood constituents network. Covalent bondings as well as secondary forces can help to avoid desorption reactions during hardening.

Johns [211] showed that isocyanates spread easily on a wood surface; 2 to 3% of isocyanate was enough to form a film completely covering the wood strands, which is not possible even with 6% of a phenolic resin. The good mobility of MDI is based on several parameters [211]:

MDI contains no water; it cannot lose its mobility during adsorption on the wood surface
its low surface tension (ca. 50 mN/m) compared to water (76 mN/m)
its low viscosity.

The impossibility of diluting PMDI with water was solved by the introduction of emulsified PMDI, often called EMDI, which allows an even distribution of the adhesive during the gluing process. EMDI is a product of the reaction of PMDI with polyglycols. EMDI is manufactured under high pressure and dispersed in water.

The isocyanate group in PMDI is characterized by high reactivity towards all substances which contain active hydrogens. The main hardening reaction proceeds via reaction with water to the final amide group, while at the same time CO_2 is split off. The water necessary to induce the hardening reaction is applied together with the PMDI (spraying together with the PMDI or spraying of an aqueous dispersion of PMDI in water) or is present in wood in sufficient amount. The amine group then reacts further with another isocyanate group to form a polyurea structure:

$$\mathrm{R{-}N{=}C{=}O + H_2O \rightarrow R{-}NH_2 + CO_2}$$

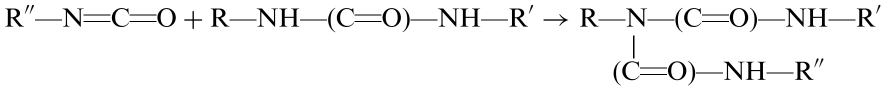
$$\mathrm{R{-}NH_2 + O{=}C{=}N - R' \rightarrow R{-}NH{-}(C{=}O){-}NH{-}R'}$$

The reaction of an isocyanate group with a hydroxyl group leads to the so-called urethane bonding:

$$\mathrm{R{-}N{=}C{=}O + HO{-}R' \rightarrow R{-}NH{-}(C{=}O){-}O{-}R'}$$

Such a reaction can theoretically also occur between an isocyanate group and an –OH group of cellulose or lignin to form a covalent bond. These bonds are usually of greater durability than purely physical bonds. If one could manage to force such a reaction to occur in an industrially useful short curing time, when the reaction of the isocyanate groups of the PMDI with water is suppressed, the probability of the formation of such covalent bonds and with this the quality of the bonding should increase, leading to higher bond strengths and especially a higher resistance against the influence of humidity.

If another isocyanate group reacts with an amide hydrogen within the polyurea structure formed, a branching point is formed (biuret group):



$$\mathrm{R''{-}N{=}C{=}O + R{-}NH{-}(C{=}O){-}NH{-}R' \rightarrow R{-}\underset{\displaystyle (C{=}O){-}NH{-}R''}{\underset{|}{N}}{-}(C{=}O){-}NH{-}R'}$$

During the hardening of PMDI Frazier et al. [212] have found the formation of urethanes, polyureas, biurets, and triurets/polyurets. The proportions of the various compounds depend on the working and hardening conditions. The forming of the network is especially influenced by the ratio between the isocyanate and water. The formation of a urethane seems to be possible for low molar mass isocyanates, as e.g., the usual industrial PMDIs, under slightly alkaline conditions. It can also be assumed that the forming of a urethane especially occurs by reaction with lignin. This bond, however, seems not to be stable at higher temperatures (120°C) for longer times.

Hydrophobic polyols should be able to repel and eliminate water from the wood surface and, therefore to fortify the reaction of the isocyanate group with the hydroxyl groups of the wood surface [213]. Umemura et al. [214] and other workers [27] compared the reaction of isocyanate with water and small amounts of polyols using DMA. The bonding strength and the thermal stability increased by adding dipropylene glycol with molar mass in the 400–1000 range.

Usually no hardeners are added during the production of wood-based panels (particle board, MDF, OSB, engineered wood products) using PMDI as adhesive. With special additives a distinct acceleration of the hardening reaction and hence shorter press times or lower press temperatures can be achieved [209]. This fact is especially interesting for cold-setting systems as well as for the production of particleboards. Possible catalysts are tertiary amines (e.g., triethanol amine, triethylamine, *N*,*N*-dimethylcyclohexylamine) and metal catalysts, based on organic compounds of tin, lead, cobalt, and mercury [208,215–218].

Compared to other adhesives, PMDI possesses various advantages, but also some disadvantages (Table 13). For the production of plywood the addition of extenders is recommended [221–226] or the mixing with other resins [191,192] as alone PMDI cannot be used for plywood. In the production of OSB (especially for the two types OSB/3 and OSB/4 according to European Norm EN 300) often PMDI is used in the core layer.

B. Polyurethane Adhesives

Polyurethane adhesives are formed by the reaction of various types of isocyanates with polyols. The polar urethane group enables bonding to various surfaces. Depending on the raw materials used, glue lines with either rubberlike behavior or elastic-to-brittle hard behavior can be achieved. The end groups determine the type of the adhesive, whether it is a reactively or a physically hardening adhesive.

Table 13 Advantages and Disadvantages of PMDI Compared to Other Adhesives, Especially UF Resins

Advantages	Higher storage stability
	Formaldehyde-free gluing, despite the fact that formaldehyde is used in the production of MDI/PMDI
	Higher reactivity
	Higher bonding strength
	Higher tolerance against humidity
	Lower consumption of adhesive
Disadvantages	Higher price, but this is compensated by the low adhesive consumptions and sometimes shorter press times
	Adhesion to all other surfaces, e.g., also press platens. This imposes the use of (i) special internal or external release agents [219], (ii) special types of PMDI [220] or (iii) the use in the board surface of adhesives other than isocyanates
	The necessary use of special emulsifiers (EMDI) or special dosing and gluing systems
	Greater worker protection requirements due to the toxicity and the low but nevertheless existing vapor pressure of monomeric MDI, which need special precautions during use

One-component isocyanate adhesive systems consist of chains with isocyanate groups on chain ends or on branching sites. These isocyanate groups can react with the moisture content of the surfaces to be bonded, and a hardened system forms from this addition reaction. Thus, at least one of the two surfaces must contain the amount of water necessary for hardening. Due to the high viscosity of these adhesives, dilution with organic solvents or higher temperatures are necessary. Additionally, the adhesive may contain various other components, such as flowing agents, fillers, antioxidants, bactericides, or dyes. The bondline reaches the necessary green strength within a few hours and hardens over a few days. During the reaction of the isocyanate group with the moisture content of the wood, CO_2 is formed, which causes some foaming of the bondline. The bondlines themselves are more or less resistant against humidity and water.

The two-component systems consist of (i) a polyol or polyamine and (ii) an isocyanate. The hardening starts with the mixing of the two components. Due to the low viscosities of the two components they can be used without addition of solvents. The weight ratio between the two components determines the properties of the bondline. Linear polyols and low amounts of isocyanates give flexible bondlines, whereas branched polyols and high amounts of isocyanates lead to hard and brittle bondlines. The pot life of the two-component systems is determined by the reactivity of the two components, the temperature, and the addition of catalysts, and can vary between 0.5 and 24 h. At room temperature hardening occurs within 3 to 20 h.

VII. WOOD ADHESIVES BASED ON NATURAL RESOURCES

Bio-based adhesive resins have been under investigation for a long time; however, extensive industrial application, at least in Europe, has not yet occurred. The use and application of adhesives based on natural and renewable resources is often thought of by the industry as well as the general public as a new approach that requires novel technologies and methods to implement. Despite the increasing trend toward the use of synthetic adhesives, processes based on the chemical modification of natural products offer opportunities for producing a new generation of high performance, high quality products. The distinct advantages in the utilization of natural materials, e.g., lower toxicity, biodegradability, and availability, need to be paralleled by more efficient and lower cost methods of production. Factors such as regional and species variation have to be considered in selecting the optimum feedstock for a particular process; additionally cost-effective manufacturing techniques have to be developed that will enable these materials to capture a wider percentage of the world market. Manufacturers need to have confidence that a continual uninterrupted supply of raw material can be sustained throughout the life cycle of a product. It is of equal importance that the feedstock should not be restricted by geographical and climatic conditions or that yield should not dramatically vary when harvested in different locations and at different times of the year. The key to an increased usage of natural products by industry is in the control of the above variables so that the end performance by the industry remains consistent [227].

A. Tannins

Tannins are polyhydroxyphenols of vegetable origin, which are soluble in water, alcohols, and acetone and can coagulate proteins. They are obtained by extraction from wood, bark, leaves, and fruits. Other components of the extraction solutions are sugars, pectins and other polymeric carbohydrates, amino acids, and other substances. The nontannin substances can reduce wood failure and decrease water resistance of glued bonds [176]. The polymeric carbohydrates especially increase the viscosity of the extracts.

The basic structures of condensed or polyflavonoid tannins are [176]

in the A-ring: resorcinol, phloroglucinol
in the B-ring: pyrogallol, catechol, and more rarely phenol.

Depending on the chemical structure of the A-rings two main types can be distinguished:

resorcinol type: in mimosa/wattle, quebracho, Douglas fir, spruce tannin extracts
phloroglucinol type (pine type): most pine species, e.g., *Pinus radiata*, *Pinus patula*, *Pinus elliotti*, *Pinus taeda*, *Pinus pinaster*, *Pinus halepensis*, Douglas fir, and *Pinus echinata*. *Pinus brutia* and *Pinus ponderosa* are mixed types with predominant resorcinol character.

The disadvantage of the phloroglucinol type is the distinct lower yield during extraction as well as the much higher reactivity of the A-ring towards formaldehyde, which if uncontrolled can cause extremely short pot lives of the glue mix.

The disadvantages of these polyphenols are the high viscosity of the solutions in the range of the concentrations of industrial application, due to the polymeric carbohydrates and high molecular weight tannins [228,229], and in some cases their short pot life. The maximum usable concentration of tannin solutions is approximately 40% by mass, except for mimosa where it can be as high as 50%. By selectively removing the polymeric carbohydrates the viscosity can be decreased and with this the possible concentration can be increased. Such purification steps using an ultracentrifuge [229–233] and an acid precipitation followed by filtration or centrifugation have been described [185,234]. However, they have not yet been introduced in industrial practice; they are only available at laboratory scale. A further possibility is the optimization of the conditions during the extraction in order to minimize the content of nontannins in the extract.

The viscosity of tannin solutions usually increases at higher pHs [185,235,236], but for some tannin types no clear dependence of the viscosity on the pH is shown. The viscosity of an extract increases with the solids content, especially if carbohydrates are present from the extraction step. There are several ways to decrease the viscosity of tannin extracts:

Dilution (lower solids content): this leads to increased moisture content of the glued particles (which is not necessarily a disadvantage, since tannins need high moisture contents of the glued particles to guarantee proper flow during pressing) as well as to a decreased content of active adhesive [176].
Degradation of the high molecular carbohydrates, e.g., by NaOH [237,238].
Addition of hydrogen bond breakers, e.g., urea [228,239,240].
Modification of the extract by sulfite or bisulfite [241]: this modification of the extracts will especially decrease the sometimes high viscosity to achieve a better performance, but also a longer pot life and a better crosslinking will be achieved; however, it can give poor results if too high a level of sulfite is used.
Modification by treatment with acetic anhydride or maleic acid anhydride as well as NaOH to decrease the viscosity [228,242–244].

Tannins are used mostly in the southern hemisphere [176]; applications in Europe are only for niche products with special properties. Depending on the resin content applied to wood, tannins can be used for interior or exterior boards. The necessary crosslinking is often done by addition of formaldehyde. This, however, can lead to some formaldehyde emission, but this is low due to the phenolic nature of the tannin. Sometimes crosslinking is performed by the addition of isocyanate. Hardening by tannin autocondensation without any aldehyde addition is also possible [245–247].

Tannins from mimosa, quebracho, and pine (*Pinus radiata*) are actually used on an industrial scale for wood gluing. The extraction itself is only performed industrially in the southern hemisphere. The tannins are produced by water extraction of the wood or of the bark. Suitable solvents are water, alcohols [248], or acetone. Some of the parameters which influence tannin extraction are:

- temperature [240,248–252]
- addition of various chemicals, e.g., NaOH or sodium carbonate [185,233,234, 248,249,253–261], sodium sulfite or bisulfite [241,248,250,262], and sulfite/bisulfite with sodium carbonate with or without urea [240]
- duration of the extraction [240,258,260]
- concentration of the extraction solution: ratio of the amount of dry bark to the amount of extraction solvent [260]
- properties of the raw material: wood species, age, time span between harvesting and extraction, storage conditions, particle sizes [176].

Usually concentrated solutions or spray dried powders are sold [176]. A purification step usually is not done at industrial scale level [176].

As tannins contain many "phenolic" type subunits one may be tempted to think that they will exhibit a similar reactivity potential to that of phenol and, therefore, procedures used in standard PF production can be transferred to those containing tannin. This, however, is not the case; the real situation is that tannin is far more reactive than unsubstituted phenol due to the resorcinol and phloroglucinol rings present in the tannin structure [263,264]. This increase in hydroxyl substitution on the two aromatic rings imparts an increase in reactivity to formaldehyde 10 to 50 times greater as compared to simple phenol. This whilst initially sounding promising creates additional problems with respect to producing an industrially applicable resin, due to limited pot lives of the ready-to-use formulations [227], although these problems have been solved and solved well even at industrial level [263,264].

Besides tannin autopolymerization, crosslinking usually is achieved via methylene or other bridges in a polycondensation reaction with formaldehyde or isocyanates. Tannins react with formaldehyde similarly to phenol, whereby the nucleophilic sites of the A-ring are more reactive than those of the B-ring. Formaldehyde reacts with a tannin in an exothermic reaction forming methylene bridges, especially between the reactive sites of the tannin A-rings. The reactive sites of the B-ring need a pH of at least 10 [265,266] to react. However, at such a high pH the reactivity of the A-ring becomes so high that no useful pot lives of the glue mix are obtained any more. Due to their size and shape the tannin molecules become immobile already at rather low degrees of condensation, so that formation of further methylene bridges is impeded or hindered, causing a low degree of hardening (crosslinking) [266]. The higher the molar mass of the tannin, the earlier this effect occurs.

At neutral pH a rapid reaction of formaldehyde with the sites 6 and 8 on the A-ring takes place. This leads to the advantage that no (high) alkaline pH as for the phenolic resins is necessary to achieve rapid gelling and that a neutral glue line is obtained. A minor disadvantage is the necessary exact adjustment of the pH, because the gelation time varies strongly with the pH [266,267].

From a purely technological point of view the gel time may not be reduced below a certain limit. Decisive factors are the pot life, the viscosity of the tannin solution, and the rate of the steam escaping from the mat and the board during hot pressing. One possible way is the separate addition of the crosslinker, e.g., by dosing paraformaldehyde via a small screw conveyor directly to the particles in the blender. Also a liquid crosslinker, e.g., a urea–formaldehyde concentrate (UFC), can be mixed with the tannin solution in a static mixer just prior to the blender. The higher viscosity of the tannin solution at higher pHs, even without addition of the crosslinker, can be overcome by warming to 30–35°C or by adding water. A higher moisture content of the glued particles is no disadvantage in tannin adhesives, on the contrary it helps to guarantee a proper flow of the tannin during hot pressing.

Possible crosslinkers are formaldehyde as aqueous solution [268], paraformaldehyde [263,265,267,269], UFC [270,271], UF resins [272], aqueous formaldehyde solution emulsified in an oil [273], dimethylolurea [274] or urea and phenol methylols with longer chains to overcome steric hindrance. Tannins can also be hardened by addition of hexamethylenetetramine (hexamine) [275], whereby these boards show a very low formaldehyde emission [269,275–281]. The autocatalytic hardening of tannins without any addition of formaldehyde or other aldehyde as crosslinker is possible, if alkaline SiO_2 is present as a catalyst at high pH or just as a consequence of the catalysis of the reaction induced by a lignocellulosic surface [282].

1. *Application of Tannins as Adhesives*

The main parameter for the application of tannins as adhesives for wood-based panels is the content of reactive polyphenols and the reactivity of these components towards formaldehyde. Tannins can be used as adhesives alone (with a formaldehyde component as crosslinker) or in combination with aminoplastic or phenolic resins. These resins can react chemically with the tannin component in a polycondensation reaction, form only two interpenetrating networks, or both. The simplest adhesive mix formulation consists of the tannin solution and powdered paraformaldehyde as crosslinker [283]. The addition of paraformaldehyde can cause in the short term a relatively high level of formaldehyde emission. Glue mixes using paraformaldehyde for the production of particleboards with low formaldehyde emission are described and used industrially [284]. In the literature a large number of papers describe the combinations of tannins with synthetic resins (Table 14).

B. Lignins

Lignins are large three-dimensional polymers produced by all vascular terrestrial plants; they are second only to cellulose in natural abundance and are essentially the “natural glue” that holds plant fibers together. Lignins are phenolic materials. They are primarily obtained as a byproduct in wood pulping processes with estimates exceeding 75 million tonnes per annum. Therefore great interest exists for possible applications. Lignins of very different chemical composition and possible applications in the wood-based panels industry (adhesives, additive for part replacement of adhesives, raw material for synthetic resins) have been described in a large number of papers and patents. Research into lignin-based adhesives dates back more than 100 years with many separate examples of resins involving lignin being cited. In reality, existing applications are very rare. No industrial use as a pure adhesive for wood is currently known despite the fact that considerable research has been directed toward producing wood adhesives from lignins. By themselves lignins offer no advantages in terms of chemical reactivity, product quality, or

Table 14 Combinations of Tannins and Synthetic Resins

Combination	Description	References
1. Tannins + aminoplastic reins		
(a) UF resins	UF resins with tannin molecules as end groups	272,285
	Addition of formaldehyde-rich UF resins	228,272,274
	Tannin + UF resin mix	272,286,287
(b) UF–resorcinol–tannin	Reaction of UF–methylols, resorcinol, and tannin	288
	UF resins with resorcinol end groups + tannin	288
	Reaction of UF–methylol + tannin followed by addition of resorcinol	288
(c) Pine tannin + MF/MUF resins		289
2. Tannins + phenolic resins		
(a) Cocondensation of tannins with phenol and formaldehyde	Replacement of various amounts of phenol of tannin extract	179,180,249,253, 254,290–295
(b) Tannins as hardening accelerator for alkali hardening PF resins	Addition of 10–20%	184,248,266,271, 296
(c) Low molar mass polymethylolphenols (PMP)	The crosslinking molecules are of greater size than formaldehyde and can, therefore, bridge better the gaps between the reactive crosslinking sites	228,266,274,297, 298
(d) mixes of tannins and PF resins; replacement of phenolic resins by tannins	Since the reaction of tannins with PF–resols and formaldehyde is accelerated strongly in the alkaline region, the pot life is reduced significantly, so PF resins with low content of alkali are used	228,234,266,274, 287,289,297, 299–301
3. Tannins with enhanced resorcinol content		
(a) Opening of the heterocyclic ring of the tannin for warm-setting resorcinol–tannin resins	Reduction of the necessary resorcinol addition by modification with sulfite (forming of resorcinol end groups from the tannin molecule by sulfite-induced cleavage of the heterocyclic ring). No free methylol groups present, addition of formaldehyde as crosslinker is necessary	302–304

(*continued*)

Table 14 Continued

Combination	Description	References
(b) Reaction of tannin with resorcinol	Replacement of resorcinol in a traditional PRF	305
(c) Cold-setting tannin–resorcinol resins (TRF)	Forming of resorcinol by intermolecular rearrangement of the tannins	285,302,306,308
	Replacement of resorcinol in a traditional PRF	302,307
(d) Cold-setting, honeymoon, separate application structural exterior adhesives (with and without resorcinol)	PRF/tannin and TRF/TRF separate-application fast-set glulam and fingerjointing adhesives	309–311
4. Tannins + isocyanate (PMDI)		
Isocyanate as crosslinker for polyflavonoid tannins	Distinct amelioration of the properties, partial reaction of the isocyanate group with the OH groups of the tannins; for a sufficient hardening of the tannin the addition of a formaldehyde component seems to be necessary	263,264,266,284, 289,312–316

color when compared to conventional wood adhesives. The greatest disadvantages of lignins in their application as adhesives are (i) their low reactivity and, therefore, slow hardening compared to phenol due to the lower number of reactive sites in the molecule, causing increased press times, and (ii) the concern over the chemical variation of the feedstock. The chemical structure of lignin is very complex with the added difficulty that unlike tannin the individual molecules are not fixed to any particular structure, therefore no true generic molecule exists for lignin from softwood, hardwood, or cereals. Lignosulfonates can be added to synthetic glue resins as extenders (by partial replacement of resin). The partial replacement of phenol during the cooking procedure of PF resins has no real industrial importance.

1. Use of Lignins as Adhesives Without Adding Other Synthetic Resins

The application of lignins as adhesives is, in principle, possible. Initial attempts needed very long press times due to the low reactivity of lignin (Pedersen process) [317,318]. This process was a condensation under strong acidic conditions, which led to considerable corrosion problems in the plant [318]. The particles are sprayed with spent sulfite liquor (pH 3 to 4) and pressed at 180°C. After this step the boards are tempered in an autoclave under pressure at 170–200°C, whereby the sulfite liquor becomes insoluble by splitting off water and SO_2. Shen [319–321], Shen and Fung [323] as well as Shen et al. [322,324] modified this process by spraying the particles with spent sulfite liquor containing sulfuric acid and pressing them at temperatures well above 210°C.

Nimz [317,325] describes the crosslinking of lignin after an oxidation of the phenolic ring in the lignin molecule using H_2O_2 in the presence of a catalyst, especially SO_2 [326]. This leads to the formation of phenoxy radicals and with this to radical coupling (but not to a condensation reaction), whereby inter- and intramolecular C–C bonds are formed.

This reaction does not necessarily need heat or acidic conditions, but is accelerated by higher temperatures (maximum 70°C) as well as lower pHs. In this way the disadvantages of the processes mentioned above (high press temperatures, long press times, use of strong acids) can be avoided [317,326]. An oxidative activation of the lignin also can be achieved by biochemical means, e.g., by adding enzymes (phenoloxidase laccase) to the spent sulfite liquor, whereby a polymerization via a radical mechanism is initiated. The enzymes are obtained from nutrient solutions of white fungi [327]. The two-component adhesive is prepared by mixing the lignin with the enzyme solution (after filtration of the mycelium). At the beginning of the press cycle the enzyme still works, since it is stable up to a temperature of 65°C. If this temperature is surpassed, the enzyme is deactivated. At such time, however, the number of quinone methides is already high enough to initiate a crosslinking reaction [86,87,327–334]. This system, however, is not capable of keeping up with the demands of modern day panel hot press times. To achieve viability this problem was solved by the addition of a smaller than usual amount of isocyanate adhesives. The use of an adhesive thus denies this system any advantage [335]; the enzymatic approach alone only achieves results and pressing times comparable to those of nonenzyme treated nonglued hardboard, a long-existing process and product.

VIII. THERMOPLASTIC WOOD ADHESIVES

A. Hot Melts

Hot melts are 100% solid thermoplastic compounds, which are compounded and applied in the molten state at elevated temperature, the resultant properties being obtained by cooling. Due to the quick cooling, bonds can be established in a very short time. Also a hot melt can be melted again, when already in the glue line. The advantages of hot melts are:

100% solid, contain no organic solvents; no water or solvent to be evaporated; low requirements concerning working and environmental safety
easy to use, short set time allows high speed operation (up to 100 m/min)
rapid bond strength increase
high bond strength
effective bonding even of difficult-to-bond surfaces: polyethylene (PE), polypropylene (PP), varnishes, and others
combination of flexibility and toughness
adhesion to a wide variety of substrates even without a primer
high variability in formulation (color, viscosity during application, temperature, and others)
practically unlimited storage life, easy storage
no time limitations in application, hence no pot life problems
no pollution of machinery and adherends, because of exactly metered application
good temperature control during application, easy to use in automated production systems

The disadvantages of hot melts are:

cold flow: hot melts creep under mechanical load, even far below the melting temperature; bonds can open slowly, this effect being accelerated by higher temperatures

low heat resistance at elevated temperatures due to thermoplastic behavior; loss of bond strength
sensitivity of certain substrates to the required application temperature
degradation at elevated temperature (color, viscosity)

1. *Composition of Hot Melts*

Polymer. The polymer determines the properties of the hot melt. Variations are possible in molar mass distribution and in chemical composition (copolymers). The polymer is the main component and backbone of the hot melt adhesive blend as it gives strength, cohesion, and mechanical properties (filmability, flexibility). Ethylene vinyl acetate (EVA) is the most used type (approximately 80%). It can be varied in viscosity (melt index) and content of acetate within a broad range of values, and once hardened it presents a predominantly amorphous structure. The vinyl acetate groups impart good adhesion ability towards many materials. The low heat stability, however, limits its areas of application. With increasing content of the vinyl acetate comonomer the adhesion ability, the wetting behavior, and the flexibility increase, but also the setting time and the price. Heat resistance and cohesion properties become worse. The higher the average molar mass of the polymer, the worse its wetting behavior, but the better the cohesion properties, the heat resistance and temperature resistance, and the higher the melting viscosity at a given temperature.

Ethylene–acrylic acid ester copolymers show high heat resistance and high elasticity at low temperatures. Amorphous poly-α-olefins (APAOs) are also used as the basic polymer and their main component monomer is propylene. They present better heat resistance than EVA. APAO shows good adhesion properties to nonpolar surfaces, good flexibility, and a high resistance to temperature and moisture.

Polyamides give the fastest setting speed, good cohesion and very high heat resistance. They are oil and solvent resistant. Due to the narrow melting region (sharp transition between the elastic and plastic areas) a short setting time during cooling is allowed. Depending on their type the melting temperature is between 105 and 190°C. Advantages are the low melt viscosity, high bond strength, and a high green tack. Disadvantages are the high price and the susceptibility for carbonization at high temperatures in the presence of oxygen. Thermoplastic polyurethanes have no reactive isocyanate groups and cannot crosslink. Thermoplastic, linear, and saturated polyesters give, depending on their chemical composition, hard or elastic and tacky bondlines. They have relatively high melt viscosities, and the bondlines are resistant against moisture, water, and ultraviolet (UV) radiation.

Tackifiers. Tackifiers usually are hydrocarbon resins (aliphatic C5, aromatic C9) or natural resins (polyterpenes, rosin and rosin derivatives, tall oil rosin ester). They improve hot tack, wetting characteristics and open time, and enhance adhesion. The content of tackifiers in a hot melt can be in the region of 10–25% of total material.

Other Components. Waxes increase the resistance against water and moisture (hydrophobization) and improve flow and lubricate during application. Inorganic fillers ($CaCO_3$ and/or $BaSO_4$) improve cohesion (small particle size) and adhesion, decrease sagging, and improve the price of the product. Pigments are also used, often in the case of white colored hot melts, the most common pigment being TiO_2. Plasticizers decrease the viscosity and the heat resistance; they ameliorate the wetting behavior and the flexibility of the bondline; however, cold flow can occur. Stabilizers improve the thermooxidative behavior of the hot melt (heat and aging stability).

2. *Curing Hot Melts*

Curing hot melts are easily meltable polyurethane prepolymers (polyaddition of polyvalent alcohols and isocyanate) with reactive isocyanate end groups ($-N=C=O$), which react with the moisture content of the wood under hardening. This leads to the formation of a crosslinked polyurethane network. Therefore, as thermoplasticity is no longer present, they cannot melt and are insoluble and show good mechanical and chemical resistance. During application a two-step bonding process takes place, the two steps running in parallel, but at different rates:

(i) quick physical solidification due to cooling: high green strength for further rapid processing
(ii) slower chemical hardening by crosslinking: the reaction of the free isocyanate groups is initiated by the moisture content of the surrounding air and of the adherend.

The advantages of the curing hot melts are:

Higher resistance against heat, moisture and steam, good aging and long term stability.
Higher mechanical bond strength.
Lower application temperatures: lower molar masses and lower softening and melting temperatures. Processing of heat susceptible adherends, e.g., PVC foils, is possible, for example at a processing temperature of 70°C. The heat resistance of the bondline is up to 120°C.
Good aging resistance

The disadvantages of curing hot melts are:

They contain monomeric isocyanate, which is toxic, and thus working safety must always be taken into account.
They have stricter requirements concerning packaging and application, namely preventing the access of water during storage and application is necessary.
They are expensive.

Two component curing hot melts consist, for example, of (i) polyamide + epoxy, or (ii) a polyol component + isocyanate. After the mixing of the two components, they possess only limited pot life.

B. Poly(Vinyl Acetate) Adhesives

Poly(vinyl acetate) (PVAc) adhesives are another important type of thermoplastic adhesive, especially in furniture manufacturing and carpentry. They form the bondline in a physical process by losing their water content to the two wooden adherends. PVAc adhesives are ready to use, have a short setting time, and give flexible and invisible joints. They are easy to clean and show long storage life. Limitations are their thermoplasticity and their creep behavior. Due to the manifold variations available (homo- or copolymerization products, unmodified or modified, with or without plasticizers) PVAc adhesives show a great variety of processing and bonding properties. The various formulations differ in viscosity, drying speed, color of the bondline, flexibility or brittleness, hardness or smoothness, and other characteristics.

The bonding priniciple of PVAc adhesives is based on the removal of the water by penetration into the wood substrate or by evaporation to the surrounding air. The forming of the bondline also requires the application of proper pressure. The final bond strength is reached after migration of the residual water away from the bondline. The minimum temperature of film formation (or white point) is 4–18°C, depending on the type of the adhesive and the addition of plasticizers. This temperature is determined mainly by the glass transition temperature T_g of the polymer used which for PVAc is approximately 28°C. Parameters influencing the drying time are the type of the adhesive, the type of wood surface, the wood substrate absorption behavior, the wood moisture content, relative humidity and temperature of the surrounding air, the amount of adhesive applied, and the temperature of the adhesive and the wood surfaces.

Depending on the formulations, various grades of water resistance can be achieved. For the two-component PVAc adhesives, crosslinking and hence a thermosetting behavior is obtained by addition of hardening resins (e.g., based on formaldehyde), complex forming salts [based on chromium (Cr III), e.g., chromium nitrate, or aluminum (Al III), e.g., aluminum nitrate] or isocyanate. The bondlines are then resistant against high temperatures and the influence of water.

The addition of comonomers during polymerization enables a higher flexibility to be obtained compared to PVAc homopolymers. This causes also a lower glass transition temperature and a lower minimum film formation temperature. Possible comonomers are acrylic acid esters (butylacrylate, 2-ethylhexylacrylate), dialkylfumarates, ethylene, and others.

Plasticizers soften the film and increase both adhesion and setting rate. The most common are phthalates, adipates, and benzoates. The amount added can be in a broad range of 10–50% by weight. They affect swelling and softening of the PVAc particles and hence ensure the film-forming capabilities at room temperature, the tack of the still wet and of the dried bondline, and a better water and moisture resistance of the bondline. Disadvantages are the lower resistance of the bondline against heat, possible migration of the plasticizers, and an enhanced cold flow.

Fillers (calcium carbonate, calcium sulfate, aluminum oxide, bentonites, wood flour) increase the solid content of the dispersion, and they are added up to 50%, based on PVAc. The purpose of their addition is the reduction of the penetration depth, a thixotropic behavior of the adhesive, gap filling properties, and the reduction of the adhesive costs. Disadvantages can be the increase of the white point and possibly the more marked tool wear rate due to greater hardness of the adhesive. Other components in PVAc formulations are defoamers, stabilizers, filler dispersants, preservatives, thickeners (hydroxyethylcellulose, carboxymethylcellulose), poly(vinyl alcohols), starch, wetting agents, tackifiers, solvents (alcohols, ketones, esters), flame retardants, and others.

The PVAc bond strength decreases at higher temperatures due to the thermoplastic behavior of the adhesive itself. The higher the average molar mass of the polymer, the smaller this temperature-dependent loss of strength. Under long term load, PVAc bondlines are susceptible to cold flow, especially when plasticizers are included in the formulation. Both effects limit the heat resistance of a PVAc bondline and generally the long term strength under load at higher temperatures (>40°C) as well.

IX. INFLUENCE OF THE ADHESIVE ON THE BONDING PROCESS AND THE PROPERTIES OF WOOD PRODUCTS

For the production of wood-based panels various adhesives are in use, including aminoplastic resins (UF, MUF, MUPF), phenolic resins (PF), and isocyanate (PMDI).

Table 15 Evaluation of the Three Adhesive Types UF, PF, and PMDI with Regard to Various Parameters

Property	UF	PF	PMDI
Price	low	medium	high
Necessary hardening temperature	low	high	low
Susceptibility to wood species	high	low	low
Efficiency	low	medium to high	high
Manipulation	easy	easy	difficult
Resistance against boiling water	no	high	high

Source: Ref. 336.

The proper choice of the adhesive depends on the required properties of the wood-based panels, on the working conditions during production as well as on the cost of the adhesive system. This does not only include the net price of the adhesive but also the overall cost of the gluing system including glue spread, capacity of the line (necessary press time), and other parameters (Table 15). Environmental aspects can also have a significant influence on the choice of the adhesive system.

A. Viscosity

The viscosity of a glue mix is determined by the viscosity of the resin (mainly depending on the degree of condensation and the resin solids content) and the composition of the glue mix. If the viscosity or the degree of condensation of the resin is too low, a large portion of the resin might penetrate into the wood, causing a starved glue line. In such a case no true glue line can be formed and hence no bonding strength can be obtained. Conversely, at a too high viscosity there might be a lack of proper wetting by the adhesive of the wood surface opposite to that surface where the adhesive was applied, consequently with no or very low penetration into the word surface and hence no mechanical interlocking of the adhesive into the substrate. Poor bond strength will also be obtained in such a case.

Besides the viscosity of the adhesive resin itself, the viscosity of the glue mix also plays an important role in the final result. A higher dilution of the resin gives a higher volume to be spread and with this a better distribution of the resin on the particles or fibers, and thus better bonding strength [337]. This also saves on costs.

B. Flow Behavior

The flowability of a resin depends on its viscosity and the solids content as well as the changes in the viscosity at elevated temperatures in the hardening glue line. A low flowability causes poor penetration of the resin into the wood surface and low bonding strengths. A too high flowability, on the other hand, leads to overpenetration of the resin into the wood and hence to starved glue lines. Flowability and hardening act against one another during the hot press curing process.

C. Surface Tension and Wetting Behavior

Aqueous adhesive resins behave similarly to water regarding surface tension and wetting behavior. For UF resins the wetting behavior strongly depends on their molecular composition [24]. The higher the F/U molar ratio the lower the surface tension, which also can be decreased by adding a detergent [24] (a practice well known in other wood adhesives too, such as resorcinol cold sets [317]) or a few percent of a PVAc adhesive [24]. The proper wetting of the wood surface is a precondition for achieving high adhesion strength between the resin and the wood surface.

D. Reactivity

The objective of the development of adhesive resins is to achieve as high reactivities as possible, while maintaining within acceptable limits other properties such as the storage stability of the resin or the pot life of the glue mix. The reactivities of the resin and of the glue mix are determined by various parameters:

- type of resin
- composition and preparation procedure
- type and amount of hardeners
- additives which might accelerate or retard the hardening process
- hardening temperature (press temperature, temperature in the glue line, temperature in the core layer)
- properties of the wood surfaces.

E. Liquid and Powdered Resins

In the production of particleboards and MDF only liquid resins are used. In OSB production in Europe liquid resins are more often used, while rather in North America powder resins are used. The advantages and disadvantages of liquid and powder resins are summarized in Table 16.

F. Combination of Various Adhesives

For the purpose of obtaining special gluing effects and results, combinations of adhesives or resins might be used, for example:

- addition of PVAc to UF resins in order to obtain better wetting of the wood surface [24] and a more elastic glue line [338]
- UF/MUF + PMDI (as accelerator, crosslinker and/or fortifier) [8,9,192,193]
- combination of adhesives in particleboard or OSB production: e.g., core layer of PMDI and face layer of MU(P)F resin or PF resin
- production of an MUF resin by mixing a UF and an MF resin or a UF resin with an MF powder resin.

X. ANALYSIS OF WOOD ADHESIVES BASED ON FORMALDEHYDE CONDENSATION RESINS

There has been considerable progress in the characterization of formaldehyde condensation resins in the past two decades. It is now possible to analyze the polydisperse nature of the resins as well as the individual structural elements in the resins, even semi quantitatively. The curing reaction can also be monitored by means of adequate methods. The main topics of analysis are: curing reaction and building up of bonding strength; evalua-

Table 16 Advantages and Disadvantages of Liquid and Powder Resins

Type	Advantages	Disadvantages
Liquid resin	Low costs No dust-related problems	Short storage stability OSB: higher resin load on wood needed because of the poorer adhesive distribution
Powder resin	Lower resin load on wood and better resin distribution on OSB strands Lower contamination of OSB resin application blenders Longer resin storage stability Quicker gelling as no evaporation of water is necessary	Higher price due to costs for spray drying and packaging Dust-related problems

tion and monitoring of the degree of condensation and the molar mass distribution; analysis of the chemical composition of the resins and of their structural components.

The characterization of formaldehyde condensation resins was for several decades only possible with basic chemical methods, including elemental analysis [339]. The application of modern spectroscopic and chromatographic methods started as late as the 1970s. One of the reasons for this delay certainly is the fact that condensation resins themselves are still systems that might change during their preparation for analysis or during the analysis itself. Furthermore, the resins' polar character as well as their relatively low solubility often render their analysis problematic. Notwithstanding this, the chemical and structural composition of condensation resins is today well known. The validity of each analytical method (Table 17) can be compared and correlated with the information derived from the resins' technological behavior and from the properties of the wood panels bonded using these resins.

Table 17 Overview of Various Analysis Methods for Formaldehyde Condensation Adhesive Resins

Chemical tests:
- purity of raw materials
- content of free formaldehyde during resin preparation and in the finished resins
- content of formaldehyde in different forms in the resins (total formaldehyde, methylol groups)
- content of urea and melamine
- content of free and total alkali
- determination of various molar ratios: F/U; $F/(NH_2)_2$; F/P; F/P/NaOH

Physical analysis:
- spectroscopic methods: IR, ^{1}H-NMR, ^{13}C-NMR, ^{15}N-NMR
- thermal analysis methods for monitoring gelling and hardening processes: DTA, DSC, TMA, DMTA, ABES

Physicochemical methods:
- determination of the molar mass distribution and the average molar masses of the resins [GPC/SEC, GPC-LALLS, vapor pressure osmometry (VPO), light scattering, intrinsic viscosity]
- chromatographic methods (HPLC, TLC) for the determination of low molar mass species and residual monomers in the resins

Table 18 Basic Technological Tests

Property	Test method description
Solids content	Drying the sample for 2 h at 120°C; results can be influenced by the test parameters
Viscosity	Using a rotation viscometer or Ford cup (DIN cup)
pH	Direct measurement using pH electrodes
Gel time and pot life	Simplified method to determine the resin's gel time Gel time at 100°C or at 70°C Pot life at 20°C or at 30°C B-time for PF resins at 100 to 140°C*

*Chapter 26, page 556.

A. Laboratory Test Results

The properties of a resin which can be determined by simple test methods are shown in Table 18. The solids content of a resin usually is determined by the so-called dish method at 120°C for 2 h [different times and sometimes lower temperatures (105°C) are often used as several variations of this method exist]. Even if it is a rather simple test, some deviations in the results might occur because not only does all water present as solvent in the liquid adhesive resin evaporate, but also a further condensation reaction with further water elimination takes place. Both liberate condensation water and this additional water is evaporated as well. The more severe the conditions during drying, the lower the solids content measured. Also some details of the test, such as the type of oven, the number of dishes in the oven at the same time, or recirculation of air or not, can influence the results of the test. The refractive index can be used as a quick method for the determination of solids content, however, the correlation between these two characteristic resin values is sometimes rather poor and not the same for all resins. The density is only important when using volumetric adhesive dosing systems, but not as a quality parameter of the adhesive.

One of the most important characteristics is the reactivity of the adhesive resin. With some methods also the start and the end point of the gelling process, the duration of its time span, the behavior of the resin during the test as well as the shape and strength of the gelled plug obtained are essential features of the gel time test. Gelling can occur within one or two seconds (as is usual for UFs) or gelation can span ten or more seconds (as is usual for melamine fortified resins). A long gel time can indicate a slow generation of cohesive bonding strength in the actual application of the resin. The behavior of the resin in the test tube (e.g., foaming) and also the consistency and strength of the gelled plug can be evaluated.

The temperature used for the gel time test should always be adjusted to the temperature of application of the resin. If the maximum temperature in a glue line during pressing is not higher than 70°C, then the gel test should be performed at such a temperature and not at water boiling point. This is recommended in order to better interpret the behavior of the resin or the resin glue mix under its conditions of industrial application.

B. Chemical Composition of Adhesive Resins

The various components and raw materials of the resins can be determined using different chemical methods (Table 19). The content of total formaldehyde is accessible by hydrolysis of an aminoplastic resin; this process, however, is not possible for PF resins. Urea can be determined in the easiest way from the resin nitrogen content. However, other possible

Table 19 Parameters to Be Determined in Adhesive Resins Analysis

Component	urea melamine phenol formaldehyde (total formaldehyde, methylol groups) alkali (free alkali, total alkali, ash)
Analysis of residual monomers	free formaldehyde unreacted urea free phenol
Molar ratios	F/U for a straight UF resin F/M for an MF resin $F/(NH_2)_2$ for an MUF resin F/P or F/P/NaOH for a PF resin

sources of nitrogen have to be taken into account. Melamine is measured via a UV method after hydrolysis in dilute hydrochloric acid. The content of phenol and of the total formaldehyde in PF resins can only be determined by NMR. Residual monomers such as free formaldehyde, unreacted urea, and residual phenol or methanol as a residual product of formaldehyde production can be determined by various methods, e.g., free phenol via high performance liquid chromatography (HPLC).

C. Structural Components

Using different spectroscopic methods such as infrared (IR), ^{1}H-NMR, ^{13}C-NMR, or ^{15}N-NMR, analysis of the adhesive structural compounds enables a deep insight into the structural composition of resins. These results are the basis for correlations of resin structural composition with their molar composition, their preparation procedure, and the properties of the panels produced and hence to development and production of tailor-made resins. Extensive information is available on the basic nature of resins and on the content of the various structural elements, including, e.g., data concerning the type of bridges between the monomers or the degree of branching.

D. Molecular Weight Distribution and Molar Mass Averages

The molecular weight distribution (MWD) can be determined by means of GPC [or size exclusion chromatography, (SEC)]. This method divides the molecules according to their hydrodynamic volume, which is proportional to their molar mass. The most important consideration in the chromatography of formaldehyde condensation resins is the poor solubility of the resins in most solvents usually used in GPC and hence the proper choice of the solvent and the mobile phase. This choice influences the solubility of the resin, the behavior of the chromatographic columns, and the effectiveness of detection. For lower molar mass PF resins, tetrahydrofuran (THF) is a suitable solvent [128], while for higher molar mass phenolics and for MF resins, dimethylformamide (DMF) can be recommended, sometimes modified e.g., by addition of small amounts of ammonium formate or other salts such as LiCl [128,340]. UF resins are only soluble in DMF (with some undissolved higher molar mass portions) and dimethylsulfoxide (DMSO). DMSO shortens the lifetime of the chromatographic columns and causes problems with high pressures because of its higher viscosity in comparison to other organic solvents and low refractive index increments [341]. The high reactivity of the functional groups of the resins additionally requires the use of the correct solvent and mobile phase, especially concerning sample preparation, in order to obtain a satisfactory reproducibility of the results.

Another problem with GPC of condensation resins is the calibration of the columns. Because in the oligomeric and polymeric regions of the resins no compounds with a special and singular molar mass and a clear molecular structure are available, similar or chemically related substances have to be used as calibration standards. However, differences in the hydrodynamic volumes even at the same molar mass cannot be excluded totally. This uncertain calibration of the columns also induces a great uncertainty in the calculation of molar mass averages on the basis of the chromatograms obtained.

Molar mass distributions of UF resins have been reported by several authors [22,125,340–345], as have mass distributions of MUF resins [71,346–348]. The molecular characterization of PF resins can also be performed without any major problems by GPC [128,134,139,349,350]. Due to newer GPC methods, modification of the PF resin before the analysis is no longer necessary.

Figure 3 shows chromatograms of two PF resins, one with a distinct high molecular weight portion, and the other with rather lower molar masses [128]. The averages of the molar mass can be (i) calculated from the gel chromatograms, taking into consideration the above-mentioned problems with the calibration of the columns, and (ii) measured by

(a) vapor pressure osmometry for the number average molar mass (UF resins [19,22,341,344], MF resins [351], PF resins [121,352,353]) and
(b) light scattering for the weight average molar mass (UF resins [19,22,341], PF resins [354]).

The weight average molar mass at each elution volume can also be monitored directly during each GPC run using GPC–LALLS. If the weight average molar mass in this case is determined directly in the eluent by light scattering, no standard calibration of

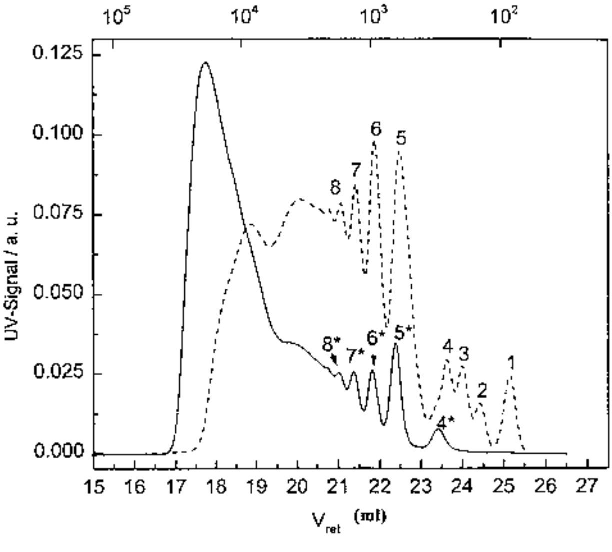


Figure 3 GPC plot of two PF resins: (——) PF resin with a distinct high molecular weight portion; (- - - -) PF resin with rather low molar masses. Column set: Merck HIBAR LiChrogel PS1 + PS4 + PS20 + PS400. Solvent and mobile phase: THF. Detection: UV–VIS, 254 and 280 nm, respectively. Concentration of samples: 1 mg/ml. Flow rate: 0.5 ml/min. (After Ref. 128.)

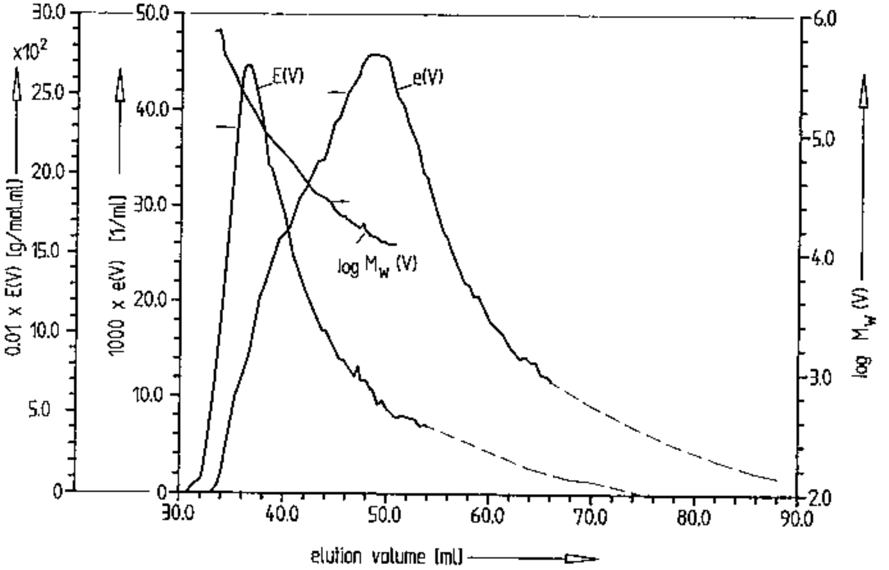


Figure 4 GPC coupled with low angle laser light scattering (GPC–LALLS) of a UF resin: e(V) = concentration signal; E(V) = normalized response of the LALLS detector; log $M_w(V) = E(V)/e(V)$ = measured weight average molar mass as a function of the elution volume V. Column set Varian Toyo Soda TSK G4000 H8+ G3000 H8+ G2000 H8+ G1000 H8. Solvent and mobile phase: 0.01 m solution of LiBr in DMF. Temperature: 40°C, flow rate: 1.1 ml/min, concentration of samples: 10–15 mg/ml. (After ref. 18.)

the column is necessary (GPC–LALLS). The eluent with the dissolved molecules passes a light scattering cell and the weight average molar mass is measured directly during each chromatographic run. However, this method is laborious and, therefore, described only in a few cases in the literature (UF [18] Fig. 4; PF [109,142,355,356]). During each run two curves are obtained: one is the concentration peak, and the other the light scattering peak, which is directly related to the actual molar mass average in the detection cell at each moment. Using these two curves, an individual calibration curve can be derived for each run. However, it must be taken into consideration that the light scattering signal can only be evaluated in the higher molar mass region and, therefore, the calibration curve is valid with sufficient accuracy only in this part of the chromatogram.

E. Monitoring of Gelling and Hardening

During gelling and hardening of the condensation resins in the hot press one can distinguish between the chemical advancement of the condensation reaction during curing of the thermosetting resin (build up of the three-dimensional network) and the progressive development of the mechanical strength of the joint (increase in cohesive bond strength). The two quantities do not progress at the same rate. The test methods that are used to follow the progression of the hardening of the resin are shown in Table 20.

The extent of chemical curing can be monitored using DTA and DSC. The exothermic behavior of the curing process is then measured as a temperature difference or directly as heat flow. Figure 5 shows a DSC plot of a PF resin [2]. The DSC run was done with pressure sealed capsules at a heating rate of 10°C/min.

Table 20 Test Methods Used to Follow Building Up of Bonding Strength

Test method	Description	References
Differential thermal analysis (DTA)	Measures the difference in temperature between two cells, these two cells are heated at a certain heating rate; one ofthe two cells contains the sample under investigation.	357–359
Differential scanning calorimetry (DSC)	Uses a similar type of instrument as DTA, but measures directly the heat flow of the exothermic and endothermic reactions occurring. The data obtained that are of interest are: shape of the curve, temperatures of the onset and the top of an exothermic or an endothermic peak, slope of the upcurve, width of the peak.	15,360–363
Differential mechanical analysis (DMA)	DMA uses a small sheet of glass fiber mats as a substrate, which is impregnated with the resin. This sample then undergoes periodic oscillations, at the same time the sample is heated following a special temperature program. The curing of the resin leads to an increase in the strength of the sample which then can be correlated with the increase of the cohesive bonding strength.	364–367
Thermomechanical analysis (TMA)	Similar to DMA but follows the adhesive hardening in situ on the real wood substrate (rather than on glass fiber). Thin wood strips are used to sandwich a liquid glue line which is then hardened. The curing of the resin leads to an increase in the strength of the sample which can then be correlated with the increase of the cohesive bonding strength as well as with the internal bond strength of wood particleboard using the same adhesive. It has been used both at constant heating rate and in isothermal mode.	368–377
Torsional braid analysis (TBA)	The damping behavior of the torsion of a glass fiber probe impregnated with the resin is characteristic for the increase of stiffness.	169,171,378
Automatic Bonding Evaluation System (ABES)	The ABES consists of a small press and a tiny testing machine in a single unit. It enables bonds to be formed under highly controlled conditions; the joints that contain the bonds which are to be measured are pressed against heated blocks for a certain time, cooled within a few seconds, and pulled immediately thereafter in shear mode. Repetition of this procedure at different curing times and temperatures yields the points (a point for each specimen) of a near-isothermal strength development curve.	96,97

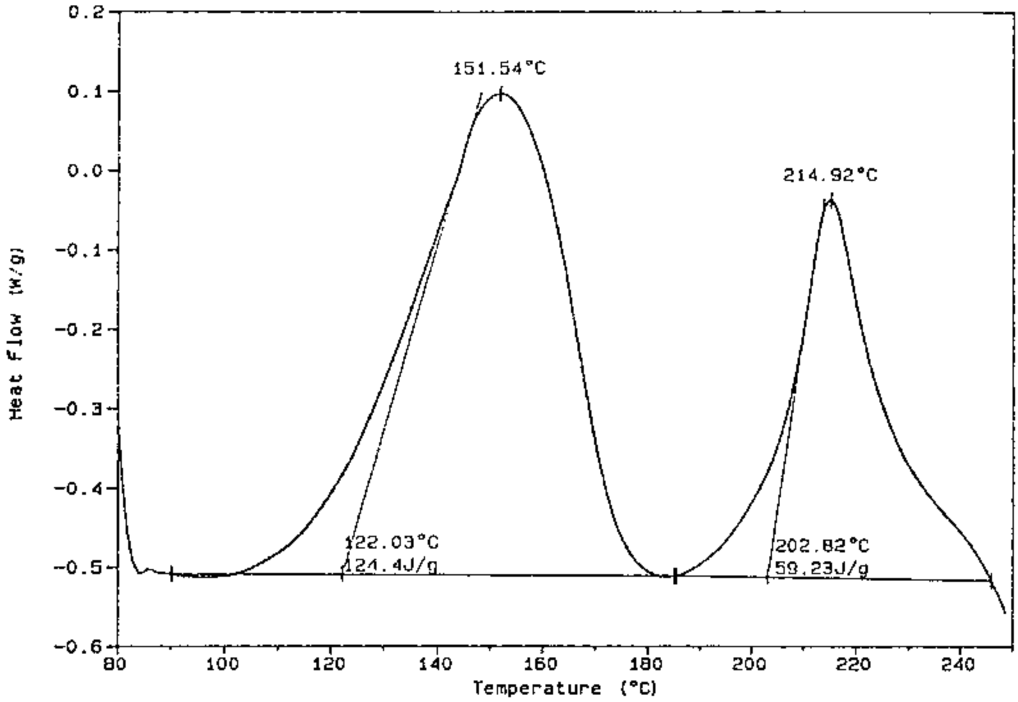


Figure 5 DSC plot of a PF resin. Pressure sealed capsules, heating rate 10°C/min. (From Ref. 2.)

During the curing of the resin the cohesive bonding strength develops step by step. Monitoring the effective strength increase (defined as the degree of mechanical curing) enables conclusions to be drawn about the suitability or not of a resin for a certain application. The best methods to use for this purpose are DMA (Fig. 6), TMA (Fig. 7) and ABES [96] (Fig. 1).

In the TMA plot in Fig. 7 it is possible to note the interactive nature of the substrate on the curing of the PF adhesive. For example, the modulus of elasticity (MOE) increase curve shows two sections (and a two peak first derivative curve). This indicates formation of entanglement networks of the resin in wood which is not possible on noninteractive substrates such as glass as in Fig. 6. Of course DMA and TMA give equally good results when used on the same wood substrate [379,380]. The ABES technique is also linearly correlated with TMA and DMA results as has been demonstrated by the linear relationship that has been found for both MUF and tannin–formaldehyde adhesives in the results of TMA and ABES [381].

In board manufacturing, when the press opens, a certain level of mechanical hardening and with this a certain bond strength is necessary to withstand the internal steam pressure in the pressed board. The full chemical curing, however, can be attained outside of the press during hot stacking. Advanced formation of the bond strength already at the same degree of chemical curing will enable shorter press times and will, therefore, increase the production capacity and reduce production costs. Plotting the chemical and mechanical degrees of curing in an *x–y* diagram shows the different hardening behaviors of various resins; such a correlation plot of the degree of chemical cure (e.g., measured by DSC) and the increase of mechanical strength (e.g., measured by TMA, DMA, or ABES) can be regarded as a fingerprint of the curing behavior of a resin [154].

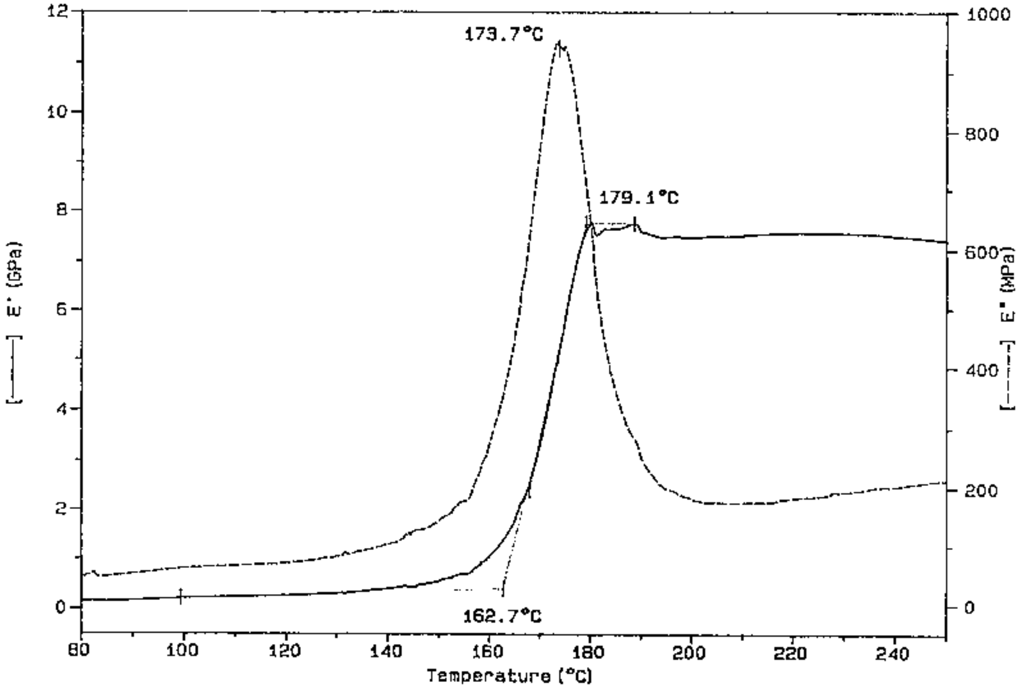


Figure 6 DMA plot of a PF resin on glass fiber. Heating rate 10°C/min. (After Ref. 2.)

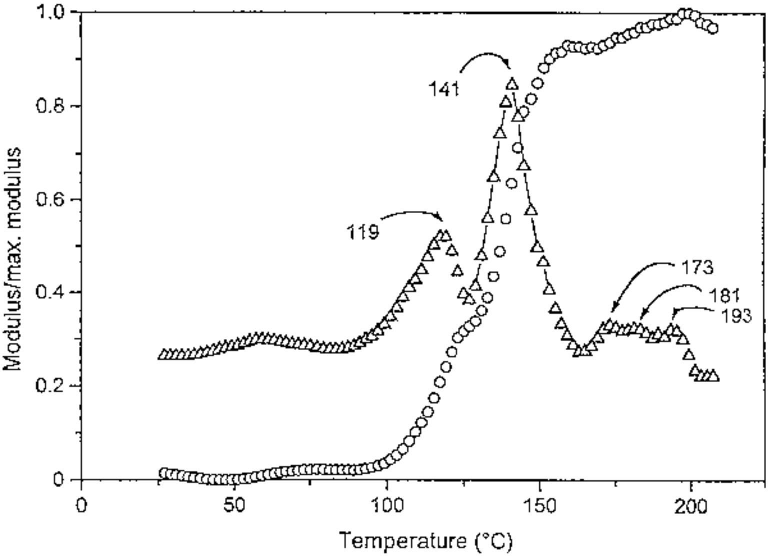


Figure 7 TMA plot of the curing of a PF resin on beech wood. Heating rate 10°C/min. Numbers in the figure are temperatures in °C. (After ref. 370.) (○) MOE curve; (△) first derivative curve.

XI. WOOD AS AN INFLUENTIAL PARAMETER IN WOOD GLUING

The properties of wood-based panels are determined, in principle, by three parameters: wood, adhesive, and processing conditions. Only if all of these three parameters are correct and well balanced in the wood bonding process, can proper bonding results be achieved. The influence of the first parameter, wood, involves several factors. Bonded wood often is described as a chain of several links: wood (substance), wood surface, interface between wood and adhesive, surface of the glue line (boundary layer), and glue line itself. As is true for all such chains, the weakest link determines the strength of the chain, and in wood gluing this is in most cases the interface.

The strength of an adhesive bond depends on various parameters:

strength of the glue line and its behavior against stresses;
influence of humidity, wood moisture content, and wood preservatives added;
wood properties, which can influence the strength of the glue line and might cause internal stresses; and
mechanical properties of the wood material.

Hence wood, especially the wood surface and its interface with the bondline plays a crucial role in the quality of bonding and therefore the quality of the wood-based panels. Low or even no bonding strength can be caused by unfavorable properties of the wood surface, e.g., low wettability.

A. Influence of Wood Species on the Properties of Wood-Based Panels

In the wood-based panels industry a great variety of wood species are used as raw materials. The choice of the wood species used is often determined just by the availability and the price of the raw material. Furthermore, large amounts of wood residues from the primary wood processing industry (e.g., saw mill waste) as well as old (recycled) wood are used. It is more than a proverb to say that the quality of a wood-based panel has already been established, to a great extent, before the wood reaches the wood storage area of the panel-producing mill. The mills generally try to maintain as constant in time as possible the composition of the wood species mix as well as the mix of wood origins and preparation modes for a certain board type. For various board types, different wood mixes (species, shape and size of the particles) are used. This is rather based on practical and empirical long term experience and often not on any reasoned thinking. Economic reasons (availability of special wood, price) can also play an important role in the choices made.

Many papers deal with special wood species in the production of wood-based panels, but the total knowledge available on this subject is not really satisfactory. Neusser and coworkers [382,383] are two of the rare examples in the literature giving a broader overview on this aspect: they have compared 18 different Austrian wood species by producing and testing laboratory particleboards. The test results obtained allowed adjustments for properties and density of laboratory boards. The best results were found for ash, followed by white beech and oak. However, these results may not be valid for all types of wood and all types of boards.

B. Wood Particle Size and Shape Before Pressing

The strength of a bond in a wood panel increases with the value of wood density for the range of approximately 0.7 to 0.8 g/cm^3. Above this density a decrease of the bond strength occurs. The performance and properties of wood-based panels are strongly influenced by the properties of the wood used. Thus, wood anisotropy as well as its heterogeneous nature, the variability of its properties, and its hygroscopicity have to be taken into account in all bonding processes. Equally, the orientation of the wood fibers and the grain angle in bonding solid wood have to be considered.

Particles as raw material for particleboards show a great variety in wood species, origin, method of preparation, age, and especially size and shape. If wood is ground into particles, a mixture of particles of very different sizes and shapes is always obtained. Particles can be described in a simple way as squared flat pieces with certain values for length l (mm), width b (mm), thickness d (mm), and slenderness ratio $s = l/\mathrm{d}$. The volume of a particle is then given as

$$V = lbd\ (\mathrm{mm}^3)$$

Considering particles with $l \gg d$, the effective gluing surface area is

$$F = 2lb\ (\mathrm{mm}^2)$$

The area form factor [384] can be considered as measure of the effective gluing surface area based on the volume. It is inversely proportional to the thickness of the particles:

$$\frac{F}{V} = \frac{2}{d} = \frac{2s}{l}$$

The influence of particle size and shape on mechanical and hygroscopic properties of boards is well described in several papers in the literature [385–390]. The central statement of these papers is an increase of bending strength, and compression and tension strength in the board plane, but a decrease of internal bond strength with increasing particle length. In particleboards the particles overlap, and thus the overlapping areas must be large enough to guarantee the transmission of the wood strength to the strength of the whole assembly.

C. Chemical Composition of Wood

Extractives contained in wood can influence the gluing process in the physical as well as chemical sense. Several authors [391–393] have indicated that the chemical composition of a wood surface after processing might be different due to the concentration on it of polar and apolar substances coming from the wood itself. Even the fiber direction of the wood surface (longitudinal, radial, tangential) can influence this composition. Extractives soluble in water or steam can migrate during the drying process to the wood surface and can decrease its wettability. In particular fatty substances and waxes might cover the wood surface. As a consequence of this, chemical weak boundary layers (CWBLs) are formed [394,395]. A chemical-induced effect can also occur if the wood extractives have a strong acidic or alkaline behavior. This might cause acceleration or retardation of the hardening process of the adhesives based on polycondensation resins.

Different wood species can show great differences in pH as well as in the buffering capacity. Even within a single wood species differences might occur due to seasonal variations, position of origin within the tree log, pH of the soil, age of the tree, time span after cutting, and drying and processing parameters.

D. Wood Surfaces

The wood surface is a complex and heterogeneous mixture of polymeric substances such as cellulose, hemicellulose, and lignin. It is also influenced by factors such as polymer morphology, wood extractives, and processing parameters. During the processing of wood and the generation of new surfaces, damage to the wood material and to the surface can occur, which might cause low quality bonding and low bond strengths. This often shows as low percent wood failure or only as a thin fiber layer. The reason for this can be a mechanical destruction of the uppermost wood layer, usually described as a mechanical weak boundary layer (MWBL) [396–398]. This layer consists of damaged wood cells caused by processing. A fracture of a bond at the interface between the wood and the adhesive can be caused by a cohesive fracture of such a weak boundary layer [399] or by a real adhesion failure at the interface [396,400].

1. Contact Angles of Wood Surfaces

A precondition for the gluing of two wood surfaces is the wetting of these surfaces by the liquid or liquified adhesive. Wetting here includes the value for the contact angle, the spreading of the liquid on the surface, and the partial penetration of the liquid into the porous adherend. Good wetting enables the creation of high adhesion forces between the wood surface and the adhesive. However, direct correlations between the contact angle and the bonding strength achieved are rather rare [401] or seem not to be universal [402]. Low contact angles ($\Theta < 45^\circ$) indicate good wetting behavior. Contact angles greater than 90° lead to incomplete wetting, which might cause low bond strengths.

The main parameters that influence the surface tension of the adhesive, when on the substrate, and therefore the possible bond strengths are:

wood species [24–26,403]
roughness of the surface [404–406]
cutting direction (radial/tangential) [24–26]
earlywood, latewood [24–26,407,408]
direction of the spreading of the droplet during measurement of the contact angle (along or lateral to the direction of the fibers) [409]
wood moisture content [410–412]
fiber angle [413]
age of the wood surface [414,415]
pH of the wood surface [416–418]
type and amount of wood extractives [401,419,420]
pretreatment of the surface, e.g., by extraction with various solvents [421]
type of adhesive: UF resins [24–26]; PF resins [406–408]

During the production of wood-based panels a certain portion of the adhesive penetrates into the wood surface. An overpenetration causes starved glue lines, whereas too low a penetration limits the contact surface between the wood and the adhesive; low penetration often is the consequence of a poor wetting behavior.

2. Modifications of the Wood Surface

Modifications of the wood surface can be implemented using various physical, mechanical, and chemical treatments. Chemical treatments are performed in particular to enhance dimensional stability of the panel, but also to improve physical and mechanical properties or to yield a higher resistance against physical, chemical, and biological degradation. To render the wood substrate hydrophobic, e.g., by acetylation, decreases the number of hydrophilic sites [422]. The OH groups of the cellulose react with acetic anhydride forming an ester. The hygroscopicity of the wood substrate decreases, and hence swelling and shrinking of the panel can be lowered [423]. Use of acetylated fibers for the production of MDF boards showed marked reduction in their thickness swelling [424,425]. It has also been reported that wood acetylation can yield reactions of the anhydride with the aromatic ring of the lignin, although the exact reaction paths are not known [426]. This chemical attack at the aromatic rings can yield some crosslinking of the constituents of the wood substrate and can, therefore, contribute to the improved wood dimensional stability.

3. *Seasonal Variations of Wood Quality in the Wood Panelboard Industry*

Hanetho [427] has discussed the experiences of the particleboard industry regarding the influence of seasonal variations of the wood quality. Some problems do occur using wood that has been harvested in the winter time and which goes into board production immediately. When these logs or chips have been stored for some time, these problems disappear. The contact angles of water and adhesive on wood are higher in the case of freshly harvested wood compared to stored chips. This means that the surface of the wood particles obtained from such a fresh wood is more hydrophobic, influencing negatively the wetting and penetration and thus the substrate gluability. It has been determined that the reason for the lower wettability of freshly harvested wood is the higher content of wood extractives. These results, however, must not be confused with the better wettability of a freshly prepared surface, independently of whether it is freshly harvested or stored wood.

Hydrophobic wood extractives and components oxidize or polymerize during storage after harvesting, as also can be seen from their lower extractibility [428]. Because of this effect the ability of wood extractives to migrate to a new surface is also reduced. Figure 8 shows this effect by plotting contact angles versus time after the

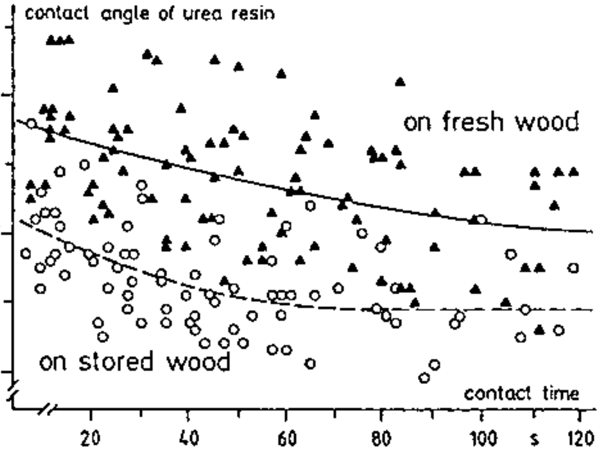


Figure 8 Contact angles of a UF resin on the surfaces of wood particles, as a function of the contact time, hence the time elapsed after the application of the droplet. The surfaces have been cut from a freshly harvested log and from a log stored for 3 months. (After ref. 428.) Water extracts from the particles made from freshly harvested wood have higher pH values, but lower buffer capacities than the surfaces made from stored chips. The lower buffer capacity might lead to prehardening if the usual amount of hardener is used, with a consequent decrease of the board strength.

application of the urea resin droplet onto the surfaces of freshly harvested wood and stored wood.

XII. PROCESSING CONDITIONS DURING PRODUCTION AS PARAMETERS INFLUENCING WOOD GLUING

A. Adhesive Consumption and Glue Spread in the Production of Particleboards

Several aspects regarding the proportion of adhesive to be used in the production of particleboards must be evaluated to obtain good results:

proportion of adhesive on individual particles
proportion of adhesive in particle mixtures and fractions
proportion of adhesive in the total particle mix
distribution of the adhesive on the surface of the particles, and proportion of the particles' surface area covered with adhesive.

The resin load content on wood as a measure of the consumption of adhesive is one of the more important parameters to consider during the production of particleboards. From a technological standpoint a certain minimum amount of resin is necessary to obtain the desired properties of the boards resulting in sufficient bonding of the individual particles. However, an excessive resin load imparts some technological disadvantages, such as high moisture content and hence possible problems with high vapor pressure during hot pressing. Furthermore, for economical reasons, the consumption of adhesive should be as low as possible as the resin contributes considerably to the costs of the finished boards. The resin load, however, is only an overall average on the total mixture of particles, without considering differences in particle size distribution and the shape of the individual particles. Moreover, the resin load gives no direct indication of the area-specific consumption of the adhesive, which is the amount of resin solids content based on the surface area of the particles. The expression "resin-robbing by the fines" is well known and describes the exceedingly high consumption of adhesive based on mass of particles owing to the great surface area of the fine particles [429,430].

The resin load on wood chips can be described in the following two ways:

mass resin load (percent or grams of resin solids content per 100 g dry particles) and
surface-specific resin load (grams of resin solids content per square meter of surface area).

If one of these two terms is known, the other can be calculated assuming a uniform distribution of the resin on the particle surfaces and estimating the total surface area of the particles.

In the production of particleboards mixtures of particles are always used as raw material, and thus the particles differ in size and shape. A size grading of the particles can be performed by sieving, where two of the three dimensions of the particle must be smaller than the standard measure of the actual sieve mesh to be passed. An exact sieving of the particles according to their size, therefore, is only possible for particles of rather similar shapes. Particles can differ widely in shape. A simplification to describe their shape is to assume that they are squared, flat with length l, width b, and thickness d for medium and coarse particles and rather cubic for the fines. Since the sieve mesh is usually graduated according to a logarithmic scale, for the theoretical calculations of the particle size

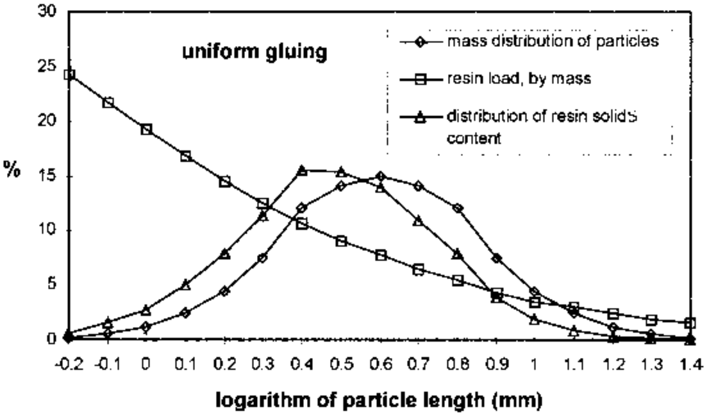


Figure 9 Example of a particle size distribution, the calculated mass resin load (gluing factor), and the distribution of the resin solids content. The overall adhesive resin consumption was assumed to be 8% resin solids content/dry wood. (After ref. 429.)

distribution this was also assumed to be logarithmic and similar to a gaussian distribution. Distributions on an industrial scale might differ from this model.

Each particle fraction has a certain relation to its resin load according to the size of the particles. Because of the great surface area of the fine particles their resin load increases strongly (linearly with the term d^{-1}). Even if there is only a small proportion of a mass fraction of very fine particles in the mixture, the high consumption of resin solids content of this fraction has a negative impact on the resin load of the coarse particles. Figure 9 shows an example of a particle size distribution with the calculated mass resin loads and the distribution of the resin solids content on the different fractions of the particle size distribution. Particle length was assumed to vary from 25 mm for the coarsest particles to 0.6 mm for wood dust, according to experience with industrial particle mixtures.

Because of the reasons discussed above, usually core layers and face layers are glued separately. In the core layer rather coarse particles predominate and in the face layer rather fine particles predominate. This separate gluing enables the use of different compositions of the glue mixes (e.g., different addition of water and hardener) and different resin loads (gluing factors) for the two layer types. An example of separate gluing is shown in Fig. 10, with separate gluing of the core layer CL (6.5% mass gluing factor) and in the face layer FL (11.0% mass gluing factor). The mass ratio of the layers CL:FL is 60:40. Figure 10 shows the particle size distributions and the mass gluing factors of the individual particle size fractions for this example of separate gluing.

Samples of industrial core layer and face layer particles, before and after gluing, can be fractionated by sieving, and thus sampling has to be done at the same time before and after blending. In the case of aminoplastic adhesives each particle fraction, glued or not, can be investigated for its nitrogen content. By knowing (i) the content of nitrogen as well as the resin solids content in the glue mix and (ii) the moisture content of the particles glued or not in the various fractions, the mass gluing factor of each glued particle size fraction can be calculated. Figure 11 shows the results of one such calculation for glued core layer and face layer particles. Even if the absolute values may differ from the calculated ones, the resin load (by weight) and the particle size show that the same shape of distribution curve is obtained.

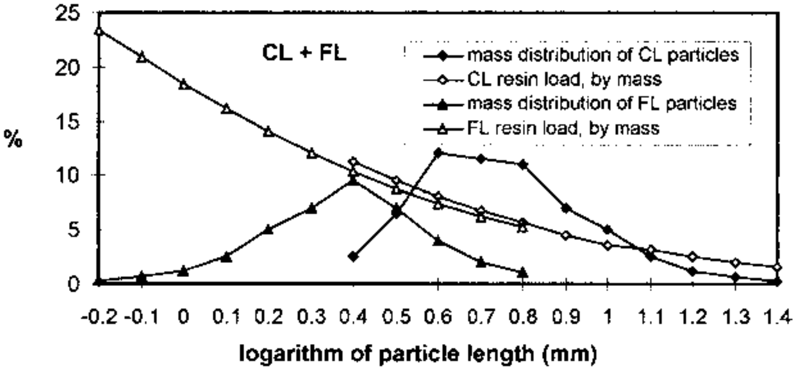


Figure 10 Particle size distribution and mass gluing factor of the individual particle size fractions for the separate gluing example "CL+FL". The resin consumption was assumed to be 6.5% resin solids content/dry wood in the core layer (CL) and 11.0% in the face layer (FL). The mass proportions are CL:FL = 60:40. (After ref. 429.)

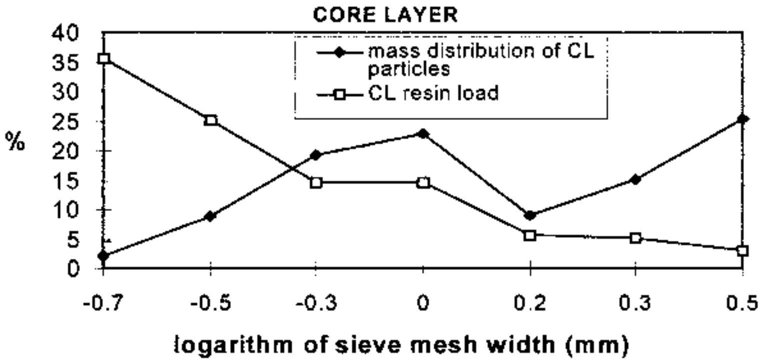


Figure 11 Fractionated mass gluing factors of industrially glued core layer particles. The mass gluing factor during blending was 9.5% resin solids/dry particles. (After ref. 429.)

Assuming that the gluing of particles of different sizes is performed randomly with their surface area as the decisive parameter, for various homogeneous particle size fractions and for different particle size mixtures the theoretical mass gluing factors and the distribution of the resin solids content can be calculated and correlated with the same values obtained experimentally, by analysis. There are some indications [431–433], however, that glue distribution is not exclusively influenced by the surface area of the particles, but has a certain preference for coarser particles. This may be due to the effectiveness of the adhesive application, thus to the separation and distribution of resin droplets, or to the mixing action in the blender after application of the resin on the wood particles (wiping effect). The concept that the particle surface area exclusively influences gluing is quite clearly invalid, if glue droplets and the surface to be glued have similar size. Meinecke and Klauditz [431] mentioned diameters of glue droplets of 8 to 110 μm, depending on the type of spraying and Lehmann [434] mentioned up to 200 μm. The latter values are of the same order of magnitude as the size of the finest particles used for the calculations above.

Besides the surface area of the particles several other parameters also have some influence on the necessary resin consumption, e.g., type of boards, thickness of the sanding zone, type and capacity of the blenders, separation and spraying of the resin (depending on if only the wiping/spreading effect occurs during blending or if instead spraying of the resin is used), shape of the particles for the same particle sizes, dependence of the slenderness ratio on particle length, concentration and viscosity of the glue resin, or a partial size degradation of the coarser particles in the blender.

New strategies in blending take into account the reality of the higher resin consumption by the finer particles, e.g., by removing the dust and the finest particles from the particle mix before blending. Also an exact screening and classifying of the particles before blending can improve the distribution of the resin on the particle surfaces and can help to spare some resin. A lower consumption of resin not only means lower costs for the raw materials, but also helps to avoid various technological disadvantages. With the resin, water is also applied to the particles; as long as this amount of water is low enough, especially in the core layer, no problem should occur with a too high vapor pressure during hot pressing. Often, however, the moisture content of the glued core particles is too high, due to an excessive gluing factor. The high vapor pressure in the board at the end of the press cycle tends to expand the fresh board; if venting is not done very carefully, blistering of the boards at the end of the continuous press or after the opening of the press might occur. Additionally, the heat transfer by the steam shock can be delayed if the vapor pressure difference betweeen the face layer and the core layer is small. If the moisture content of the glued core layer particles is high, the moisture in the glued face layer particles must be reduced. Also spraying water onto the belt before the forming station and onto the surface of the formed mat cannot be done due to the problems with the too high moisture content in the mat and hence with the too high vapor pressure.

Gluing of particles is usually done in quickly rotating blenders by spraying the resin mix into the blender. Due to the rotation of the blender a partial degradation in the size of the particles can occur. While blending OSB strands this degradation must be avoided; this is done by using slowly rotating big blender drums with a diameter of approximately 3 m. The liquid adhesive is distributed by several atomizers in this blender drum.

Gluing of fibers in MDF production is usually done in the so-called blowline between the refiner and the dryer. The advantage of this method is that it avoids resin spots at the surface of the board. The disadvantage, however, is the fact that the resin passes the dryer and can suffer part precuring. This causes some loss of usable resin (approximately 0.5 to 2% in absolute figures); therefore the glue consumption in blowline blending is higher than in the mechanical blending. Due to this fact mechanical blenders have lately been installed again in a few factories. The theory of turbulent flow blowline-gluing is not yet clearly defined [435,436]. However, some equations attempting to describe it have been recently presented [436].

B. Wood Moisture Content

The wood moisture content influences several important processes such as wetting, flow of the adhesive, penetration into the wood surface, and hardening of the adhesive in the gluing and production of wood-based panels. In bonding solid wood usually a wood moisture content of 6 to 14% is seen as optimal. Lower wood moisture contents can cause a quick dryout of the glue spread due to a strong absorption of the water into the wood surface as well as wetting problems. High moisture contents can lead to a high flow and an enhanced penetration into the wood, causing starved glue lines.

Additionally a high steam pressure can be generated which might give problems of blistering when the press opens or at the end of the continuous press. Also the hardening of a condensation resin might be retarded or even hindered.

During the hot press cycle of the particleboard or MDF production, quick changes of temperature, moisture content, and steam pressure occur. The gradients of temperature and moisture content determine significantly the hardening rate of the resin and hence the board properties. These gradients together with the mechanical pressure applied to densify the mat are decisive for generating the density profile and hence for the application properties and performance of the boards. The higher the moisture content of the glued face layer particles, the steeper the moisture gradient between the surface and the core of the mat and the quicker the heating up of the mat occurs. In the fiber mat in MDF production no differences are seen in the moisture content of the outer layer and the inner layer due to the temperature applied to the mat, nevertheless a vapor pressure gradient occurs.

The moisture content of the glued particles is the sum of the wood moisture content and the water that is part of the applied glue mix. Therefore, the moisture content of the glued particles mainly depends on the gluing factor. Usual moisture contents of glued particles are: (a) for UF, 6.5–8.5% in the core layer and 10–13% in the face layer; (b) for PF, 11–14% in the core layer and 14–18% in the face layer. The optimal moisture content of the glued and dried MDF fibers in the mat before the press is in the region of 9–11%. The higher the moisture content of particles, the easier the face layer can be densified at the start of the press cycle; this leads to a lower density in the core layer.

Blistering at the end of the press cycle or at the end of the continuous press occurs if the steam pressure within the fresh, and still hot, board exceeds the internal bond strength of the board. It should be noted that the bond strengths at higher temperatures are always lower than after cooling the board. If blistering occurs using resins with low formaldehyde content, press time should be shortened instead of prolonged, because a longer press time would not increase the bond strength but certainly would increase the steam pressure in the board. Careful venting as well as decreasing the moisture content of the glued particles and reducing the press temperature will help.

C. Press Cycle

During the hot press cycle the hardening of the resin and possible reactions of the adhesive with the wood substance take place. The influential parameters are especially the press temperature and the moisture content in the mat. Additional parameters are the wood density, porosity, swelling and shrinking behavior of the wood, structure at the surface, and wetting behavior. During the press cycle several processes take place:

transport of heat and moisture
densification, increasing internal stresses, followed by relaxation processes
adhesion between the particles or fibers
increase of the bond strength in the glue line (cohesion).

Models describing what occurs in a panel during hot pressing have been published [437–443]. These take into consideration various conditions occurring during the hot press cycle such as heat transfer, temperature gradients, moisture content, steam pressure, bond strengths, and presence or absence of postcuring [437–443].

Table 21 Press Strategy for Production of Particleboards

Different particle structures: coarser in the core, finer in the face layer.
Press temperature:
As high as possible, to enable a quick heating up of the core layer due to an optimal steam shock effect. In continuous lines press temperatures decrease from the entrance to the outlet of the press. In the last zone of the press even active cooling in a few cases is possible (decreasing steam pressure in the core layer).
Moisture content of the glued particles:
Core layer as dry as possible (ca. 6–7% in the case of UF resins), face layer as high as possible (11–14%, depending on the proportion of the face layer in the board). Too high a moisture content can cause blistering.
Spraying of water onto both surfaces in order to enhance the steam shock, amount ca. 20–40 g/m^2.
Press pressure profile:
The variation of pressure during hot pressing can follow different sequences. Quick densification with pressure maximum to enable a high density of the face layer and hence high modulus of elasticity (MOE). Sometimes a second densification step is used.

Table 22 Press Strategy for Production of MDF

Despite the uniform fiber material, a certain density profile is created due to the action of heat and compression.
Two-step pressure profile with quick densification at the start of the hot press cycle and a second densification step for the inner layer.
Uniform moisture content of the glued and dried fibers across the thickness of the mat. Higher moisture content in the outer layer would require a three-layer mat or spraying of water.

Tables 21 and 22 summarize the usual press strategies for the production of particleboards and MDF. The warming up of the mat is performed by the so-called steam shock effect [442–447]. The precondition for this is the high permeability to steam and gases of the particle or fiber mat [442,443,448,449]. High moisture contents of the face layers and spraying of water on the surface layers sustain this effect. The press temperature influences the possible press time and by this the capacity of the production line. The minimum press time has to guarantee that the bond strength of the still hot board can withstand the internal steam pressure as well as the elastic springback in board thickness at press opening.

XIII. CONCLUSIONS

Wood is a very complex material. Wood adhesives technology is an advanced science which blends the technology of adhesive preparation and formulation with a multitude of advanced application technologies to different wood products. In many fields other than wood, good bonding depends mainly on the use of a good adhesive. The situation is not as straightforward in wood gluing: in general one can obtain excellent wood panels when using a decidedly poor adhesive if the parameters governing the technology of manufacture of the wood product are well mastered. This indicates the extent to which a high level application technology can play a predominant role in this field. This is not valid for all wood products. Of course, good results are better or easier to obtain if one uses an excellent adhesive. However, just the use of a good adhesive gives no assurance of good bonding in this field. It is the essential interaction of the equally important adhesive and its application technology that this chapter has tried to describe. It is exactly this interaction that is so important in a field that comprises more than 60% by volume of all the adhesives used today in the world for any application. Without mastering this interaction between adhesive technology and wood product manufacturing technology there cannot be wood bonding of any consequence.

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Bioadhesives in Drug Delivery

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I. INTRODUCTION

The use of bioadhesives in drug delivery systems is by no means new, although increased interest in its unique applications in therapy is evidenced by the recent spate of publications. Bioadhesives complement drug delivery systems through increased residence time in the various routes of administration. Prolonged contact time can offer very substantial improvements in local drug therapy as well as significant increases in bioavailability for some drugs. Indeed, for a number of drugs that can only be administered by injection, because of either poor membrane absorption or excessive drug degradation, prolonged residence time at a particular site can obviate the need for an injectable mode of drug administration.

A *bioadhesive* can be defined as any substance that can adhere to a biological substrate and is capable of being retained on that surface for an extended period of time [1,2]. Drug delivery systems using bioadhesives usually adhere to membrane surfaces or the mucin layer coating such surfaces. The majority of the targeted areas used in drug delivery have a coating of mucus, and bioadhesive polymers that attach to this mucus coating are generally called *mucoadhesives*. Their residence times on these surfaces are controlled by whether the bioadhesive is water soluble or insoluble. In the case of water-soluble bioadhesives, contact time is generally only a few hours, depending on the adhesive and flow of biological fluid at the site of drug administration. Water-insoluble polymers, in contrast, remain in place until the mucin or tissue replaces itself, typically a period of about 4 to 72 h.

Contact between the adhesive and the mucosal membrane or its coating can be seen as a two-step process, the initial contact between the bioadhesive and substrate and the subsequent formation of bonds between the two surfaces. Success of the initial contact appears dependent on similarity of physicochemical properties between the adhesive and substrate and is often associated with "wetting" of the substrate surface. Formation of bonds, which can be electrostatic, hydrophobic, or hydrogen bonds, permit the bioadhesive (and drug delivery system) to attach to the substrate. To better understand the use

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of bioadhesives in drug delivery, it is necessary to consider the physicochemical characteristics of the bioadhesive, the substrate, and the drug. To optimize adhesion, physiological parameters of the targeted tissue must also be addressed.

II. BIOLOGICAL SUBSTRATE

A. Mucus Layer

All external cavities of the body are lined with a continuous, thick, gel-like structure called *mucin*. Although the thickness varies depending on the type of tissue [3,4], this layer serves as a protective barrier between the cell surface and its external surroundings. Mucin is secreted by goblet cells and special exocrine glands [5] and can be considered a natural bioadhesive capable of binding to the underlying epithelial tissue. This binding results in a continuous, unstirred gel layer over the mucosa and thus serves as a barrier between a drug delivery system and the underlying mucosal epithelium. Mucus is a mixture of mucin glycoproteins, water, electrolytes, enzymes, bacteria, and sloughed epithelial cells [5]. Most of the content of mucus is an aqueous fluid containing macromolecules [6], with the mucin glycoproteins making up less than 5% of the total weight [7].

Mucin glycoproteins are macromolecules linked together by cross-linking disulfide bonds, physical entanglement [6], and secondary bonds to form a continuous network. These glycoproteins have an abundance of oligosaccharide side chains [6], with their terminal ends usually being either sialic acid [8,9] or L-fucose [10,11]. The entire mucin network at physiological pH has a net negative charge due to these sialic acid residues ($\mathrm{p}K_a = 2.6$) and additional sulfate residues [12]. Thus mucin can be viewed as an anionic polyelectrolyte consisting of hydrated, cross-linked, linear, flexible glycoprotein molecules with sufficient overlap and interpenetration to form a continuous network. Since mucus is continually being formed, secreted, and removed from these tissues, its turnover rate must be taken into consideration when designing a bioadhesive dosage form.

B. Epithelial Surface

Most animal cell membrane surfaces are covered with glycoproteins and glycolipids extending from the cell exterior [13]. Collectively, all the polysaccharide structures on the outer surface of the cell are referred to as the glycocalyx [14]. The glycocalyx is continually being synthesized by the underlying cells [14] and is thought to be partly responsible for the adhesive property of the cell. Like mucus, the surface of cell membranes has a net negative charge due to the presence of charged groups [8,9], and the binding of mucin to the cell layer then results primarily from interaction between two surfaces of the same charge with additional secondary forces providing stabilization. The primary adhesive force for most bioadhesives is thought to be hydrogen bonding.

Adherence of a drug delivery system directly to any mucosal membrane can occur if the mucus layer is disturbed or the bioadhesive penetrates the mucin. Disruption of the mucus layer can be by abrasion, cell sloughing, chemical alterations by mucolytic agents, or disease state of the tissue [15]. If such an interruption occurs, bioadhesives can serve (1) to maintain continuity of the mucus layer and minimize the exposed area, (2) replace the mucus layer and provide a protective covering for the underlying cell layers from physical and chemical injury, and (3) act as a platform for drug delivery to local tissues and facilitate recovery of the damaged or diseased cell layers.

III. BIOADHESIVES

A. Bioadhesive Examples

The majority of work using bioadhesives in drug delivery has been with a small number of water-soluble and water-insoluble polymers. Water-soluble polymers are not cross-linked, whereas water-insoluble polymers are often swellable networks joined by cross-linking agents. Bioadhesives can be natural or synthetic in origin, but in drug delivery systems, nonbiological macromolecules or hydrocolloid materials are often used. Some examples of bioadhesives are given in Table 1.

B. Physicochemical Criteria for Bioadhesion

The physicochemical criteria for potential bioadhesion have been studied extensively for both natural and synthetic polymers. Past studies have shown that polyethylene glycols [16], sodium carboxymethyl cellulose [17], and potassium carrageenan [16] need a minimum molecular weight for bioadhesion. Further, the molecular weight of a compound has been shown to be proportional to its bioadhesive strength. For most polymers, increasing the molecular weight means an increase in length of the molecule, which can have an effect on the physical penetration and subsequent entanglement of the polymer with the substrate. Interpenetration and entanglement of an adhesive polymer with a mucin substrate is partly responsible for its bioadhesive strength [17], and any parameter that alters this process will have an effect on bioadhesive–mucin interaction.

The chains of water-insoluble swellable polymers are connected to cross-linking agents. As the amount of cross-linking is increased, the diffusion coefficient of the polymer chains is decreased with a subsequent decrease in interdiffusion between the polymer and substrate and a decrease in the polymer's bioadhesive properties [18,19]. This increase in cross-linking also lowers chain-segment mobility and flexibility, which can reduce the

Table 1 Examples of Bioadhesives

Type	Example	Refs.
Water soluble		
Cationic	Polylysine	22
	Poly(vinylmethylimidazole)	22
	Polybrene	22
Anionic	Alginic acid	16,17
	Carrageenan	16
	Carboxymethyl cellulose (sodium)	16,17
Neutral	Polyethelene glycol	16,22
	Poly(vinylpyrrolidone)	22
	Hydroxypropyl cellulose	68,69,70
Water insoluble		
Cationic	Gelatin	37
Anionic	Carbopol 934	70,72
	Polycarbophil	23
	Cross-linked polymethacrylic acid	23
Neutral	Hydroxypropylmethyl cellulose	17
	Poly(methyl methacrylate)	91
	Ethyl cellulose	92

amount of interpenetration and entanglement of the polymer with its substrate. It has been suggested that there is an optimal chain mobility because too little or too much flexibility of the side chains can lead to a decrease in interpenetration with the mucus [20].

The interactions between bioadhesives and their substrates occur through covalent bonds, electrostatic interactions, and hydrogen-bond formation. Due to the potential toxicity involved in covalent bonding of an adhesive to a biological substrate (e.g., cyanoacrylate "superglue"), polymers that adhere via electrostatic interactions and hydrogen bonding are preferred. Anionic, cationic, and neutral polymers have been studied extensively for their bioadhesive properties [21–23]. When the bioadhesive strength of the hydrocolloids, acrylic acid and 2-hydroxyethyl methacrylate (containing carboxyl groups and neutral groups, respectively) were measured, the role of the negatively charged groups was clearly established [23]. It was also determined that both the charge sign and density are important [21,24]. When both toxicity and bioadhesive properties are considered, polyanionic polymers appear to be better bioadhesives than polycations. Also, polyanions with carboxyl groups appear to be better than those with sulfate groups when only toxicity is considered. Thus the pH of the media can play a significant role in a polymer's bioadhesive strength, depending on the pK_a of the adhesive. Since, as mentioned above, the mucus layer and the mucosal epithelium both carry a net negative charge, electrostatic interactions are likely to occur with polyanionic molecules leading to increased bioadhesion.

Many polymers show significant bioadhesive strength when they are not ionized. Bioadhesive polymers often have numerous hydrophilic functional groups such as carboxyl, hydroxyl, amide, and sulfate groups which can form hydrogen bonds with the biological substrates [16]. These bonds may play a larger role in bioadhesion than the electrostatic interactions mentioned above. Studies using cross-linked polyacrylic acid ($pK_a = 4.75$) show that the adhesion is greatest when the carboxylate groups are in the free acid form and show a significant drop in adhesive strength above pH 4.0 [18], thus illustrating that hydrogen bonding is the dominant mechanism.

Sufficient hydration of a polymer is also of importance in bioadhesion. As bioadhesives hydrate in aqueous media, they swell and form gels with fixed charged groups inside the network. These fixed charged groups result in the development of a swelling force or a net osmotic pressure which drives the surrounding solvent from the more dilute external bulk solution into the polymer network [25]. It was found that the degree of hydration decreases as the number of charged acrylic acid groups decreases or the amount of uncharged groups on methyl methacrylate increases [26]. Thus the rate and extent of water uptake by a polymer is dependent on the type and number of hydrophilic functional groups present in the polymer and also on the ionic strength and pH of the surrounding media.

The degree of hydration of a polymer is pertinent to its adhesive properties because sufficient water is needed to properly hydrate and expand the adhesive. If insufficient amounts of solvent are available or hydration is slow, the polymer is not fully hydrated and this limits the flexibility and mobility of the polymer chains, which is crucial to their diffusion and penetration into a substrate.

Pores in the hydrated polymer are formed due to chain flexibility and chain movement [27] and are a characteristic of the expanded nature of the polymer network. Formation of pores is lowered with decreased hydration and this limits the active adhesive sites available on the polymer network. As the degree of hydration increases with an increase in the density of charged groups [26], so does the mesh size of the network. Indeed, it was determined that the tensile strength of a mucoadhesive is directly proportional to the mesh size of the polymer network [28]. Thus as with mucin, the expanded nature of the network of an adhesive is an important factor in controlling adhesive strength.

If a drug delivery system using bioadhesives is placed in an aqueous medium, the polymer will absorb water. This absorption of water leads to the formation of aqueous channels and subsequent desorption of water-soluble drug [29–31] (i.e., the hydration of the polymer allows the polymer chains to extend and form aqueous pores in the polymer matrices and allows diffusion of drug molecules out of the polymer matrix to the underlying absorbing epithelium). Controlling the swelling rate [32], the cross-linking density of the polymer network [33], ionicity and pH of the media [33,34], solubility of the active drug, and so on, of a drug delivery system containing a bioadhesive can all be manipulated to optimize release of the drug from the delivery system to the targeted membrane.

C. Methods to Quantify Bioadhesion

Various techniques have been designed to study the strength of adhesion between biological substrates and water-soluble or water-insoluble polymers. Adhesive quantitation of water-insoluble polymers usually involves measurement of tensile and shear strength of adhesion. In an appropriate buffer solution, the polymer is sandwiched between either two biological membranes or a membrane and a nonbiological substrate, and the detachment force is measured. Using a modified tensiometer, the tensile strength can be measured from the vertical force of detachment [18,26] and the shear strength can be measured from the horizontal force of detachment [26]. When measured under controlled conditions of constant surface area, rate of removal, and applied force, these two parameters can give a comparative measure of adhesive performance. These methods allow the selection of suitable tissues for adherence as well as control of the bathing medium. Although the preferred substrate for bioadhesion, the use of tissue samples can be costly, and thus other less expensive methods are sometimes sought. One such approach is to use red colloidal gold particles which form a conjugate with mucin [35]. Upon interaction with a polymer, the intensity of the red color of the conjugate–polymer can be measured spectrophotometrically. Whereas the techniques discussed above measure adhesion strength, this method measures adhesion number.

Adhesive measurement of water-soluble polymers is more difficult, but a number of techniques have been reported to assess adhesive strength adequately. One method is to coat a plate of glass with a soluble polymer and, using a tensiometer, measure the force to move it through a mucus solution [17]. Fluorescent probes have also been used to measure bioadhesion of soluble polymers to cell membranes [22]. With this approach adhesive strength is measured as a function of membrane viscosity differences before and after polymer binding using the fluorescent probe pyrene, which is incorporated into the lipid bilayer. Others have described methods on the static and dynamic adhesiveness of polymers in mucin solutions based on fluid mechanics [36]. More recently, researchers have studied bioadhesion by measuring viscometric differences in a mixture of polymer and gastric mucin [37].

IV. APPLICATIONS

Along with the physicochemical characteristics of the bioadhesive and mucin–epithelium surface, physiological events in the area in which adhesion occurs must be addressed to optimize the drug delivery system. Most delivery systems utilizing bioadhesives are designed to be topically applied to a targeted tissue. Drug delivery systems using bioadhesives can be applied to many areas of the body, such as the oral cavity, gastric, intestinal, rectal, vaginal, ocular, and dermal areas. Each tissue type has its own unique properties which can be exploited for the delivery of drugs. Each biological membrane has its own permeability, enzymatic activity, and immunology, which have to be taken into consideration if both satisfactory bioadhesion and improved bioavailability of drug are to be achieved.

A. Gastrointestinal

Most drug delivery systems are taken orally with the absorption of the drug occurring mainly in the proximal small intestine. To be effective either locally or systematically, a bioadhesive drug delivery system must be able to overcome the harsh gastric environment, motility of the gastrointestinal (GI) tract, immunogenic responses, enzymatic degradation, and dynamic changes in localization of the drug. The intestinal route is a desirable one despite these conditions because of its high absorptive characteristics compared to other routes of administration, which often need permeability enhancement of the tissue to increase bioavailability of the drug.

For a bioadhesive to adhere to either the stomach or intestine for an extended period of time, it must overcome the shear force associated with the motility patterns (parastalsis) of the GI tract, which can physically dislodge the adhesive from the mucus surface. GI motility patterns differ whether the subject is in a fasted (interdigestive) or a fed (digestive) state. Fasted-state motility has distinct phases of varying contractile magnitude, with the largest force occurring during what is called the housekeeper wave [38,39]. This phase serves to clear the upper GI tract of indigestible materials, and any bioadhesive system must therefore bind strongly enough to withstand this physical force if it is to be localized for an extended period of time. The digestive state motility pattern differs from the fasted state in that there are continuous contractions of approximately equal magnitude but only half the magnitude of the housekeeper wave. These continual contractions, as well as the physical removal of the bioadhesive by food, also need to be considered if a bioadhesive is to adhere to the mucus or underlying mucosal layer for an extended period of time.

The gastric turnover of mucin in both the fasted and fed state is a significant issue for bioadhesion in the oral route. The relatively rapid and continual production and subsequent removal of older mucus by luminal peptic activity [40] makes long-term (i.e., 24 to 48 h) bioadhesion to the gastric mucin layer impractical. Some researchers have tried to deliver drugs to the intestine at a controlled rate using bioadhesives in the stomach [41,42] but because of the mucus exchange and the motility conditions discussed above, little can be expected in long-term gastric retention in humans.

Because of the high turnover rate of gastric mucin, for a bioadhesive to remain in the stomach for an extended period of time it would therefore need to adhere to the epithelial layer instead of the mucus. This has been exploited in the use of an antiulcer drug that can adhere to damaged gastric epithelial tissue. Ulcerations are formed in the gastric and intestinal regions, where the protective mucus layer has been altered, and the underlying tissue is thus subject to proteolytic degradation by pepsins and bacteria. The antiulcer drug Sucralfate is used for the treatment of peptic ulcers and has been shown to bind to damaged gastric mucosa [43]. Sucralfate, an aluminum salt of sulfated sucrose, has been shown to protect the gastric mucosa from noxious materials such as alcohol, aspirin, and nonsteroidal anti-inflammatory drugs (NSAIDs) [44–46]. Sucralfate polymerizes upon addition to acid and forms a viscous mass that binds to the gastric mucosa [47,48]. Its protective qualities against ulcerations are thought to be due to the enhancement of gel viscosity, hydrophobicity, and mucin content of the gastric mucus in the ulcer vicinity, as well as inhibition of prostaglandin synthetase [49].

Controlled intestinal release of drugs through the use of bioadhesives has certain advantages due to the high absorptivity and neutral pH of the intestinal lumen. Barring enzymatic and immunogenic responses, tissue absorption of drugs from a bioadhesive platform can be high if retained in the intestine for extended periods of time. In situ experiments in rats [50] have shown increased residence time of certain cross-linked acrylic polymers in the intestine. This increased residence time in the lumen of the intestine increased the bioavailability of poorly absorbed drugs.

Enzymatic and immunogenic degradation of both drug and bioadhesive must be addressed in any route of administration but seems to be very important in the GI tract. A detailed review of these parameters with regard to bioadhesion is beyond the scope of this chapter, but suffice it to say that any absorption of drugs via the intestinal epithelium presupposes adequate protection against enzymatic degradation associated with the stomach and intestine as well as immune responses to antigens in the GI tract. Another drawback to the gastrointestinal route is that drugs that enter the general circulation are subject to first-pass metabolism as they pass through the hepatic-portal system leading to lower systemic availability. Most of the work to date associated with bioadhesives in drug delivery systems has focused on other routes of administration, which avoid such adverse conditions.

B. Rectal

Most recently administered drugs for either local or systemic therapy are given in suppository form. Systemic availability of rectally administered drugs is maximal when the dosage form is close to the anus [51]. Normally, after insertion, suppositories tend gradually to migrate and rest in the upper portion of the rectum. Drugs that are absorbed through this area into the bloodstream enter the hepatic-portal system and are subject to first-pass metabolism, which in turn degrades many susceptible drugs and leaves them ineffective. The lower rectum's blood flow, however, drains directly into the general circulation, and first-pass metabolism of a drug can be avoided if the delivery system can be maintained in the lower region [52,53]. Suppositories containing bioadhesives can reduce this migration toward the upper rectum and hence improve drug bioavailability.

Penetration enhancers that improve the uptake of compounds into the epithelium can also be incorporated into such a delivery system. These enhancers are often used for hydrophilic compounds (especially peptides and proteins), which show low permeability through the barrier membrane. Although penetration enhancers have obvious benefits in absorption of drugs through the epithelium, they may also cause adverse effects to the tissue as well as local or systemic side effects [54]. Yet because of the delivery system's localization, the concentration of enhancers can be minimized, thus reducing adverse effects. Indeed, promising results were shown in using enhancers in the rectum for compounds that normally show poor bioavailability. For example, insulin uptake into the bloodstream has been shown to increase when enhancers are used in rectal administration [55,56]. Controlled release of antipyrine and theophylline using cross-linked hydroxyethyl methacrylate (HEMA) as a bioadhesive was shown to sustain the availability of rectally applied drug in humans [57]. The combination of permeability enhancement and localization by bioadhesives has the potential to increase drug bioavailability significantly via the rectal route of administration.

C. Nasal

Nasal delivery systems are usually in the form of aqueous sprays in which the drug is distributed into the nasal cavity. This area provides an excellent route for drug absorption because of its large surface area and vascularity [58] as well as a thin layer of mucus secreted from local mucosal glands [59]. Absorption into the bloodstream via the nasal route also eliminates hepatic first-pass metabolism. This combination makes the nasal cavity an excellent route for localized treatment (e.g., nasal inflammation and allergic responses) as well as for systemic drug delivery. A suitable bioadhesive could then be hydrated by the nasal mucus and form a viscous gel covering the nasal cavity. The ciliary removal of mucus must be taken into consideration when using bioadhesives in the nasal cavity.

Many researchers have taken advantage of this potential route using bioadhesives as a delivery system. Hydrophilic compounds that are normally poorly absorbed in the nasal cavity [60] can still be utilized using penetration enhancers in conjunction with a retained delivery system [61]. Using degradable starch microspheres and a penetration enhancer, the nasal absorption of gentamicin [62] was shown to be improved. These microspheres form a gel when in contact with the moist nasal mucosa. Using these degradable starch microspheres, nasal administration of insulin has been shown to be improved when administered with penetration enhancers [63]. Insulin has also been administered in freeze-dried form with Carbopol 934 (a cross-linked polyacrylic acid polymer) to achieve a sustained release effect, which increased with increasing Carbopol concentration [64]. Using polyacrylic acid, other research has shown increased availability of both insulin and calcitonin by nasal administration in rats [65]. Using the nasal route of administration for insulin, as opposed to the daily subcutaneous injections commonly used, has obvious benefits with respect to patient compliance, although systemic levels of drug thus far are lower with the same dosage concentration, even with the addition of enhancers.

D. Vaginal

The vaginal and cervical route of administration is unique from other routes in that the tissue environment is subject to many changes throughout a women's life. Depending on whether the woman is pre- or postmenopausal, the tissue and mucus of the vaginal and cervical areas can be vastly different. Decreased endogenous levels of estrogen, cervical shrinkage, cell atrophy, and lower cervical mucus levels [66] are characteristic of postmenopausal women. Thus a vaginal bioadhesive delivery system geared to older women would need to address these conditions to optimize drug availability.

A women's menstrual cycle can also affect the vaginal environment. Vaginal mucus originates in the cervix, then migrates into the vaginal area. Monthly fluctuations in the properties of cervical mucin have been documented [67], showing lower viscoelasticity when estrogen is dominant and thicker, more viscoelastic mucin when progesterone dominates. Again, a bioadhesive delivery system must take these considerations into account to optimize the bioavailability of drug to the tissue.

Most vaginally administered drugs ware delivered via creams, foams, suppositories, gels, or tablets. The women's health care market is very large and profitable and hence a number of delivery systems utilizing bioadhesives have started to appear. The patented use of a soluble hydroxypropyl cellulose (HPC) cartridge for vaginal delivery of drugs has been shown to release the drug for an extended period of time [68]. The polymer forms a hydrated gel of sufficient viscosity in the vaginal cavity and releases the drug directly to the vaginal area. The anticancer drugs bleomycin, carbazilquinone, and 5-fluorouracil have been administered directly to the cervix using disk- and rod-shaped dosage forms containing a combination of HPC and Carbopol [69,70]. These dosage forms were shown to stay in the diseased area for a longer period of time than vaginal suppositories containing the same drug. Compared to suppositories, local side effects of these dosage forms were also reduced. Such a system has the possibility, then, to treat cancer of the cervix locally.

During a woman's reproductive years, the vaginal bacterial flora is capable of maintaining an acidic environment which can reduce vaginal infection by limiting the bacterial growth often associated with other disease states [71]. Maintenance of this slightly acidic pH is then crucial for vaginal health, and thus drug delivery systems that address this phenomenon have obvious therapeutic benefits. A vaginal moisturizer containing the bioadhesive polycarbophil has been shown to alleviate postmenopausal vaginal dryness (Replens, Columbia Laboratories, Hollywood, Florida). The cream has the ability to remain in the vaginal cavity for 2 to 3 days after only one administration and maintains a healthier vaginal environment through its hydration of the mucosa. Because of polycarbophil's pK_a value of 4.75, the cream also can maintain a nearly normal acidic vaginal pH, which, as discussed above, has certain health-related advantages.

E. Oral Cavity

Drug administration to the oral cavity has many advantages from both a patient and a therapeutic point of view. Both local and systemic availability can be achieved using bioadhesives in the oral cavity. Anesthetic, anti-inflammatory, and antimicrobial agents can be administered locally for increased residence time using bioadhesives. Besides the use of adhesives for retention of dentures, the dental industry has taken advantage of using bioadhesives for other localized applications. The anesthetic lidocaine, used locally for toothaches, has been shown to have an increased duration of activity when administered in a mucoadhesive tablet containing a combination of freeze-dried hydroxypropyl cellulose and Carbopol 934 [72]. This has advantages over the usual forms of topical administration, which show little precision in site specificity and can quickly be washed away by saliva. The analgesic lignocaine has also been studied when applied by a bioadhesive patch [73]. Various polymer systems have been employed to deliver fluorides to the oral cavity [74,75]. Others have reported therapeutic treatment of buccal lesions, such as aphthae and lichen planus using bioadhesives [76–78]. These dosage forms have the advantage over standard oral ointments of being applied directly to the lesion and achieving high drug levels because of increased duration at the site of inflammation.

Systemic delivery of drugs through the mouth has gained popularity in recent years. Drugs that are susceptible to degradation by the harshness of the gastrointestinal route can be administered via the mouth. This avoids first-pass metabolism of susceptible compounds by the hepatic system and offers the patient a more desirable route of administration than injection. Due to the limited area of the oral cavity, the delivery system itself is restricted in size, and hence potent compounds, such as proteins and peptides, are often more suited to such delivery systems.

The oral cavity can be divided into three distinct functional areas: the lining mucosa (buccal, sublingal, and soft palate), the masticatory mucosa (hard palate and gingiva), and the specialized mucosa (dorsal tongue). The thickness and keratinization of the tissue differs between these regions [79] and hence the permeability of each is unique [80]. The hard palate and gingiva are highly keratinized and subsequently offer limited permeability for drug delivery. The use of enhancers, however, has been shown to increase the permeability through keratinized tissues from bioadhesive platforms [81,82]. The majority of the work with systemic delivery systems using bioadhesives in the oral cavity has been concentrated on the buccal (cheek) route of administration because of its large surface area and nonkeratinization. Bioadhesive buccal tablets or patches have been utilized as delivery systems. They are usually designed to be unidirectional in their delivery (i.e., delivering the drug from the side of the patch attached to the buccal mucosa and not to rest of the mouth). This is often accomplished by an impermeable backing facing the oral cavity. The bioadhesive of choice can then serve two purposes: as an adhesive keeping the delivery system in place and/or as a drug-containing matrix in which the compound diffuses from the matrix and permeates the mucosa into the general circulation.

When administered in a mucoadhesive tablet, similar to the tablet containing lidocaine above but with the addition of an oil base and the penetration enhancer glycocholate, insulin has shown increased absorption through the oral mucosa [83]. Insulin blood levels, however, were significantly lower in comparison to systemic levels achieved by intramuscular injection. The reason for the low bioavailability could be due to poor tissue permeability, even with the enhancer. Mucoadhesive dosage forms have also been used for the treatment of cardiovascular disorders such as angina and hypertension [84–86]. When administered by an adhesive delivery system, nifedipine showed plateau drug levels after 8 h and was sustained there until removal of the delivery system. Another delivery system using nitroglycerin in a bioadhesive buccal tablet has also been shown to have a sustained effect.

F. Ocular

Drug delivery to the eyes is made difficult by dilution of drug in the tears and the natural mechanisms of blinking and high tear turnover rate, which protect the eye from external contaminants. Traditional aqueous, ocular delivery systems are administered dropwise, and due to the foregoing conditions, bioavailability is severely limited for either local or systemic therapy. Although many attempts have been made to prolong drug release of ocular delivery systems, few have proven to be completely successful when patient acceptance, drug bioavailability, and cost are considered. For a drug to be sustained in the eye, it must be maintained in the precorneal area and deliver drug to this area for an extended period of time. Ocular bioadhesive delivery systems could therefore show a sustained effect if they penetrate the aqueous tear film and interact with the underlying mucin or cell layer. If firmly attached to the surface, the dosage form could remain in the preocular area longer than conventional ocular dosage forms, and if dissolution of drug release is controlled, utilization of water-soluble drug can be increased significantly.

Pilocarpine is a drug commonly used in glaucoma therapy to relieve intraocular pressure (IOP), which is a cause of great discomfort to the patient. Piloplex is a sustained-release product based on an emulsion system of pilocarpine bound to a polymeric carrier [87,88]. Piloplex was shown to prolong a reduction in IOP as compared to standard pilocarpine hydrochloride drops. This is attributed to its bioadhesive properties, which keep the drug in the precorneal area longer than do conventional ocular dosage forms.

The release of progesterone used as a model drug in an ocular delivery system consisting of cross-linked acrylic acid has been shown to be sustained [89]. The delivery system showed increased bioavailability 4.2 times greater than a suspension without polymer and showed excellent bioadhesion to the conjunctinal mucosa of the albino rabbit. Another system utilizing polycarbophil also showed increased bioavailability of a fluorometholone steroid suspension used for the treatment of inflammation [90]. Aqueous humor drug levels were maintained above the therapeutic minimum for 8 h in albino rabbits, and the mean residence time of fluorometholone was increased 1.7 times over an aqueous suspension.

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Bonding Materials and Techniques in Dentistry

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I. INTRODUCTION

The success of modern restorative dentistry in the repair, restoration, and replacement of tooth structure is critically dependent on the availability of specialized metallic and nonmetallic materials and on procedures for their proficient application. Most of the nonmetallics are polymeric in nature, and on a volume basis, the greatest share by far of these polymeric materials find use in the construction of dentures, and to a lesser extent also in the preparation of impression materials and prosthetic restorations such as crowns or bridges. Materials of this type do not display adhesive functions; at best, they may act as adherends. Yet there are different procedures, generally in operative dentistry, where certain polymers, sometimes in combination with inorganic compounds, have come to assume leading roles as active participants in adhesion processes in addition to other vital functions associated with their particular applications in restorative and preventive dentistry. In the classification of the FDI (Fédérale Dentaire Internationale), polymers of this type fall under the description of group M1 (dental filling and related materials) and include such items as luting agents, cavity liners, pit and fissure sealants, and finally, the important class of cavity-filling cements. Although some of these materials truly conform to the characteristics of an adhesive—namely, to bond two surfaces together—others, such as the cavity-filling cements, are in a sense half-sided adhesives insofar as they bond to one adherend surface only; yet they are included here because their one-sided bonding represents a realistic process of retention. The bonding reaction may involve mechanical interlocking, and this is indeed the mechanism utilized in the majority of adhesion processes encountered in dentistry. Alternatively, it may involve a chemical, generally ionic or covalent, bond-forming process, which one finds invariably coupled with smaller or larger contributions by the mechanical retention mode.

To facilitate presentation and digest of the subject, this chapter has been subdivided into four main sections in accordance with fields of application rather than composition of materials. Brief discussions of the applications and materials requirements are followed in each category by presentations of the working materials of choice, their mode of action, and where applicable, their strong and weak points in performance. In view of the abundance of publications in the field of dental materials, no attempt has been made to provide a comprehensive compilation of references. Instead, preference has been given to the citation of selected recent publications by leading specialists, in which reference has been made to previous work on the subject. Fundamental facts and relationships presented as background information, which are considered textbook knowledge, have not been referenced. Exemplifying texts to be consulted for details are those of McCabe [1] and Wilson et al. [2].

II. LUTING

Cements are adhesive substances capable of bonding different bodies together; they are generally applied as liquids or viscous fluids, which set (harden, cure) in situ to solid materials. Dental cements used for luting or cavity lining are similar in composition and related in function; accordingly, certain data presented here are pertinent as well to Section IV. Luting cements are employed for the attachment of restorations and orthodontic bands to the tooth structure.* Luted restorations include crowns, inlays, and metal posts, as well as some of the older bridge constructions. In general, they are of a permanent nature. Temporary appliances, however (e.g., temporary crowns or splints), also require luting cements, and such appliances are similar in composition to those used for permanent luting except that they are designed for weaker bonding to facilitate future removal.

A. Requirements

A luting agent should have minimal solubility in the aqueous oral fluids while displaying good wetting properties. It should possess low initial viscosity to allow for proper seating of the restoration and for adequate narrowing of the margin between restoration and tooth. A wide margin, commensurate with a thick layer of poorly flowing, viscous cement in the luting space, will cause exposure of a proportionately large area of cement to the oral environment with consequent erosion effects, the development of microleakage, and potential secondary caries resulting from bacterial ingress. The cement should not be toxic or irritant to the pulp; it should provide thermal and, ideally, electrical insulation, features of particular importance for the luting of metallic restorations, such as gold crowns. In an ideal luting process the cement should bond chemically to the enamel and restoration adherends; with currently available materials, however, the bonding effect is largely or entirely one of micromechanical interlocking, as the material, utilizing existing surface roughness, flows into, and occupies, the microscopic interstices on the adherend surfaces. Once hardened in the assembly, the cement must assume sufficient

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*The hard tissue of the tooth substance consists of a protective outer coat of *enamel* and an underlying *dentin* phase. The latter, in turn, connects to the inner core of soft tissue (*pulp*), which is interpenetrated by nerve strands and blood vessels. The enamel, which covers essentially the visible part of the tooth and indeed represents the hardest tissue in the body, is composed almost entirely (97% by weight) of mineral-type hydroxyapatite (a crystalline calcium phosphate) in addition to a few percent of water and organic, mostly proteinaceous, matter. Dentin, constituting the major proportion of tooth substance, contains less mineralized phase (69% hydroxyapatite) but a comparatively large proportion of organic matter and water. Compositional and physical property data for enamel and dentin [3] are summarized in Tables 1 and 2.

Table 1 Composition of Tooth Structure

Component	Content[a] Enamel Percent by weight	Content[a] Enamel Percent by volume	Content[a] Dentin Percent by weight	Content[a] Dentin Percent by volume
Mineral matter (mostly hydroxyapatite)	97	92	69	48
Organic matter (mostly proteinaceous)	1	2	20[b]	29[b]
Water	2	6	11	23

[a] From Ref. 3; data approximate.
[b] Essentially collagen.

Table 2 Selected Physical Properties of Tooth Structure

Property	Enamel	Dentin
Compressive strength (MPa)	100–380[a]	250–350
Tensile strength (MPa)	10[b]	20–50
Modulus of elasticity (GPa)	10–80	11–15
Knoop hardness number	360–390	75
Vickers hardness number	350	60
Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	0.88–0.92	0.59–0.63
Coefficient of thermal expansion ($10^{-6}\ {}^{\circ}C^{-1}$)	11	8–9

[a] Depending on orientation of test sample and other factors.
[b] Measured in tension.
Source: Refs. 1 to 3.

strength for the microscopic protrusions into the interstices (tags) to withstand without fracture the occlusal masticatory (compressive and deformation) forces exerted onto the restored tooth.

B. Materials

The development of luting agents with ever more satisfactory bonding characteristics has been an ongoing objective in dental materials research for many decades. Although numerous adhesive compositions have been, and continue to be, commercialized, no perfect universal bonding systems have as yet reached the market. Important classes of luting materials include the zinc phosphate and silicophosphate cements, resin cements, chelating agents of the zinc oxide–eugenol and zinc oxide–ethoxybenzoic acid types, the polycarboxylates, the glass ionomer cements, and finally, a number of materials based on mono- and diacrylate resin systems, some of these possessing special adhesive properties.

1. *Zinc Phosphates*

Luting cements based on zinc phosphate have been known for more than a century and are still in major use today. The fundamental process leading to cementation is the formation of hydrated zinc phosphate from zinc oxide and phosphoric acid:

$$3ZnO + 2H_3PO_4 + H_2O \rightarrow Zn_3(PO_4)_2 \cdot 4H_2O$$

Accordingly, the material is supplied as a two-part system: a powder component consisting predominantly of zinc oxide, and an aqueous solution of phosphoric acid (50 to 60 wt%) and other minor ingredients. The two components are mixed by the clinician in a controlled fashion immediately prior to use. The reaction is vigorous and strongly exothermic. For clinical application some retardation is called for; in most commercial products this is achieved by high-temperature (>1300°C) sintering of the zinc oxide reactant with some 10% of other, less reactive oxides, such as MgO, resulting in partial deactivation. To buffer the reaction further, up to 10% of aluminum and zinc phosphates are added to the phosphoric acid solution. With a powder/liquid ratio of 1.4 g/mL the mixture possesses adequate fluidity and working time to permit thin-film (ideally, 35 to 40 μm) application and allow for proper seating of the restoration. The lute so prepared sets within 4 to 7 min and undergoes further hardening thereafter; ultimate compressive strength after more than 24 h is typically in the vicinity of 80 MPa.*

To achieve satisfactory mechanical characteristics of the cement, the lute margin requires protection from moisture during the setting period (e.g., by varnish application); otherwise, phosphoric acid leaches out from the fresh cement, and the latter turns chalky and porous. The retention effects of the zinc phosphate cement rest on mechanical interlocking rather than chemical bond formation to the adherends. Surface roughness therefore contributes decisively to lute retention, although a limit is set by the inherent strength of the cured cement. The shear bond strengths of the phosphate and other classical luting cements to the tooth structure are in a very low range, generally not exceeding 2 MPa. Cement solubility in the aqueous oral fluids is slight but noticeable and leads to slow lute erosion and loss of retention. The erosion is affected by lute margin width, zinc oxide load, and particle size. Taken together, such erosion effects render the zinc phosphates inferior in this respect to most resin and composite cements.

2. *Silicophosphates*

Closely related to the zinc phosphate luting cements, the silicophosphate materials are two-part bonding systems, which are mixed and applied essentially as described in the preceding section. Whereas the liquid component is a buffered aqueous phosphoric acid solution as before, the solid is a powdered mixture of a fluoride-containing, ion-leachable aluminosilicate glass and zinc oxide, and the hardening process yields a matrix of phosphates of zinc and aluminum, embedding zinc oxide, and glass particles. The fully set cement is less soluble than zinc phosphate in aqueous media, yet still prone to erosion, especially under acidic oral conditions. The fluoride content is beneficial in retarding secondary cavity formation, as fluoride ion gradually leaches from the lute. Because of their superior translucency, the silicophosphates are preferentially used for luting porcelain crowns, although their bonding mode is one of micromechanical interlocking, requiring specialized surface treatment of the porcelain restoration. The cements are weak under tensile and flexural loads but adequate in compression (Table 4).

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*The retention of most crown restorations and the older types of bride design is largely secured by the compressive forces exerted in vivo during mastication. Compressive strength data are therefore routinely specified for luting and cavity-lining cements. Representative data have been compiled in Table 3.

Table 3 Typical Compressive Strength of Luting, Cavity-Lining, and Endodontic Cements

Material	Compressive strength (MPa)
Calcium hydroxide	
Conventional	8
Resin-modified	20
Zinc phosphate	
Luting	80
Lining	140
Zinc oxide–eugenol (ZOE)	
Conventional	20
Poly(methyl methacrylate)-modified	40
Zinc oxide–ethoxybenzoic acid (EBA)	85
Methyl methacrylate resin, unfilled	85
Composite resin	180
Polycarboxylate	90
Glass ionomer	
Conventional	160
Light-cured	90
Calcium phosphate	35

Source: Ref. 1 and other literature.

Table 4 Selected Physical Properties of Restoratives

Material	Compressive strength (MPa)	Tensile strength (MPa)	Modulus of elasticity (GPa)	Thermal coefficient of expansion ($10^{-6}\,K^{-1}$)
Silicate	180–220	10–15	15–25	8–10
Acrylic				
Unfilled[a]	70–80	25–35	2	80–100
Glass ionomer				
Conventional and light-cured	180–250	11–13	1–6	13–16
Composite				
Conventional	200–260	35–55	9–15	20–35
Microfilled	250–260	30–40	6	50–75
Hybrid	300	50	14–16	
Amalgam				
Conventional	380–450	6	14–19	25

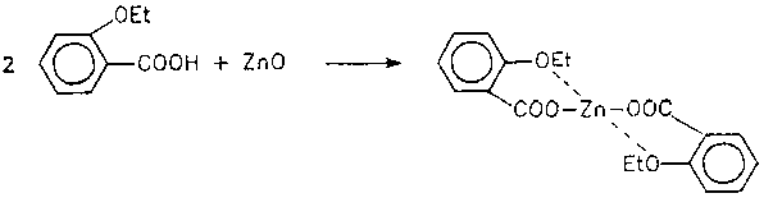
[a] No longer in use; data for comparison only.
Source: Ref. 1 and other literature.

3. *Zinc Oxide–Eugenol Cements*

Falling under the heading of metal chelate compounds, the zinc oxide–eugenol (ZOE) cements in the hardened state are essentially zinc phenolates formed by reaction of zinc oxide and eugenol (4-allyl-2-methoxyphenol) in the presence of moisture, embedding unreacted ZnO and eugenol. The products are stabilized through coordinative bonding of the metal center to two ether oxygen atoms with generation of five-membered chelate rings. The commercial products are two-part systems supplied either as powder–liquid or paste–paste combinations. In the former case, the powder is composed of zinc oxide as the primary ingredient, usually containing 1 to 5% zinc acetate added to accelerate the reaction, and the liquid component is made up of eugenol mixed with small proportions (5 to 15%) of cottonseed or olive oils, added for viscosity control. The paste–paste combinations, supplied for greater ease of mixing, generally contain the ZnO–ZnOAc solids admixed to a plant oil, on the one hand, and the eugenol admixed to an inert mineral filler, on the other. In the absence of water, the two parts mixed together by the clinician can be handled conveniently without premature setting; once applied, the mixture, now exposed to the moist and slightly warmer oral environment, sets rapidly. The cement is weak, however, having a compressive strength of no more than 10 to 20 MPa (somewhat higher upon additional resin reinforcement). In addition, eugenol leaching from the lute and subsequent hydrolysis may lead to significant deterioration of the material. For this reason, the ZOE cements should be used only for temporary luting.

4. *Zinc Oxide–Ethoxybenzoic Acid Cements*

These two-part powder/liquid materials, close relatives of the ZOE cements, in the ultimate form are zinc chelates, resulting for the most part from reaction of ZnO with *ortho*-ethoxybenzoic acid:



The zinc oxide–ethoxybenzoic acid (EBA) cements can thus be classified as zinc carboxylates in which the metal center is additionally bonded coordinatively to two ether oxygen atoms, forming electronically stabilized six-membered chelate ring structures. The powder component, again, contains zinc oxide, typically 60%, in addition to some 35% fused quartz filler and other resin ingredients, whereas the liquid part may typically consist of a 60:40 mixture of ethoxybenzoic acid and eugenol. Hence Zn eugenolate chelates are present as well in the hardened matrix. As with the ZOE materials, and much to the convenience of the clinician, the setting is accelerated by moisture in the oral environment. The hardened cement is comparatively strong under compressive load, ultimate compressive strength values reaching 80 to 85 MPa; in addition, it is less soluble than the ZOE cements in water. Both factors combine to render the EBA materials suitable for permanent luting.

5. *Polycarboxylates*

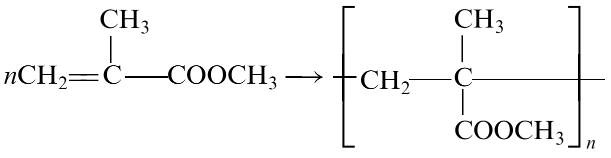
Developed some 35 years ago, the polycarboxylate materials are based on polycarboxylic acids, such as poly(acrylic acid), poly(maleic acid) and various acrylic acid copolymers, and their principal setting reaction involves carboxylate salt and chelate formation with polyvalent cations, mainly Zn^{2+}. Because of the polyvalent nature of the cations, the reaction leads to three-dimensional cross-linking. The polycarboxylates are generally supplied as two-part, solid–liquid systems. Finely powdered zinc oxide, sometimes admixed with magnesium oxide and other oxides, represents the solid component, whereas the liquid is a solution of poly(acrylic acid) (ca. 40%) and other polyacids in water. Rapid reaction occurs on mixing of the components; within 15 min some 75% of ultimate strength (compressive; approximately 80 MPa) is attained. Other commercial products are supplied as powders, which require mixing with water for cementation. These solids are composed of zinc oxide and anhydrous poly(acrylic acid) in the proper proportions, and reaction sets in upon admixture of water, which provides the vehicle for the ionic reaction sequence. Some materials contain fluoridation agents such as tin(II) fluoride in the powder component, thus providing protection of adjacent tooth structure against secondary caries without affecting the bonding characteristics. The polycarboxylate cements are more readily soluble than the phosphates in aqueous media. On the other hand, they offer an additional contribution to retention insofar as they form ionic bonds through salt formation of free carboxyl groups with the cationic calcium present in the hydroxyapatite tooth structure. The micromechanical bonding contribution in polycarboxylate cementation nevertheless is a major one, rendered highly efficacious as a result of surface porosity and wettability of the enamel adherend brought about by etching with the poly(acrylic acid). Bonding to dentinal tooth structure (invariably much weaker than to enamel) may also involve carboxyl group interaction with reactive groups (OH, NH_2) in the collagen constituent, which makes up a substantial proportion (Table 1). The polycarboxylates bond strongly to stainless steel, whereas there is little or no chemical adhesive bonding to noble metal alloys, porcelain, and resin restorations.

6. *Glass Ionomers*

For the development of cements of the glass ionomer (GI) type, features have been borrowed from both the polycarboxylates and the silicate cements. In the fundamental cementation process, polyacids, such as poly(acrylic acid) and acrylic–maleic or acrylic–itaconic acid copolymers, interact with inorganic cationic constituents of sodium aluminosilicate glass possessing a high Al content. The reaction involves a complex interplay between hydronium ions from the polyacids penetrating into the glass core and calcium and aluminum cations migrating out of the core into an outer gel phase for subsequent salt and complex formation with the polyacids. Tartaric acid is commonly added as a controlling agent of the setting characteristics. The application forms, powder–liquid and powder–water, are similar to those of the polycarboxylates. The cured cements are quite strong under compressive load, ultimate compressive strength values approximating 140 to 180 MPa, and sonication immediately after mixing of the components, resulting in void reduction, appears to have an enhancing effect on compressive strength. The adhesion characteristics resemble those of the polycarboxylates, provided that early moisture access is avoided, for example, by protecting the fresh lute margin with a coat of varnish. Typical shear bond strength data measured in vitro on conventional cements bonded to enamel and dentin, respectively, are 9 to 10 and 3 to 5 MPa [4,5]. Because of the rather low (ca. 12 MPa) inherent tensile strength of the glass ionomers, tensile failure is cohesive in the cement, setting a limit to overall expected bond strengths. For a novel stainless steel-reinforced GI cement, corresponding strength values of about 14 and 10 MPa, respectively, have been reported [5]. As the predominant use of the GI cements is in cavity lining, the reader is referred to Section IV.B.5 for additional details.

7. *Resin Cements*

Basically composed of poly(methyl methacrylate) upon setting, the acrylic resin cements in the unfilled state are simpler, linear organic polymers.



$$n\mathrm{CH_2{=}}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{{-}COOCH_3} \longrightarrow \left[\mathrm{CH_2{-}}\underset{\underset{\mathrm{COOCH_3}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}{-}\right]_n$$

Although known in dentistry for several decades, they have not as such enjoyed much acceptance because of considerable volume shrinkage on polymerization (21 to 22%) [6] and consequent microleakage, a high coefficient of thermal expansion (about 10 times greater than observed for tooth substance), high exothermicity of the polymerization reaction, and other shortcomings. Strong points, on the other hand, include low solubility in oral fluids, good thermal insulation, outstanding transparency, and ease of manipulation in the virgin (uncured) state. The commercial products generally are two-part systems made up, first, of a powder that contains fine ($< 50\,\mu$m) beads of poly(methyl methacrylate) and a peroxide-type initiator, and second, a liquid composed of methyl methacrylate monomer and a chemical activator, usually a tertiary amine, such as *N*,*N*-dimethyl-*p*-toluidine. More recent products use peroxide/alkylborane, peroxide/sulfinic acid, and other initiator/activator systems. The set cements bond mechanically to the tooth structure.

The development of filled resin cements (composites) has helped overcome some of the shortcomings of the unfilled resins. The two-part materials comprise a powder component, such as silanized silica of small (10 to 15 μm) particle size, combined with peroxide initiator, and a liquid component consisting of a bisacrylate monomer, such as 2,2-bis[4-(2-hydroxy-3-(methacryloyloxy)propoxy)phenyl]propane (bis-GMA), a diluent comonomer, usually triethylene glycol dimethacrylate (TEGDMA), and some 0.5% of a tertiary amine activator. Paste–paste and paste–liquid systems comprising the aforementioned reactants and activators are also on the market. The recent advent of light-activated composite materials for restorative applications has prompted the development of similarly composed, single-paste composite cements for luting purposes. Such light-cured cements contain certain diketones (0.03 to 0.09 wt %), the most popular being camphorquinone, which in the presence of amines generate free radicals upon irradiation with visible light. Halogen lamps (400 to 500 nm) are the standard light sources, although argon ion lasers (476.5 nm) are being used in current experimental studies with variable results. The free radicals so generated then initiate methacrylate polymerization. Also in use are *dual-cure composites*, in which a primary polymerization phase is photoinitiated, to be followed by chemically initiated secondary polymerization. Composite hardening proceeds with comparatively low polymerization shrinkage (1.2 to 2.7%) and low exothermicity, and the set cements feature low solubility and coefficients of thermal expansion significantly lower than observed with the unfilled resin materials. Both chemically and photochemically initiated low-viscosity resin systems of the bis-GMA–TEGDMA type as presented in the foregoing, yet containing little or no filler reinforcement, are now widely employed as pit and fissure sealing materials. Such sealants serve to protect natural enamel faults from becoming carious and thus represent a vital tool in preventive dentistry. Irrespective of the specifics of application, use of methacrylate-type resins requires brief

(20 to 60 s) acid-etching pre-treatment of enamel surfaces, generally with aqueous phosphoric acid as detailed in Section V.B.3. The surface roughening so achieved will allow resin tags to anchor to the enamel adherend; hence the mode of bonding to tooth structure is of the micromechanical kind. In view of the predominant part played by the composite resins as cavity-filling restoratives, the topic will be discussed in more detail in Section V.B.2.

8. *Adhesive Resins*

The luting cements based on silicates, phosphates, ZOE, EBA, and simple methacrylate resins provide little, if any, chemical adhesion, and as pointed out before, the existing bonding forces, for the most part involving micromechanical retention, are weak. However, special biphasic resin compositions are available which, on account of the presence of both hydrophilic and hydrophobic molecular constituents, experience enhanced retention to the enamel and dentinal domains of the tooth substance and to the restoration, although still largely by micromechanical interlocking. This feature is exploited for the luting of porcelain and composite inlays or onlays and for the bonding of porcelain veneers onto buccal tooth surfaces.* Resins of the biphasic type find their major use as dentin bonding agents and hence will be explored more thoroughly in Section V.B.3. Only two exemplifying luting agents for porcelain inlays are presented in this section. One of these is based on 4-(2-methacryloyloxyethoxycarbonyl)phthalic anhydride (4-META) as the key monomer. The material consists of a base, a mixture of 4-META and methyl methacrylate (MMA) which is combined with the (preoxidized) tributylborane initiator prior to application. As the material also adheres strongly to etched base alloy, it is an efficacious bonding agent for the attachment of metallic bridges to acid-etched enamel of the tooth structure. Enamel–metal joints with this 4-META-based resin system have been reported to attain mean tensile bond strengths near 26 MPa [9]. Typical shear bond strengths to both dentin and base metal alloys are 20 MPa [10]. With similar values determined for the bond to porcelain, the resin is also useful for the repair of porcelain restorations [11]. The second bonding system consists of a weakly filled, modified phosphate ester of bis-GMA. The application procedure includes etching of the enamel with aqueous phosphoric acid for surface roughening, application of the bonding resin, and placement of the restoration. The resin hardens through chemically initiated polymerization; temporary superficial protection from oxygen is required for proper conversion [12]. In order to achieve acceptable retention, the porcelain surfaces are properly pretreated.*This affords enamel–porcelain joints with representative bond strengths of 14 to 18 MPa. Typical shear bond strength values for the adhesive itself, attached to silanized composite, are in the vicinity of 25 MPa [8]. Adhering strongly to base metal alloys [12–14], this bonding system also finds use in prosthodontics for the fastening of bridges

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*For optimal retention, the surfaces of the restoration require special pre-treatment generally performed in the technician's workshop. For example, the bonding surfaces of porcelain restorations are commonly subjected to microsandblasting, followed by silanizing with a silane coupling agent, such as 3-methacryloyloxypropyl(trimethoxy)silane, or simply by acid etching with hydrofluoric acid. Combined acid-etching and silanizing procedures are also popular, as are the more recently developed methods of silica coating by various techniques [7]. Similar silanizing treatments have been proposed for composite resin inlays [8]. The mechanism of adhesion to silica-coated and/or silanized adherend surfaces includes chemical bonding through Si—O links and major or minor contributions by micromechanical interlocking.

as in the preceding case. Usefulness as an orthodontic bracket adhesive is also indicated [12], with shear bond strengths near 16 MPa and fracture in tension observed to occur at the metal surface [15]. For another highly efficacious adhesive-type luting agent, based on a biphenyldimethacrylate (BPDM) primer, the reader is referred to Section V.B.3.

III. ENDODONTIC SEALANTS

Dental root treatment commonly comprises removal of the necrotic pulp or its remnants, cleaning, widening, and sterilization of the root canal, and filling of the prepared canal with core and sealing materials. Popular core materials are silver, gutta-percha, and silicon rubber points, and these are sealed in place by a cement sealer.

A. Requirements

The filling materials are in direct contact with the dentin of the canal walls and in a more indirect contact with the soft connective tissue in the apical area. Accordingly, various features of biocompatibility are a prime requirement of the endodontic sealant cements. These cements must also display acceptably low levels of solubility in aqueous media in addition to providing a good seal along the entire contact area for prevention of ingress of bacteria. Setting characteristics must be such that placement in the moist and warm endodontic environment can be accomplished without premature hardening; hence moisture activation, as observed with certain luting cements of the ZOE type, cannot be tolerated. Radiopaqueness is a property frequently called for whenever radiographic control of the filling geometry is indicated.

B. Materials

Although covered as a separate group (M2) in the FDI classification, the endodontic cements are to a large extent similar to the luting materials covered in Section II.B. One of the most frequently used cements is based on the ZOE system (see Section II.B.3) for reasons of simple and conventional application techniques and good setting properties. The irritating effects of the eugenol constituent are generally tolerated. Modified ZOE products containing various additives for consistency or setting time control dominate the market. Related sealer materials based on zinc oxide and ketone-type Zn-chelating agents, sometimes further modified with vinyl polymers, are also commercially available, as are certain retarder-modified calcium hydroxide–zinc oxide–salicylate combinations similar to the calcium hydroxide cavity-lining materials of Section IV.B.1. With a different class of sealing agents, which contain acrylate monomers resulting from epoxy–bisphenol A addition reactions, good dimensional stability and sealing capacity are attained, although irritation caused by acrylic monomers diffusing into soft connecting tissue may be problematic.

Among the newer materials advocated for root canal sealing and reviewed by Chow et al. [16] is an apatitic calcium phosphate cement formed under ambient conditions from calcium hydrogen phosphate and a tetracalcium phosphate formally composed of equimolar quantities of CaO and $Ca_3(PO_4)_2$:

$$CaHPO_4 \cdot 2H_2O + Ca_4(PO_4)_2O \rightarrow Ca_5(PO_4)_3OH + 2H_2O$$

Being hydroxyapatitic in structure, cements of this type are particularly tissue-compatible, and fluoride can be introduced (OH replaced by F) to provide protection against caries. Compressive strengths of these phosphates are in the relatively low range of 30 to 50 MPa, depending on formulation and application details. Increased strength and reduced setting time are achieved by compounding the phosphates with polyalkenoic acids, such as poly(-acrylic acid).

For the most part, the sealer cements used at present exert bonding effects to adjacent surfaces of points or dentinal tooth structure by the micromechanical mode. Only the polyalkenoic acid-modified cements are likely to undergo additional weak retention through chemical bonding involving the carboxyl functions and apatitic hydroxyl groups of the dentin.

IV. CAVITY LINING

The dentinal tooth substance exposed by the clinician in the process of cavity preparation has direct access to the sensitive pulp via the dentinal tubules and so is highly responsive to irritating effects and attacks originating from, or transferred through, the cavity-filling material. Although such effects are minimal and clinically acceptable with many of the nonmetallic restoratives in current use, some of the more ‘‘classical’’ filling materials, notably amalgam, require pre-treatment of the prepared cavity with a cement acting as a base or liner with the specific function of providing a protective barrier between restoration and dentin.

A. Requirements

In the process of hardening, the overlying filling material may exert considerable pressure on the liner. Additional forces, mostly compressive in nature, will be transmitted to the liner through the hardened restorative as the completed restoration is subjected to the stresses of mastication. To prevent liner deformation and flow under the packing load in the process of cavity filling, it is important for the lining cement to have undergone sufficient hardening before the filling step is initiated. Application of the cement requires a pastelike consistency, and this contrasts with the low-viscosity materials used for luting. As a rule, depending on type of cavity, type of restorative, filling technique, and other variables, a lining cement must attain a compressive strength of up to 26 MPa prior to filling, and a sufficiently long time interval between placement of the liner and that of the restorative is therefore indicated. Ideally, a liner should display good micromechanical and/or chemical bonding characteristics vis-à-vis both the tooth structure and the restorative so as to minimize microleakage. In terms of strength and mechanism, the bonding effects depend on the materials’ composition; in practice, they are found to be rather weak.

The base or liner should provide a chemical barrier protecting the underlying dentin from attack by acids or acrylic monomers and other irritants that may diffuse out of the restoration. Needless to say, cements emitting irritants themselves may be restricted in use to the lining of shallow cavities where pulp irritation represents a less severe problem. Another important function of the cement base or lining, especially with amalgam fillings in deep cavities, is thermal and electrical insulation, so as to minimize heat transfer or transmission of electrical currents to the sensitive pulp area. Although electrical conduction is not always prevented by the common water-based ionic or metal-chelating cements, their thermally insulating properties generally are more than adequate for the purpose.

B. Materials

Not unexpectedly in view of the related functions of luting and lining materials, most of the materials discussed in Section II.B as luting agents are more or less equally useful as cavity base and liner cements. Cements classified as cavity liners include the calcium hydroxide materials, the zinc phosphates, zinc chelating agents, polycarboxylates, and glass ionomers.

1. Calcium Hydroxide Cements

One of the oldest lining materials in use, calcium hydroxide cement still enjoys some popularity in this field, although in a vastly modified form. It has antibacterial properties, is biocompatible, and promotes pulp recovery and regrowth of dentin. In the original form used—namely, as a suspension of calcium hydroxide in water—it yielded cements too weak for acceptable clinical performance. Coapplication of bonding agents such as methyl or carboxymethyl cellulose marginally raised the tensile and compressive strengths to 1 to 2 MPa and 7 to 8 MPa, respectively, and in order to apply the material as a liner under amalgam, an underlay by a different, stronger cement was required. More recent products are of the two-part type, with zinc oxide (typically, 10%) in combination with calcium hydroxide (50%) in one part, and salicylic esters exemplified by 1,3-butylene glycol disalicylate (40%) in the other. Cementation hence involves chelation, as in the more commonly used zinc oxide–eugenol cements discussed in Section II.B.3.

The latest development in the field of calcium hydroxide cements aims at light-activated compositions. The setting reaction in these products is quite different from the chelate formation mechanism of the calcium–zinc salicylate cements insofar as the materials harden through light-induced, chemically activated polymerization of dimethacrylate (bis-GMA) and monomethacrylate (HEMA) monomers as coingredients with calcium hydroxide. Although compressive strength values of present-day materials are still quite low (ca. 20 MPa), lining under amalgam is practicable under restricted conditions of cavity geometry. More often, these products are used as liners under silicate- or resin-based fillings. The bonding mode of the calcium hydroxide cements is largely micromechanical.

2. Zinc Phosphates

The zinc phosphate materials, discussed in Section II.B.1 as luting agents, are also in use for cavity lining. The major difference, compared to the luting cements, is the more putty-like consistency required for base or lining purposes and brought about by increasing the powder/liquid ratio to, maximally, 3.2 g/mL. A cement of this composition sets in 7 min or less to a hardness sufficient for amalgam filling without liner displacement, and the ultimate compressive strength may be as high as 140 MPa. Retention to the adherends, as in the luting application, utilizes micromechanical interlocking. The cements provide good thermal insulation, but the chemical barrier properties of these inherently acidic materials are poor. The former feature is beneficial, and the latter acceptable, for restoration with amalgam.

3. Zinc Oxide–Eugenol and Zinc Oxide–Ethoxybenzoate Acid Cements

The compositional and performance features of the zinc oxide–eugenol and zinc oxide–*ortho*-ethoxybenzoic acid cements were dealt with in Sections II.B.3 and II.B.4. While employed for temporary luting and filling, the ZOE materials find their major use in cavity lining. The fundamentally weak cement materials are usually reinforced for this purpose with poly(methyl methacrylate) filler in powder form, and compressive strengths of 40 to 50 MPa can thus be attained. The rather high degree of solubility and eugenol leaching, presenting a drawback in luting applications, can be tolerated for lining purposes even in deep cavities, where use of the phosphates is contraindicated. Occasionally, therefore, ZOE cements are placed as sublinings to be overlaid with zinc phosphate. They are not useful, however, as liners under resin-based restorations because free eugenol may interfere with the free-radical polymerization hardening of the resin filling materials.

Although employed predominantly as luting agents, the EBA cements, because of their high silica filler content (ca. 35%), are more resistant to flow in the uncured state, and possess higher compressive strength (80 to 85 MPa), than the ZOE cements. Therefore, they provide a useful lining function, notably under amalgam. As in luting applications, the bonding effects of both ZOE and EBA materials toward dentin and restorative are of the micromechanical mode and hence are quite weak.

4. *Polycarboxylates*

Once again, one is dealing here with a class of materials described in Section II.B.5 as luting agents, and indeed the only major difference compared to luting agents is that of consistency, the polycarboxylates used as cavity base or lining materials having a higher viscosity as a consequence of a higher concentration of the aqueous poly(acrylic acid) solution. Because of the possibility of pulp irritation by the free polyacid present in the uncured material, use of the polycarboxylates is generally restricted to the lining of shallow cavities unless the linings are underlaid by protective calcium hydroxide or ZOE sublinings. As pointed out before, the polycarboxylates stand out against the phosphates and chelating cements because of their capability of bond formation between carboxyl groups and apatitic calcium cations of enamel and dentin. Compressive strength values of the hardened cement materials typically attain 90 MPa.

5. *Glass Ionomers*

Although originally used as direct filling materials, the glass ionomer (GI) cements have since proven their worth in a number of different dental applications, including the previously discussed luting of restorations. Their use as cavity base and lining materials has increased rapidly in recent years, and in this area the glass ionomers have established themselves as a major materials class for reasons of compatibility with resin restorations, biological acceptability, good thermal insulating properties, fluoride release,* and good strength and bonding characteristics, the latter accentuated by a low coefficient of thermal expansion (typically, $15 \times 10^{-6}\ {}^\circ\mathrm{C}^{-1}$), matching that of dentin (Table 2), thus minimizing microleakage caused by expansion differentials under thermocycling conditions. Similar in composition and hardening properties to the luting variety, the lining materials contain an ion-leachable (generally, calcium fluoride-modified) sodium fluoroaluminosilicate glass and an acrylic acid homo- or copolymer as the principal reactants. The powder–liquid products comprise the finely ground glass filler in the powder component, and an aqueous

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*The release of fluoride ions to combat caries and encourage remineralization, although not directly pertinent to the adhesion problem, may affect bonding indirectly through creation of porous structures that would enhance leakage and ultimate weakening of the bond. The development of fluoride release mechanisms devoid of detrimental effects on existing bonds to restorations and restoratives or removable appliances is therefore a prime concern in dental materials research. See, for example, Cooley et al. [17,18].

solution of poly(acrylic acid) or copolymer, sometimes in combination with tartaric acid. A high aluminum content in the glass serves to increase the reactivity with the polyacid. The tartaric acid additive undergoes early complex formation with Al^{3+} ions liberated from the glass surface, thus facilitating calcium ion accessibility in the glass for acid attack; it remains an important participant in subsequent reaction steps leading to ultimate cross-linking.

Powder–water products differ from the powder–liquid products insofar as the solid component contains both the glass and the anhydrous polyacid, whereas the aqueous phase here is either plain water or a diluted aqueous tartaric acid solution. Both application forms produce the same type of end product, a cement comprising surface-gelled glass particle filler and polyacid matrix cross-linked through three-dimensional calcium and aluminum salt formation. Residual free carboxyl groups in the cement are left available for calcium salt formation involving adjacent dentin, and this represents an important, although weak chemical dentin-bonding mode utilized to advantage in GI applications. A further increase in the dentin–GI bond strength reportedly results from preconditioning the exposed dentin surface with aqueous poly(acrylic acid) solution; the conditioner etches the surface and serves to dissolve (and, perhaps, reprecipitate) the so-called smear layer, a thin (ca. 1 μm), mineral-rich zone of dentinal debris collecting on the freshly prepared dentin surface, which, if left untreated, is widely considered detrimental to the bonding process. Deep dentin surfaces, which possess a lower apatite content and show stronger resistance than upper dentin surfaces to bonding, can be activated for bonding by a mineralization treatment, which induces calcium phosphate crystallization and thus increases the Ca^{2+} ion concentration on the dentinal adherend.

GI adhesion to the enamel of the tooth structure is more efficacious than to dentin because, in addition to the calcium carboxylate bond formation with Ca^{2+} present in a higher concentration in the enamel adherend (Table 1), the free polyacid in the cement exerts an etching effect on the enamel surface, resulting in increased surface roughness and concomitantly improved micromechanical retention. Typical GI–enamel and GI–dentin bond strength data are provided in Section II.B.6. While GI liners are rarely used under amalgam, their beneficial application under composite fillings, where resin compatibility is important, has been widely accepted. Adhesion between liner and composite filling material can be improved further by etching the liner surface with phosphoric acid prior to packing of the restorative. Shear bond strength values of joints so prepared typically average 10 MPa (6.5 MPa without liner etching), and fracture occurs predominantly in the cement [19]. A weakened bond between liner and dentin, on the other hand, is often a consequence of this treatment. As the packed composite undergoes polymerization shrinkage, the firmly bonded GI liner, being subjected to tensile and/or shear stresses, tends to retreat from the dentin surface and, in the process, cause detrimental enhancement of leakage in the liner–dentin interface. With increasing success in research toward composite materials devoid of polymerization shrinkage (see Section V.B.2), one can expect this liner–dentin debonding problem to become less relevant.

The advent of light-activation methods for resin composites has prompted research into light-activated GI cements. Representative products now on the market are powder/liquid combinations. The powder, again, constitutes an ion-leachable fluoroaluminosilicate glass containing a light-activated initiator. The liquid is an aqueous solution of a polycarboxylic acid modified with methacryloyloxy side groups, for example, a poly(acrylic acid-co-methacryloyloxyethyl acrylate), hydroxyethyl methacrylate, and the light-sensitizer part of the light-activating system. Combinations of this type provide adequately long working times, as the purely chemical hardening process, utilizing the calcium cation–carboxylate interaction, proceeds at a conveniently slow rate. After completed placement, the material may be light activated, which initiates polymerization of the methacrylate side groups and entails rapid hardening. The presence of residual free carboxyl groups ensures chemical cement bonding to the enamel–dentin adherend as in the conventional products. Slow continuing reaction of polyacid and glass filler, following the light-curing step, leads to further maturation of the cement. Typical shear bond strength values for light-cured GI cements bonded to dentin range from about 3 to 5 MPa (occasionally even higher [20]), and similar values are obtained for bonds to amalgam.

Numerous other so-called "light-curing" GI cements have recently been commercialized that are related to the glass ionomers only insofar as they contain a powdery filler made up of GI powder and calcium phosphate as the principal ingredients. The matrix component of these materials is a light-curing mixture of mono- and diacrylate monomers. As a consequence, their setting shrinkage is considerably larger than that of the conventional GI cements [21]. Furthermore, containing no polyacids, these materials are unable to undergo the chemical bonding reaction to enamel–dentin characteristic of the glass ionomers proper, although other bonding mechanisms associated with the acrylate monomers may be quite efficacious. Procedural details for GI liner application have been described [22], and a good review of developments in this field is available [23].

V. CAVITY FILLING

While dental amalgam is still the most widely used cavity filling material for the direct restoration of defects in posterior teeth, the retention of amalgam filling is due entirely to macromechanical containment in the undercut cavity. The same holds true for the silicate filling materials, which have for many decades been used for anterior restoration. These two classes of restoratives are therefore outside the scope of this chapter. Of interest as adhesion-active filling materials under the present heading are the glass ionomer cements, including their metal-reinforced varieties (cermets), and the composite resins.

A. Requirements

In addition to certain biological requirements, such as cariostatic properties and lack of pulp irritability or systemic toxicity, a filling material should possess low water absorption and should not dissolve in the oral fluids. The dimensional changes (generally involving contraction) on hardening of the material should be minimal so as to preclude tensile and/or shear stress concentrations at the interface with tooth structure with resultant development of microleakage, and the thermal properties (e.g., coefficient of thermal expansion and thermal diffusivity) should resemble as far as possible those of the tooth substance so as to minimize the development of interfacial shear and tensile stresses. Ideally, the mechanical properties, notably strength and stiffness, should match those of enamel and dentin, and some bonding mechanisms, micromechanical and/or chemical, should be operative between cement and cavosurface. Additional requirements, of no major interest in the present context, are concerned with cosmetic considerations, radiopacity, and rheological behavior, the last-named two features being of importance in the clinical application.

B. Materials

1. *Glass Ionomers*

Although prevalently used as luting and cavity-lining cements, the glass ionomers play a moderate part as cavity-filling materials, largely on the strength of their adhesion to the enamel and dentin of the tooth structure, the polyacid components participating in ionic bond formation with calcium cations of the hydroxyapatite in addition to undergoing weak ionic and/or covalent bonding with basic or nucleophilic sites in the dentinal collagen. The structural features and bonding mechanisms were discussed in Sections II.B.6 and IV.B.5. The compositions and properties of the GI filling materials are quite similar to those of the luting and lining varieties, the main difference being a more viscous consistency of the filling material, brought about by increased filler/liquid ratios and/or varied types and sizes of the glass–particulate fillers. As pointed out earlier, the weak link in GI–enamel bonding frequently is not so much the interface but the cement itself, which is quite brittle and possesses low flexural (15 to 20 MPa) and diametral tensile (8 to 12 MPa) strengths. It is largely for this reason that the GI cements are not routinely employed for restoration of permanent teeth, where premature failure would be expected under the load of masticating forces.

Metal-containing GI materials, known as cermets, are the latest in specialty development in the field of dental ionomer cements. The cermets contain a filler phase obtained by fusing silver and other metals or alloys together with aluminosilicate glass and pulverizing the molten mass. This is then combined with poly(acrylic acid) in one- or two-part fashion as described in Section II.B.6. The cermets display setting and bonding characteristics resembling those of the metal-free parent cements while displaying better fatigue limits, and in properly poly(acrylic acid)-conditioned cavities, cause significantly less marginal leakage. However, there appears to be no clear superiority with respect to other strength characteristics, both tensile and compressive strength values being in the same ranges as observed for representative GI cements, although for a silver–tin–zinc alloy as the metal component, encouraging compressive and diametral tensile strength data (187 and 18 MPa, respectively) have been reported [24]. An interesting potential application for reinforced-glass ionomers in restorative dentistry suggests itself for building up cores in severely destructed teeth prior to the placement of crowns. Perfect dimensional stability is required for a core to support a superimposed crown efficaciously. Conventional composites exposed to moisture are not sufficiently stable dimensionally for this kind of application as a consequence of unduly high water sorption, and there are indications that reinforced GI cements, on account of better dimensional stability, may more adequately fulfill that requirement [25].

2. *Composites*

The shortcomings of the unfilled acrylic resins as luting agents were emphasized in Section II.B.7, and for similar reasons, these clear acrylics have failed to establish themselves as restorative materials. The composite resins on the other hand, after a lengthy development period have come to be recognized as one of the most useful and versatile classes of dental materials now available to the clinician for both anterior and posterior restorations [26]. Composite resins are essentially ceramic-filled, polymerizable dimethacrylates, the curing (hardening) of which, as pointed out before, involves three-dimensional cross-linking through free-radical polymerization of the acrylic groups, initiated either chemically (i.e., through peroxide–amine redox initiation) or photolytically (i.e., through a light-activated process commonly involving α-diketone photooxidants and amine-type photoreductants). Contrasted with the unfilled acrylic, the present-day composite resin systems feature low exotherms and comparatively low polymerization shrinkage (typically, 1.5%), low water absorption and solubility, yet improved thermal properties, esthetics, biocompatibility, and mechanical stiffness.

The dimethacrylate resins constituting the matrix generally contain aromatic ring structures to impart rigidity and high viscosity. The most common representative, bis-GMA, a bisphenol A derivative, was introduced in Section II.B.7. Other partly aromatic and highly viscous, yet less hydrophilic dimethacrylates as currently used matrix components, imparting enhanced dimensional stability, are 2,2-bis(4-methacryloyloxyphenyl) propane (bis-MA) and 2,2-bis[4-(3-methacryloyloxypropoxy)phenyl]propane (bis-PMA). To optimize clinical manipulation, the matrix contains low-viscosity comonomers, including the previously introduced TEGDMA and a large variety of aliphatic and aromatic urethanedimethacrylates. Although the degree of conversion and cross-linking increases with raised concentrations of the low-viscosity monomers, at the same time it causes increased polymerization shrinkage with obvious detrimental effects on adhesion to the tooth material. Although incremental placement of the composite, with intermittent partial curing of the individual layers, is being practiced in an effort to minimize contraction on curing, this technique tends to reduce the ultimate fracture toughness within the interface between the layers of the restorative. A recently described method of compensating for contraction during polymerization utilizes ammonia-treated montmorillonite as a low-percentage additive [27]. More promising pointers toward overcoming the polymerization shrinkage problem are found in the excellent work currently performed, inter alia, in the laboratories of Eick [6,28,29] and of Stansbury and Bailey [30] on cyclic monomers consisting of spiro-orthocarbonates, such as the cis–trans isomers of 2,3,8,9-di(tetramethylene)-1,5,7,11-tetraoxaspiro-[5.5]undecane or similar structures possessing exocyclic polymerizable double bonds. Monomers of this type undergo polymerization with volume expansion, and the reaction can be photoinitiated, for example, with (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate. Structural design features have been discussed and methods for volume change measurement presented [31]. The presence of exocyclic double bonds may facilitate polymerization, and methacryloyloxy-substituted spiro-orthocarbonates, which also polymerize with volume expansion, offer the potential for copolymerization reactions with conventional resin systems. Further advancement in this field can be expected, and this should contribute significantly to the retention properties of composite materials.

The discontinuous, reinforcing phase of the composites, which on a mass basis constitutes some 50 to 85% of the total cement, consists of siliceous ceramic filler particles, generally crystalline quartz, barium or strontium aluminoborate silica, aluminosilicate glasses, prepolymerized composite material, and specialty biphasic glasses. Depending on filler particle size, one distinguishes the conventional composites, with a filler size of 1 to 50 μm, from an important intermediate class of composites featuring 1- to 5-μm filler size, a third class known as microfilled composites with a mean particle size of 0.04 μm, and finally, the so-called hybrid composites, which for most efficient packing and highest fracture toughness, typically incorporate some 70 to 75% of conventional filler and 8 to 10% of submicron-size silica filler. These variations of filler type, size, and concentration play a major part in affecting the physical and performance characteristics and thus the optimal clinical conditions for application of each one of the numerous types of compositions on the market.

The strength, fracture toughness, and general durability of the resin–filler combinations in the oral environment are all critically dependent on a strong bond between resin matrix and reinforcement particles. Weak interfacial bonding leads to marginal degradation, penetration of oral fluids, and premature wear under the masticatory forces. Untreated filler materials are anchored to the matrix essentially by the micromechanical mode, as the polymerizing resin locks into the surface voids and crevasses of the filler or penetrates into the pores of especially porous filler materials. Introduction of a chemical adhesion component in the form of coupling agents improves the bonding dramatically. The commonly utilized compounds are methacrylate-terminated alkoxysilanes [e.g., 3-methacryloyloxypropyl(trimethoxy)silane], occasionally in combination with zirconates and other co-coupling agents. The rationale behind this structural choice is the expectation that, upon treatment of the filler materials (glassy fillers requiring preetching) with coupling agents of this type, silyl ether bonds are formed with surface hydroxyl groups of the filler, while polymerizable vinyl groups protrude from the surface layer and, on compounding with the resin, should be available for copolymerization and cross-linking with the embedding matrix. In practice, however, most of the vinyl groups of the silanized filler surface appear to undergo homopolymerization, and the actual resin bonding involves formation of an interpenetrating, rather than cross-linking, network on the interface as the polymerizing matrix resin diffuses into the polymethacrylate surface layer. Irrespective of the actual bonding mechanism operative in the interface, silanizing of filler materials prior to compounding with the matrix is generally the accepted method of efficaciously enhancing resin–filler adhesion. Typical diametral tensile bond strength values reported for a light-cured, zirconate-treated bis-GMA resin composite containing a silanized glass filler are 55 to 56 MPa, as against 32 MPa for a composite containing untreated glass [32].

3. *Bonding Agents*

One of the most intensely pursued objectives in dental materials research over the past three decades is the achievement of clinically acceptable retention, by micromechanical and/or chemical bonding mechanisms, of the restorative to the prepared enamel and dentinal tooth structure. Perfect retention, in addition to providing a major contribution to the longevity of the restoration, would offer the best protection against microleakage of oral fluids along the tooth–restorative interface, with its detrimental consequences of bacterial ingress and secondary caries development. Optimally effective interfacial bonding requires complete wetting of the adherend surfaces by the adhesive and the attainment of durable bond strengths matching the inherent strength levels of the dental and restorative components of the joint. Although materials science is still a long way from reaching such perfection, much has been accomplished in recent years in pursuit of this goal. In view of the importance of dentinal and enamel bonding in restorative practice, the subject is being treated in this section under its own separate heading. Also covered here briefly are bonding methods used for prosthodontic and orthodontic attachments and repair.

The retention of restoratives and restorations to the tooth structure is customarily measured in terms of shear bond strength and, less commonly, tensile bond strength. Peel strength measurements, as routinely performed in other segments of adhesion technology, are not particularly predictive here and hence are seldom utilized in restorative dentistry. The bond strength data reported in the dental materials literature tend to show considerable variability because of marked sensitivity to the materials and techniques employed. Type, age, and preconditioning of the tooth material, type and geometry of the prepared cavity (or other adhesion surface), and the application variables of primer and filling material all are of critical importance, and so are the details of postconditioning (e.g., storage in saline and thermocycling) of the prepared joints, and the techniques and devices used for bond strength testing.* The strength data given in the text should thus be accepted at best as representative, useful indicators of general bonding performance. It is equally important to realize that the data reported in the literature have been derived almost entirely from in vitro tests and thus cannot simply be correlated with in vivo results, although their value as predictors of clinical performance remains undisputed.

The composite materials presently on the market do not per se possess adhesive properties conducive to bonding to the hard tissue of tooth structure. Auxiliary techniques are available, however, which enable the clinician to overcome this inherent deficiency, and composite-type restorations are routinely placed nowadays under conditions leading to an acceptable, if not perfect degree of bond formation with the cavosurface. Thanks to these advances in dental material technology, cavity preparation with large undercuts, as with amalgam fillings, is no longer a necessity for successful restoration, and the beneficial consequences in terms of preservation of healthy tooth structure and minimization of secondary caries through reduction of microleakage are obvious. Because of differences in some of the bonding mechanisms between the resin–enamel and resin–dentin adherend pairs, the techniques required for resin bonding to enamel on the one hand, and to the dentinal tooth component on the other, differ in certain aspects. Enamel is a biomaterial of low free surface energy and thus will resist wetting by a potential adhesive. Moreover, as pointed out before, it consists of 97 wt % mineral constituent, essentially hydroxyapatite. Any adhesion process would therefore have to rely almost exclusively on reactions with the exposed apatitic hydroxyl groups, as has been established for the polycarboxylate and ionomer cements (Sections II.B.5 and II.B.6). Reactive partners of this type, however, are absent in the resin-based materials. For a mechanical joint, on the other hand, the cut enamel surface, having grooves substantially shallower than 100 nm, lacks the roughness required for retention of the intruding resin tags. The advent of the acid etch technique, developed by Buonocore in 1955, changed the situation dramatically. Acid etching, in essence an enamel-conditioning process, and by now a standard clinical procedure, involves a brief treatment of the clinically prepared enamel surface with acids, most commonly phosphoric acid, applied as an aqueous (30 to 50%) solution or, more conveniently, as an aqueous gel. The resultant increase in free surface energy enhances the wetting characteristics and so enlarges the interfacial contact area. In addition, the etching creates microporosity, which allows the subsequently placed resin to flow into the pores,

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*The divergence of test methods currently employed in different laboratories has prompted numerous calls for international standardization, exemplified by recent proposals to standardize methods for dentinal bond strength determination and, herewith related, for the evaluation of microleakage and marginal gap dimensions [33]. On a more universal scale, several years ago, with the aim of developing standardized test methods, a working group was convened by D.R. Beech of the Australian Dental Standards Laboratory under the auspices of the International Standards Organisation (ISO) Technical Committee 106 (Dentistry). A draft report, completed in 1991, CD TR 11405, entitled *Dental Materials Guidance on Testing of Adhesion to Tooth Structure*, presents precise details of screening tests, bond strength measurements, gap and microleakage tests, and clinical usage tests. A useful tool for assessment of the reliability of a bond is the Weibull analysis approach [34]. The method, utilized now in many laboratories, allows for determination of the probability of bond failure as a function of applied stress.

forming resin tags with a typical length of 25 μm, thus efficaciously anchoring the composite to the enamel in a micromechanical fashion. The depth of hard-tissue penetration is not necessarily, however, the prime contributor to the bonding effect; tag density and inherent strength both are of at least equal importance. The placement of heavily filled and viscous composites, including the hybrid types, which may find it difficult to penetrate into the pores, is frequently preceded by application of a layer of unfilled resin of low viscosity compatible with the composite, although the success of this method is questioned by others. Typical tensile bond strengths attained between composite resin and acid-etched enamel range from 16 to 23 MPa, highest bond strength values generally being associated with surfaces cut transversely to the enamel crystallites [35]. The topic of acid etching has been reviewed by Gwinnett [36] and by Retief [37]. In addition to the acid etching technique, methods of enamel etching by laser treatment have more recently been introduced and in general appear to be similarly effective, or even superior, although more cumbersome in clinical practice.

The development of chemical coupling or bonding agents for resin adhesion to hard tooth structure, pioneered by Bowen several decades ago [38] and more recently reviewed by that author [39], represents a challenging chapter in contemporary dental materials research. Although applicable to resin–enamel bonding, the chemical adhesive materials currently available find their major use in resin–dentin bonding applications.

Contrasted with enamel, dentin contains only 69% hydroxyapatite matter in addition to an increased percentage of organic substance of low surface energy and aqueous fluids, which occupy the dental tubules (Table 1). On a volume basis, the overall organic–aqueous domain makes up more than one-half of the dentinal substance. The dentin surface is thus a strongly hydrophilic adherend. The bis-GMA and related resin components of the composite, on the other hand, represent hydrophobic constituents. A bonding agent intended to join dentinal and composite adherends durably must therefore be hydrophilic enough to displace the aqueous phase from the dentinal surface for subsequent bonding, by whatever mechanism, to the dentinal substrate. At the same time, however, it must comprise hydrophobic molecular entities compatible with, and capable of bonding to, the resinous restorative. Based on this rationale, early biphasic, surface-active dentin bonding agents, developed in Bowen's laboratory [38], were of the type *N*-[2-hydroxy-3-(methacryloyloxy)propyl]-*N*-phenylglycine (NPG-GMA), *N*-[2-hydroxy-3-(methacryloyloxy)propyl]-*N*-(4-tolyl)glycine (NTG-GMA), and related structures. These compounds are distinguished (1) by the presence of hydrophilic functional amino acid groups capable of chelating or ionic bonding to the apatitic surface calcium and other multivalent cations and to reactive amino groups in the organic (collagen) domains of dentin, and (2) by the presence of reactive vinyl groups capable of copolymerization with composite resin. Other first-generation bonding agents contained isocyanatoacrylates or diisocyanate-terminated oligourethanes designed so as to form cross-links between dentinal hydroxyl and amine functions and filler hydroxyl groups. Halogenated phosphate esters of bis-GMA, HEMA, and other methacrylate substrates, believed to function through calcium phosphate bonding to dentin and vinyl-type copolymerization with composite resin, were also developed at that time. The compounds were applied as thin layers to variously conditioned dentinal surfaces, followed by the placement of standard composites. Athough initial results were by no means impressive, shear bond strengths at the very best attaining 10 MPa, these early pioneering investigations provided a powerful impetus to dental bonding research activities worldwide, and although many a development product fell by the wayside for reasons of poor long-term clinical performance, others were developed in the following years to a fairly high level of effectiveness and produced encouraging (although not necessarily clinically acceptable) results. Among the bonding systems that have reached the third-generation stage and compete for present-day clinical acceptance are those based on combinations of (1) glutaraldehyde with HEMA; (2) arylglycine-type surface-active monomers with PMDM, the adduct of HEMA to pyromellitic dianhydride; (3) hydrophilic HEMA with hydrophobic bis-GMA; and (4) methyl methacrylate with 4-META, the adduct of HEMA to trimellitic acid anhydride. A brief discussion of these examplify bonding systems follows.

The original glutaraldehyde–HEMA system, developed in Asmussen's laboratory [40] and commonly known as GLUMA, contains as the critical component a primer consisting of an aqueous solution of glutaraldehyde (5%) and HEMA (35%), which was applied onto the dental surface precleansed with alkali-neutralized (pH 7.4) ethylenediaminetetraacetic acid (17% in water) for smear layer removal and superficial decalcification. This was overlaid with a sealer consisting of unfilled, light-cured resin of the bis-GMA type, onto which in turn the composite was placed. The primer mixture in this system interpenetrates and forms bonds with the top zone of the partly demineralized dentin matrix, to which it anchors the resinous overlays upon free-radical homo- and copolymerization. The bonding effects achieved with this early system were unsatisfactory; average shear bond strengths generally failed to exceed 10 MPa even after the implementation of further (minor) improvements. Bond failure occurred along the weakened decalcified dentin zone, as neither the primer nor the sealer diffused through that zone into the underlying calcified matrix. Adhesive failure at the sealer–composite interface was also observed [41]. Subsequent improvements and simplifications of the GLUMA system included changes in pre-treatment and conversion of the primer into a self-contained bonding resin through inclusion of bis-GMA monomer and initiator. A typical present-day GLUMA bonding procedure [42] comprises the following steps:

1. Cavosurface cleansing by treatment with an aqueous solution of aluminum oxalate (ca. 5%) and glycine (2.5%) adjusted to pH 1.5. This results in both enamel and dentin etching and in amino acid infiltration into the etched dentin.
2. Brush application of bonding resin consisting of glutaraldehyde (5%), HEMA (33%), bis-GMA (2%), camphorquinone photoinitiator (0.1%), water (55%), and acetone (5%), followed by light curing.
3. Conventional placement of composite resin.

In this and similar systems (e.g., with pyruvic acid and glycine as cleanser components) [43,44] the amino acid infiltrated into the dentinal surface zone adds to the concentration of amino groups in that layer and thus contributes to glutaraldehyde bonding; in addition, it is believed to act as the reductant in conjunction with the camphorquinone photooxidant component in the interpenetrating resin, thus upon photoirradiation, initiating resin polymerization right along the contact surface with the cleanser. Shear bond strength values as high as 16 to 18 MPa to dentin, and up to 23 MPa to enamel, can be attained with this and similar third-generation GLUMA recipes.

In the field of bonding agents based on arylglycine–PMDM combinations, numerous advanced versions have originated from Bowen's early concept of biphasic monomers with both hydrophilic and hydrophobic functional sites as exemplified by the aforementioned NPG-GMA system. In our initial version, a second biphasic monomer, 2,5-bis[2-(methacryloyloxy)ethoxycarbonyl]terephthalic acid (PMDM), an addition product of HEMA to pyromellitic dianhydride, was added. The dentinal surface was first conditioned with an aqueous acidic solution of iron(III) oxalate, which removed the smear layer and deposited iron cations, contributing to the bonding effect through chelation. Next, an acetone solution of NPG-GMA or NTG-GMA was applied, followed by treatment with an acetone solution of PMDM and placement of the composite. The PMDM comonomer interacted synergistically with the precursor component, spontaneously inducing free-radical polymerization. Having passed through various stages of improvement, a current version, available commercially, comprises dentin conditioning with aluminum oxalate (6%) in dilute (2.5%) aqueous nitric acid, followed by application of a premixed acetone solution of NTG-GMA and PMDM. After solvent volatilization, this is overlaid with an unfilled, light-curing bis-GMA resin of low viscosity, to be followed by composite placement [39]. The micromechanical processes constituting the overall bonding effect have been studied by transmission and scanning electron microscopy* techniques [41,46]. Mean shear bond strengths of 17 to 18 MPa have been reported [47,48]; however, lower and quite variable values are also on record, once again stressing the need for standardization of bonding and testing techniques [49].

The recent finding in Bowen's laboratory that the oxalate conditioning and subsequent NPG-GMA coating steps can be replaced by a treatment with acidic NPG without loss of bonding strength has led to a related bonding system, also available commercially, in which the dentin is pretreated with a dilute (2.5%) aqueous nitric acid containing NPG (4%) [39]. This removes the smear layer, partially decalcifies the upper dentin layer, and permits interpenetration of the amino acid. Subsequent application of a 5% acetone solution of PMDM, with or without added HEMA, provides an overlay of resin, which penetrates into, and through, the decalcified zone and polymerizes spontaneously in contact with the amino acid, forming a resin-reinforced demineralized zone, which then bonds to the subsequently placed composite [46]. Tensile bond strengths are 12 to 16 MPa at best, and frequently much lower. On the other hand, and in contrast to the behavior of most other contemporary bonding agents, strength tends to increase slightly upon saline storage and thermocycling [50]. Failure typically occurs along the adhesive–tooth surface, and the adhesive resin itself is probably the weakest part of the joint.

Outstanding adhesion perfomance has recently been documented for a modified system in which the key ingredient is a combination of NTG-GMA and BPDM, a biphenyldimethacrylate derivative related to PMDM. The two components (called primers), dissolved in acetone, are premixed just prior to multiple-brush application onto the dentinal surface preconditioned either by etching with 10% aqueous phosphoric acid or by treatment with a succinic anhydride-modified HEMA (SA-HEMA) (a hydrophilic/hydrophobic methacrylate possessing a propanoic acid terminal). The low-viscosity primer mixture displaces surface moisture on the dentin and interpenetrates the partly demineralized collagen layer exposed by the etching process and fills the dentinal tubule orifices. Subsequent application of an unfilled, photocuring methacrylate bonding resin causes further resin reinforcement of the demineralized zone and subsequent copolymerization. This is followed by conventional composite application. Mean shear bond strengths range from about 27 to nearly 40 MPa, depending on details of the application technique, and failure is cohesive in dentin. The phosphoric acid-etching pre-treatment and tolerance of a

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*Although not specifically indicated in the text, the techniques of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) represent indispensable tools in the study of bonding processes and are widely used for the qualitative and quantitative evaluation of adherend surfaces, wetting and penetration, gap dimensions, and fracture mechanisms. Roulet et al. [45] have discussed the use of SEM in margin analysis, and publications dealing with preparatory methods for TEM and SEM investigations have been referenced by Eick et al. [46].

certain degree of surface moisture (by blotting or mild air drying) both combine to result in optimal bonding, whereas aggressively air-dried surfaces give considerably weaker bonds [51]. The system described also lends itself exceedingly well to metal and porcelain bonding and has therefore found application in luting operations and prosthodontics [51,52]. For example, a Ni–Cr–Be base metal alloy is bonded to composite with a mean shear bond strength in the vicinity of 25 MPa. Key aspects of the NTG-GMA–BPDM primer application have recently been discussed in some detail [52].

The development of HEMA–bis-GMA combinations as bonding agents has culminated in a number of recipes showing encouraging performance, and one major representative now on the market, defined as a dentin–enamel bonding system, has received wide attention. In a typical protocol, the enamel portions of the prepared cavity are conventionally acid etched, and the dentinal surfaces are primed with an aqueous solution of the hydrophilic HEMA and maleic acid as comonomers. This removes the smear layer and provides dentin interpenetration by the two monomers. Priming is followed by brush application, in a fairly thick layer (75 to 100 μm), of a resin adhesive composed of HEMA, bis-GMA, and a photoinitiator, with a few percent of a low-viscosity monomer added for viscosity reduction. After brief light curing of the adhesive coat, the composite is placed conventionally. Because of polymerization inhibition by oxygen, a reactive surface layer containing incompletely polymerized resin is left on the adhesive coat, and subsequent copolymerization with the composite resin overlay affords effective adhesive–composite bonding. Although earlier strength data reported were not particularly convincing, recent publications [41] cite mean shear bond strength values as high as 23 MPa, well on a par with enamel bonding data, with fracture for the major part cohesive in dentin or composite. Excellent performance with respect to minimal microleakage and marginal gap dimensions relative to competitive bonding systems tested are also on record [53]. On the other hand, this bonding system has been found to weaken on storage and thermocycling [41,50].

A combination of modified features of the last-named two bonding systems is realized in an adhesive application known as the Kanca technique, in which dentin and enamel pre-treatment by phosphoric acid etching is followed by the consecutive layering of NTG-GMA, PMDM, and HEMA–bis-GMA adhesive resins, onto which the restorative is placed by conventional manipulation. Low microleakage, and composite shear bond strengths to enamel/dentin at the 18-MPa level, have been reported [54].

The last bonding system to be dealt with in this section, presented in Section II.B.8 as a luting agent, contains as the key monomer the addition product of HEMA to trimellitic acid anhydride, 4-(2-methacryloyloxyethoxycarbonyl)phthalic anhydride (4-META). Following early reports of excellent dentin–composite bonding results with 4-META-containing adhesives (tensile bond strengths typically 17 to 18 MPa), preeminently from Nakabayashi's group and reviewed by that researcher [55], the 4-META system has since been refined to the stage of commercialization and routine clinical use [10,56]. It typically comprises the following steps:

1. Short (10 to 30 s) pre-treatment of prepared dentinal surface with the familiar citric acid–iron(III) chloride system (10% and 3%, respectively, in water).
2. Application of bonding resin, composed of 5% 4-META in MMA and premixed with the initiator, a partially oxidized tri-*n*-butylborane [57].
3. Overlaying of bonding resin coat with a thin layer of powdered poly(methyl methacrylate), followed by placement of composite.

The acidic iron(III) chloride etchant, as pointed out before, removes the smear layer and acts as a decalcifying agent. In addition, just like 4-META itself, it appears to promote acrylate monomer penetration into the etched and partly demineralized dentinal surface. The interpenetrated bonding agent containing the hydrophilic–hydrophobic 4-META comonomer may be retained inside the demineralized zone by adsorption onto the hydrophilic and hydrophobic domains present in that zone so that, upon polymerization, a *hybrid* zone is generated, which consists of resin-reinforced dentinal matter capable of copolymerization with the adjacent overlay of composite restorative. Restricting the duration of the etching treatment to the short period indicated is a vital prerequisite for strong dentin–composite bond formation, as this will keep the depth of demineralization to less than 5μm (ca. 2 μm in noncarious dentin) and maintain the collagen phase in a reactive (nondenatured) state, thus ensuring complete penetration of the demineralized stratum by the MMA/4-META agent down to the virgin (calcified) dentin matrix before polymerization sets in under the influence of the borane initiator. This, in turn, will ensure that no interlayer of decalcified and weakened dentinal material is left between virgin dentin and resin-impregnated stratum, as the exposed collagen, unprotected by infiltrated resin, is susceptible to degradation in an aqueous environment and thus would represent a weak link of the joint [56,58]. An outstanding advantage of the borane derivative as the initiator of this 4-META bonding system rests on its activation by water and oxygen as described by Nakabayashi et al. [58]. The moisture on the dental surfaces in combination with air triggers free-radical generation and thus the initiation of polymerization by the borane at the dentin interface rather than throughout the bulk of the resin layer as in other free-radical-initiated systems. This ensures that resin shrinkage proceeds toward the dentin adherend rather than away from it and so provides forceful counteraction against microleakage. In a further (commercialized) version, etching with citric acid–iron(III) chloride [containing poly(vinyl alcohol) for viscosity control] is followed by brush application of HEMA monomer (containing hydroquinone monomethyl ether), a subsequent application of the HEMA–4-META combination premixed with the tributylborane initiator, and the final placement of the restorative resin [59]. Excellent shear bond strength data, up to nearly 23 MPa, paired with a remarkably low degree of microleakage, have variously been reported [10,41,59,60], and fracture is cohesive in dentine and/or composite. The last-named adhesive system is also quite efficacious in prosthodontic and orthodontic bonding applications [61] and in the bonding of amalgam fillings, which in general practice, plugging into an undercut cavity, are retained solely by a micromechanical mode. Although dentin–amalgam shear bond strengths, just above 3 MPa, are weak in relation to corresponding dentin–composite strength data, the bond is effective in reducing microleakage appreciably in comparison to conventionally placed amalgam restorative.

Representative shear bond strength ranges for the bonding agents discussed in the foregoing are listed in Table 5, and the structural representations and universally used abbreviations for the principal methacrylate and dimethacrylate monomers are found in Tables 6 and 7. Detailed characterization techniques for methacrylates and derived polymers have been described by Ruyter and Øysaed [62].

VI. CONCLUSIONS

The foremost objective of operative dentistry is the durable placement of restoratives and the seating of restorations and prosthetic appliances with minimal loss of healthy tooth

Table 5 Representative Bond Strength Data for Present-Day Dentin Bonding Agents

Bonding agent[a]	Dentin conditioning	Composite–dentin shear bond strength (MPa)
Glutaraldehyde, HEMA	Al oxalate, glycine	10–18
NTG-GMA, PMDM	Al oxalate, diluted HNO_3	8–18
PMDM	NPG, diluted HNO_3	7–16
NTG-GMA, BPDM	SA-HEMA or diluted H_3PO_4	15–29
HEMA, bis-GMA	HEMA, maleic acid	8–23
4-META, MMA	Fe(III) chloride, citric acid	10–23
4-META, HEMA	Fe(III) chloride, citric acid, then HEMA	9–22

[a] See Section V.B.3 and Table 6.
Source: Literature in period 1989–1993.

Table 6 Structures and Abbreviations of Representative Monomethacrylate Monomers

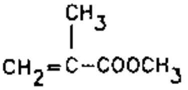
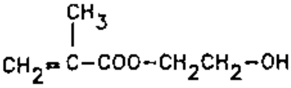
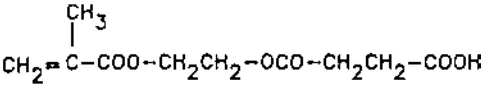
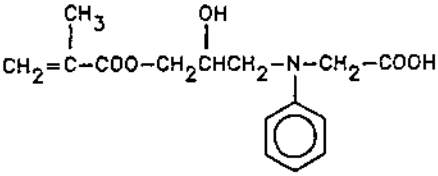
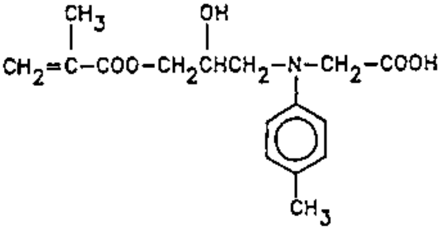
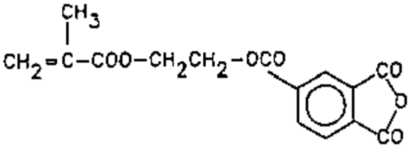
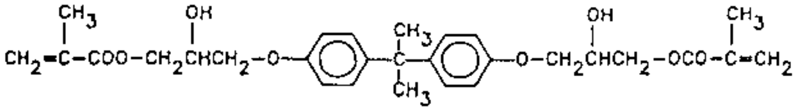
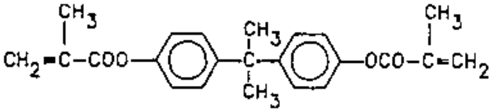
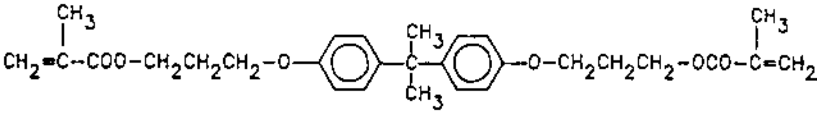
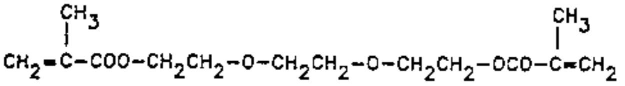
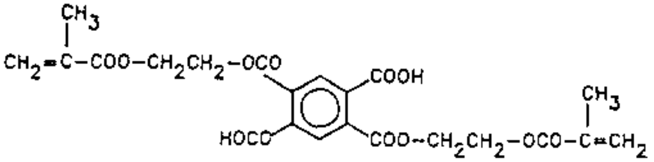
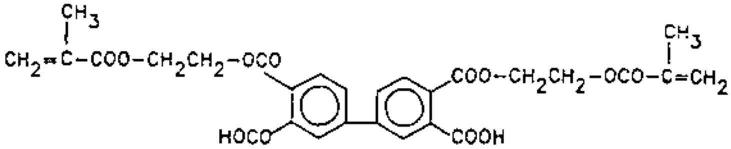
Structure	Abbreviation
 $CH_2{=}\overset{CH_3}{\overset{\vert}{C}}{-}COOCH_3$	MMA
 $CH_2{=}\overset{CH_3}{\overset{\vert}{C}}{-}COO{-}CH_2CH_2{-}OH$	HEMA
 $CH_2{=}\overset{CH_3}{\overset{\vert}{C}}{-}COO{-}CH_2CH_2{-}OCO{-}CH_2CH_2{-}COOH$	SA-HEMA
	NPG-GMA
	NTG-GMA
	4-META

Table 7 Structures and Abbreviations of Representative Dimethacrylate Monomers

Structure	Abbreviation
	Bis-GMA
	Bis-MA
	Bis-PMA
 $CH_2{=}\overset{CH_3}{C}-COO-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-OCO-\overset{CH_3}{C}{=}CH_2$	TEGDMA
	PMDM
 and positional isomer	BPDM

substance. With the realization that adhesion technology can be a powerful ally in this endeavor, advanced bonding techniques have in recent years been placed in ever-increasing numbers at the clinician's disposal in an effort to approach, and ultimately attain, this goal. Promising results are evident particularly in the design of bonding techniques permitting enhanced retention of composite restoratives to the enamel and dentinal phases of the tooth substance. Progress is also apparent in the development of adhesive systems allowing for the simplified and more efficacious attachment of bridges, inlays, onlays, and veneers to the tooth structure. Emphasis in future development work will focus less on the achievement of ever-greater bond strengths than on perfection of adhesion in terms of complete surface wetting, absence of interfacial microleakage with associated cariogenic factors, and enhanced durability of both the adhesive interface and the restorative adherend.

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Adhesives in the Automotive Industry

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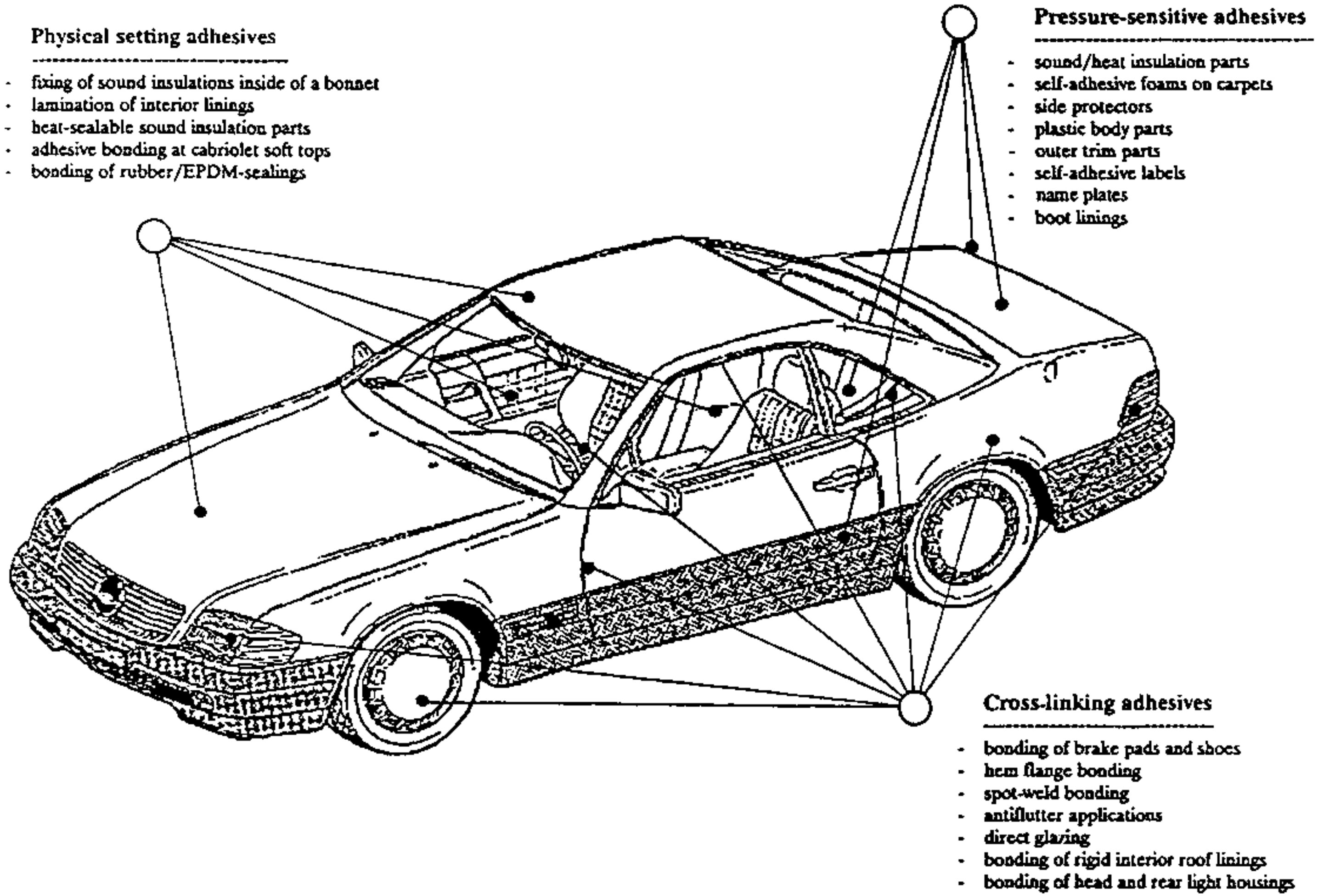
I. INTRODUCTION

Adhesive bonding and sealing are used for various applications in the modern automotive industry, ranging from flexible car body sealings to high-performance structural adhesives (Fig. 1). Adhesive types with specific properties are available for miscellaneous processing. The requirements for adhesive bonds have increased due to the extended life of the car. In adhesive processing, industrial health and environmental protection aspects have become more and more important. Therefore, it is more difficult but nevertheless necessary to determine requirements for the adhesives to be used in the future. In addition, the demand for quality standards requiring better quality management is increasing.

II. ADHESIVE APPLICATIONS IN THE AUTOMOTIVE INDUSTRY

In this chapter, adhesive bonding and sealing in automobile production are subdivided schematically into five ranges of application: (1) mechanical parts production, (2) the body shop, (3) the paint shop, (4) the assembly shop, and (5) the manufacturing of components. Depending on the variety of applications, adhesives must satisfy a wide range of requirements. On principle, all body shop adhesives must be usable without risk to the paint shop and they must resist the high temperature of the paint bake ovens. Generally, the bond strength and/or sealing ability must perform under severe conditions for the life of the car. Further requirements depend on:

1. *Function of the material* (e.g., spot-weld sealants): good corrosion protection, weldability, no HCl or chlorine emitted to cause corrosion when overbaked, good adhesion on the substrates
2. *Processing technique*: manual or automatic application, bonding at the assembly line or at a separate working site
3. *Specific material characteristics* (e.g., moisture and/or hot-curing adhesive): curing time, stability in storage, flexibility at low temperatures, hydrolytic stability, aging resistance, adhesion properties



Physical setting adhesives

- fixing of sound insulations inside of a bonnet
- lamination of interior linings
- heat-sealable sound insulation parts
- adhesive bonding at cabriolet soft tops
- bonding of rubber/EPDM-sealings

Pressure-sensitive adhesives

- sound/heat insulation parts
- self-adhesive foams on carpets
- side protectors
- plastic body parts
- outer trim parts
- self-adhesive labels
- name plates
- boot linings

Cross-linking adhesives

- bonding of brake pads and shoes
- hem flange bonding
- spot-weld bonding
- antiflutter applications
- direct glazing
- bonding of rigid interior roof linings
- bonding of head and rear light housings

Figure 1 Samples of adhesive applications in car production.

For all ranges of application the adhesives must not only meet the functional requirements but also retain them under a wide variety of conditions during use: impacts, vibrations, climate conditions, extreme changes in temperature, corrosion, and so on.

A. Adhesives for Mechanical Applications

In this range of applications, adhesives are used for fastener locking, formed-in-place gaskets, and bonding of mechanical parts. Mainly cyanoacrylates, anaerobic and encapsulated adhesives, modified acrylates, and elastomer or resin-based compounds are applied. Examples of applications are listed in Table 1. To choose a suitable adhesive, the required strength and mechanical properties as well as the chemical conditions for the specific application should be well known. For example, for the curing of dimethacrylates, the catalytic effect of the glued surface, the absence of oxygen, the temperature, the mold of the bond line, and the type of material to be bonded are important. Depending on the type of bonding, the requirements differ. The bond strength, temperature and aging stability, and the resistance to chemical reagents must fit the application load. The specific conditions of the joint performance have to be taken into consideration.

Table 1 Adhesive and Sealant Applications in Mechanical Parts Production

Type of adhesive	Method of curing	Applications
Anaerobic adhesives	Absence of oxygen and metal contact	Gaskets Flat surface bonding Adhesive bonding of electric and electronical components Fastener locking Shaft/hub bonding
Cyanoacrylates	Moisture	Gaskets Thread sealing Flat surface bonding Bonding of caps in cylinder head covers, gearboxes, crankcases, axle housings Shaft/hub bonding
Epoxy resin adhesive foils	Heat treatment	Bonding of heat exchanger
Synthetic resin sealants	Solvent evaporation	Gaskets Common sealing
Encapsulated adhesives	Anaerobic or with hardener after bursting of the capsules	Fastener locking
Modified acrylates	Activator and absence of oxygen	Bonding of flat surfaces
Phenolic adhesive foils	Heat treatment	Bonding of brake straps Bonding of clutch and brake linings
Silicone rubbers	Moisture or hardener	Sealing of oil pans and housing covers

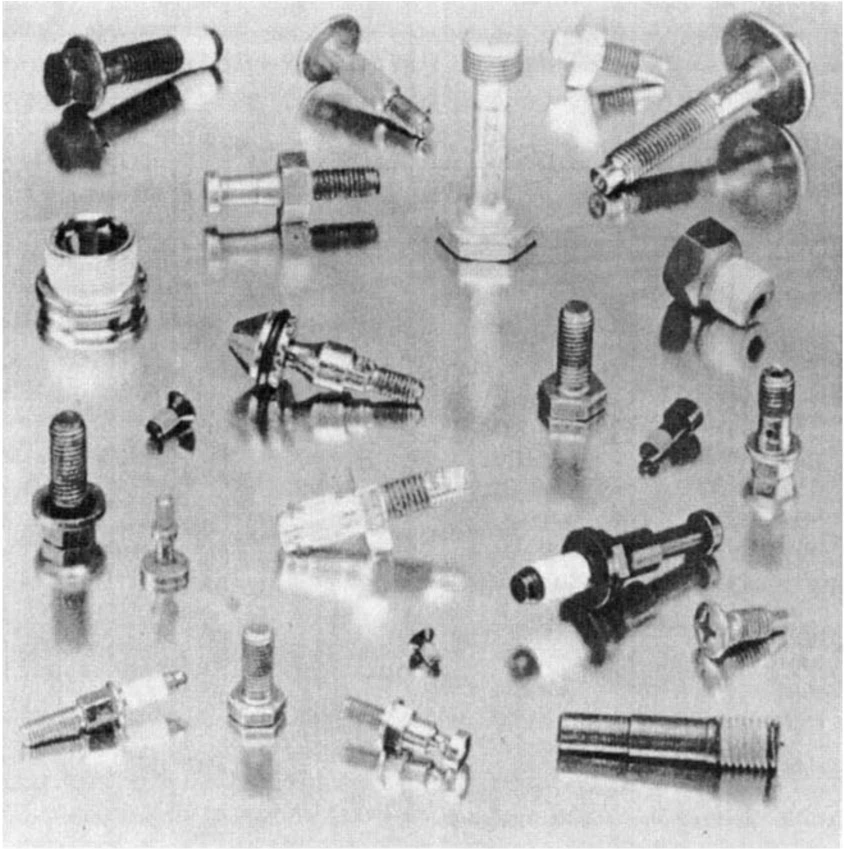


Figure 2 Examples of fasteners coated with encapsulated adhesives. (Courtesy of Loctite Deutschland GmbH).

For adhesive bonding of plastics to plastics and plastics to metal the cyanoacrylates are usually better than anaerobic compounds, which are more suitable for metal-to-metal bonding because of their greater resistance to mechanical vibrations and impacts. Encapsulated adhesives can be used to coat the fastener by the supplier. The curing takes place after fastening and locking are done. Figure 2 shows the great variety of available coated fasteners. Formed-in-place gaskets and adhesive sealants are used in various mechanical applications to seal and bond surfaces. There are cyanoacrylates, anaerobic adhesives, and modified acrylates and solvent-based rubber or resin compounds as well as silicones. The products are applied manually or automatically on the surfaces just prior to assembly. Figure 3 shows a sealant application extruded automatically onto an oil pan flange.

B. Adhesive Applications in the Body Shop

There are adhesives and sealants in the body shop with basically four different functions (Table 2):

1. Sealants for body joints
2. Spot-welding sealants and tapes

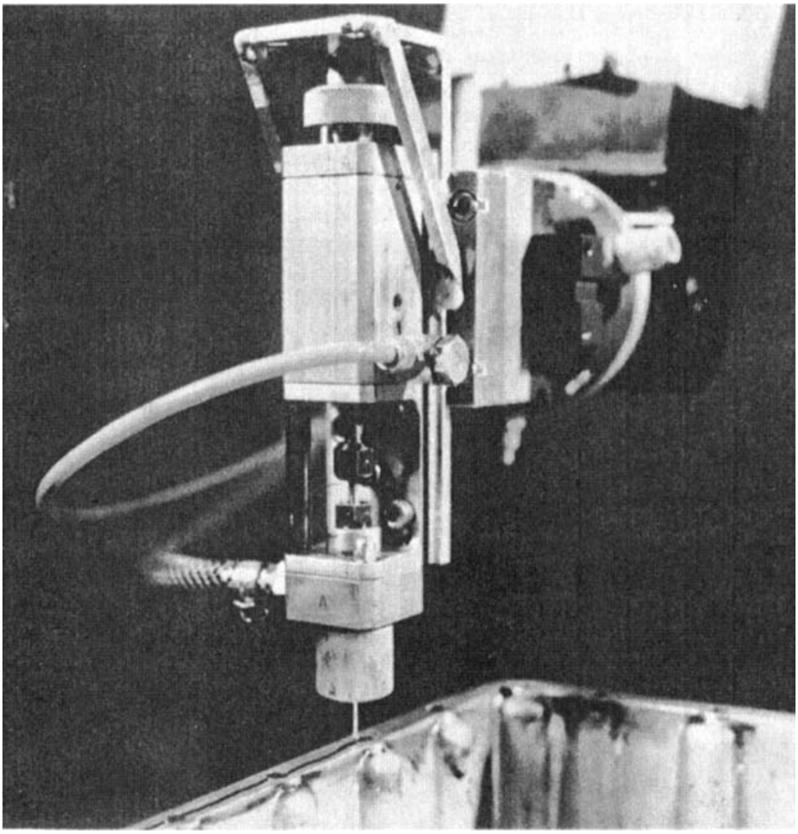


Figure 3 Application of a sealant automatically extruded onto an oil pan flange.

Table 2 Main Adhesive Bonding and Sealing Applications in the Body Shop

	Application			
Shear strength range (MPa)	Structural adhesive bonding and hem flange sealing	Antiflutter bonding	Body joint sealing	Spot-weld sealing
30				
⋮	Epoxies			
15				
⋮	Polymer blends			
7	Polyurethanes	Polyurethanes	Polyurethanes	
⋮				
4	Acrylic plastisols	PVC plastisols	PVC plastisols	
		Acrylic plastisols	Acrylic plastisols	Acrylic plastisols
⋮				
2		Reactive butyls	Reactive butyls	Reactive butyls
⋮			Butyls	Butyls
0			Nonsetting rubber compounds	Nonsetting rubber compounds

3. Antiflutter bonding
4. Structural adhesive bonding and hem flange sealing

Examples of these applications are shown in Figs. 4 and 5. The sealants for body joints are applied after assembly. They are extruded over the welded joints and have to seal out dust and water and avoid corrosion. A typical application is shown in Fig. 6. The following materials are in use:

1. Moisture and/or heat curing one-component polyurethanes
2. PVC plastisols
3. Pregelling compounds based on synthetic rubber
4. Butyls

Spot-weld sealants and tapes are used in spot-welded flanges to protect against corrosion. They are applied to the flanges before joining, then the body parts are pressed together and spot-welded. Figure 4 shows the application points on a body shop car schematically. The application of spot-weld sealing on the flange between the front section

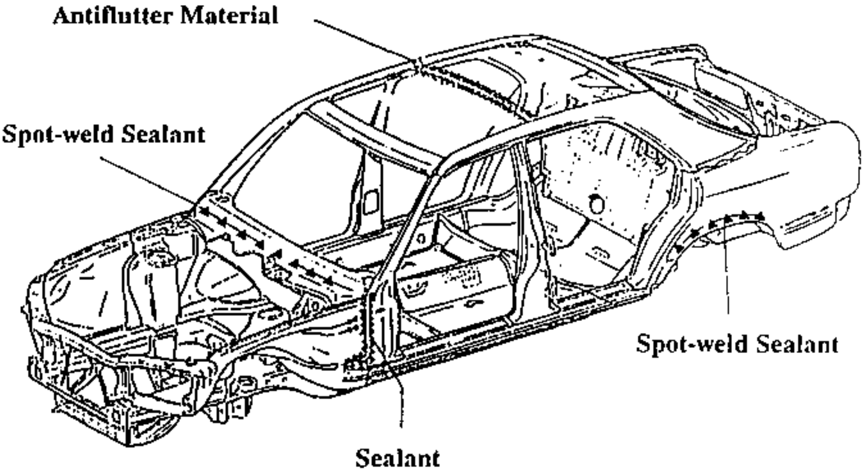


Figure 4 Examples of adhesive and sealant applications in the body shop.

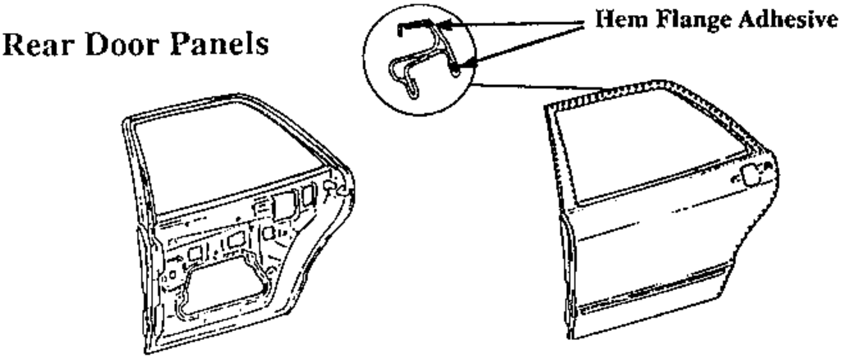


Figure 5 Applications of a hem flange adhesive in the body shop.

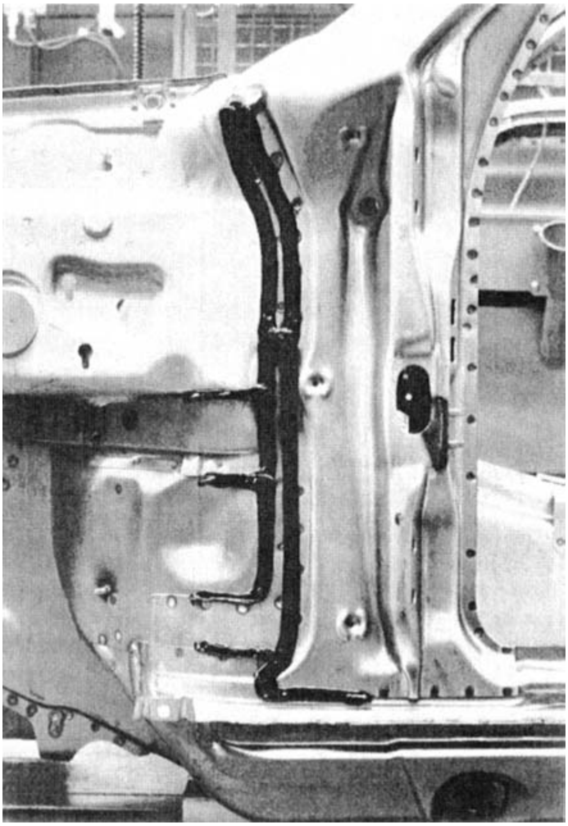


Figure 6 Example of a sealant application for body joints in the body shop.

and the lower windshield and on the inner flange of the rear fender can be seen as an example. The extrusion of a spot-weld sealant on the inner side of the fender is shown in Fig. 7. In use are:

1. PVC plastisols
2. Acrylic plastisols
3. Warm-applied butyls
4. Butyl tapes
5. Rubber-based pastes

The solvent-based compounds used formerly are no longer used.

Outer car body panels are stiffened with reinforcements to avoid flutter and the so-called "oil can" effect. In this way the strength of the body component is also improved. In Fig. 4 the use of an expandable butyl as antiflutter material is shown. Figure 8 gives an example of the use of an intermediate layer for antiflutter bonding on a hood. The following materials are used:

1. Bituminous or acrylic-soaked foams
2. Warm-applied butyls
3. Vulcanizable expandable butyls
4. Hot-curing one-component polyurethanes

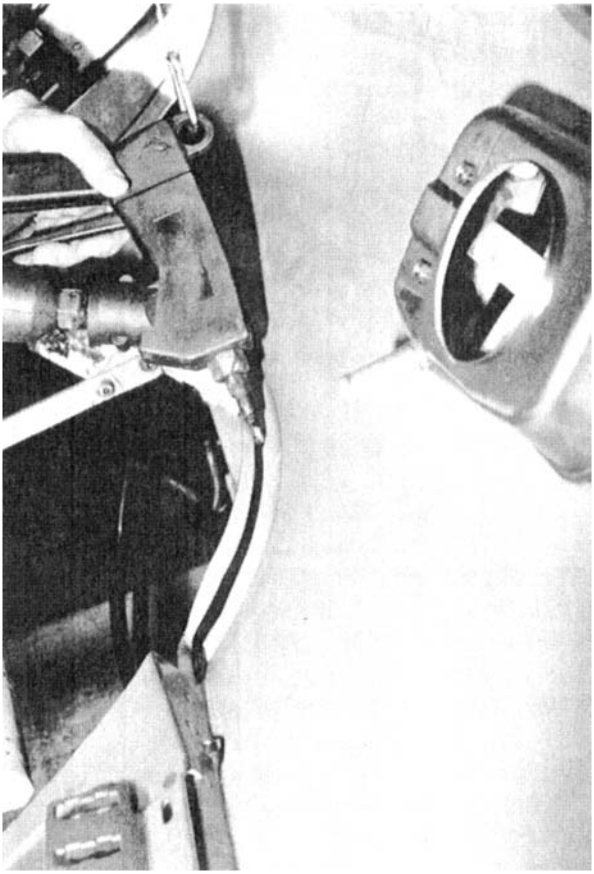


Figure 7 Extrusion of a spot-weld sealant on the inner side of a fender.

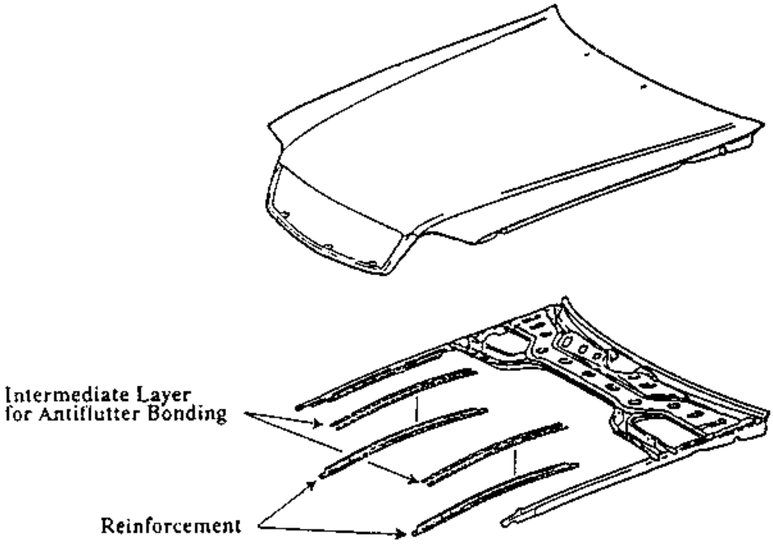


Figure 8 Sketch of inner and outer hood panels.

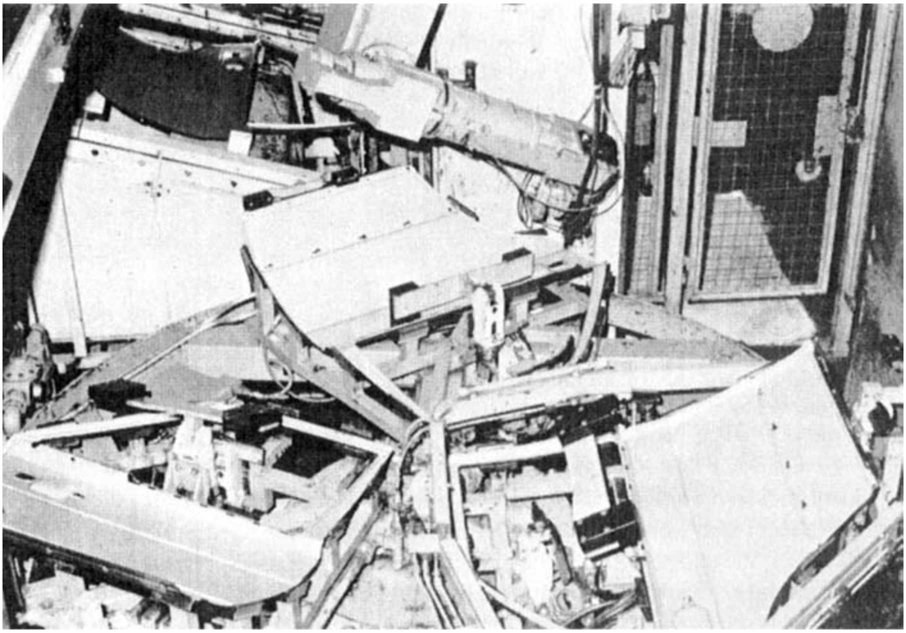


Figure 9 Robotized application of a hem flange adhesive on a rotary table.

Metal-to-metal adhesives are used to bond and seal hem flanges as well as for structural bonding of body shop components. As an example, Fig. 5 shows the adhesive bonding of inner and outer door panels. In Fig. 9 the robotized application of an adhesive on a rotary table can be seen. The adhesive bonding of hem flanges enables a homogeneous stress distribution along the bond line, through which the stiffness of the bonded component is better than in a conventional spot-welded joint. Often, adhesive bonding is combined with spot welding, which provides some advantages: the adhesive can replace a large number of spot-welding points, which reduces expensive surface finishing at outer panels; the components can be handled immediately after joining, before the adhesive is cured; and improved strength is achieved. Moreover, the spot-welding points hinder the attack of peel forces, which is harmful to the bond line. Instead of spot welding, other joining techniques (rivet fastening, screw fastening, "clinchen," "toxen," etc.) can be used in combination with the adhesive bonding.

Corrosion protection is often mentioned as a principal advantage of adhesive flange bonding, but today, coated sheet metal and aluminum are used more and more in the body shop, so this advantage is no longer the primary one. With the increasing use of coated sheet metal, the adhesive choice becomes more important. The bond strength is poor if the adhesive used is not adapted to the particular properties of the coatings. For adhesive metal bonding the following compounds are in use:

1. PVC or acrylic plastisols if no higher strength is required
2. One-component hot-curing or two-component cold-setting polyurethanes with medium strength
3. Epoxy-based adhesives, hot or cold curing, as one- or two-component pastes or as adhesive films for structural bonding with significant loads
4. Polyurethane/epoxy-based polymer blends (so-called "toughened" epoxies)

The conventional epoxy–resin adhesives give good sheer strength results, but they show brittle fracture under impact loads, particularly in cold conditions. Polyurethane compounds are more flexible and tougher, but they give lower strength in adhesive bondings. Adhesive applications in the body shop had usually been confined to low-loaded components. Nowadays adhesive bonding is also used more and more for parts that have to transmit significant structural loads (e.g., chassis components, floor panels, and side rails). The deformation ability of the adhesive-bonded components must be high to absorb the impact energy to give the car body good crash behavior. That requires a toughened adhesive with as high a strength as possible and was the reason for the development of polymer blends.

Worthwhile mentioning also are the adhesive applications in car body manufacturing, where the traditional sheet steel construction is replaced by steel or light metal space frames with plastic exterior body panels. A growing demand exists for the use of exterior body components made of plastic or metal–plastic composites, as doors, tailgates, trunk lids, hoods, roofs, and so on. Using these components to build a car body has forced the manufacturing process to be altered from the conventional flow of manufacture. That has influenced adhesive processing and caused modifications in the adhesives. Polyurethane-based adhesives, which are one-component moisture-curing or two-component cold-setting compounds, are generally used in these applications.

C. Adhesives and Sealants in the Paint Shop

Apart from underbody coating (usually PVC based), which is not explained further, the majority of bonding and sealing products in the paint shop are also PVC compounds. Acrylate plastisols are not often used and polyurethane-based sealants are rarely found. The main applications are in seam sealing and antiflutter bonding. On a small scale there are adhesive applications to bond and seal caps and to fix sound deadeners. In addition, foams and butyls as well as bituminous or acrylic-based sealants are used to fill car body holes.

D. Adhesive and Sealant Applications in the Assembly Shop

There are lots of adhesive applications in the assembly shop and in the manufacture of components. A complete list is not given, but adhesive use is illustrated by examples. The larger quantities of adhesives used on the assembly line are for bonding of insulation pads, interior fittings, instrument panels, and roof modules, and for direct glazing. When the applications do not require a surface coating adhesive or when smaller assembly pads are to be bonded or a droplike or continuous extrusion of the adhesive is sufficient, hot melts can be used with advantage. When higher strength is not necessary, ethylene–vinyl acetate (EVA), polyamide (PA), or thermoplastic rubber compounds can be chosen. Otherwise, reactive hot-melt adhesives would be preferred. They can be applied as common hot melts, but they are cross-linking afterward and therefore provide bond strength like that of two-part urethane adhesives and good durability at higher temperatures. In some cases, adhesive bonding with cyanoacrylates or methacrylates, which cure in a few seconds, is used only as a temporary fixative to assist assembly.

When joining is required over the entire surface, pressure-sensitive adhesives. adhesive tape systems, or hot-melt adhesive foils can be used. For health reasons, conventional rubber-based solvent cements are used rarely today. There is a trend to replace them with hot melts or water-based adhesives. With new application techniques the hot melts can be coated on substrates like solvent-based adhesives. Water-based adhesive systems frequently have the disadvantages of a longer open time and insufficient tack. An additional mechanical fixing is often necessary. The adhesive bonding of interior roof linings is an example of the use of water-based instead of solvent-based adhesives.

The primary sealants in common use in the assembly shop (e.g., for sealing of assembled air-conditioning systems or air filters) are:

1. Polyisobutylene-based compounds
2. Butyls
3. Moisture-curing one-component polyurethane adhesives

The adhesive bonding of plastic assembly components such as instrument panels, spoilers, spare wheel boxes, roof parts, trim assembles, and fenders is generally with one- or two-component polyurethanes. Frequently, a primer is used as pretreatment to improve adhesion. Adhesive tape systems can provide good results for the bonding of dash panels, trim lines, insignia parts, and rear view mirrors, for example.

Today the use of polyurethane adhesives is a common practice for adhesive bonding of windows in a car body, called direct glazing. Compared to the former glazing technique using rubber seals or polysulfide materials, direct glazing has the following significant advantages:

1. Possibility of completely automatic application (see Fig. 10)
2. High-performance sealing, matching the safety standards
3. Higher body strength
4. Smoothly designed car bodies
5. Improved aerodynamics

In addition, with direct glazing windows can be used as design and engineering elements of a car body (flush glazing). One- or two-component adhesives are used, which can be applied either warm or at room temperature and which are moisture- or hot-curing or

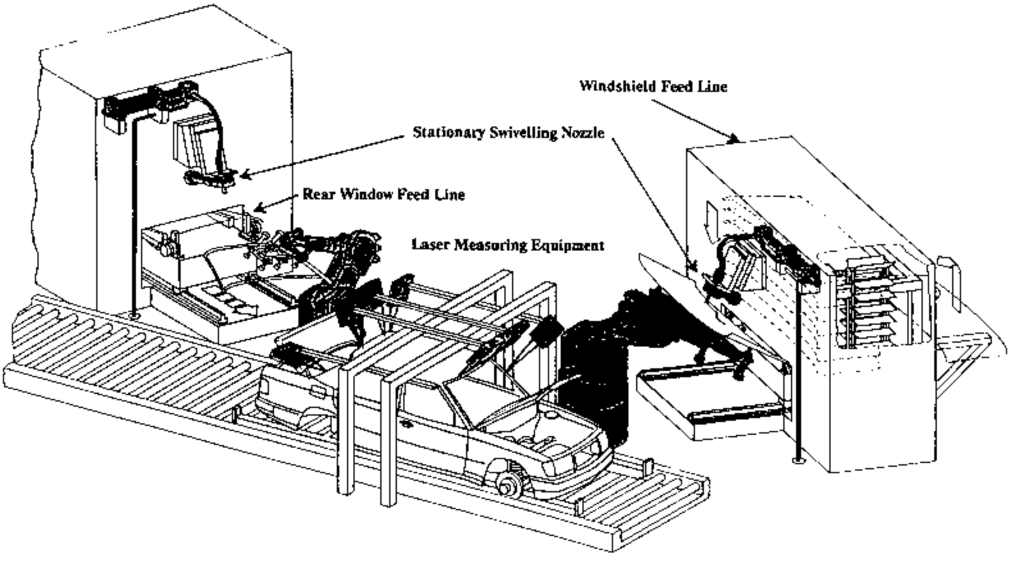


Figure 10 Sketch of automatic manufacturing equipment for direct glazing.

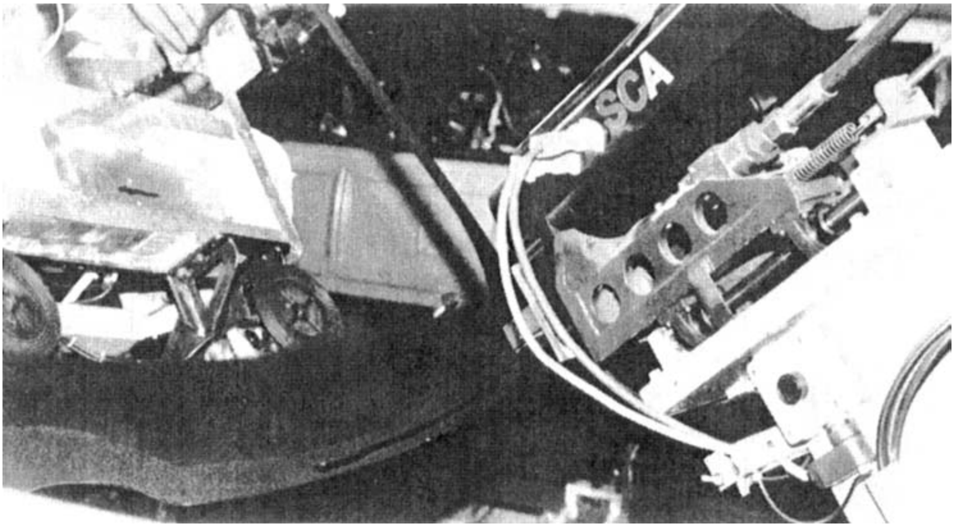


Figure 11 Robotized extrusion of a polyurethane adhesive onto a windshield.

curing with hardener. One-component moisture-curing compounds are very common. Generally, the bonding process includes pretreatments using specific cleaner and primer for both the glass surface and the car body flange. To protect the adhesive joint against ultraviolet rays, ceramic silk-screen printing on the glass and a black glass primer are used. New developments utilize their requirement primerless direct glazing. As mentioned above, the complete process of direct glazing can be performed fully automatically. Figure 10 shows a sketch as an example of such manufacturing equipment. In Fig. 11 a robotized extrusion onto a windshield is shown. The robot is holding the windshield and leads it along a stationary swiveling nozzle, and after the adhesive is applied, puts it in the body opening (see Fig. 12). The accuracy in fitting is controlled by sensors.

E. Adhesive Applications in Component Manufacturing

The use of adhesives in component manufacturing ranges from automotive headlamps to plastic body components (e.g., hoods, tailgates) to interior fittings to cabriolet soft tops, including a wide range of adhesives employed. Table 3 lists applications without any claim to being complete. Looking at the plastic components it is obvious that there are many different types of polymers, but the adhesives selected are basically polyurethane and epoxy-based compounds. The latter are rarely used. The main difference among them is in the way they are formulated: one or two components, cold setting or curing at higher temperature, liquid or paste, and so on. Because of the easy processing, the newly developed two-part acrylic adhesives, which are applied in a no-mix formulation, are very interesting. The A component is applied to one side and the B component to the other side of the surfaces to be bonded. After being fixed together, the adhesive cross-links in a few minutes. Bondings manufactured using this type of adhesive show good shear and peel strength results and high durability at impact loads. Applications include the bonding of protection plates to the sill beam or the joining of exterior lighting housings.

In cabriolet-cover manufacturing, solvent adhesives, synthetic rubber- or polyurethane-based, are used for sealing the folding top seams and for bonding the soft

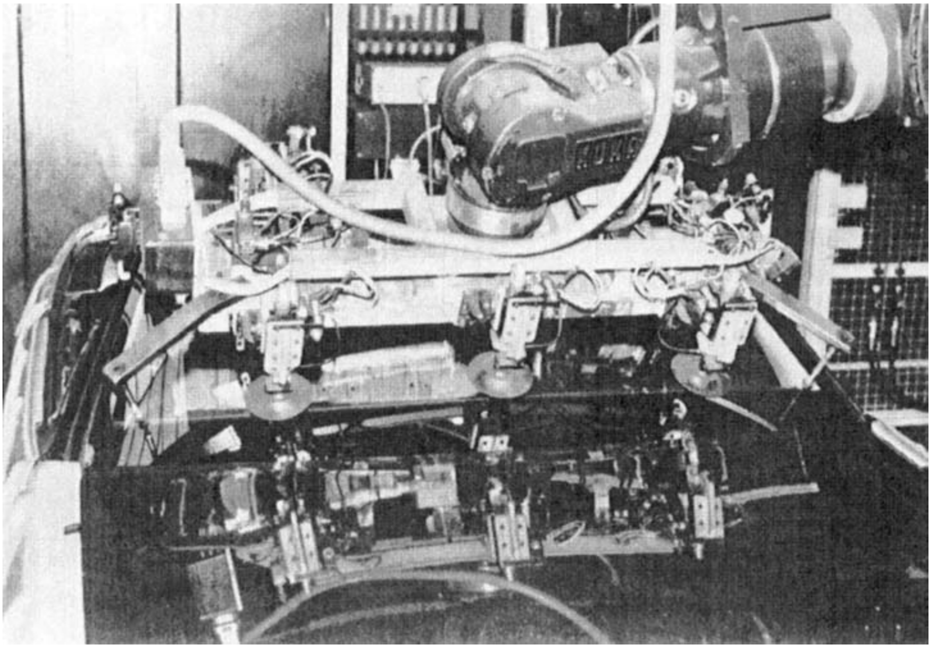


Figure 12 Robotized assembly of a windshield.

cover to the hood linkage. Adhesives are often mixed with hardener to improve the heat resistance of the bonding. Hot-melt adhesive foils are also employed. Preformed butyls or butyl sealant pastes or moisture-curing polyurethane adhesives are used for additional sealing.

Many interior fittings (e.g., instrument panel, door and sidewall panels, package trays, seat linings, boot carpetings, rear window shelves, etc.) are often manufactured by vacuum drawing and laminating the cover sheet material (leatherette, textile, leather, etc.) onto the trim panel. The use of hot-melt (also cross-linking) adhesives and water-based polyurethane adhesives (with hardener) is state of the art for this type of component production.

III. SOME CONSIDERATIONS REGARDING TRENDS IN AUTOMOTIVE ADHESIVE BONDING

For the future the evolution of adhesive bonding as a joining technique in automobile production points in two directions. On the one hand, well-known applications have to be optimized and improved to make them cost-effective but nevertheless reliable and trustful processes enjoying increasing acceptance for adhesive bonding. On the other hand, there will be new applications with different adhesive requirements, and adhesive suppliers must anticipate these changes and develop compatible adhesive compounds to satisfy the new requirements.

As to the first point mentioned above, cost-cutting steps have to be taken seriously. Increasing automation of the adhesive application is imperative. Adhesive bonding processes without extra pretreatment of joint surfaces and without using a primer but with

Table 3 Adhesive Bonding and Sealing Applications in the Assembly Shop and in Components Manufacturing

Type of adhesive	Method of curing	Applications
Anaerobic adhesives	Absence of oxygen and metal contact	Fastener locking Flat surface bonding Gaskets
Cyanoacrylates	Moisture	Flat surface bonding Metal-to-metal bonding Metal-to-plastic bonding Plastic-to-plastic bonding Adhesive bonding or rubber and EPDM parts Adhesive bonding to assist assembly
Adhesive dispersion	Drying and/or heat supply, pressure	Laminating at interior fittings Adhesive joining of seat linings Adhesive bonding of headliners
Adhesive tape systems	No curing, joining under heat supply and pressure	Bonding of: Moldings Protective strips Name plates Pattern plates Mirrors Rubber seals Wheelhouse covers Flared wheel arches Chassis beam panels Insulating parts Draught excludors Reflectors
Epoxy resin adhesives	Heat supply or hardener	Radiators
Rubber sealant	Solvent evaporation	Common sealing in the assembly shop
Solvent-based cements	Solvent evaporation	Sundry (no further data, not state of the art)
Encapsulated adhesives	Anaerobic or with hardener after bursting of the capsules	Fastener locking
Modified acrylates	Activator	Bonding of flat surfaces Bonding of lighting housings Glass–metal bonding (e.g., quarter-window adjuster, rear view mirror)
Polyurethanes	Moisture or hardner	Assembly bonding of plastic components: Spoiler Side protectors Spare wheel compartments Fender Instrument consoles Air ducts systems Window guiderails

(*continued*)

Table 3 Continued

Type of adhesive	Method of curing	Applications
		Window lifter rails Roofs and sun roofs Rigid roof linings Bonding of plastic components: Bonnets Tailgates Multipiece spoiler Impact protection parts Bumper Heating and ventilation systems Seat buckets Backrest linings Head and rear light housings Direct glazing Adhesive bonding and sealing at cabriolet hard and soft tops
Hot-melt adhesives (also cross-linking)	Cool down (moisture)	Bonding of wiring harnesses Sealing of radiators Rear view mirrors Laminating at interior fittings Assembly bonding of moldings Bonding of headlight lenses Adhesive bonding of sound systems Antiflutter bonding Bonding of insulation pads and sound deadeners Adhesive bonding at filters and filter housings, heating and ventilation channels Bonding of insignia parts at wheel caps Bonding of brackets at interior door panels Adhesive bonding and sealing at cabriolet hoods

reliable efficiency are required. Pregelling of body shop adhesives will be eliminated and oven temperatures for adhesive curing will be lowered to reduce energy costs. Increased use of reactive hot melts is conceivable. Multifunctional adhesives will be welcome: for example, hem flange adhesive bonding and seam sealing with only one material in one procedure. For ecological and personnel safety reasons, the use of harmful adhesives (e.g., solvent-based cements) will be reduced. Costs for toxic waste disposal, exhauster, reheat, or solvent recovery equipment will be reduced.

New applications of adhesive bonding can be expected where the specific advantages of this joining technique will be usable. Due to lightweight construction, which will be more and more important, outside panels must be used as supporting parts of the body structure. Conventional sheet steel constructions often show welded joints at the visible outer skin of the car body, which should be avoided in a smooth aerodynamic body design. In hybrid constructions different materials must be bonded. For both techniques adhesive bonding is preferred to welding or soldering. Adhesive bonding can also be combined with two new joining techniques, *clinchen* and *toxen*.

Structural adhesive bonding processes could be transferred from the body shop into the assembly shop to get clean and better defined glue surfaces. Temperature loadings to glue joints in paint bake ovens could be dropped, which would be an additional advantage, Components could be manufactured in a subsystem production process and adhesive bonded to the car body in the assembly shop. Adhesive bonding processes separate from the assembly line, performed at special working sites with specific adhesive equipment, would have advantages.

Recycling aspects will get more attention. Components should be recoverable and the adhesives applied must not disturb the reprocessing. New improvements are being developed to manufacture laminated interior fittings, in which coverings and form substrates are made of the same or similar materials, so reprocessing can be done without prior delaminating of the layers. In this case the adhesives used had to fit with the substrate materials. The future number of adhesive bonding applications in the automotive industry will depend on the success of the adhesive bonding processes. The quality and the safety reproducibility, especially of high-performance structural adhesive bondings, will be more and more important for large-scale productions. A quality system including planning and surveillance should support these requirements.

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