Flexible Packaging Adhesives – The Basics

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Abstract

Flexible packaging adhesives are predominately based on urethane and acrylic chemistry. Backbone options create unique performance properties. Changes in composition determine whether the adhesive will be solvent, water or solventless based. While the starting components are limited to FDA compliance lists, the resultant adhesives are complex. These meet the challenges from simple, non-demanding packages to the most severe requirements. This paper will discuss basic chemistries, end use performance levels and some chemical features that dictate performance.

Adhesives in Flexible Packaging

Flexible packing for foods and others consumer goods has been around for a long time and now is essential for efficient distribution, protection and economics. Today's packaging could not exist in its myriad forms and functionalities without, amongst many other components, the integral part played by flexible packaging adhesives.

One of the earliest classes of material used for adhesives to marry dissimilar materials together were natural products based on waxes, petroleum exudates, pine gums, and various sugars, starches and proteins. These are still used, but not in the scope of today's more sophisticated packaging, and will not be discussed here. Rather the focus will be on synthetic materials created specifically for the laminating adhesives

We will discuss products used in the dry bond lamination process.

In this paper on the basics of adhesives, we will touch on

- the types of adhesives commonly used
- some relationships of chemical and physical properties
- the forms these types are commonly applied
- expected performance from the types used

In today's packaging adhesives, the composition generally complies to various food laws, most notably the Food and Drug Administration's Title 21 Code of Federal Regulation parts 175.105, 177.1390 and 177.1395 in North America.

General Components of a Polyurethane Adhesive

The general polyurethane adhesive contains some sort of a polyol or mixtures, and some sort of an isocyanate or mixtures. Other extenders and alternate cross-linking chemistry may also be present.

Polyol

The nature of the polyol defines the type of generic urethane created. For example, one polyol that can be used is based upon Polytetramethylene ether glycol (PTMEG). The number of glycol ether units repeats, and mixed types allow varied molecular weight and flexibility in the linear backbone. The polyether polyol typically used has secondary (rather than primary) hydroxyl groups, to be less reactive than the primary alcohol polyols. The polyether backbone is generalized by the **(- C – O – C -)** linkage. When reacted or extended with isocyanate, the resulting adhesive could be called a **polyether urethane**.

Some properties derived from using an ether backbone in adhesives are:

- Hydrolysis resistance - retain their properties longer in conditions of extreme moisture, such as those found in wet and humid environments, resistance to some oxidizing agents.
- Microbe resistance - resistant to biological decay and won't degrade with soil or food contact.
- Low-temperature properties - retain their elasticity and flexibility at extremely low temperatures.
- Dynamic properties and resilience - exhibit excellent dynamic properties including high flexibility, elongation and tensile properties; tends to 'feel' soft and more rubbery.

The basis of polyester is a condensation reaction of a di-acid and a di-alcohol. There are many choices of starting materials here, some aromatic while others are aliphatic. Saturated polyesters are based mainly on adipic acid, aromatic acids, various linear or branched glycols, and, less commonly, dicarboxylic acids. The multitude of linear and branched polyesters that can be produced from these building blocks offer many valuable performance properties. By varying the base ingredients and the methods used to combine them, the balance of properties can be tailored to suit a wide variety of requirements.

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The **polyester urethanes** made from polyester polyols have higher polarity, and show generally better metal adhesion than adhesives derived from polyether polyols.

Some properties derived from using an ester backbone in adhesives are:

- Chemical resistance – resist absorption or attack by chemicals or solvents, but are attacked by strong basic or acidic environments; resistant to UV light and outdoor exposures; hydrolytically stable.
- Adhesion – more polar, have a stronger specific adhesion to more materials, especially metal.
- Low temperature properties – tend to be more brittle in low temperatures.
- Crystallinity – can have low to high backbone crystallinity, resulting in soft to hard segments that vary flexibility, adhesion and chemical resistance.

Backbone Modifiers

Many other short to medium length chain extenders are incorporated to provide specific properties or to enhance performance.

For example 1,4 – butanediol can be used in conjunction with polyether or polyester backbones to add properties. In some cases, the 1,4 – butanediol can be made into polyester to provide soft segments, or in combination with the proper isocyanate, hard segments. 1,4 – butanediol can also be used as the cross linker of a two part adhesive where the major resin side is isocyanate terminated, or as a chain extender during the synthesis phase of the adhesive. In this case, the molecular weight is very low with a very high hydroxyl number. This modifier produces a good balance between hardness and low temperature flexibility.

Another example is Trimethylolpropane (TMP), a liquid polyol with secondary hydroxyl groups. This molecule is used as a chain extender, to control certain properties of synthesis and to increase functionality. Important improvements to physical properties derived are: high tensile, elongation, hardness, modulus and resilience properties to the polyurethane elastomer.

Isocyanate.

There are many isocyanates available for industrial use, but only a limited number approved by food laws useful for packaging adhesive. The two general classes of isocyanates are aromatic and aliphatic. Aromatic isocyanates are faster reacting by a factor of between 2 –10, depending on their chemical structure.

In the aromatic class, the principal ones used are Toluene diisocyanate, (TDI) and Diphenylmethane 4,4' diisocyanate, (MDI). This leads to the so-called TDI-based or MDI-based adhesives.

In the aliphatic class, typical ones include Isophorone diisocyanate, (IPDI) and Hexamethylene diisocyanate, (HDI). Other aliphatic materials are used for more specialized adhesive applications. The aliphatic isocyanates are much more costly than aromatic. They bring different, often unique and safer chemistry for elevated temperature packaging. In some applications, only the aliphatic isocyanate is permitted by food law regulation.

Creation of Urethane

The urethane is formed by the reaction of the hydroxyl from the polyether or polyester polyol with a suitable diisocyanate. The diisocyanate continues to react with another polyol's hydroxyl group, leading to chain extension and molecular weight build. The link thus formed is called a urethane link.

The make up of the adhesive is further complicated depending upon the starting materials. The polyol can be:

- low to high molecular weight of singular or mixed materials,
- a polyurethane prepolymer, hydroxyl terminated,
- mixtures of the two

These are reacted with low to medium molecular weight diisocyanate prepolymer and allowed to cross-link to form the urethane link and the final cured adhesive. This would be called a 2-part adhesive system.

In some cases, the prepolymer adhesive is created and terminated in isocyanate. This one-part adhesive is allowed to cure with ambient moisture to form a different linkage, called urea. This is sometimes called a moisture cure adhesive.

There is always the potential for water reacting with the isocyanate, even in a 2-part adhesive, due to humidity in the air and water in solvents. Though in this case the goal is to create polyurethane adhesive, there might be some small amount of polyurea formed as well.

The combination of polyol monomer and prepolymer with various isocyanate types is almost endless, resulting in many unique adhesives and properties, as well as general adhesives suitable for many applications.

To further complicate the description, acrylic polyol can be used, either as the base backbone material or as mixtures with the polyether and polyester polyols. The resulting adhesives acquire some of the properties of acrylic chemistry and can be called acrylic urethane, polyester-acrylic urethane or polyether-acrylic urethane.

In some adhesive systems, the prepolymer backbone may be polyurethane, but is terminated in amine, epoxy or some other chemistry. These terminations are then reacted, as a 2-part adhesive with a corresponding epoxy or amine prepolymer, or some other corresponding chemistry. While they are cross-linked or cured differently, in most cases they are still referred as polyether, polyester or acrylic urethanes.

Care is needed to ensure that FDA sanctioned materials are used. There can be confusion in other parts of the world, where different food laws are cited. The ingredients used may or may not match up with the FDA guidelines.

The urethane chemistry is commercially used in three forms as one-part and two-part adhesives: solvent based solution, 100 % solids and polyurethane dispersion (PUD).

Advantages – Solvent Based:

- well known history of performance
- types available for all types of food packaging laminations
- can be one-part for simplicity of handling

- two-part has enhanced heat, chemical and, in some cases, bond performance
- excellent clarity
- adhesion to wide range of substrates
- newer chemistries allow higher solids application

Disadvantages – Solvent Based:

- contain volatile organic compounds (VOC), though many Hazardous Air Pollutant (HAP) free
- can be economical to costly on dried applied basis
- health and safety concerns
- fire hazard
- water of alcohol contamination will compromise cure
- rate of drying often limiting step
- takes time for cure to develop
- two-part requires proper mixing and ratio, especially in higher performance applications – chance for error

Advantages – 100 % Solids: (sometimes called solventless, solvent free)

- little or no VOC and no HAP
- high application speeds
- very competitive on applied cost
- often lower applied weight
- adhesion to wide range of substrates
- types available for low to high demand packaging
- excellent clarity
- reduced waste of adhesive

Disadvantages – 100 % Solids

- need dedicated laminator to apply
- need transfer pumps for one-part
- need meter-mix-dispense pump for two-part – chance for error
- little initial bond, no shear resistance initially
- some need pre-heat to pump and apply
- takes time for bond and final cure to develop

Advantages – PUD:

- medium to high solids at lower viscosity
- little to no VOC
- performance equal to general purpose and medium performance solvent base and 100 % solid adhesive
- good bonds to wide range of substrates
- good to excellent clarity
- can be cost competitive
- reduced health and safety issues

Disadvantages – PUD:

- tendency to generate foam
- usually not freeze/thaw stable
- requires careful addition and mixing of coreactant to ensure proper dispersion – chance for error

Acrylic Based adhesives

Acrylic is a general term for polymers made from acrylic acid. Acrylates, such as methyl and ethyl acrylate, are derivatives of acrylic acid. Acrylic esters such as methyl, ethyl, butyl and 2-ethylhexyl acrylates are made from technical-grade acrylic acid. Co-polymers and blends of various acrylates like methyl methacrylate, butyl acrylate and ethyl hexyl acrylate are used in the creation of the acrylic adhesives.

Acrylic esters may be polymerized or catalyzed by heat and oxidizing agents in solution or emulsion methods to form long-chain thermoplastic resins. Broadly, acrylic ester polymers are colourless, insoluble in aliphatic hydrocarbons and resistant to alkali, mineral oils and water. With good resistance to degradation and good adhesion to many substrates, they have been used sparingly in the past and are now starting to be widely used in flexible packaging.

The acrylic based polymers are usually mid- to high-molecular weight and are emulsified in water. This produces very small particles dispersed in water and allows high percent solids at very low viscosity. Many of these adhesives are used as one-part with either no cross-linking or some self cross-linking. In essence, they remain pressure sensitive and rely on their inherent molecular weight for the properties of adhesion, tack, and intrinsic bond strength and shear resistance.

For higher performance, a suitable cross linker can be used to create a two-part system. There are water dispersible isocyanates that can form acrylic urethane polymers when cured. This allows the performance and benefits of both the acrylic and the urethane chemistry. Another approach is to use amine – epoxy cross-linking for the cure. The acrylic polymer is terminated either in amine or epoxy, and the opposite prepolymer is used for the cure. Many other cross-linking materials are available for acrylic based adhesives, but few have status in the food laws.

The acrylic adhesives have the following characteristics.

Advantages:

- higher solids in water
- low viscosity, apply as supplied
- easy to dry, low film forming temperature
- no VOC
- crystal clear when dry
- some aroma barrier properties
- low demand laminations as one-part adhesive (can replace many solvent and solventless applications)
- enhanced performance as two-part adhesive (can replace some solvent and solventless adhesive applications)
- economic on a dry applied basis

Disadvantages:

- low bond performance as one-part
- low chemical and heat resistance as one-part
- mix ratio and measuring as two-part - chance for error

PVDC Based Adhesives

PVDC (polyvinylidene chloride) is normally considered for barrier coatings and a heat seal medium. Certain types however, have the properties of an adhesive as well as providing some barrier properties.

Pure PVDC is too hard and brittle to be used as a coating, let alone an adhesive. Therefore, co monomers are reacted into the backbone to provide specific properties of flexibility and adhesion to substrates. The resulting polymer is of very high molecular weight and is emulsified or dispersed into water. High solids content at very low viscosity is achieved.

Solvent solution PVDC are lower molecular weight and are seldom used for adhesives in flexible packaging.

The PVDC designed to be an adhesive has the following characteristics.

Advantages:

- high solids in water
- low viscosity, apply as supplied
- easy to dry, low film forming temperature
- no VOC
- crystal clear when dry
- very high shear and tunnel resistance
- bonds well on most plastic films
- barrier build in dry and wet environments
- high aroma and chemical barrier
- economic on a dried applied basis
- no second component

Disadvantages:

- low pH – acidic and corrosive to soft metals
- requires higher nipping temperatures
- requires time to develop full barrier properties
- not normally used on metallized films or aluminum foil
- hard to recycle due to chlorine content

Energy Cured Adhesives

There has been much interest lately in using ultraviolet light (UV) or electron beam (EB) adhesives for food packaging. These systems have been used in non-food applications for a number of years. While the allure of instant cure and reduced work-in-process inventory is very high, there are some drawbacks in food compliance and specific adhesion to some substrates.

In general, the UV adhesives have very good adhesion to many substrates, but the components are not well governed by food laws. Curing is accomplished by exposure to ultraviolet light. The cured adhesive is tack-free, and a permanent bond with good chemical and heat resistance can be achieved. The process involves UV curing through one of the film layers; therefore, at least one of the layers must be transparent to allow penetration of the UV light. These systems include acrylics and acrylates, epoxies, polyurethanes (PUR), polyesters, silicones, and vinyl and vinyl esters and incorporate various photoinitiators, monomers, oligomers and additives. Cationic photoinitiators may also be used. Acrylics are the most common components of UV curable adhesives. The concern from the food safety point of view is that the components have little standing in the food laws and can migrate if the adhesive is under cured.

With EB adhesives, the lack of a photoinitiator for EB curing results in lower-cost formulations than for UV and improves the potential for FDA applications. Though generally composed of the same chemistry, greater strides have been made in gaining approval for food packaging through specific testing of the final structure. The cure is energy dependent and produces much less migration of adhesive materials. This testing helps to determine FDA compliance of the EB curable chemistry by supporting the “No Migration/No Food Additive” and “Functional Barrier Doctrine”. In general, EB adhesives have not found wide spread application in food packaging yet.

Advantages – Energy Cured Adhesives

- 100 percent solids, no volatiles
- almost instant to instant cure
- reduced turn time in work in process inventory
- reduced waste

- fast application speeds
- reduced energy costs to apply

Disadvantages – Energy Cured Adhesives

- need dedicated application and cure equipment
- cost of equipment and adhesive
- skin sensitizer of chemistry – potential health and safety issues
- food law compliance needs to be confirmed
- impact of energy on packaging films

The following is a simple guide for selection of adhesive chemistry type for different packaging. In some cases, only two-part adhesive systems from a chemistry class will be successful. There are two considerations for selection of the adhesive type used: mechanical performance for the application and adherence to the applicable food laws.

Adhesive Class	Snack	Low Demand General Purpose	Medium Performance Chemical Resistant	High performance Chemical resistant	Hot Fill	Boil, Cook-in Retort
Solvent Urethane	OK	OK	OK	OK	OK	OK
100 % Solids PUR	OK	OK	OK	(OK)	OK	OK
PUD	OK	OK	(OK)	NO	OK	NO
Acrylic	OK	OK	(OK)	NO	OK	NO
PVDC	OK	OK	(OK)	NO	(OK)	NO
Energy Curable	(OK)	(OK)	(OK)	(OK)	(OK)	(OK)

(OK) needs to be carefully tested for the application

Summary

In the last 40 years, flexible packaging adhesives have evolved to the point where competing technologies can be used for the same applications. Polyurethane chemistry is still dominantly used in solvent based, 100 % solids and water based. Even though the more mature chemistry, new products in this class are still being developed.

Water based acrylic chemistry has, until recently, remained suitable for snack and low demand laminations. Recent advances in hybrids with urethane and cure mechanisms have broadened its use, especially with the economic advantage and low EPA restrictions. There remains a small but viable market of PVDC lamination adhesives as well.

Energy curable adhesives are starting to enter the food lamination market. Against the constraints of higher cost and food law acceptability, the drive to faster cure is generating much interest. This chemistry is still in the early stages of evolving and bears watching for developments.