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Synthetic Polymer-Polymer Composites

Sample Chapter 1:
Manufacturing and Processing of Polymer Composites

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Preface

The awareness about adverse environmental impacts of synthetic, petroleum-based polymers is steadily increasing and has already caused some worldwide concern. What is more, this concern is ascending because of the use of synthetic polymers is increasing rather than decreasing. A good example in this respect is the usage of poly(ethylene terephthalate) (PET) whose production has an annual growth of 10%, mostly due to its excellent properties as packaging material for various products that include pressurized beverages, food articles and medicines. The expected future growth is strongly supported by the fact that a large percentage of food products is often wasted because of bad or lack of packaging. In their efforts to change the situation, many countries, such as China and India, are likely to increase the usage of plastics packaging containers. However, in many countries legislations are introduced to control the amount of plastics used. For example, in the European Union, it will be not allowed after 2015 to use in the cars manufacturing plastics having more than 5 wt% incineration quota*.

A decade or so ago, researchers believed that the commonly used polymer composites, comprising about 30% glass fibers, would be replaced by nanocomposites having only 2 to 5 wt% nano-sized materials as reinforcement. Unfortunately, this expectation has turned out to be somewhat elusive and researchers have started to look for alternative ways of replacing the traditional glass fibers with natural, biodegradable materials, mostly with fibrous structure. The potential of this approach has been demonstrated in our book entitled *Engineering Biopolymers: Homopolymers, Blends and Composites* (Hanser Publication, 2007).

In this book we show another approach for replacing glass and other inorganic fibers as reinforcements for polymer composites. This replacement could be again synthetic, petroleum-based polymer but prepared as fibers, micro- or nanofibrils. Of course, this approach is not as advantageous as using natural fibers that are biodegradable and eco-friendly. At the same time, the synthetic polymer-polymer composites seem to be much more acceptable from the environmental point of view because they, being organic in

* A. Bismarck *et al.*, Plant fibres as reinforcement for green composites, in *Natural Fibres, Biopolymers, and Biocomposites* (Eds. A. Mohanty, M. Misra and L. T. Drzal) CRC/Taylor & Francis, 2005, pp. 37–108.

nature, are prone to incineration process. In addition to their environmental advantages, compared to the polymer composites with mineral reinforcements with high weight/volume fractions, they are likely to possess much better specific mechanical properties. This positive attribute allows them to be used to manufacture lightweight products and structures, a fact that has particular importance in the transportation and packaging industries.

This book is an attempt to collate information from a group internationally known researchers and demonstrate the state-of-the-art applications of synthetic, but organic in nature, materials as carbon fibers, carbon nanotubes, synthetic polymers in the forms of fibers, and micro-/nanofibrils as replacements of mineral reinforcements. We would like to thank all the contributors for their willingness to participate in this exercise and being patient during the compilation work. The editors also wish to thank the Centre for Advanced Composite Materials, University of Auckland for providing a range of facilities and the Ministry of Science and Innovation, New Zealand for financially supporting Dr. Fakirov.

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Auckland, November 2011

PART I
INTRODUCTION

Chapter 1

Manufacturing and Processing of Polymer Composites

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1.1. Introduction

Composite materials consisting of two or more components are likely to be more difficult to process than isotropic one-component materials. However, it is obvious that the success of a material is always dependent on its processability. Over the last decades, enormous progress has been made in this field, leading composites out of its niche as material for military purpose and aviation use, to commercial applications and possibly for daily life. Besides the continuous pultrusion process for rapid production of profiles and hand lay-up for small series production of aircraft structures such as vertical tails; thermoforming, liquid composite molding, tape-laying and filament winding have been developed into competitive mass production methods. The best proof for this development is the attempt of BMW to build a car with a carbon fiber passenger cell, which shall be produced about 150 000 times per year starting 2013.

The nature of composites with its basic components matrix and fibers, which are available in a broad variety of semifinished products, allow the manufacturing of composite parts through a wide range of different processes (Figure 1.1). The first differentiation made in Figure 1.1 does not relate to the definition of short fibers having a length shorter than the critical length, but are due to a more process related approach. Thus, the longest short fibers shall be the ones used for injection molding (Long Fiber Thermoplastics – LFTs) with approximately 25 mm. However, the Long Discontinuous Fibers (LDF) developed by DuPont and used for thermoforming with an average fiber length of 50 mm can be considered as the shortest long fibers with this regard. Multiroving processing covers all sorts of textile processes to produce woven and nonwoven fabrics such as weaving, knitting, *etc.*

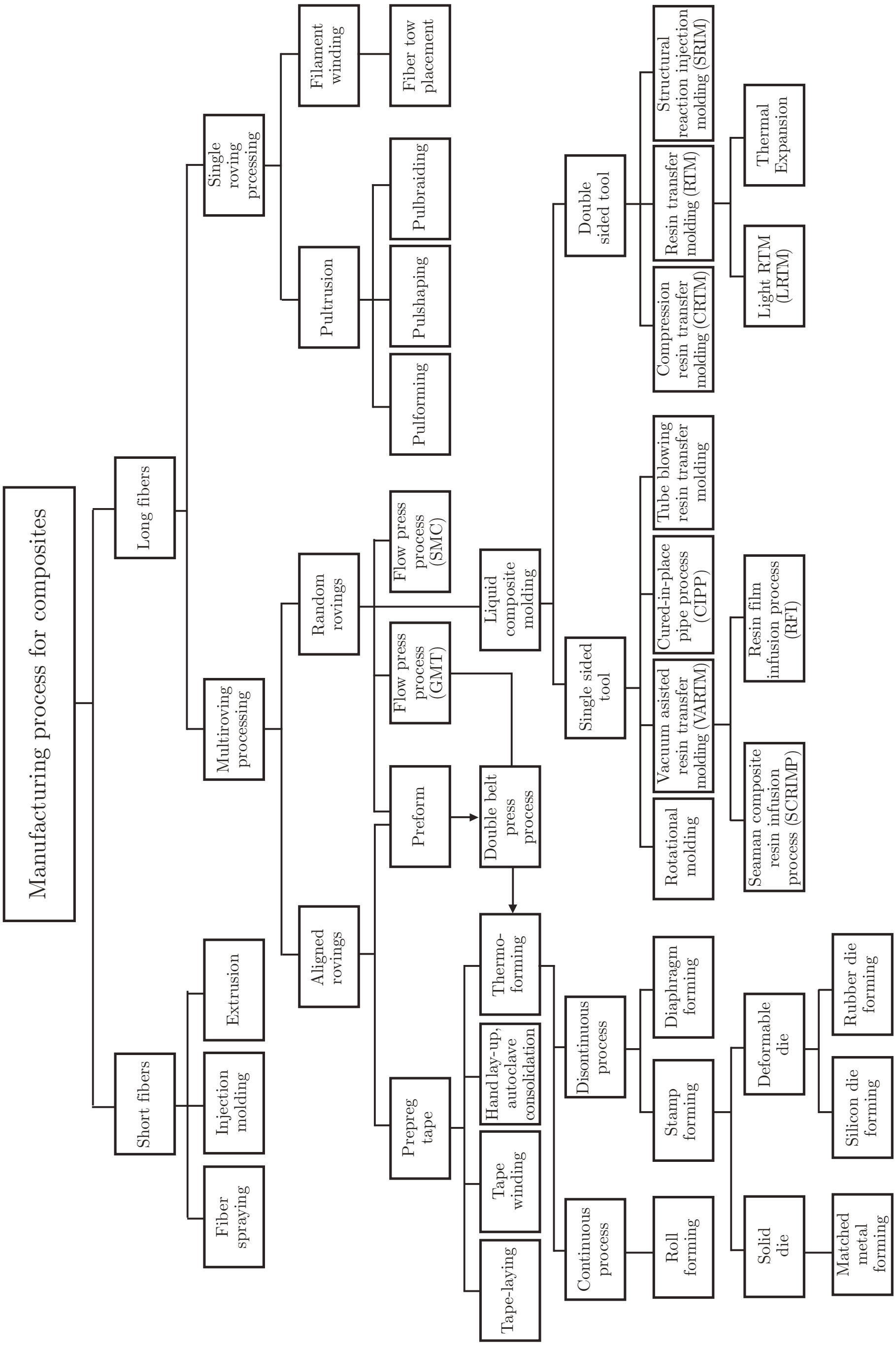

Figure 1.1. Systematic order of manufacturing processes for composites

This schematic structure allows for the perception of some processes from a different point of view. For example, rotational molding is a special liquid molding process with the resin drawn by centrifugal forces and roll forming is a continuous thermoforming process.

1.2. Autoclave-processing

1.2.1. *Introduction*

Invented in 1879, autoclaves have been used since the beginning of the 20th century for processing rubber products [1]. Although sophisticated processing techniques for composites have developed over the last several decades, autoclave-processing is still the dominant consolidation method for prepreg-made aircraft, space, and leisure industry parts such as the tail fin of the Airbus A380 aircraft. Autoclave-processing combines almost no shape limitation, a high flexibility with a precise positioning of fibers in a prior hand lay-up or tape-laying process. The often manual insertion of inserts is possible. However, this manufacturing method is economically suitable only for small series production.

1.2.2. *Equipment*

An autoclave is a chamber in which temperature, heating rate, cooling rate, and pressure can be precisely controlled. Conventional autoclaves work with convection heating and cooling. In addition, the pressure required is provided by air or nitrogen. Autoclaves with a capacity of up to 850 m^3 have been built. In smaller versions, pressures up to 70 bar, and temperatures up to 650°C have been realized [1]. Nitrogen gas has to be used in order to apply higher pressures and/or temperatures because the oxygen in the air becomes very reactive causing fire inside the autoclave. Nitrogen pressured autoclaves have to be handled with care because huge amounts of nitrogen released into small environments may cause suffocation.

Microwave heating of composites has been developed for almost 20 years. In microwave processing, energy is supplied by an electromagnetic field directly into the material. This results in rapid heating throughout the material thickness with reduced thermal gradients. Such volumetric heating can also reduce processing times and save energy. The microwave field and the dielectric response of a material govern its ability to be subjected to microwave heating [2]. Microwave autoclaves are being introduced for industrial use as shown in Figure 1.2 [3].

1.2.3. *Laminate assembly*

Prior to autoclave-processing, sheets or tapes with preimpregnated fibers with resin or thermoplastics (prepreg) have to be laid-up in a specific order. Prepreg is manufactured by laying the fiber and the resin between sheets of siliconized paper or plastic film, which are pressed or rolled to ensure consolidation and wetting out of the fibers. This process allows excellent alignment of the fibers in unidirectional layers [4]. A lay-up is formed by stacking up the prepregs according to the design criteria. In order to derive warpage-free parts, a symmetrical lay-up sequence has to be preferred. Thermoplastic prepregs can only be used for one-dimensionally curved structures due to their limited drapability. In

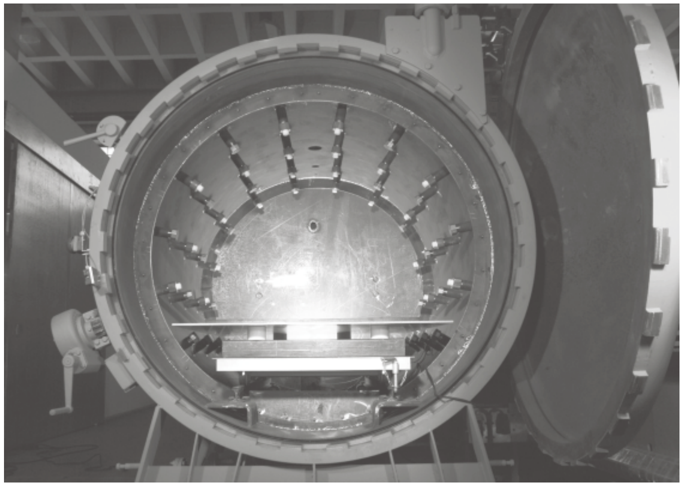

Figure 1.2. Microwave autoclave [3]

such cases the lay-up can be performed with fabrics and polymer films or fabrics consisting of reinforcing and polymer fibers (commingled yarns).

The standard lay-up structure is shown in Figure 1.3. The bleeder material sucks excessive resin coming from the prepreg. Peel-ply fabrics and release films are positioned above and below the prepreg to allow part removal without residue of excessive resin.

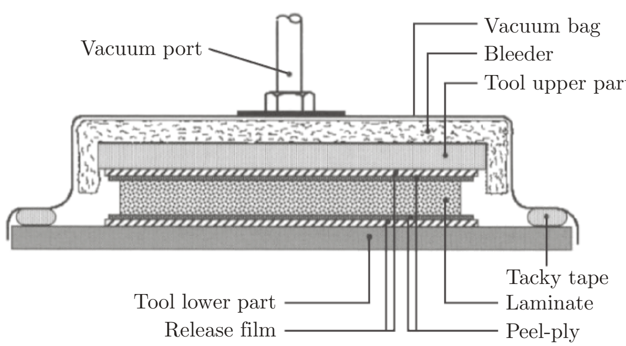

Figure 1.3. Lay-up structure for autoclave curing [1]

1.2.4. *Process description*

The thermoplastic or thermoset matrix based composite lay-up is subjected to a defined temperature-pressure course which can last between two to twelve hours. To cure thermosetting-systems, the temperature can vary depending on the type of resin between 80°

and 180 °C along with pressures between 6 and 10 bar (0.6–1 MPa). The temperature rise initiates the curing reaction of thermosets while the pressure applied effects the complete impregnation and good consolidation.

In terms of thermoplastic matrices, the temperature rise results in melting of the matrix. Therefore, the temperature can be as high as 390 °C for PEEK-systems and is significantly higher in comparison to thermosets. The pressure applied, up to 25 bar (2.5 MPa), is also higher than for resins due to a higher viscosity of thermoplastic matrices. Successive cooling supported by pressure effects the consolidation. A vacuum is applied to remove gaseous substances from the composite sealed in a vacuum bag. Thus, the effective pressure on the composite is the difference between the applied pressure and the under pressure (vacuum) applied.

1.2.5. *Further developments*

Although being a relatively old technology to process composites, the autoclave technique is still a matter of research. Besides the previously mentioned microwave development, research is being conducted to simulate the autoclave process and to derive models for time-based cost calculations [5,6]. In addition, efforts are being undertaken in the field of tooling and the effect of the tool on the part quality [7,8].

A different approach is to entirely substitute the autoclave process was undertaken by using heating and cooling fluids in a pressure chamber. The so-called Quickstep-process is about three times faster than the conventional autoclave process while providing better mechanical properties of the composite part [9].

1.3. Pultrusion

1.3.1. *Introduction*

Pultrusion is an automated process for continuous production of endless composite profiles of constant cross-section. It is the only fully continuous production method for profiles which is unreservedly regarded to be suitable for mass production. Specific characteristics of the process are a fully automated process causing low labor costs, little waste, and no need for auxiliary material. Pultruded profiles are mainly stock articles with cylindrical or rectangular hollow cross-sections or L-, U-, T-, or H-shapes. The application of these profiles is widespread. Typical examples are window frames, reinforcing for concrete, stairways, fences, wires, exterior covering for railroad cars and container parts [10].

Pultrusion is mainly used to process glass-, aramide-, carbon fiber rovings with a wide variety of thermoset matrices such as polyester-, vinylester- and epoxy-resins [10]. The processing speed can be up to 5 m/min. In addition, thermoplastic matrix based composite pultrusion has been developed over the last 20 years. Due to the higher viscosity of thermoplastics in comparison to thermosets, the processing speed is about ten times slower in terms of thermoplastic pultrusion [11].

1.3.2. *Equipment*

In general, the pultrusion process incorporates three processing steps determining the partial functions of a pultruder:

- Impregnation
- Forming and
- Curing/Cooling

Therefore, a pultruder consists of a resin impregnation device where the rovings coming from a creel are pulled through. An impregnation device is not installed if either thermoplastic or thermoset prepregs (or such rovings) are processed. Fabrics or nonwoven mats are often used as surface layers to enhance the transverse properties of the pultruded material. This can cause difficulties during impregnation due to friction induced shear forces leading to changes in fiber directions. Furthermore, the impregnation equipment consists of a preformer bundling and draping the wetted reinforcing material. After final forming and curing in a die, successive cooling happens at ambient air or by means of cooling devices under tension load provided by the pulling device. Finally, the continuous profiles are cut into desired lengths (Figure 1.4).

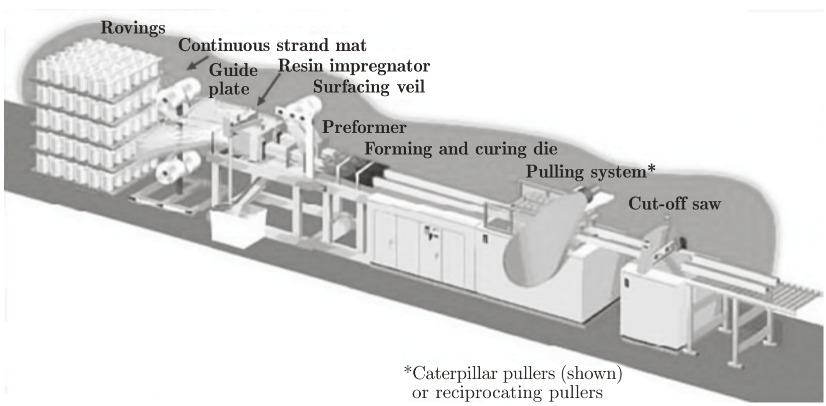

Figure 1.4. Pultrusion machine [12]

1.3.3. *Process description*

Thermoplastic and thermoset pultrusion differ mainly in the field of impregnation. In conventional thermoset pultrusion machines, the rovings are passed through a resin wet-out tank containing the liquid resin. However, due to environmental and quality aspects, a separate resin injection chamber, upstream of the heated die, is introduced, where resin is injected into the rovings *via* injection ports [10,13,14]. Impregnation is completed in the preformer where its tapered passageway provokes intensive resin flow. The wetted reinforcement is pulled through a heated die to be correctly shaped and completely cured. The entire impregnation and curing process, especially the very important pulling, has to be optimized and controlled to derive a good product quality [15]. The pultrusion process can also be improved by means of simulation using finite elements or neural networks [16–19].

Naturally, impregnating rovings with thermoplastic material works differently than with resins. In general, two different strategies are possible:

- Reactive impregnation and
- Nonreactive impregnation.

As be seen on Figure 1.5, reactive thermoplastic pultrusion can be regarded as a combination of the manufacturing principles of thermoset and nonreactive thermoplastic pultrusion [20]. Thus, a thermoplastic reactive pultrusion machine is very similar to a thermoset pultruder. During reactive impregnation, the monomers are brought in contact with the rovings by means of injection while they are reacting to a polymer. This very innovative and still developing procedure is limited to only a few polymers like polyamides, polymethylmethacrylate, and polyurethanes.

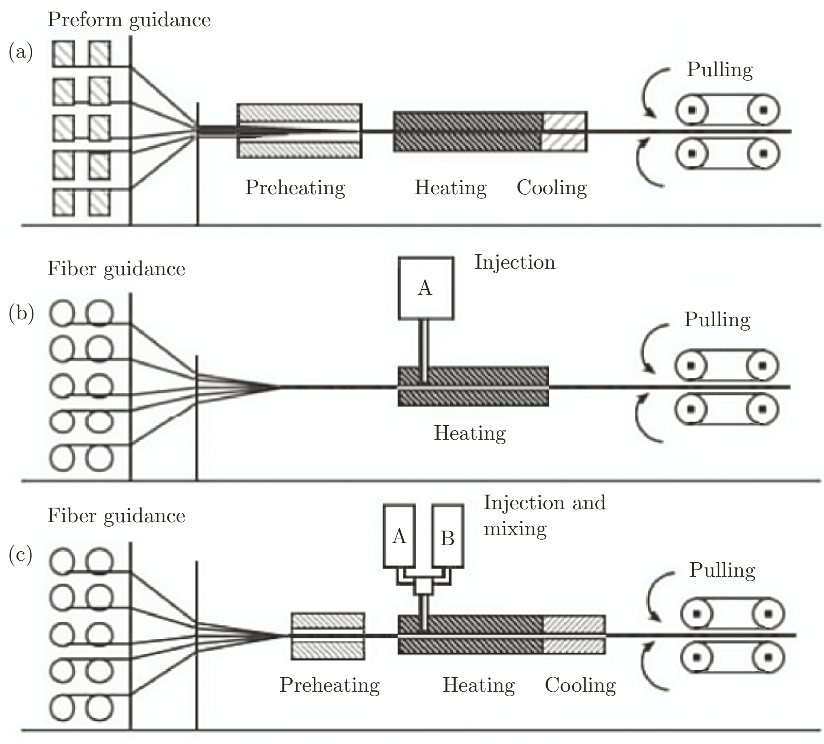

Figure 1.5. Diagrams of different pultusion processes: (a) nonreactive pultrusion of thermoplastic preforms; (b) reactive pultrusion for thermoset composites; and (c) reactive pultrusion for thermoplastic composites [20]

Nonreactive thermoplastic pultrusion utilizes completely polymerized plastics in various preprocessed states such as powder, granulates, filaments, or solutions. The use of preimpregnated fibers is advised due to short flow paths. These preimpregnated fibers can be fed into the pultruder as commingled yarns, thermoplastically coated yarns or tapes. Since impregnation is already done, no impregnation device is needed. Instead, due to the low thermal conductivity of the matrix material and its limited deterioration temperature, a preheating zone has to be used to heat up the material as high as possible before entering the forming die. Preheating can be realized by means of hot air, hot gases, radiation, conduction pins, or a combination of these methods. A new heating technique has been developed using microwave heating [21]. Investigations have shown that heat transfer by conduction is most effective [10]. Final impregnation is performed in a forming die, which is also heated by conduction or convection.

The main advantage of thermoplastic pultrusion is a possible later shaping process to derive curved or even spiral beams [22,23]. In addition, concurrently happening processes such as braiding, filament winding, and thermoforming have been combined with pultrusion to overcome the constraint of constant cross-section [24,25]. Pulwinding and pulbraiding allow helical and hoop filaments glued or welded in-line on pultruded sections leading to superior mechanical properties in different directions (Figure 1.6) [10,22,24]. Pulforming and pulshaping are intermittent processes with a single mold or run in a continuous process with circulating mold pairs allowing curved shapes to be formed with variable cross-sections such as leaf springs [24,26,27].

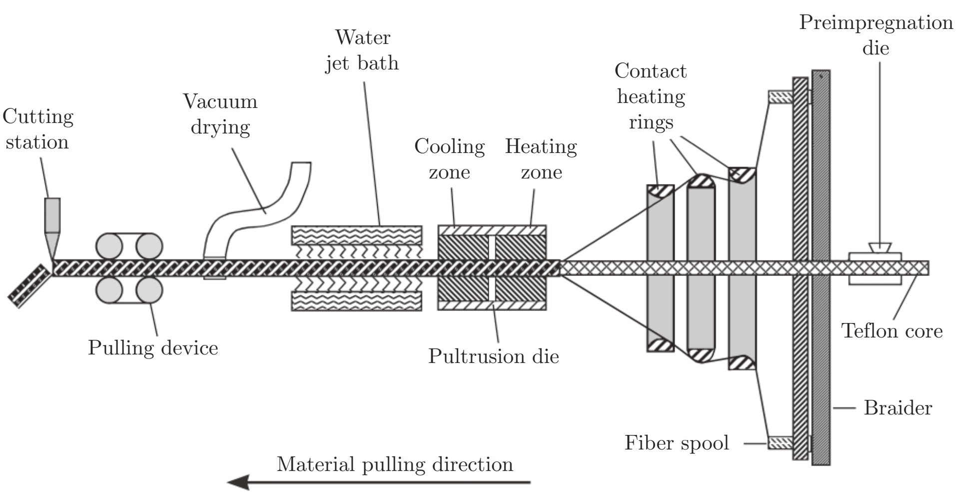

Figure 1.6. Pulbraiding line with contact preheating

1.4. Filament winding and placement techniques

1.4.1. *Filament winding*

Introduction

Filament winding is a discontinuous process of forming circular composite parts such as vessels, tubes, shafts, and rods by winding rovings or tapes previously impregnated with resin or thermoplastic material onto a mandrel. The concept of filament winding was introduced during World War II and improved until the 1960's when the first industrial series