# 5 Manufacturing

A key ingredient in the successful production application of a material or a component is a cost-effective and reliable manufacturing method. Cost-effectiveness depends largely on the rate of production, and reliability requires a uniform quality from part to part.

The early manufacturing method for fiber-reinforced composite structural parts used a hand layup technique. Although hand layup is a reliable process, it is by nature very slow and labor-intensive. In recent years, particularly due to the interest generated in the automotive industry, there is more emphasis on the development of manufacturing methods that can support mass production rates. Compression molding, pultrusion, and filament winding represent three such manufacturing processes. Although they have existed for many years, investigations on their basic characteristics and process optimization started mostly in the mid-1970s. Resin transfer molding (RTM) is another manufacturing process that has received significant attention in both aerospace and automotive industries for its ability to produce composite parts with complex shapes at relatively high production rates. With the introduction of automation, fast-curing resins, new fiber forms, high-resolution quality control tools, and so on, the manufacturing technology for fiber-reinforced polymer composites has advanced at a remarkably rapid pace.

This chapter describes the basic characteristics of major manufacturing methods used in the fiber-reinforced polymer industry. Emphasis is given to process parameters and their relation to product quality. Quality inspection methods and cost issues are also discussed in this chapter.

## 5.1 FUNDAMENTALS

Transformation of uncured or partially cured fiber-reinforced thermoset polymers into composite parts or structures involves curing the material at elevated temperatures and pressures for a predetermined length of time. High cure temperatures are required to initiate and sustain the chemical reaction that transforms the uncured or partially cured material into a fully cured solid. High pressures are used to provide the force needed for the flow of the highly viscous resin or fiber–resin mixture in the mold, as well as for the consolidation of individual unbonded plies into a bonded laminate. The magnitude of these two important process parameters, as well as their duration, significantly affects the quality and performance of the molded product. The length of time required to properly cure a part is called the cure cycle. Since the cure cycle determines the production rate for a part, it is desirable to achieve the proper cure in the shortest amount of time. It should be noted that the cure cycle depends on a number of factors, including resin chemistry, catalyst reactivity, cure temperature, and the presence of inhibitors or accelerators.

## 5.1.1 DEGREE OF CURE

A number of investigators [1–3] have experimentally measured the heat evolved in a curing reaction and related it to the degree of cure achieved at any time during the curing process. Experiments are performed in a differential scanning calorimeter (DSC) in which a small sample, weighing a few milligrams, is heated either isothermally (i.e., at constant temperature) or dynamically (i.e., with uniformly increasing temperature). The instrumentation in DSC monitors the rate of heat generation as a function of time and records it. Figure 5.1 schematically illustrates the rate of heat generation curves for isothermal and dynamic heating.

The total heat generation to complete a curing reaction (i.e., 100% degree of cure) is equal to the area under the rate of heat generation–time curve obtained in a dynamic heating experiment. It is expressed as

$$H_{\rm R} = \int_0^{t_{\rm f}} \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{\rm d} \mathrm{d}t,\tag{5.1}$$

where

 $H_{\rm R}$  = heat of reaction  $(dQ/dt)_{\rm d}$  = rate of heat generation in a dynamic experiment  $t_{\rm f}$  = time required to complete the reaction



**FIGURE 5.1** Schematic representation of the rate of heat generation in (a) dynamic and (b) isothermal heating of a thermoset polymer in a differential scanning calorimeter (DSC).

The amount of heat released in time t at a constant curing temperature T is determined from isothermal experiments. The area under the rate of heat generation-time curve obtained in an isothermal experiment is expressed as

$$H = \int_0^t \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{\mathrm{i}} \mathrm{d}t,\tag{5.2}$$

where *H* is the amount of heat released in time *t* and  $(dQ/dt)_i$  is the rate of heat generation in an isothermal experiment conducted at a constant temperature *T*.

The degree of cure  $\alpha_c$  at any time t is defined as

$$\alpha_{\rm c} = \frac{H}{H_{\rm R}}.$$
(5.3)

Figure 5.2 shows a number of curves relating the degree of cure  $\alpha_c$  to cure time for a vinyl ester resin at various cure temperatures. From this figure, it can be seen that  $\alpha_c$  increases with both time and temperature; however, the rate of cure,  $d\alpha_c/dt$ , is decreased as the degree of cure attains asymptotically a maximum value. If the cure temperature is too low, the degree of cure may not reach a 100% level for any reasonable length of time. The rate of cure  $d\alpha_c/dt$ , obtained from the slope of  $\alpha_c$  vs. t curve and plotted in Figure 5.3, exhibits



FIGURE 5.2 Degree of cure for a vinyl ester resin at various cure temperatures. (After Han, C.D. and Lem, K.W., J. Appl. Polym. Sci., 29, 1878, 1984.)



FIGURE 5.3 Rate of cure for a vinyl ester resin at various cure temperatures. (After Han, C.D. and Lem, K.W., J. Appl. Polym. Sci., 29, 1878, 1984.)

a maximum value at 10%-40% of the total cure achieved. Higher cure temperatures increase the rate of cure and produce the maximum degree of cure in shorter periods of time. On the other hand, the addition of a low-profile agent, such as a thermoplastic polymer, to a polyester or a vinyl ester resin decreases the cure rate.

Kamal and Sourour [4] have proposed the following expression for the isothermal cure rate of a thermoset resin:

$$\frac{\mathrm{d}\alpha_{\mathrm{c}}}{\mathrm{d}t} = (k_1 + k_2 \alpha_{\mathrm{c}}^m)(1 - \alpha_{\mathrm{c}})^n, \qquad (5.4)$$

where  $k_1$  and  $k_2$  are reaction rate constants and *m* and *n* are constants describing the order of reaction. The parameters *m* and *n* do not vary significantly with the cure temperature, but  $k_1$  and  $k_2$  depend strongly on the cure temperature. With the assumption of a second-order reaction (i.e., m + n = 2), Equation 5.4 has been used to describe the isothermal cure kinetics of epoxy, unsaturated polyester, and vinyl ester resins. The values of  $k_1$ ,  $k_2$ , *m*, and *n* are determined by nonlinear least-squares curve fit to the  $d\alpha_c/dt$  vs.  $\alpha_c$  data. Typical values of these constants for a number of resins are listed in Table 5.1.

	Temperature,	Kinetic Parameters in Equation 5.4							
Resin	°C (°F)	k <sub>1</sub> (per min)	$k_2$ (per min)	т	n				
Polyester	45 (113)	0.0131	0.351	0.23	1.77				
	60 (140)	0.0924	1.57	0.40	1.60				
Low-profile polyester	45 (113)	0.0084	0.144	0.27	1.73				
(with 20% polyvinyl acetate)	60 (140)	0.0264	0.282	0.27	1.73				
Vinyl ester	45 (113)	0.0073	0.219	0.33	1.76				
	60 (140)	0.0624	1.59	0.49	1.51				

## TABLE 5.1 Kinetic Parameters for Various Resin Systems

Source: Adapted from Lem, K.W. and Han, C.D., Polym. Eng. Sci., 24, 175, 1984.

#### 5.1.2 VISCOSITY

Viscosity of a fluid is a measure of its resistance to flow under shear stresses. Low-molecular-weight fluids, such as water and motor oil, have low viscosities and flow readily. High-molecular-weight fluids, such as polymer melts, have high viscosities and flow only under high stresses.

The two most important factors determining the viscosity of a fluid are the temperature and shear rate. For all fluids, the viscosity decreases with increasing temperature. Shear rate does not have any influence on the viscosity of low-molecular-weight fluids, whereas it tends to either increase (shear thickening) or decrease (shear thinning) the viscosity of a high-molecular-weight fluids (Figure 5.4). Polymer melts, in general, are shear-thinning fluids since their viscosity decreases with increasing intensity of shearing.

The starting material for a thermoset resin is a low-viscosity fluid. However, its viscosity increases with curing and approaches a very large value as it transforms into a solid mass. Variation of viscosity during isothermal curing of an epoxy resin is shown in Figure 5.5. Similar viscosity–time curves are also observed for polyester [3] and vinyl ester [5] resins. In all cases, the viscosity increases with increasing cure time and temperature. The rate of viscosity increase is low at the early stage of curing. After a threshold degree of cure is achieved, the resin viscosity increases at a very rapid rate. The time at which this occurs is called the *gel time*. The gel time is an important molding parameter, since the flow of resin in the mold becomes increasingly difficult at the end of this time period.

A number of important observations can be made from the viscosity data reported in the literature:



**FIGURE 5.4** Schematic shear stress vs. shear rate curves for various types of liquids. Note that the viscosity is defined as the slope of the shear stress–shear rate curve.

- 1. A B-staged or a thickened resin has a much higher viscosity than the neat resin at all stages of curing.
- 2. The addition of fillers, such as CaCO<sub>3</sub>, to the neat resin increases its viscosity as well as the rate of viscosity increase during curing. On the



FIGURE 5.5 Variation of viscosity during isothermal curing of an epoxy resin. (After Kamal, M.R., *Polym. Eng. Sci.*, 14, 231, 1974.)

other hand, the addition of thermoplastic additives (such as those added in low-profile polyester and vinyl ester resins) tends to reduce the rate of viscosity increase during curing.

- 3. The increase in viscosity with cure time is less if the shear rate is increased. This phenomenon, known as shear thinning, is more pronounced in B-staged or thickened resins than in neat resins. Fillers and thermoplastic additives also tend to increase the shear-thinning phenomenon.
- 4. The viscosity  $\eta$  of a thermoset resin during the curing process is a function of cure temperature *T*, shear rate  $\dot{\gamma}$ , and the degree of cure  $\alpha_c$

$$\eta = \eta(T, \dot{\gamma}, \alpha_{\rm c}). \tag{5.5}$$

The viscosity function for thermosets is significantly different from that for thermoplastics. Since no in situ chemical reaction occurs during the processing of a thermoplastic polymer, its viscosity depends on temperature and shear rate.

5. At a constant shear rate and for the same degree of cure, the  $\eta$  vs. 1/T plot is linear (Figure 5.6). This suggests that the viscous flow of a



FIGURE 5.6 Viscosity-temperature relationships for an epoxy resin at different levels of cure. (After Kamal, M.R., *Polym. Eng. Sci.*, 14, 231, 1974.)

thermoset polymer is an energy-activated process. Thus, its viscosity as a function of temperature can be written as

$$\eta = \eta_{\rm o} \exp\left(\frac{E}{RT}\right),\tag{5.6}$$

where

 $\eta$  = viscosity\* (Pa s or poise) E = flow activation energy (cal/g mol) R = universal gas constant T = cure temperature (°K)  $\eta_{o}$  = constant

The activation energy for viscous flow increases with the degree of cure and approaches a very high value near the gel point.

## 5.1.3 RESIN FLOW

Proper flow of resin through a dry fiber network (in liquid composite molding [LCM]) or a prepreg layup (in bag molding) is critical in producing void-free parts and good fiber wet-out. In thermoset resins, curing may take place simultaneously with resin flow, and if the resin viscosity rises too rapidly due to curing, its flow may be inhibited, causing voids and poor interlaminar adhesion.

Resin flow through fiber network has been modeled using Darcy's equation, which was derived for flow of Newtonian fluids through a porous medium. This equation relates the volumetric resin-flow rate q per unit area to the pressure gradient that causes the flow to occur. For one-dimensional flow in the x direction,

$$q = -\frac{P_0}{\eta} \left(\frac{\mathrm{d}p}{\mathrm{d}x}\right),\tag{5.7}$$

where

q = volumetric flow rate per unit area (m/s) in the x direction

- $P_0 =$  permeability (m<sup>2</sup>)
- $\eta = \text{viscosity} (\text{N} \text{s}/\text{m}^2)$
- $\frac{dp}{dx}$  = pressure gradient (N/m<sup>3</sup>), which is negative in the direction of flow (positive x direction)

\* Unit of viscosity: 1 Pas =  $1 \text{ Ns/m}^2 = 10 \text{ poise (P)} = 1000 \text{ centipoise (cP)}.$ 

The *permeability* is determined by the following equation known as the Kozeny-Carman equation:

$$P_0 = \frac{d_{\rm f}^2}{16K} \frac{(1 - v_{\rm f})^3}{v_{\rm f}^2},\tag{5.8}$$

where

 $d_{\rm f} = {\rm fiber \ diameter}$ 

 $v_f\,=\,fiber\;volume\;fraction$ 

K = Kozeny constant

Equations 5.7 and 5.8, although simplistic, have been used by many investigators in modeling resin flow from prepregs in bag-molding process and mold filling in RTM. Equation 5.8 assumes that the porous medium is isotropic, and the pore size and distribution are uniform. However, fiber networks are nonisotropic and therefore, the Kozeny constant, K, is not the same in all directions. For example, for a fiber network with unidirectional fiber orientation, the Kozeny constant in the transverse direction ( $K_{22}$ ) is an order of magnitude higher than the Kozeny constant in the longitudinal direction ( $K_{11}$ ). This means that the resin flow in the transverse direction is much lower than that in the longitudinal direction. Furthermore, the fiber packing in a fiber network is not uniform, which also affects the Kozeny constant, and therefore the resin flow.

Equation 5.8 works well for predicting resin flow in the fiber direction. However, Equation 5.8 is not valid for resin flow in the transverse direction, since according to this equation resin flow between the fibers does not stop even when the fiber volume fraction reaches the maximum value at which the fibers touch each other and there are no gaps between them. Gebart [6] derived the following permeability equations in the fiber direction and normal to the fiber direction for unidirectional continuous fiber network with regularly arranged, parallel fibers.

In the fiber direction: 
$$P_{11} = \frac{2d_{\rm f}^2}{C_1} \frac{(1 - {\rm v}_{\rm f}^3)}{{\rm v}_{\rm f}^2},$$
 (5.9a)

Normal to the fiber direction: 
$$P_{22} = C_2 \left( \sqrt{\frac{\mathbf{v}_{\mathrm{f,max}}}{\mathbf{v}_{\mathrm{f}}}} - 1 \right)^{5/2} \frac{d_{\mathrm{f}}^2}{4},$$
 (5.9b)

where

 $C_1$  = hydraulic radius between the fibers

 $C_2$  = a constant

 $v_{f,max}$  = maximum fiber volume fraction (i.e., at maximum fiber packing)

The parameters  $C_1$ ,  $C_2$ , and  $v_{f,max}$  depend on the fiber arrangement in the network. For a square arrangement of fibers,  $C_1 = 57$ ,  $C_2 = 0.4$ , and  $v_{f,max} = 0.785$ . For a hexagonal arrangement of fibers (see Problem P2.18),  $C_1 = 53$ ,  $C_2 = 0.231$ , and  $v_{f,max} = 0.906$ . Note that Equation 5.9a for resin flow parallel to the fiber direction has the same form as the Kozeny-Carman equation 5.8. According to Equation 5.9b, which is applicable for resin flow transverse to the flow direction,  $P_{22} = 0$  at  $v_f = v_{f,max}$ , and therefore, the transverse resin flow stops at the maximum fiber volume fraction.

The permeability equations assume that the fiber distribution is uniform, the gaps between the fibers are the same throughout the network, the fibers are perfectly aligned, and all fibers in the network have the same diameter. These assumptions are not valid in practice, and therefore, the permeability predictions using Equation 5.8 or 5.9 can only be considered approximate.

#### 5.1.4 CONSOLIDATION

Consolidation of layers in a fiber network or a prepreg layup requires good resin flow and compaction; otherwise, the resulting composite laminate may contain a variety of defects, including voids, interply cracks, resin-rich areas, or resin-poor areas. Good resin flow by itself is not sufficient to produce good consolidation [7].

Both resin flow and compaction require the application of pressure during processing in a direction normal to the dry fiber network or prepreg layup. The pressure is applied to squeeze out the trapped air or volatiles, as the liquid resin flows through the fiber network or prepreg layup, suppresses voids, and attains uniform fiber volume fraction. Gutowski et al. [8] developed a model for consolidation in which it is assumed that the applied pressure is shared by the fiber network and the resin so that

$$p = \sigma + \bar{p}_{\rm r},\tag{5.10}$$

where

p = applied pressure  $\sigma =$  average effective stress on the fiber network

 $\bar{p}_{\rm r}$  = average pressure on the resin

The average effective pressure on the fiber network increases with increasing fiber volume fraction and is given by

$$\sigma = A \frac{1 - \sqrt{\frac{V_{\rm f}}{V_{\rm o}}}}{\left(\sqrt{\frac{V_{\rm a}}{V_{\rm f}}} - 1\right)^4},\tag{5.11}$$

#### where

A is a constant

 $v_o$  is the initial fiber volume fraction in the fiber network (before compaction)  $v_f$  is the fiber volume fraction at any instant during compaction

v<sub>a</sub> is the maximum possible fiber volume fraction

The constant A in Equation 5.11 depends on the fiber stiffness and the fiber waviness, and is a measure of the deformability of the fiber network. Since the fiber volume fraction,  $v_f$ , increases with increasing compaction, Equation 5.11 predicts that  $\sigma$  also increases with increasing compaction, that is, the fiber network begins to take up an increasing amount of the applied pressure. On the other hand, the average pressure on the resin decreases with increasing compaction, which can lead to void formation.

## 5.1.5 GEL-TIME TEST

The curing characteristics of a resin–catalyst combination are frequently determined by the gel-time test. In this test, a measured amount (10 g) of a thoroughly mixed resin–catalyst combination is poured into a standard test tube. The temperature rise in the material is monitored as a function of time by means of a thermocouple while the test tube is suspended in a  $82^{\circ}C$  ( $180^{\circ}F$ ) water bath.

A typical temperature–time curve (also known as *exotherm curve*) obtained in a gel-time test is illustrated in Figure 5.7. On this curve, point A indicates the time required for the resin–catalyst mixture to attain the bath temperature. The beginning of temperature rise indicates the initiation of the curing reaction. As the curing reaction begins, the liquid mix begins to transform into a gel-like mass. Heat generated by the exothermic curing reaction increases the mix temperature, which in turn causes the catalyst to decompose at a faster rate and the reaction to proceed at a progressively increasing speed. Since the rate of heat generation is higher than the rate of heat loss to the surrounding medium, the temperature rises rapidly to high values. As the curing reaction nears completion, the rate of heat generation is reduced and a decrease in temperature follows. The exothermic peak temperature observed in a gel-time test is a function of the resin chemistry (level of unsaturation) and the resin–catalyst ratio. The slope of the exotherm curve is a measure of cure rate, which depends primarily on the catalyst reactivity.

Shortly after the curing reaction begins at point A, the resin viscosity increases very rapidly owing to the increasing number of cross-links formed by the curing reaction. The time at which a rapid increase in viscosity ensues is called the gel time and is indicated by point B in Figure 5.7. According to one standard, the time at which the exotherm temperature increases by  $5.5^{\circ}C$  (10°F) above the bath temperature is considered the gel time. It is sometimes measured by probing the surface of the reacting mass with a clean wooden applicator stick every 15 s until the reacting material no longer adheres to the end of a clean stick.



FIGURE 5.7 Typical temperature-time curve obtained in a gel-time test.

#### 5.1.6 SHRINKAGE

Shrinkage is the reduction in volume or linear dimensions caused by curing as well as thermal contraction. Curing shrinkage occurs because of the rearrangement of polymer molecules into a more compact mass as the curing reaction proceeds. The thermal shrinkage occurs during the cooling period that follows the curing reaction and may take place both inside and outside the mold.

The volumetric shrinkage for cast-epoxy resins is of the order of 1%-5% and that for polyester and vinyl ester resins may range from 5% to 12%. The addition of fibers or fillers reduces the volumetric shrinkage of a resin. However, in the case of unidirectional fibers, the reduction in shrinkage in the longitudinal direction is higher than in the transverse direction.

High shrinkage in polyester or vinyl ester resins can be reduced significantly by the addition of low shrink additives (also called low-profile agents), which are thermoplastic polymers, such as polyethylene, polymethyl acrylate, polyvinyl acetate, and polycaprolactone (see Chapter 2). These thermoplastic additives are usually mixed in styrene monomer during blending with the liquid resin. On curing, the thermoplastic polymer becomes incompatible with the cross-linked resin and forms a dispersed second phase in the cured resin. High resin shrinkage is desirable for easy release of the part from the mold surface; however, at the same time, high resin shrinkage can contribute to many molding defects, such as warpage and sink marks. These defects are described in Section 5.3.

## 5.1.7 Voids

Among the various defects produced during the molding of a composite laminate, the presence of voids is considered the most critical defect in influencing its mechanical properties. The most common cause for void formation is the inability of the resin to displace air from the fiber surface during the time fibers are coated with the liquid resin. The rate at which the fibers are pulled through the liquid resin, the resin viscosity, the relative values of fiber and resin surface energies, and the mechanical manipulation of fibers in the liquid resin affect air entrapment at the fiber–resin interface. Voids may also be caused by air bubbles and volatiles entrapped in the liquid resin. Solvents used for resin viscosity control, moisture, and chemical contaminants in the resin, as well as styrene monomer, may remain dissolved in the resin mix and volatilize during elevated temperature curing. In addition, air is also entrapped between various layers during the lamination process.

Much of the air or volatiles entrapped at the premolding stages can be removed by (1) degassing the liquid resin, (2) applying vacuum during the molding process, and (3) allowing the resin mix to flow freely in the mold, which helps in carrying the air and volatiles out through the vents in the mold. The various process parameters controlling the resin flow are described in later sections.

The presence of large volume fractions of voids in a composite laminate can significantly reduce its tensile, compressive, and flexural strengths. Large reductions in interlaminar shear strength are observed even if the void content is only 2%-3% by volume (Figure 5.8). The presence of voids generally increases the rate and amount of moisture absorption in a humid environment, which in turn increases the physical dimensions of the part and reduces its matrix-dominated properties.

## 5.2 BAG-MOLDING PROCESS

The bag-molding process is used predominantly in the aerospace industry where high production rate is not an important consideration. The starting material for bag-molding processes is a prepreg that contains fibers in a partially cured (B-staged) epoxy resin. Typically, a prepreg contains 42 wt% of resin. If this prepreg is allowed to cure without any resin loss, the cured laminate would contain 50 vol% of fibers. Since nearly 10 wt% of resin flows out during the molding process, the actual fiber content in the cured laminate is



FIGURE 5.8 Effect of void volume fraction on the interlaminar shear strength of a composite laminate. (After Yokota, M.J., *SAMPE J.*, 11, 1978.)

60 vol% which is considered an industry standard for aerospace applications. The excess resin flowing out from the prepreg removes the entrapped air and residual solvents, which in turn reduces the void content in the laminate. However, the recent trend is to employ a near-net resin content, typically 34 wt%, and to allow only 1-2 wt% resin loss during molding.

Figure 5.9 shows the schematic of a bag-molding process. The mold surface is covered with a Teflon-coated glass fabric separator (used for preventing sticking in the mold) on which the prepreg plies are laid up in the desired fiber orientation angle as well as in the desired sequence. Plies are trimmed from the prepreg roll into the desired shape, size, and orientation by means of a cutting device, which may simply be a mat knife. Laser beams, high-speed water jets, or trimming dies are also used. The layer-by-layer stacking operation can be performed either manually (by hand) or by numerically controlled automatic tape-laying machines. Before laying up the prepreg, the backup release film is peeled off from each ply. Slight compaction pressure is applied to adhere the prepreg to the Teflon-coated glass fabric or to the preceding ply in the layup.

After the layup operation is complete, a porous release cloth and a few layers of bleeder papers are placed on top of the prepreg stack. The bleeder papers are used to absorb the excess resin in the prepreg as it flows out during the molding process. The complete layup is covered with another sheet of



FIGURE 5.9 Schematic of a bag-molding process.

Teflon-coated glass fabric separator, a caul plate, and then a thin heat-resistant vacuum bag, which is closed around its periphery by a sealant. The entire assembly is placed inside an autoclave where a combination of external pressure, vacuum, and heat is applied to consolidate and densify separate plies into a solid laminate. The vacuum is applied to remove air and volatiles, while the pressure is required to consolidate individual layers into a laminate.

As the prepreg is heated in the autoclave, the resin viscosity in the B-staged prepreg plies first decreases, attains a minimum, and then increases rapidly (gels) as the curing (cross-linking) reaction begins and proceeds toward completion. Figure 5.10 shows a typical two-stage cure cycle for a carbon fiber–epoxy prepreg. The first stage in this cure cycle consists of increasing the temperature at a controlled rate (say, 2°C/min) up to 130°C and dwelling at this temperature for nearly 60 min when the minimum resin viscosity is reached.



FIGURE 5.10 Typical two-stage cure cycle for a carbon fiber-epoxy prepreg.

During this period of temperature dwell, an external pressure is applied on the prepreg stack that causes the excess resin to flow out into the bleeder papers. The resin flow is critical since it allows the removal of entrapped air and volatiles from the prepreg and thus reduces the void content in the cured laminate. At the end of the temperature dwell, the autoclave temperature is increased to the actual curing temperature for the resin. The cure temperature and pressure are maintained for 2 h or more until a predetermined level of cure has occurred. At the end of the cure cycle, the temperature is slowly reduced while the laminate is still under pressure. The laminate is removed from the vacuum bag and, if needed, postcured at an elevated temperature in an aircirculating oven.

The flow of excess resin from the prepregs is extremely important in reducing the void content in the cured laminate. In a bag-molding process for producing thin shell or plate structures, resin flow by face bleeding (normal to the top laminate face) is preferred over edge bleeding. Face bleeding is more effective since the resin-flow path before gelation is shorter in the thickness direction than in the edge directions. Since the resin-flow path is relatively long in the edge directions, it is difficult to remove entrapped air and volatiles from the central areas of the laminate by the edge bleeding process.

The resin flow from the prepregs reduces significantly and may even stop after the gel time, which can be increased by reducing the heat-up rate as well as the dwell temperature (Figure 5.11). Dwelling at a temperature lower than the curing temperature is important for two reasons: (1) it allows the layup to achieve a uniform temperature throughout the thickness and (2) it provides



FIGURE 5.11 Effect of dwelling on gel time. (Adapted from Purslaw, D. and Childs, R., *Composites*, 17, 757, 1986.)

time for the resin to achieve a low viscosity. A small batch-to-batch variation in dwell temperature may cause a large variation in gel time, as evidenced in Figure 5.11.

The cure temperature and pressure are selected to meet the following requirements:

- 1. The resin is cured uniformly and attains a specified degree of cure in the shortest possible time.
- 2. The temperature at any position inside the prepreg does not exceed a prescribed limit during the cure.
- 3. The cure pressure is sufficiently high to squeeze out all of the excess resin from every ply before the resin gels (increases in viscosity) at any location inside the prepreg.

Loos and Springer [9] developed a theoretical model for the complex thermomechanical phenomenon that takes place in a vacuum bag-molding process. Based on their model and experimental works, the following observations can be made regarding the various molding parameters.

The maximum temperature inside the layup depends on (1) the maximum cure temperature, (2) the heating rate, and (3) the initial layup thickness. The maximum cure temperature is usually prescribed by the prepreg manufacturer for the particular resin–catalyst system used in the prepreg and is determined from the time–temperature–viscosity characteristics of the resin–catalyst system. At low heating rates, the temperature distribution remains uniform within the layup. At high heating rates and increased layup thickness, the heat generated by the curing reaction is faster than the heat transferred to the mold surfaces and a temperature "overshoot" occurs.

Resin flow in the layup depends on the maximum pressure, layup thickness, and heating rate, as well as the pressure application rate. A cure pressure sufficient to squeeze out all excess resin from 16 to 32 layups was found to be inadequate for squeezing out resin from the layers closer to the bottom surface in a 64-ply layup. Similarly, if the heating rate is very high, the resin may start to gel before the excess resin is squeezed out from every ply in the layup.

Loos and Springer [9] have pointed out that the cure cycle recommended by prepreg manufactures may not be adequate to squeeze out excess resin from thick layups. Since the compaction and resin flow progress inward from the top, the plies adjacent to the bottom mold surface may remain uncompacted and rich in resin, thereby creating weak interlaminar layers in the laminate.

Excess resin must be squeezed out of every ply before the gel point is reached at any location in the prepreg. Therefore, the maximum cure pressure should be applied just before the resin viscosity in the top ply becomes sufficiently low for the resin flow to occur. If the cure pressure is applied too early, excess resin loss would occur owing to very low viscosity in the pregel period.

## TABLE 5.2Cure Time for 90% Degree of Cure in a 32-PlyCarbon Fiber-Epoxy Laminate<sup>a</sup>

Cure Temperature, °C (°F)	Heating Rate, °C/min (°F/min)	Cure Time (min)			
135 (275)	2.8 (5)	236			
163 (325)	2.8 (5)	110			
177 (351)	2.8 (5)	89			
177 (351)	5.6 (10)	65			
177 (351)	11.1 (20)	52			

<sup>a</sup> Based on a theoretical model developed by Loos and Springer — Loos, A.C. and Springer, G.S., *J. Compos. Mater.*, 17, 135, 1983.

If on the other hand the cure pressure is applied after the gel time, the resin may not be able to flow into the bleeder cloth because of the high viscosity it quickly attains in the postgel period. Thus the pressure application time is an important molding parameter in a bag-molding process. In general, it decreases with increasing cure pressure as well as increasing heating rate.

The uniformity of cure in the laminate requires a uniform temperature distribution in the laminate. The time needed for completing the desired degree of cure is reduced by increasing the cure temperature as well as increasing the heating rate (Table 5.2).

Besides voids and improper cure, defects in bag-molded laminates relate to the ply layup and trimming operations. Close control must be maintained over the fiber orientation in each ply, the stacking sequence, and the total number of plies in the stack. Since prepreg tapes are not as wide as the part itself, each layer may contain a number of identical plies laid side by side to cover the entire mold surface. A filament gap in a single layer should not exceed 0.76 mm (0.03 in.), and the distance between any two gaps should not be <38 mm (1.5 in.) [10]. Care must also be taken to avoid filament crossovers. Broken filaments, foreign matter, and debris should not be permitted. To prevent moisture pickup, the prepreg roll on removal from the cold storage should be warmed to room temperature before use.

## 5.3 COMPRESSION MOLDING

Compression molding is used for transforming sheet-molding compounds (SMC) into finished products in matched molds. The principal advantage of compression molding is its ability to produce parts of complex geometry in short periods of time. Nonuniform thickness, ribs, bosses, flanges, holes, and shoulders, for example, can be incorporated during the compression-molding



FIGURE 5.12 Schematic of a compression-molding process.

process. Thus, it allows the possibility of eliminating a number of secondary finishing operations, such as drilling, forming, and welding. The entire molding process, including mold preparation and placement of SMC in the mold, as well as part removal from the mold, can be automated. Thus, the compressionmolding process is suitable for the high-volume production of composite parts. It is considered the primary method of manufacturing for many structural automotive components, including road wheels, bumpers, and leaf springs.

The compression-molding operation begins with the placement of a precut and weighed amount of SMC, usually a stack of several rectangular plies called the charge, onto the bottom half of a preheated mold cavity (Figure 5.12). The ply dimensions are selected to cover 60%–70% of the mold surface area. The mold is closed quickly after the charge placement, and the top half of the mold is lowered at a constant rate until the pressure on the charge increases to a preset level. With increasing pressure, the SMC material in the mold starts to flow and fill the cavity. Flow of the material is required to expel air entrapped in the mold as well as in the charge. Depending on the part complexity, length of flow, and fiber content (which controls the viscosity of SMC), the molding pressure may vary from 1.4 to 34.5 MPa (200–5000 psi). Usually, high pressures are required for molding parts that contain deep ribs and bosses. The mold temperature is usually in the range of  $130^{\circ}C$ – $160^{\circ}C$  (270°F–320°F). After a



FIGURE 5.13 Temperature distribution at various locations across the thickness of an SMC during the compression-molding operation. (After Mallick, P.K. and Raghupathi, N., *Polym. Eng. Sci.*, 19, 774, 1979.)

reasonable degree of cure is achieved under pressure, the mold is opened and the part is removed, often with the aid of ejector pins.

During molding, a complex heat transfer and a viscous flow phenomenon take place in the cavity. A review of the current understanding of the flow and cure characteristics of compression-molded SMC is given in Ref. [11]. Temperature-time curves measured at the outer surface, subsurface, and centerline of thick E-glass fiber-SMC moldings (Figure 5.13) show that the charge surface temperature quickly attains the mold temperature and remains relatively uniform compared with the centerline temperature. However, owing to the low thermal conductivity of E-glass fiber-SMC, the centerline temperature increases slowly until the curing reaction is initiated at the mid-thickness of the part. Since the SMC material has a relatively low thermal conductivity, the heat generated by the exothermic curing reaction in the interior of the SMC charge is not efficiently conducted to the mold surface and the centerline temperature increases rapidly to a peak value. As the curing reaction nears completion, the centerline temperature decreases gradually to the mold surface temperature. For thin parts, the temperature rise is nearly uniform across the thickness and the maximum temperature in the material seldom exceeds the mold temperature.

Since the surface temperature first attains the resin gel temperature, curing begins first at the surface and progresses inward. Curing occurs more rapidly at higher mold temperatures (Figure 5.14); however, the peak exotherm temperature may also increase. Since peak exotherm temperature of 200°C or higher may cause burning and chemical degradation in the resin, high molding temperatures in thick parts should be avoided.



**FIGURE 5.14** Curing time vs. mold temperature of SMC sheets. Note that the shaded area represents undesirable molding conditions due to the exotherm temperature exceeding 200°C. (After Panter, M.R., The effect to processing variables on curing time and thermal degradation of compression molded SMC, *Proceedings 36th Annual Conference*, Society of the Plastics Industry, February 1981.)

Increasing the filler content in SMC formulations decreases the peak exotherm temperature since it replaces part of the resin and thereby decreases the total amount of heat liberated. It also acts as a heat sink within the material. The time to reach peak exotherm, which increases almost linearly with the part thickness, is also reduced with increasing filler content. Thus fillers can play a significant role in reducing the cure cycle of a part. Another efficient way of reducing the cure time in the mold is to preheat the charge to pregel temperatures outside the mold and finish curing with high mold-closing speeds inside the mold. Preheating can be accomplished by dielectric heaters that increase the temperature rapidly and uniformly throughout the charge volume. During molding, the thermal gradient remains nearly constant across the thickness of a preheated charge, which allows uniform curing in the thickness direction. As a result, residual curing stresses in the molded part are also reduced.

As the temperature of SMC charge increases in the mold, the network structure created by the thickening reaction with MgO (see Chapter 2) breaks down and the resin viscosity is reduced (Figure 5.15). If the material does not attain a low viscosity before gelling, its flow in the mold is severely restricted. If premature gelation occurs before the mold is filled, the molded part will be incomplete and may contain voids and interlaminar cracks. A number of investigators have studied the basic flow behavior of random fiber SMC with multicolored layers in flat plaque mold cavities [12–14]. At fast mold-closing speeds, the layers flow with uniform extension (plug flow), with slip occurring at the mold surface (Figure 5.16a). The charge thickness does not influence this flow pattern at fast mold-closing speeds. At slow mold-closing speeds, on the other hand, SMC flow pattern depends very much on the charge thickness.



**FIGURE 5.15** Viscosity variation of an SMC before and during the compressionmolding operation.

For thick charges, the viscosity of SMC in layers adjacent to the hot mold surfaces decreases rapidly while the viscosity in the interior layers is still quite high. As a result, the outer layers begin to flow before the interior layers and may even squirt into the uncovered areas of the mold (Figure 5.16b). Thus the outer layers in this case undergo greater extensional deformation than



**FIGURE 5.16** Flow of various layers of an SMC charge during compression molding at (a) fast mold-closing speeds and (b) slow mold-closing speeds. (After Barone, M.R. and Caulk, D.A., *Polym. Compos.*, 6, 105, 1985.)

## TABLE 5.3 Common Surface Defects in Compression-Molded SMC

Possible Contributing Factors					
Coarse filler particles, filler particle agglomeration					
Resin shrinkage, glass fiber distribution					
Poor dispersion of the lubricant (zinc stearate)					
Resin shrinkage, fiber distribution, fiber length, fiber orientation					
Resin shrinkage, fiber bundle integrity, strand dimensions, fiber distribution					
Styrene loss from the surface					
Subsurface voids due to trapped air and volatiles					

the interior layers, with slip occurring between the layers as well as at the mold surface. As the charge thickness is reduced, the extensional deformation becomes more uniform and approaches the same flow pattern observed at fast mold-closing speeds. For a good molded part, a rapid mold-closing speed is desirable since it avoids the possibility of premature gelation and produces the most uniform flow pattern regardless of the charge thickness [14].

Compression-molded SMC parts may contain a wide variety of surface and internal defects (Table 5.3). The surface defects usually create a poor surface appearance or unacceptable surface finish, and the internal defects may affect performance of the molded part. The origin of some of these defects is discussed as follows.

Porosity is the result of small internal voids or surface pits (Figure 5.17a) caused by the entrapment of air or other gases in the molded part. Air is introduced into the SMC at a number of stages, namely, (1) in the resin paste during mechanical blending of liquid resin, styrene monomer, and fillers, (2) at the fiber–resin interface owing to inefficient wetting, (3) in the SMC sheet during compaction between carrier films, (4) between layers of SMC sheets in the charge, and (5) in the closed mold. Air entrapped in the SMC before mold closure is squeezed into small volumes by the pressure exerted during molding. A substantial amount of these air volumes can be carried away by the material flowing toward the vents and shear edges. However, if proper venting is not provided in the mold or the material viscosity is high during its flow, these air volumes may remain entrapped as voids in the molded part.

Blisters are interlaminar cracks (Figure 5.17b) formed at the end of molding due to excessive gas pressure in the interior region of the molded part. The internal gas pressure is generated during molding from unreacted styrene monomer in undercured parts or from large pockets of entrapped air between the stacked layers. If this internal pressure is high, interlaminar cracks may form at the time of mold opening. The delaminated area near the surface may bulge



FIGURE 5.17 Various defects in a compression-molded SMC part.

into a dome-shaped blister by the entrapped gas pressure. Blisters may also appear during some postmolding operations, such as high-temperature baking in a paint oven, which causes expansion of entrapped air or gases.

Griffith and Shanoski [15] suggested two possible ways of reducing blisters:

- 1. Minimize the entrapped air. The most effective method for minimizing the entrapped air is vacuum molding, in which air from the mold is evacuated just as the mold is closed. A second method of reducing the entrapped air is to allow more radial flow by stacking more plies over a smaller area instead of stacking fewer plies over a larger area.
- 2. Increase the interlaminar shear strength by changing the resin type, using coupling agents, reducing contamination between layers, decreasing the molding temperature, and assuring proper cure before the mold pressure is released.

In any molding operation involving long flow paths, it is extremely difficult to control the preferential orientation of fibers. With compression molding of SMC-R, abrupt changes in thickness, any obstruction in the flow path, or the

presence of high shear zones can create fiber orientations that deviate from the ideal random orientation. As a result, the molded part may become locally anisotropic with its strength and modulus higher in the direction of flow than in the transverse direction. In the compression molding of SMC-R, it is common practice to cover only 60%–70% of the mold surface with the charge, and then use high normal pressure to spread it over the entire mold cavity. When the flow front contacts the cavity edges, discontinuous fibers in the SMC-R tend to rotate normal to the flow direction (Figure 5.17c). This results in strength reduction normal to the flow direction and makes the edges prone to early cracking.

Compression molding of SMC-CR or XMC containing continuous fibers is normally performed with 90%–95% initial mold surface coverage. For these materials, flow is possible only in the transverse direction of fibers. If excessive transverse flow is allowed, continuous fibers in the surface and subsurface layers of both SMC-CR and XMC may buckle (bow out) near the end of the flow path (Figure 5.17d). In addition, the included angle between the X-patterned fibers in XMC may also increase. As a result, the longitudinal tensile strengths of SMC-CR and XMC are reduced in areas with fiber misorientation [16]. However, since severe fiber misorientations are generally restricted to the outer layers, increasing the number of plies improves the longitudinal strength to the level observed with no misorientation.

Knit lines are linear domains of aligned fiber orientation and are formed at the joining of two divided flow fronts (Figure 5.17e), such as behind a metal insert or pin or where two or more separate flow fronts arising from multiple charge pieces meet. Multiple charge pieces are used for compression molding of large and complex parts. Since fibers tend to align themselves along the knit line, the strength of the part in a direction normal to the knit line is reduced.

The formation of knit lines can be reduced by proper charge placement in the mold. A common location of knit lines in behind a core pin used in forming molded-in holes. Thus if the holes are in a high-stress area, it is better to drill them instead of using core pins, since knit lines formed behind such core pins may extend to the edge and initiate premature cracking.

Warpage is critical in thin-section moldings and is caused by variations in cooling rate between sections of different thicknesses or different fiber orientations. Differential cooling rates may also lead to complex residual stresses, which may ultimately reduce the strength of a molded part.

Nonuniform cure is critical in thick-section moldings and can create a gradient of properties in the thickness direction. Since the curing reaction is initiated at the surfaces and progresses inward, it is likely that insufficient molding time will leave the interior undercured. As a result, the interlaminar shear strength of the molded part is reduced.

The effect of various molding times on the development of throughthickness properties of a thick-section molding is demonstrated in Figure 5.18. This figure was developed by sectioning 12 mm (0.5 in.) thick compression-molded specimens along the center plane and testing each half in flexure, one with the



FIGURE 5.18 Effect of cure time on the development of flexural strength in a compressionmolded SMC-R laminate. (After Mallick, P.K. and Raghupathi, N., *Polym. Eng. Sci.*, 19, 774, 1979.)

outer skin in tension and the other with the exposed center in tension. For short mold-opening times the center has a much lower strength than the outer skin, indicating that the part was removed before completion of cure at the center. The difference in strength is reduced at higher molding times.

Sink marks are small surface depressions normally observed above the ribs in compression-molded SMC parts (Figure 5.17f). Jutte [17] has shown that the flow of material into a rib creates a fiber-rich zone near its base and resin-rich zone near the opposite surface. Since the resin-rich zone has a higher coefficient of thermal contraction, it shrinks more than the surrounding material, which contains uniform fiber distribution. As a result, the surface opposite to a rib will depress and a sink mark will appear.

A nonuniform flow pattern of material is generally considered the reason for the separation of resin from fibers at or near the base of a rib. Smith and Suh [18] have shown that protruding rib corners (Figure 5.19) create less sink



**FIGURE 5.19** Rib design in SMC parts: (a) rounded corner, (b) sharp corner, and (c) protruded corner.

depths than either sharp or rounded rib corners. Their experiments also show that sink depths in 12 mm (0.5 in.) long fiber-reinforced SMC are lower than those in 25 mm (1 in.) long fiber-reinforced SMC. Uneven part thickness on the two sides of a rib tends to reduce the sink depth as well as shift the sink mark toward the thicker section.

A poor surface finish caused by sink marks is undesirable in highly visible exterior automotive body panels, such as a hood or a door panel, made of compression-molded SMC. Short ribs are commonly used on the back surface of these panels to improve their flexural stiffness. However, sink marks formed on the top surface reduce the surface finish to lower than the Class A (mirror) finish. Although sink depths can be controlled by using longer ribs, a combination of long and short fibers in the SMC-R sheets, or a low-profile resin, they are not completely eliminated. The current approach is to mask these and other surface imperfections by coating the outer surface with a flexible paint. Just after the completion of the cure cycle, the top mold is retracted by a small amount and the liquid paint is injected over the top surface. This process is known as *in-mold coating*.

### 5.4 PULTRUSION

Pultrusion is a continuous molding process for producing long, straight structural members of constant cross-sectional area. Among the common pultruded products are solid rods, hollow tubes, flat sheets, and beams of a variety of cross sections, including angles, channels, hat sections, and wide-flanged sections. Pultrusion processes for producing variable cross sections along the length as well as curved members have also been developed.

The major constituent in a pultruded product is longitudinally oriented continuous strand rovings. Several layers of mats or woven rovings are added at or near the outer surface (Figure 5.20) to improve its transverse strength. The total fiber content in a pultruded member may be as high as 70% by weight; however, owing to the presence of mats or woven rovings, its longitudinal

Continuous	0	~	0	0	0	~	0	~	0	~	0	~	0	~	0	~	0		0	~	0
strand rovings	0	0	0	0	0	<u> </u>	0	0	0	0	0	0	0	0	0	0	0	_	0	<u> </u>	0
Mat layers																					
,	o		0		0		0		0		0		0		0		0		0		0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	ິ	C	ິ	С	0
	_		_		<u> </u>		<u> </u>		<u> </u>		<u> </u>		<u> </u>				<u> </u>		<u> </u>		_
																					_
	0	~	0	~	0	~	0	~	0	~	0	~	0	~	0	~	0	2	0	0	0
	0	0	0	0	0	0	0	0	0	Ű	0	0	0	0	0	Ő	0	-	0	0	0

FIGURE 5.20 Typical construction of a pultruded sheet.

TABLE 5.4			
<b>Mechanical Properties</b>	of Pultruded E-Glass	–Polyester	Sheets

Total Fiber Content					
(wt%)	70	60	50	40	30
Continuous roving content (wt%)	38.8	28.8	18.8	18.8	16.1
Mat content (wt%)	31.2	31.2	31.2	20.8	13.9
Roving-mat ratio	1.24	0.92	0.60	0.90	1.16
Roving end count	79	58	38	29	33
No. mat layers	2	3	3	3	2
Mat weight (oz)	1.5	1.5	1.5	1.5	1
Tensile strength, MPa (ksi)					
Longitudinal	373.1 (54.1)	332.4 (48.2)	282.1 (40.9)	265.5 (38.5)	217.2 (31.5)
Transverse	86.9 (12.6)	93.1 (13.5)	94.5 (13.7)	84.8 (12.3)	67.6 (9.8)
Tensile modulus, GPa (Msi)					
Longitudinal	28.8 (4.17)	23.6 (3.42)	18.4 (2.67)	17.1 (2.48)	15.4 (2.24)
Transverse	8.34 (1.21)	9.31 (1.35)	8.55 (1.24)	7.1 (1.03)	5.24 (0.76)
Flexural strength, MPa (ksi)					
Longitudinal	412.4 (59.8)	375.9 (54.5)	325.5 (47.2)	338.6 (49.1)	180.7 (26.2)
Transverse	204.1 (29.6)	199.3 (28.9)	220.0 (31.9)	181.4 (26.3)	169 (24.5)

Source: Adapted from Evans, D.J., Classifying pultruded products by glass loading, *Proceedings* 41st Annual Conference, Society of the Plastics Industry, January 1986.

strength and modulus are lower than those obtained with all unidirectional  $0^{\circ}$  fiber strands. The ratio of continuous strand rovings to mats or woven rovings determines its mechanical properties (Table 5.4).

In commercial applications, polyester and vinyl ester resins are used as the matrix material. Epoxies have also been used; however, they require longer cure times and do not release easily from the pultrusion die. Pultrusion process has also been used with thermoplastic polymers, such as PEEK and polysulfone.

Figure 5.21 is a schematic of a typical pultrusion line. Continuous strand rovings and mats are pulled from one end of the line into a resin bath that contains liquid resin, curing agent (initiator), and other ingredients, such as colorant, ultraviolet (UV) stabilizer, and fire retardant. The viscosity of the liquid resin, residence time, and mechanical action on the fibers (such as looping of fibers) in the resin bath are adjusted to ensure a complete wet-out of fibers with the resin. Thermoplastic polyester surfacing veils are added to the fiber–resin stream just outside the resin bath to improve the surface smoothness of the molded product. The fiber–resin stream is pulled first through a series of preformers and then through a long preheated die. The preformers distribute



FIGURE 5.21 Schematic of a pultrusion process.

the fiber bundles evenly, squeeze out the excess resin, and bring the material into its final configuration. Final shaping, compaction, and curing take place in the die, which has a gradually tapering section along its length. The entrance section of the die is usually water cooled to prevent premature gelling, and the rest of the die is heated in a controlled manner either by oil heaters or by electric heaters. Infrared heating has also been used to speed up the curing process. A number of pulling rolls or blocks pull the cured pultruded member out of the die. The die temperature, die length, and pulling speed are controlled to ensure that the resin has cured completely before the pultruded member exits from the die. After cooling with air or water, it is cut into desired lengths by a diamondimpregnated saw at the end of the line.

The most important factor controlling the mechanical performance of a pultruded member is the fiber wet-out. The ability to wet out the fibers with the resin depends on the initial resin viscosity, residence time in the resin bath, resin bath temperature, and mechanical action applied to fibers in the resin bath. For a given resin viscosity, the degree of wet-out is improved as (1) the residence time is prolonged by using slower line speeds or longer baths, (2) the resin bath temperature is increased (which reduces the resin viscosity), or (3) the degree of mechanical working on fibers is increased. Since each roving pulled through the resin bath contains a large number of fiber bundles, it is extremely important that the resin penetrates inside the roving and coats each bundle uniformly. Resin penetration takes place through capillary action as well as lateral squeezing between the bundles. Lateral pressure at the resin squeeze-out bushings (located at the resin bath exit), preformers, and die entrance also improves the resin penetration in the bundles. Generally, slower line speed and lower resin viscosity favor resin penetration by capillary action, and faster line speed and higher resin viscosity improve the amount of resin pickup owing to increased drag force [19]. The fiber and resin surface energies are also important parameters in improving the amount of resin coating on fiber rovings. Thus, Kevlar 49 fibers, by virtue of their high surface energies, pick up more resin in the resin bath than either E-glass or carbon fibers under similar process conditions.

The resin viscosity in commercial pultrusion lines may range from 0.4 to 5 Pa s (400–5000 cP). Resin viscosities >5 Pa s may result in poor fiber wet-out,

slower line speed, and frequent fiber breakage at the resin squeeze-out bushings. On the other hand, very low resin viscosities may cause excessive resin draining from the fiber-resin stream after it leaves the resin bath. Resin viscosity can be lowered by increasing the bath temperature; however, if it reduces to 0.2 Pas or lower, the fiber-resin stream must be cooled at the resin bath exit to increase the resin viscosity and prevent excessive draining.

As the fiber–resin stream enters the heated die, the resin viscosity first decreases, which aids in the continued wet-out of uncoated fibers. However, the curing reaction begins a short distance from the die entrance, and soon after the resin viscosity increases rapidly, as shown in Figure 5.22. If the die temperature is not gradually increased in the die entrance zone, a cured resin skin may quickly form on the die walls. The separation of uncured material from the skin results in poor surface quality for the pultruded product. This problem can be alleviated by preheating the fiber–resin stream just outside the die, which reduces the temperature gradient at the die entrance zone.

The curing reaction continues at an increasing rate as the fiber–resin stream moves toward the exit end of the die. Heat generated by the exothermic curing reaction raises the temperature in the fiber–resin stream. The location of the exothermic peak depends on the speed of pulling the fiber–resin stream through



FIGURE 5.22 Viscosity change of a thermosetting resin in a pultrusion die.



**FIGURE 5.23** Temperature distribution along the length of a pultrusion die. (After Sumerak, J.E. and Martin, J.D., Applying internal temperature measurement data to pultrusion process control, *Proceedings 41st Annual Conference*, Society of the Plastics Industry, January 1986.)

the die (Figure 5.23). As the curing reaction nears completion, the exotherm temperature decreases and a cooling period begins. The rate of heat transfer from the cured material into the die walls is increased owing to a lower die temperature near the exit zone. This allows rapid cooling of the entire cured section while it is still under the confinement of the die walls. If the temperature in the interior of the cured section remains high at the time of exit from the die, interlaminar cracks may form within the pultruded member.

Unlike many other molding processes, no external pressure is applied in a pultrusion process. However, experiments performed by Sumerak [20] have demonstrated that the pressure in the die entrance zone is in the range of 1.7–8.6 MPa (250–1250 psi). The principal source for such high internal pressure is the volumetric expansion of the resin as it is heated in the die entrance zone. However, as the curing reaction begins, the polymerization shrinkage reduces the pressure to near-zero values at approximately the midlength of the die. In general, the internal pressure can be increased by controlling the resin chemistry and the fiber volume fraction. Although increasing the internal pressure may also result in a higher pulling force, it will improve fiber–resin consolidation in the pultruded section.

Depending on the part complexity, resin viscosity, and cure schedule, the line speed in a commercial pultrusion process may range from 50-75 mm/min (2–3 in./min) to 3–4.5 m/min (10–15 ft./min). High line speeds usually shift the

location of the peak exotherm temperature toward the exit end of the die and increase the pulling force. Although the production rate is increased at high line speeds, the product quality may deteriorate owing to poor fiber wet-out, unfinished curing, and roving migration within the cross section. If high output is desired, it is often better to use multiple dies instead of high line speeds.

The pulling force applied to the pulling mechanism at the end of the pultrusion line must overcome the combined effects of (1) the frictional force of fibers sliding against the die wall, (2) the shear viscous force between a very thin layer of resin and the die wall, and (3) the backflow force or drag resistance between the fibers and the backflowing resin at the die entrance. The contribution from each of these forces to the total pulling force varies along the length of the die. For example, the shear viscous force and the backflow force have larger contributions near the die entrance. As curing progresses along the die length and the liquid resin transforms into a solid mass, the frictional force becomes more predominant. The theoretical model developed by Bibbo and Gutowski [21] shows that the pulling force increases with increasing fiber volume fraction, resin viscosity, line speed, and compaction ratio (i.e., the ratio of the die entrance opening to the die exit opening). However, contributions from each of these parameters on the frictional force, shear viscous force, and backflow force are not uniform. Control of the pulling force and the design of the fiber guidance system are extremely important since they influence the fiber alignment as well as fiber wet-out. Some of the defects found in pultruded products, such as fiber bunching, fiber shifting, wrinkles, and folding of mats or woven rovings, are related to these factors.

## 5.5 FILAMENT WINDING

In a filament-winding process, a band of continuous resin-impregnated rovings or monofilaments is wrapped around a rotating mandrel and cured to produce axisymmetric hollow parts. Among the applications of filament winding are automotive drive shafts, helicopter blades, oxygen tanks, pipelines, spherical pressure vessels, conical rocket motor cases, and large underground gasoline storage tanks. The filament-winding process is also used to manufacture prepreg sheets or continuous fiber-reinforced sheet-molding compounds, such as XMC. The sheet is formed by slitting the wound shape parallel to the mandrel axis.

Figure 5.24 shows the schematic of a basic filament-winding process. A large number of fiber rovings are pulled from a series of creels into a liquid resin bath containing liquid resin, catalyst, and other ingredients, such as pigments and UV absorbers. Fiber tension is controlled using the fiber guides or scissor bars located between each creel and the resin bath. Just before entering the resin bath, the rovings are usually gathered into a band by passing them through a textile thread board or a stainless steel comb.

At the end of the resin tank, the resin-impregnated rovings are pulled through a wiping device that removes the excess resin from the rovings and



FIGURE 5.24 Schematic of a filament-winding process.

controls the resin coating thickness around each roving. The most commonly used wiping device is a set of squeeze rollers in which the position of the top roller is adjusted to control the resin content as well as the tension in fiber rovings. Another technique for wiping the resin-impregnated rovings is to pull each roving separately through an orifice, very much like the procedure in a wire drawing process. This latter technique provides better control of resin content. However, in the case of fiber breakage during a filament-winding operation, it becomes difficult to rethread the broken roving line through its orifice.

Once the rovings have been thoroughly impregnated and wiped, they are gathered together in a flat band and positioned on the mandrel. Band formation can be achieved by using a straight bar, a ring, or a comb. The band former is usually located on a carriage, which traverses back and forth parallel to the mandrel, like a tool stock in a lathe machine. The traversing speed of the carriage and the winding speed of the mandrel are controlled to create the desired winding angle patterns. Typical winding speeds range from 90 to 110 linear m/min (300–360 linear ft./min). However, for more precise winding, slower speeds are recommended.

The basic filament-winding process described earlier creates a helical winding pattern (Figure 5.25) and is called the helical winding process. The angle of the roving band with respect to the mandrel axis is called the wind angle. By adjusting the carriage feed rate and the mandrel's rotational speed, any wind angle between near 0° (i.e., longitudinal winding) to near 90° (i.e., hoop winding) can be obtained. Since the feed carriage moves backward and forward, fiber bands crisscross at plus and minus the wind angle and create a weaving or interlocking effect. It is also possible to produce a helical winding by keeping the feed carriage stationary and traversing the rotating mandrel back and forth. The mechanical properties of the helically wound part depend strongly on the



**FIGURE 5.25** (a) Schematic of helical winding pattern and (b) a helically wound cylindrical tank. (Courtesy of En-Tec Technology, Inc. With permission.)

wind angle, as shown in Figure 5.26. In another type of filament-winding process, called polar winding, the carriage rotates about the longitudinal axis of a stationary (but indexable) mandrel. After each rotation of the carriage, the mandrel is indexed to advance one fiber bandwidth. Thus, the fiber bands lie adjacent to each other and there are no fiber crossovers. A complete wrap consists of two plies oriented at plus and minus the wind angle on two sides of the mandrel (Figure 5.27).

After winding a number of layers to generate the desired thickness, the filament-wound part is generally cured on the mandrel. The mandrel is then extracted from the cured part. To facilitate mandrel extraction, collapsible mandrels, either segmented or inflatable, are used for products in which the end closures are integrally wound, as in pressure vessels. For prototyping or for



**FIGURE 5.26** Mechanical property variation in a filament-wound part as a function of wind angle.

low-volume productions, soluble plasters, eutectic salts, or low-melting alloys are also used. However, a proper mandrel material must be able to resist sagging due to its own weight, withstand the applied winding tension, and keep its form during curing at elevated temperatures.

Both helical and polar winding processes require winding the fiber band around the mandrel ends. Hemispherical domes with central openings are commonly used at the mandrel ends for manufacturing pressure vessels. The central openings are necessary to extract the mandrel from the cured pressure vessel. Pins or rounded edges at the mandrel ends are used for manufacturing open-ended products, such as a pipe or a drive shaft.

Conventional filament-winding machines use a driving motor to rotate the mandrel and a chain and sprocket to move the carriage back and forth parallel to the mandrel (Figure 5.28). The main sprocket is connected to the mandrel shaft through a set of gears so that the carriage feed can be controlled in relation to the mandrel rotation by changing the gear ratios or the sprocket size. For a



FIGURE 5.27 Polar winding pattern.



FIGURE 5.28 Schematic of a conventional filament-winding machine.

circular mandrel rotating with a constant rotational speed of N revolutions per minute and a constant carriage feed of V, the wind angle is given by

$$\theta = \frac{2\pi Nr}{V},\tag{5.12}$$

where r is the radius of the mandrel. Equation 5.12 shows that a constant wind angle can be maintained in a thick part only if the ratio N/V is adjusted from layer to layer. Winding with the conventional machine also requires the carriage to travel extra lengths on both sides of the mandrel.

The versatility of filament-winding process is improved tremendously if numerical controls are added to the filament-winding machine [22,23]. In numerically controlled machines, independent drives are used for the mandrel as well as for the carriage. In addition, a cross (transverse) feed mechanism and a rotating pay-out eye (Figure 5.29) allow an unequal fiber placement on the mandrel. The cross feed mechanism is mounted on the carriage and can move in and out radially; the pay-out eye can be controlled to rotate about a horizontal axis. The combination of these two motions prevents fiber slippage as well as fiber bunching on mandrels of irregular shape. Although each mechanism is driven by its own hydraulic motor, their movements are related to the mandrel rotation by numerical controls. Since no mechanical connections are involved, wind angles can be varied without much manual operation. With conventional filament-winding machines, the shapes that can be created are limited to surfaces of revolution, such as cylinders of various cross sections, cones, box beams, or spheroids (Figure 5.30). The computer-controlled multiaxis machines can wind irregular and complex shapes with no axis of symmetry, such as the aerodynamic shape of a helicopter blade.


FIGURE 5.29 Schematic of a numerically controlled filament-winding machine.

The important process parameters in a filament-winding operation are fiber tension, fiber wet-out, and resin content. Adequate fiber tension is required to maintain fiber alignment on the mandrel as well as to control the resin content in the filament-wound part. Excessive fiber tension can cause differences in resin content in the inner and outer layers, undesirable residual stresses in the finished product, and large mandrel deflections. Typical tension values range from 1.1 to 4.4 N (0.25–1 lb) per end.

Fiber tension is created by pulling the rovings through a number of fiber guides placed between the creels and the resin bath. Figure 5.31 illustrates three



FIGURE 5.30 Cross sections of possible filament-wound parts (a and b); (c) demonstrates a cross section that cannot be filament wound.



FIGURE 5.31 Typical fiber guides used in controlling fiber tension in a filamentwinding line.

common types of fiber guides. Mechanical action on the fibers in the resin bath, such as looping, generates additional fiber tension.

Good fiber wet-out is essential for reducing voids in a filament-wound part. The following material and process parameters control the fiber wet-out:

- 1. Viscosity of the catalyzed resin in the resin bath, which depends on the resin type and resin bath temperature, as well as cure advancement in the resin bath
- 2. Number of strands (or ends) in a roving, which determines the accessibility of resin to each strand
- 3. Fiber tension, which controls the pressure on various layers already wound around the mandrel
- 4. Speed of winding and length of the resin bath

There are two essential requirements for the resin used in filament winding:

- 1. The viscosity of the mixed resin system (which may include a solvent) should be low enough for impregnating the moving fiber strands in the resin bath, yet not so low that the resin drips and runs out easily from the impregnated fiber strands. Usually, a viscosity level of 1–2 Pas (1000–2000 cP) is preferred.
- 2. The resin must have a relatively long pot life so that large structures can be filament-wound without premature gelation or excessive exotherm. Furthermore, the resin bath is usually heated to lower the viscosity level of the mixed resin system. Since increased temperature of the resin bath may reduce the pot life, a resin with short pot life at room temperature has a limited usefulness in filament winding.

As a rule of thumb, each roving should be under the resin surface level for 1/3-1/2 s. In a line moving at 60 m/min (200 ft./min), this means that the length of

roving under the resin surface level be  $\sim 30$  cm (1 ft.). For good wetting, the minimum roving length under the resin surface level is 15 cm (6 in.).

Proper resin content and uniform resin distribution are required for good mechanical properties as well as for weight and thickness control. Resin content is controlled by proper wiping action at the squeegee bars or stripper die, fiber tension, and resin viscosity. Dry winding in which prepregs are wound around a mandrel often provides a better uniform resin distribution than the wet winding process.

Fiber collimation in a multiple-strand roving is also an important consideration to create uniform tension in each strand as well as to coat each strand evenly with the resin. For good fiber collimation, single-strand rovings are often preferred over conventional multiple-strand rovings. Differences in strand lengths in conventional multiple-strand rovings can cause sagging (catenary) in the filament-winding line.

In a helical winding operation, the fiber bands crisscross at several points along the length of the mandrel, and one complete layer consists of a balanced helical pattern with fiber oriented in the  $+\theta^{\circ}/-\theta^{\circ}$  directions. The thickness of a layer depends on the band density (i.e., the number of rovings per unit length of a band), the roving count (i.e., the number of strands or ends per roving), and the resin content. For the same band density, a high roving count results in larger amounts of fibers and, therefore, thicker layers. Increasing the resin content also results in thicker layers. An example is shown in Figure 5.32.



**FIGURE 5.32** Effects of roving count, fiber weight fraction, and matrix density (in g/cm<sup>3</sup>) of the thickness of a filament-wound E-glass fiber-reinforced epoxy part. (Adapted from Filament Winding, Publication No. 5-CR-6516, Owens-Corning Fiberglas, 1974.)

The common defects in filament-wound parts are voids, delaminations, and fiber wrinkles. Voids may appear because of poor fiber wet-out, the presence of air bubbles in the resin bath, an improper bandwidth resulting in gapping or overlapping, or excessive resin squeeze-out from the interior layers caused by high winding tension. In large filament-wound parts, an excessive time lapse between two consecutive layers of windings can result in delaminations, especially if the resin has a limited pot life. Reducing the time lapse and brushing the wound layer with fresh resin just before starting the next winding are recommended for reducing delaminations. Wrinkles result from improper winding tension and misaligned rovings. Unstable fiber paths that cause fibers to slip on the mandrel may cause fibers to bunch, bridge, and improperly orient in the wound part.

## 5.6 LIQUID COMPOSITE MOLDING PROCESSES

In liquid composite molding (LCM) processes, a premixed liquid thermoset resin is injected into a dry fiber perform in a closed mold. As the liquid spreads through the preform, it coats the fibers, fills the space between the fibers, expels air, and finally as it cures, it transforms into the matrix. This section describes two LCM processes, namely RTM and structural reaction injection molding (SRIM).

## 5.6.1 RESIN TRANSFER MOLDING

In RTM, several layers of dry continuous strand mat, woven roving, or cloth are placed in the bottom half of a two-part mold, the mold is closed, and a catalyzed liquid resin is injected into the mold via a centrally located sprue. The resin injection point is usually at the lowest point of the mold cavity. The injection pressure is in the range of 69–690 kPa (10–100 psi). As the resin flows and spreads throughout the mold, it fills the space between the fiber yarns in the dry fiber preform, displaces the entrapped air through the air vents in the mold, and coats the fibers. Depending on the type of the resin–catalyst system used, curing is performed either at room temperature or at an elevated temperature in an air-circulating oven. After the cured part is pulled out of the mold, it is often necessary to trim the part at the outer edges to conform to the exact dimensions.

Instead of using flat-reinforcing layers, such as a continuous strand mat, the starting material in an RTM process can be a preform that already has the shape of the desired product (Figure 5.33). The advantages of using a preform are good moldability with complicated shapes (particularly with deep draws) and the elimination of the trimming operation, which is often the most labor-intensive step in an RTM process.

There are various methods of producing preforms. One of them is the spray-up process in which 12.7-76.2 mm (0.5-3 in.) long fibers, chopped from



FIGURE 5.33 Schematic of RTM process.

continuous fiber rovings, are sprayed onto a preshaped screen. Vacuum applied to the rear side of the screen holds the fibers securely on the screen. A binder sprayed with the fibers keeps them in place and maintains the preformed shape. Continuous strand mats containing random fibers can be preformed by a stamping operation using a simple press and a preshaped die (Figure 5.34). Both thermoplastic and thermoset binders are available for retaining the formed shape after stamping. With woven fabric containing bidirectional fibers, a "cut and sew" method is used in which various patterns are first cut from the fabric and then stitched together by polyester, glass, or Kevlar sewing threads into the shape of the part that is being produced. Braiding and textile weaving processes have also been used to produce two- or three-dimensional preforms [24]. Braiding is particularly suitable for producing tubular preforms.

Compared with the compression-molding process, RTM has a very low tooling cost and simple mold clamping requirements. In some cases, a ratchet clamp or a series of nuts and bolts can be used to hold the two mold halves together. RTM is a low-pressure process, and therefore parts can be resin transfer molded in low-tonnage presses. A second advantage of the RTM process is its ability to encapsulate metal inserts, stiffeners, washers, and so on within the molded laminate. It is also possible to encapsulate a foam core between the top and bottom preforms of a hollow part, which adds stiffness to



**FIGURE 5.34** Photograph of a preform stamped from multiple layers of continuous strand random glass fiber mat. (Courtesy of Ford Motor Co. With permission.)

the structure and allows molding of complex three-dimensional shapes in one piece. The RTM process has been successfully used in molding such parts as cabinet walls, chair or bench seats, hoppers, water tanks, bathtubs, and boat hulls. It also offers a cost-saving alternative to the labor-intensive bag-molding process or the capital-intensive compression-molding process. It is particularly suitable for producing low- to midvolume parts, say 5,000–50,000 parts a year.

There are several variations of the basic RTM process described earlier. In one of these variations, known as vacuum-assisted RTM (VARTM), vacuum is used in addition to the resin injection system to pull the liquid resin into the preform. Another variation of the RTM process is SCRIMP, which stands for Seemann's Composite Resin Infusion Molding Process, a patented process named after its inventor William Seemann. Vacuum is also used in SCRIMP to pull the liquid resin into the dry fiber preform, but in this process, a porous layer is placed on the preform to distribute the resin uniformly throughout the preform. The porous layer is selected such that it has a very low resistance to flow and it provides the liquid resin an easy flow path to the preform. In both VARTM and SCRIMP, a single-sided hard mold is used. The preform is placed on the hard mold surface (Figure 5.35) and covered with a vacuum bag, much like the bag-molding process described in Section 5.2.

### 5.6.2 Structural Reaction Injection Molding

Another manufacturing process very similar to RTM is called structural reaction injection molding (SRIM). It also uses dry fiber preform that is



FIGURE 5.35 Vacuum-assisted resin transfer molding (VARTM).

placed in the mold before resin injection. The difference in RTM and SRIM is mainly in the resin reactivity, which is much higher for SRIM resins than for RTM resins. SRIM is based on the reaction injection molding (RIM) technology [25] in which two highly reactive, low-viscosity liquid streams are impinged on each other at high speeds in a mixing chamber immediately before injecting the liquid mix into a closed mold cavity (Figure 5.36).



FIGURE 5.36 Schematic of SRIM process.

Commercial RIM resins are mostly based on polyurethane chemistry, although epoxies have also been used. The curing temperature for polyurethane resins is between 60°C and 120°C.

The reaction rate for the resins used in RIM or SRIM is much faster than epoxy, polyester, or vinyl ester resins that are commonly used for the RTM process. The curing time for the SRIM resins is in the range of a few seconds compared with a few minutes for the RTM resins. The molding pressure for both processes is in the range of 0.5-1.5 MPa (70–210 psi).

In both RTM and SRIM processes, the liquid resin flows through layers of dry fiber preform while the curing reaction continues. For producing good quality parts, it is imperative that the resin fills the mold completely and wets out the reinforcement before arriving at the gel point. Therefore, the resin viscosity in both processes must be low. However, since the curing reaction is much faster in SRIM, the initial viscosity of SRIM resins must be lower than that for RTM resins. Preferred room temperature viscosity range for SRIM resins is 0.01–0.1 Pa s (10–100 cP) compared with 0.1–1 Pa s (100–1000 cP) for RTM resins. Since the reaction rate of the liquid resin mix in SRIM is very high, its viscosity increases rapidly, and therefore, the mold must be filled very quickly. For this reason, preforms in SRIM are, in general, lower in fiber content and simpler in shape than in RTM.

The quality of liquid composite-molded parts depends on resin flow through the dry fiber preform, since it determines mold filling, fiber surface wetting, and void formation. The principal molding problems observed are incomplete filling, dry spots, nonuniform resin distribution, void formation, nonuniform cure, and low degree of cure. The main source of void formation is the air entrapped in the complex fiber network in the preform. Good resin flow and mold venting are essential in reducing the void content in the composite. There may also be fiber displacement and preform distortion as the liquid resin moves through the fiber preform, especially if the viscosity increases rapidly before the mold filling is complete.

## 5.7 OTHER MANUFACTURING PROCESSES

### 5.7.1 RESIN FILM INFUSION

In the resin film infusion (RFI) process, a precatalyzed resin film placed under the dry fiber preform provides the liquid resin that flows through the preform and on curing, becomes the matrix. The process starts by covering the mold surface with the resin film and then placing the dry fiber preform on top of the resin film (Figure 5.37). The thickness of the resin film depends on the quantity of resin needed to completely infiltrate the preform.

RFI can be carried out using the bag-molding technique described in Section 5.2. In that case, the assembly of resin film and dry fiber preform is covered with a vacuum bag and placed inside an autoclave. The full vacuum



FIGURE 5.37 Schematic of resin film infusion process.

is applied at the beginning to remove the trapped air from the preform. As the temperature is increased in the autoclave, the resin viscosity decreases and the resin starts to flow through the dry fiber preform. Pressure is applied to force the liquid resin to infiltrate the preform and wet out the fibers. With the temperature now raised to the prescribed curing temperature, the curing reaction begins and the liquid resin starts to gel. If an epoxy film is used, the curing cycle is similar to that shown in Figure 5.10 and may take several minutes to several hours depending on the resin type and the curing conditions used.

## 5.7.2 ELASTIC RESERVOIR MOLDING

In elastic reservoir molding (ERM), a sandwich of liquid resin-impregnated open-celled foam and face layers of dry continuous strand mat, woven roving, or cloth placed in a heated mold (Figure 5.38) are pressed with a molding pressure of 520–1030 kPa (75–150 psi). The foam in the center of the sandwich



FIGURE 5.38 Schematic of the elastic reservoir molding process.



FIGURE 5.39 Schematic of various tube-rolling methods.

is usually a flexible polyurethane that acts as an elastic reservoir for the catalyzed liquid resin. As the foam is compressed, resin flows out vertically and wets the face layers. On curing, a sandwich of low-density core and fiber-reinforced skins is formed.

Among the advantages of an ERM process are low-cost tooling, better control of properties (since there is no horizontal flow), and a better stiffness–weight ratio (due to the sandwich construction). It is generally restricted to molding thin panels of simple geometry. Examples of ERM applications are bus roof panels, radar reflecting surfaces, automotive body panels, and luggage carriers.

### 5.7.3 TUBE ROLLING

Circular tubes for space truss or bicycle frame, for example, are often fabricated from prepregs using the tube-rolling technique. In this process, precut lengths of a prepreg are rolled onto a removable mandrel, as illustrated in Figure 5.39. The uncured tube is wrapped with a heat-shrinkable film or sleeve and cured at elevated temperatures in an air-circulating oven. As the outer wrap shrinks tightly on the rolled prepreg, air entrapped between the layers is squeezed out through the ends. For a better surface finish, the curing operation can be performed in a close-fitting steel tube or a split steel mold. The outer steel mold also prevents the mandrel from sagging at the high temperatures used for curing. After curing, the mandrel is removed and a hollow tube is formed. The advantages of the tube-rolling process over the filament-winding process are low tooling cost, simple operation, better control of resin content and resin distribution, and faster production rate. However, this process is generally more suitable for simple layups containing 0° and 90° layers.

# 5.8 MANUFACTURING PROCESSES FOR THERMOPLASTIC MATRIX COMPOSITES

Many of the manufacturing processes described earlier for thermoset matrix composites are also used for thermoplastic matrix composites. However, there

are some critical differences that arise due to the differences in physical and thermal characteristics of these two types of polymers. For example, thermoplastic prepregs are not tacky (sticky). They are also not very flexible, which poses problems in draping them into contoured mold surfaces. To overcome the problem associated with the lack of stickiness, thermoplastic prepreg layups are spot-welded together along the outside edges. One method of spot welding is to use a hot soldering iron and light pressure, which causes the matrix to melt and fuse at the edges. Laser beams have also been used to melt and fuse thermoplastic prepregs in continuous tape-laying processes.

The processing temperatures required for thermoplastic matrix composites are much higher than the curing temperatures required for thermoset matrix composites. Therefore, if a bag-molding process is used, the bagging material and sealant tapes must be of high-temperature type.

Unlike thermoset matrix composites, no chemical reaction occurs during the processing of thermoplastic matrix composites. However, individual plies in the stack must still be consolidated to form a laminate, which requires both high temperature and pressure. The stacked layup can be heated rapidly by means of quartz lamps or infrared heaters. The consolidation time may range from a few seconds to several minutes, depending on the laminate thickness and geometry. After consolidation, the laminate must be cooled at a controlled rate to solidify the matrix without causing residual stresses, warpage, and so on. For a semicrystalline thermoplastic matrix, such as PEEK, the crystallinity in the solidified matrix depends very much on the cooling rate (Figure 5.40). Slower cooling rate produces a higher crystallinity in the matrix, which in turn may influence the matrix properties, particularly its fracture toughness.



**FIGURE 5.40** Crystallinity in PEEK thermoplastic matrix composite as a function of cooling rate.



**FIGURE 5.41** Forming methods for thermoplastic matrix composites: (a) matched die forming, (b) hydroforming, and (c) thermoforming.

Since thermoplastic matrix composites can be shaped and formed repeatedly by the application of heat and pressure, they can be processed using some metal-working as well as thermoplastic forming techniques, such as matched die forming, hydroforming, and thermoforming [26]. These are highly efficient processes for converting flat sheets into three-dimensional objects at relatively high production rates.

Matched die forming is a widely used forming technique for sheet metals. It uses two matching metal dies mounted in a hydraulic press (Figure 5.41a). The deformation produced in the sheet during forming is a combination of stretching, bending, and drawing. It is suitable for forming constant thickness parts, since the dies are generally designed to a fixed gap with close tolerances. The forming pressure for thermoplastic matrix composites is considerably lower than that for metals. However, if a thickness variation exists in the part, the pressure distribution will be nonuniform, which may result in nonuniform ply consolidation.

Hydroforming uses a hydraulic fluid inside an elastomeric diaphragm to generate pressure required for deforming and consolidating the layup (Figure 5.41b). Only one metal die is required for the hydroforming operation. Although this process is limited due to temperature limitation of the elastomeric diaphragm, it allows a better control on the forming pressure distribution in parts with nonuniform thickness.

Thermoforming is a common manufacturing technique in the plastics industry for forming unreinforced thermoplastic sheets into trays, cups, packages, bathtubs, small boats, and so on. In this process, the sheet is preheated to the forming temperature, placed in the mold, clamped around the edges, and formed into the mold cavity by the application of either vacuum, pressure, or both (Figure 5.41c). The forming temperature is usually higher than the glass transition temperature  $T_g$  of the polymer. After forming, the part is cooled



FIGURE 5.42 Schematic of diaphragm forming.

under pressure to below the glass transition temperature before it is removed from the mold. If this process is applied to thermoplastic matrix composites, various layers in the layup must be consolidated into a laminated sheet before thermoforming. If consolidation takes place during the thermoforming process, the forming temperature will be close to the melt temperature of the polymer.

In the forming operation, the sheet is both stretched and drawn into the final shape. However, for thermoplastic matrix composites containing continuous fibers that are inextensible, it is not possible to stretch the individual plies in the fiber direction without breaking the fibers. Therefore, the thermoplastic matrix composite layup cannot be clamped and fixed around its edges. On the other hand, if the plies are not in tension during forming, some of them may wrinkle. To overcome this problem, the layup is placed between two thin, highly deformable diaphragms, which are clamped around their edges (Figure 5.42). As the forming pressure is applied, the deformation of diaphragms creates a biaxial tension in the layup, which prevents the plies from wrinkling. Common diaphragm materials are superplastic aluminum alloys and polyimide films.

A typical process cycle for diaphragm forming of carbon fiber-reinforced PEEK in an autoclave is shown in Figure 5.43. The temperature in the autoclave is slowly increased to  $380^{\circ}$ C, which is ~40°C above the melting point of PEEK. The autoclave pressure is increased to ~0.4 MPa (60 psi) to force the layup into the mold cavity and is maintained at that pressure to consolidate the laminate. The thickness of the layup decreases during consolidation as the free spaces between the plies are eliminated and interlaminar adhesion builds up. There may also be some rearrangement of fibers and matrix squeeze-out during consolidation.

Figure 5.44 depicts the four basic mechanisms that may occur during consolidation and forming of thermoplastic matrix composites [27]:

- 1. Percolation or flow of molten polymer through fiber layers
- 2. Transverse flow (movement in the thickness direction) of fibers or fiber networks



**FIGURE 5.43** Typical process cycle in diaphragm forming. (Adapted from Mallon, P.J., O'Bradaigh, C.M., and Pipes, R.B., *Composites*, 20, 48, 1989.)



FIGURE 5.44 Basic mechanisms during forming of thermoplastic matrix composites. (Adapted from Cogswell, F.N., *Int. Polym. Proc.*, 1, 157, 1987.)

- 3. Intraply shearing which allows fibers within each ply to move relative to each other in the axial as well as in the transverse direction
- 4. Interply slip, by which plies slide over each other while conforming to the shape of the die

The first two mechanisms are essential for good consolidation, since they help reduce the gaps and voids that exist between the plies as well as within each ply and create good interlaminar adhesion. The other two mechanisms help in forming contoured shapes without fiber wrinkling, splitting, or local thinning.

# 5.9 QUALITY INSPECTION METHODS

The mechanical properties of a molded part and their variations from part to part depend on many factors, including the quality of raw materials, the degree of cure, and the presence of molding defects in the part. Many of the molding defects can be either eliminated or reduced by proper part and mold designs as well as by controlling the various process parameters described in the earlier sections. Since complete elimination of all molding defects is not possible, it is important that the quality of the molded parts be inspected regularly for critical defects that can cause premature failure in a part during its service. The criticality of a defect or a group of defects is established through extensive testing at the prototype development stage. The quality inspection techniques and the part acceptance criteria are also established at the prototype development stage.

## 5.9.1 RAW MATERIALS

Among the raw materials, the two most important candidates for close quality inspection are fibers and resin. Measurements of tensile strength and modulus are the primary screening methods for continuous fibers. For the resin, curing agents, or diluents, the standard quality inspection items are the density, viscosity, color, and moisture content. Additional tests recommended for the incoming resin and other components [28] are (1) wet chemical analysis to determine the amount of functional groups (such as epoxide groups in epoxies or acid numbers in polyesters) in the material, (2) infrared (IR) spectroscopy or nuclear magnetic resonance (NMR) spectroscopy to fingerprint the chemical structure and impurities, and (3) liquid chromatography or gel permeation chromatography (GPC) to determine the weight-average molecular weight and molecular weight distribution of the resin molecules.

The average molecular weight and molecular weight distribution are two very important characteristics of a resin that control its viscosity and mechanical properties. Burns et al. [29] have shown that high fractions of low-molecular-weight molecules in a polyester resin reduce the rate of thickening (viscosity increase) in SMC sheets. The viscosity of a polyester resin with low-average molecular weight may not attain the level required for proper handling  $(0.5-1.3 \times 10^6 \text{ P})$  even after a thickening period of 7 days or more. Another factor in controlling the thickening rate of polyester resins was found to be the moisture content.

Raw materials are often purchased by the part manufacturer in the form of prepreg rolls. The prepreg characteristics that influence its moldability as well as its mechanical properties are resin content, volatile content, filament count, filament diameter, gel time, and resin flow. The gel-time and resin-flow tests can indicate cure advancement in the B-staged resin, which in turn is related to the tackiness and drapability of the prepreg as well as to the fluidity of the resin during the molding process. Proper tack is required to (1) adhere the prepreg to the mold surface as well as to the preceding ply and (2) release the backup film without separating the resin from the prepreg. The prepreg should also be sufficiently drapable to conform to the contour of the mold surface.

The gel-time and resin-flow tests are inadequate to detect variations in resin formulation. To improve the quality assurance of the B-staged resin in the prepreg, chemical and rheological tests, such as liquid chromatography, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA), should be adopted [30].

### 5.9.2 CURE CYCLE MONITORING

Cure cycle monitoring during production runs is important to ensure that each molded part has the same degree of cure as has been established earlier in the prototype development stage. Accurate control over the cure cycle helps achieve greater consistency between the parts and reduce the amount of scrap or waste.

Many research tools are available for monitoring the curing process of a fiber-reinforced thermoset polymer. They include wet chemical analysis, infrared spectroscopy, NMR, DSC, DMA, and dielectrometry. Among these, dielectrometry is considered the most promising technique to monitor cure cycle during a production molding operation [31]. In this technique, the dielectric loss factor of the resin is measured as a function of cure time. The instrumentation includes two conductor probes (electrodes), which are usually embedded in the top and bottom mold surfaces and are connected to an alternating electric field. Since polymers are dielectric materials, the combination of these probes and fiber–resin system forms a parallel-plate capacitor. The charge accumulated in this capacitor depends on the ability of the dipoles and ions present in polymer molecules to follow the alternating electric field at different stages of curing. The loss factor of a resin represents the energy expended in aligning its dipoles and moving its ions in accordance with the direction of the alternating electric field.

A typical dielectric loss factor plot obtained during the molding of a fiberreinforced thermoset polymer is shown in Figure 5.45. At the beginning of the



**FIGURE 5.45** Dielectric loss factor as a function of cure time and frequency of the oscillating electric field.

cure cycle, the resin viscosity in the uncured prepreg is relatively high so that the dipole and ion mobilities are restricted. This results in low loss factor just after the uncured prepreg is placed in the mold. As the temperature of the prepreg increases in the mold, the resin viscosity is reduced and the loss factor increases owing to greater dipole and ion mobilities. As soon as the gel point is reached, the resin viscosity increases rapidly and the loss factor decreases. At a full degree of cure, the loss factor levels off to a constant value.

#### 5.9.3 CURED COMPOSITE PART

Quality inspection of cured composite parts includes both destructive and nondestructive tests (NDT). Examples of routine destructive tests are burn-off tests for checking the fiber weight fraction and tension tests on specimens cut from the finished parts for checking their strength and modulus values. Performance tests on randomly selected parts are also recommended. Simple NDT include thickness measurements, visual inspection for surface defects, and proof tests. In proof tests, each part is loaded to predetermined stress levels, which are usually lower than the design stress level.

A cured composite part may contain a multitude of internal defects, such as voids, delaminations, fiber misorientations, and nonuniform fiber distribution. Some of these internal defects may act as or grow into critical flaws during the service operation of a part and severely affect its performance. During a production process, these defects are detected by NDT, and parts are either accepted or rejected on the basis of defect quality standards developed earlier at the prototype development stage. In the event of service failure, the NDT records can also serve a useful purpose in analyzing the cause of failure. At the present time, both ultrasonic and radiographic tests are performed on structural composites used in aircraft or aerospace applications. Other NDT methods, such as the acoustic emission test, thermography, and the acoustoultrasonic test, are used mostly as research tools to monitor damage development during mechanical tests of composite specimens. A common problem with all these tests, including ultrasonic and radiography, is the lack of standards that can be used to distinguish between critical and noncritical defects.

### 5.9.3.1 Radiography

In radiographic techniques, the internal structure of a molded part is examined by impinging a beam of radiation on one of its surfaces and recording the intensity of the beam as it emerges from the opposite surface. Conventional radiography uses x-rays (in the range of 7–30 keV) as the source of radiation and records the internal defects as shadow images on a photographic film. Gamma rays are more useful in thicker parts, since they possess shorter wavelengths and, hence, greater penetrating power than x-rays. Other radiation beams, such as beta irradiation and neutron radiation, are also used. Imaging techniques, such as displaying the image on a fluorescent screen (fluoroscopy) or cross-sectional scanning [32] by computed tomography (CT), are also available. The former is more useful for on-line inspection of production parts than the photographic technique.

In fiber-reinforced composite structures, radiography is capable of detecting large voids, foreign inclusions, translaminar cracks, and nonuniform fiber distribution, as well as fiber misorientation (such as weld lines or fiber wrinkles). These defects change the intensity of the radiation beam by varying amounts and create images of different shades and contrasts on the photographic film. Thus, for example, large voids appear as dark spots and fiber-rich areas appear as light streaks on an x-ray film. The detection of microvoids and delaminations is possible by using radiopaque penetrants, such as sulfur, trichloroethylene, or carbon tetrachloride. The detection of fiber misorientation may require the use of lead glass tracers in the prepreg or SMC.

## 5.9.3.2 Ultrasonic

Ultrasonic inspection uses the energy levels of high-frequency (1–25 MHz) sound waves to detect internal defects in a test material. The ultrasonic sound energy is generated by electrically exciting a piezoelectric transducer and is introduced into the surface of a molded part by means of a coupling medium. As the ultrasonic waves propagate through the material, their energy levels are attenuated by the presence of defects. Although some of the attenuated



FIGURE 5.46 Pulse-echo method of ultrasonic testing.

ultrasonic waves are transmitted through the part thickness, others are reflected back to the input surface. The energy levels of these transmitted and reflected ultrasonic waves are converted into electrical signals by a receiving transducer and are then compared with a preset threshold and displayed on a cathode ray tube (CRT) screen or a computer screen.

The following methods are commonly used for ultrasonic inspection of defects in a fiber-reinforced composite material.

*Pulse-echo method*: In this method, echos reflecting from the front surface, back surface, and internal defects are picked up either by the transmitting transducer or by a separate receiving transducer. All reflected pulses are displayed as distinct peaks on the monitor (Figure 5.46). Pulse-echo depths are determined by measuring the time intervals between the front surface reflection peak and other significant peaks. Knowing the ultrasonic wave velocity in the material, these time intervals can be converted into defect location (depth) or part thickness measurements.

*Through-transmission method*: In this method, ultrasonic waves transmitted through the part thickness are picked up by a receiving transducer on the other side of the part (Figure 5.47). Since the transmitted wave interacting with a



FIGURE 5.47 Through-transmission method of ultrasonic testing.



**FIGURE 5.48** A-scan representation of internal defects: peak A for front surface reflection, peak B for reflection from a defect, and peak C for back surface reflection.

defect has a lower energy level than an uninterrupted wave, it is displayed as a smaller peak. In contrast to the pulse-echo method, the through-transmission method requires access to both surfaces of the part.

In general, part surfaces are scanned at regular intervals by piezoelectric transducers and an ultrasonic map of the entire part is generated. The three different procedures used for data presentation are A scan, B scan, and C scan. In the A-scan procedure, output signal amplitudes are displayed against a time scale (Figure 5.48) and the depths of various defect locations are judged from the positions of the signal peaks on the time sweep. The B-scan procedure profiles the top and bottom surfaces of a defect (Figure 5.49). The C-scan procedure, on the other hand, displays the plan view of the defect boundaries in the material (Figure 5.50).



FIGURE 5.49 B-scan representation of internal defects.



FIGURE 5.50 C-scan representation of internal defects.

C-scan images of through-transmission waves are commonly used for on-line inspection of large molded parts. In gray-level C scans, weaker transmitted signals are either dark gray or black. Thus, defects are identified as dark patches in a light gray background. The through-the-thickness location of any defect observed in a C scan can be obtained by using the pulse-echo method and by recording the A-scan image of the reflected pulse.

The ultrasonic inspection has been successfully used to detect large voids, delaminations, clusters of microvoids, and foreign materials. Reynolds [33] has reported the widespread application of ultrasonic C scanning in the aircraft industry. Water is the most commonly used coupling medium for ultrasonic scanning. The composite part may be squirted with water on its surface or may be completely immersed in a water tank for more uniform coupling.

#### 5.9.3.3 Acoustic Emission

Acoustic emission (AE) refers to the transient elastic stress waves generated by the release of sound energy at stress-induced microscopic damage sites in the material. In metals, localized plastic deformation, crack initiation, and crack propagation are the primary sources of acoustic emission. In fiber-reinforced composites, acoustic emission is generated by the development of matrix microcracking, fiber-matrix interfacial debonding, localized delamination, fiber pullout, and fiber breakage. If the applied stress level is relatively low, these failure modes are likely to occur at the sites of inherent defects. Thus by monitoring the acoustic emission at low proof stress levels, it may be possible to locate and map critical defects in a molded part.

Acoustic emissions in a stressed part are detected by an array of highly sensitive piezoelectric transducers attached at various locations on its surface. These transducers measure the surface displacements caused by stress waves originating at the defect sites. Through proper instrumentation and a multiplechannel recorder, the electrical signal output from each transducer is amplified, stored, and recorded for further analysis.

Figure 5.51 illustrates the electrical signal output associated with an acoustic emission event. The most important AE parameter obtained from such output records is the cumulative event count. This is defined as the total



FIGURE 5.51 An acoustic emission signal (event) and associated nomenclatures.

number of events that contain signal amplitudes higher than a preset threshold. In general, the cumulative event count increases almost exponentially with increasing stress level. If the stress is held constant, the cumulative event count levels off, unless the part continues to deform owing to creep.

Figure 5.52 shows the cumulative AE event count recorded during a quasistatic loading–unloading cycle of a notched carbon–epoxy tensile specimen.



**FIGURE 5.52** Typical AE event count as a function of loading on a fiber-reinforced laminate.

The acoustic emission begins only after the applied load in the first cycle exceeds a minimum value, and then the cumulative event count increases rapidly with increasing load. If the specimen is unloaded, the acoustic emission stops. If the load is reapplied, the acoustic emission occurs even before the previous maximum load is reached. This unique AE characteristic of a fiber-reinforced composite is not observed in metals and is called the felicity effect [34]. The load at which the AE begins on the (n + 1)th load cycle divided by the maximum load reached on the *n*th load cycle is termed the felicity ratio. The value of the felicity ratio indicates the extent of damage in the material and can be used as a potential acceptance or rejection criterion [35].

The difference in arrival times of a given event at various transducers can be used to locate the source of an acoustic emission. However, since a fiberreinforced composite structure emits numerous bursts of emission in successive order, the transducers may not always be able to isolate a specific event. Furthermore, signal attenuation in fiber-reinforced polymers is high. Since low-frequency waves (typically 20–111 kHz) attenuate less and therefore travel longer distances than high-frequency waves, transducers designed to detect this frequency range are preferred for fiber-reinforced composite structures. Usually, high-frequency transducers are used in local areas of probable emission in conjunction with low-frequency transducers.

Acoustic emission has been used by a number of investigators to study the development and progression of damage with increasing time or stress. Some of these studies have also included the effects of various process and material parameters, such as cure temperature, cooling rate, matrix flexibility, and fiber orientation, on the acoustic emission activities of fiber-reinforced polymers. Standard practices have been developed for acoustic emission testing of glass fiber-reinforced plastic tanks and pressure vessels [36]. However, as Hamstad [37] has noted, acoustic emission in fiber-reinforced composites is a complex phenomenon and may lead to erroneous source identification if proper attention is not paid to the nature of wave attenuation and extraneous noise generation.

#### 5.9.3.4 Acousto-Ultrasonic

Acousto-ultrasonic testing combines aspects of ultrasonic testing with acoustic emission signal analysis techniques to measure the severity of subtle internal flaws and inhomogeneity in a material. Examples of such flaws in a composite material are porosity, fiber breaks, fiber bunching, resin-rich zones, improper curing, fiber misorientations, and fiber–matrix debonding. While these flaws are not always considered as critical as delaminations or large voids, collectively they can reduce the mechanical properties or structural response of a material [38].

In acousto-ultrasonic method, a broad-band piezoelectric transducer is used to introduce a series of repeating ultrasonic pulses in the material. When these pulses interact with various flaws in the material, spontaneous stress



FIGURE 5.53 Acousto-ultrasonic measurements.

waves are produced that simulate acoustic emission events. The attenuated stress waves are detected by another piezoelectric transducer, which is commonly located on the same surface, but at some distance away from the sender transducer (Figure 5.53).

Acousto-ultrasonic signals received at the second transducer resemble acoustic emission burst-type waves that decay exponentially. They are processed using acoustic emission methodology, for example, ring-down count or voltage peak. The degree of attenuation of the transmitted waves is converted into a numerical value, called the stress wave factor (SWF). It is used as an indirect measure for the criticality of total flaw population present in the material. A low SWF that occurs due to high attenuation of stress waves indicates a severe flaw population. High values of SWF indicate an efficient transmission of stress waves through the material and, therefore, a relatively defect-free material.

The SWF has been correlated with mechanical properties, such as tensile strength or interlaminar shear strength. The SWF is also a sensitive indicator of accumulated damage in composite laminates subjected to fatigue cycling or impact loads. However, it is not suited for detecting isolated gross flaws, such as delaminations or voids, for which ultrasonic testing is recommended.

#### 5.9.3.5 Thermography

Thermography or thermal imaging is based on the principle that the thermal conductivity of a material is altered locally due to the presence of defects, such as delaminations or inclusions. If the material containing such defects is



FIGURE 5.54 Surface temperature difference over delaminated and away from delaminated areas in a eight-ply carbon fiber–epoxy laminate. The delamination size is 5 mm between plies 1 and 2. (Adapted from Mirchandani, M.G. and McLaughlin, P.V., Jr., *Quantitative Nondestructive Evaluation*, Vol. 5B, Plenum Press, New York, 1986.)

subjected to a uniform heat source on one surface, the heat flow through its thickness will be uneven as a result of local variation of thermal conductivity. This will result in a nonuniform surface temperature distribution, which is detected and related to the presence of defects in the interior of the material [39]. For example, heat flow obstructed by a delaminated area increases the surface temperature above the delaminated area compared with that in the surrounding area (Figure 5.54).

The most common technique in thermography is to apply a uniform heat source on one surface of the material and record the transient temperature contours on the other surface by means of either liquid crystals or an infrared heat detection camera. The heat source can be as simple as hot water bags, hot air-dryers, a bank of light bulbs, or a photographic flash gun. Planar location and planar size of the defect can be easily detected from the thermogram.

A modified form of thermography is called vibrothermography [40], in which low-amplitude mechanical vibrations are used to induce localized heating in the material. It has been observed that localized heating occurs preferentially around internal defects, such as delaminations and large matrix cracks. The resulting temperature contours are recorded as before.

## 5.10 COST ISSUES

One major obstacle to greater use of fiber-reinforced composites in structural applications is their cost. Although carbon fiber-reinforced composites are used in large quantities in aerospace applications, their high cost is still a concern. The automotive industry is significantly more cost-conscious and has used carbon fiber-reinforced composites in a very limited amount. Most of the structural composite parts used in automobiles today are manufactured from glass fiber-reinforced polyurethane using SRIM. Even with their lower cost, they cannot always compete with low carbon steel, which is less than half as expensive. It has been shown that carbon fiber-reinforced polymers can greatly reduce the weight of automotive body and chassis components due to their high modulus-weight ratio and fatigue resistance, but the high cost of carbon fibers has prevented their use in the automotive industry. The same argument can be made for many other nonaerospace industries as well.

The high cost of fibers is not the only reason for the high cost of fiberreinforced polymers. The cost of the matrix can also be very high, especially if it is a high-temperature polymer. For the total material cost, one must also include the cost of preparing the material, for example, for making prepreg or for making sheet-molding compound sheet. The standard unidirectional carbon fiber–epoxy prepreg is typically about 1.5–2 times the cost of carbon fibers [41]. The cost of making toughened epoxy prepreg or high temperature thermoplastic matrix prepreg can be as much as three times higher than that of making standard epoxy prepregs.

The second item in the cost consideration is the fabrication cost of fiberreinforced polymer parts, which depends on part design and the manufacturing process selected for fabrication. In the early days of composite applications in the aerospace industry, hand layup of prepreg stacks followed by vacuum bagging and autoclave curing was the most common method of producing carbon fiberreinforced epoxy parts. The processing steps involved in autoclave molding are

- 1. Cutting the prepreg material (template layout, actual cutting and marking of the cut plies)
- 2. Laying up the plies (orienting the plies, building up the stack, and tacking or debulking)
- 3. Bagging and autoclave preparation
- 4. Autoclave cycle
- 5. Demolding
- 6. Trimming the part to final dimensions
- 7. Inspection, including nondestructive testing

Most of the operations involved in autoclave molding are done manually, may take several minutes to several hours, and require the use of highly skilled workers. It is a labor-intensive process and the direct labor cost for such a process may be 3–3.5 times the direct material cost. While vacuum bagging is still the most common manufacturing process in the aerospace industry, the use of computer-controlled prepreg cutting and tape-laying machines has reduced the labor cost; albeit at a higher equipment cost. RTM is also increasingly used in manufacturing many aircraft composite parts. Filament winding and pultrusion are less labor-intensive, can be highly automated, and can produce higher number of parts per hour; however, as discussed earlier in this chapter, they are suitable for making relatively simple structures.

Another aspect of the cost issue is the tooling cost, which includes the mold material cost and mold making cost. The selection of the mold material depends on part design (both size and complexity), production rate, and volume of production. For thermoset matrix prepregs, alloy steel tools are commonly used for high-volume production runs. For thermoplastic matrix prepregs, the processing temperature is higher, typically in the range of 260°C–300°C compared with 175°C or lower for thermoset matrix prepregs. At high processing temperatures, the difference in thermal expansions of the tool material and the prepreg must be minimized; otherwise, there may be fiber motion during cooling, which can cause fiber buckling and fiber breakage. Many low CTE mold materials are available—for example, monolithic graphite, castable ceramic, and chemically bonded ceramic. However, these materials are very expensive and they are easily damaged during transport, demolding, and temperature ramp-up.

Next, the cost of assembly must also be considered. Even though reduction in the number of parts achieved through parts integration reduces the number of assembly operations, there may still be a few needed to construct a large or complex composite structure. Assembly operations are also needed to attach composite parts with metal parts. Mechanical assembly using rivets and bolts is the primary assembly technique used in the aerospace industry. Cocuring and cobonding are also becoming assembly techniques. Mechanical assembly is often preferred over adhesive bonding, since it does not require surface preparation and long cycle time as is needed for the adhesive curing process and it allows disassembly for inspection and repair. However, the close tolerance required for mechanical assembly or secondary adhesive bonding is often not achieved with fiber-reinforced polymers, and shimming is used to assure a good fit and avoid damage to composite part during assembly. Thus, even with mechanical assembly, the assembly cost may be close to the part fabrication cost.

Finally, the cost of quality inspection must also be added. For highperformance parts requiring safe operation during their life time, 100% of the parts may need to be inspected for manufacturing defects, such as voids, delaminations, ply gap, resin-rich or resin-starved areas, misoriented plies, and so on. In the aerospace industry, the most common quality inspection technique for many of these defects is the through-transmission ultrasonic testing. Depending on the part complexity and the level as well as frequency of inspection needed, the cost of quality inspection can be in the range of 25%-100% of the fabrication cost [41].

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#### PROBLEMS

P5.1. The following isothermal cure rate equation was found to fit the DSC data for a thermoset resin:

$$\frac{\mathrm{d}\alpha_{\mathrm{c}}}{\mathrm{d}t} = k(1-\alpha_{\mathrm{c}})^2,$$

where k is a temperature-dependent constant. Solve this differential equation to show that time required to achieve a cure level  $\alpha_c$  is given by

$$t = \frac{\alpha_{\rm c}}{k(1-\alpha_{\rm c})}.$$

P5.2. In Problem 5.1, the constant k (per minute) is given by the following Arrhenius equation:

$$k = 2.3 \times 10^6 \exp\left(-\frac{14.8}{RT}\right),$$

where

R is the universal gas constant (kcal/mol K) T is the absolute temperature (K)

Calculate the cure times for 50%, 80%, and 99.9% cure levels in the thermoset resin at 100°C and 150°C. State the observations you will make from these calculations.

P5.3. The degree of cure of a vinyl ester resin used for RTM as a function of cure time is given by the following equation.

$$\alpha_{\rm c} = \frac{kt}{1+kt},$$

where

$$k = 1.25 \times 10^6 \exp\left(-\frac{5000}{T}\right)$$

t is the cure time in minutes T is the temperature in °K

- (a) Assuming that the presence of fibers does not influence the cure kinetics, determine the temperature that should be used to achieve 80% cure in 1 min cure time.
- (b) What is the cure rate at 80% cure in (a)?
- (c) What temperature should be used if the cure rate needs to be doubled at 80% cure? What will be the cure time now?
- P5.4. The isothermal rate of cure for a thermoset polyester system is given by the following equation:

$$\frac{\mathrm{d}\alpha_{\mathrm{c}}}{\mathrm{d}t} = k\alpha_{\mathrm{c}}^{m}(1-\alpha_{\mathrm{c}})^{n}.$$

Show that the maximum rate of cure for this polyester system is obtained at a cure level

$$\alpha_{\rm c} = \frac{m}{m+n}.$$

P5.5. The isothermal cure rate of a DGEBA epoxy cured with *m*-phenylene diamine is given by Equation 5.4. The kinetic parameters, determined from DSC data, are

$$m = 0.45$$
  
 $n = 1.55$   
 $k_1 = 2.17 \times 10^6 \exp(-E_1/RT)$  per minute  
 $k_2 = 1.21 \times 10^6 \exp(-E_2/RT)$  per minute  
 $E_1 = 13,600$  cal/mol  
 $E_2 = 13,700$  cal/mol

- 1. Graphically compare the cure rates of this epoxy resin at 100°C, 125°C, and 150°C as a function of the degree of cure,  $\alpha_c$ . State the observations you will make from the graphs.
- 2. Determine the maximum cure rate at each temperature.

P5.6. The following isothermal viscosity data were obtained in a parallel-plate viscometer for an epoxy system cured at 125°C:

Time (min)	Viscosity (cP)
0	79.5
20	100
40	148
60	162
80	263
100	512
120	1,480
140	6,160
160	44,600
180	513,000
200	14,781,000

Plot the data on a semilog scale and schematically show how the nature of this curve may change if (a) the curing temperature is  $150^{\circ}$ C, (b) the curing temperature is  $100^{\circ}$ C, and (c) the epoxy system is B-staged before curing at  $125^{\circ}$ C.

P5.7. Let et al. [1] fitted the following equation to the viscosity  $(\eta)$  data (in Pa s) for an epoxy system:

$$\eta = 7.9 imes 10^{-14} \exp\left(rac{E}{RT} + 14lpha_{
m c}
ight) \quad {
m for} \; lpha_{
m c} < 0.5,$$

where

- E = activation energy for viscosity = 9 × 10<sup>4</sup> J/mol
- R = universal gas constant (J/mol K)
- T = absolute temperature (K)
- $\alpha_{\rm c} = \text{degree of cure}$

Using this equation, estimate the viscosity of the epoxy system at  $100^{\circ}$ C and  $150^{\circ}$ C (a) at the beginning of the curing reaction, (b) at 20% cure, and (c) at 40% cure.

P5.8. Roller\* has represented the isothermal viscosity data for a B-staged epoxy resin, by the following four-parameter equation:

<sup>\*</sup> M.B. Roller, Characterization of the time-temperature-viscosity behavior of curing B-staged epoxy resin, *Polym. Eng. Sci.*, 15:406 (1975).

$$\ln \eta = \ln \eta_{\infty} + \frac{E_1}{RT} + tk \exp\left(-\frac{E_2}{RT}\right),$$

where

 $E_1$  and  $E_2$  are activation energies k is a kinetic parameter (which depends on the resin type, curing agent concentration, and other factors)  $\eta_{\infty}$  is the calculated viscosity at  $T = \infty$ T is the absolute temperature t is the time at temperature T R is the universal gas constant

For a particular B-staged epoxy resin, the four parameters in the isothermal viscosity equation are:  $E_1 = 27,000 \text{ cal/mol}, E_2 = 19,000 \text{ cal/} \text{mol}, k = 6.4 \times 10^7 \text{ per second}, \text{ and } \eta_{\infty} = 2 \times 10^{-11} \text{ cP}$ . Determine the gel-time viscosity of the resin at 170°C if the gel time is 200 s at this temperature.

P5.9. A gel-time test on an epoxy resulted in the following data:

T (°C)	Time (min)
140	4
130	7.5
120	14
110	25
105	34.3

- 1. Plot ln(gel time) vs. 1/T is (where T is the temperature in K).
- 2. Assume that gel time can be represented by Arrhenius equation:

$$t_{\rm gel} = A \exp\left(\frac{E}{RT}\right),\,$$

where

- E =activation energy
- R = universal gas constant
- A = constant

Determine the values of A and E.

3. Determine the gel time at 100°C and 150°C using the Arrhenius equation.

P5.10. The following figure shows two cure cycles and the corresponding viscosity-time curves for an epoxy-based prepreg. Which of these two cure cycles is expected to produce better and more uniform mechanical properties, and why?



P5.11. The following figure shows the viscosity and gel-time curves for two epoxy resin systems. Which of the two resin systems will be more suitable for a bag-molding process, and why?



P5.12. The following figure shows a typical isothermal DSC curve for a polyester resin system. It contains *t*-butyl perbenzoate (TBPB) as the initiator for the curing reaction. The three important time parameters relevant for the compression-molding cycle of this material are also indicated in the figure. Explain how these time parameters may be affected by (a) an increase in cure temperature, (b) an increase in the initiator concentration, (c) the presence of an inhibitor, (d) the use of a lower temperature initiator, and (e) a combination of TBPB and a lower temperature initiator. From the standpoint of flow in the mold, which one of these changes would be more desirable?



- P5.13. As a part of the manufacturing study of an SMC-R material, you are asked to investigate the effects of SMC machine variables as well as molding variables on the mechanical properties of compression-molded flat plaques. The study was instigated by the wide variation in tensile strengths and failure locations observed in a prototype molded part. Select the experimental variables that might be of primary importance in this investigation, and design an experimental program (including test methods, specimen location, and so on) for this study.
- P5.14. A thin-walled cylinder with closed ends contains oxygen at a high internal pressure, which creates a hoop tensile stress twice the axial tensile stress in its wall. Assume that the fibers carry all load and there is no interaction between the layers. Show that the optimum helix angle in the filament-wound cylinder is 54.74°.
- P5.15. The price of carbon fibers is lower when there are 25,000–50,000 filaments per tow instead of 1,000–5,000 filaments per tow. Discuss the advantages and disadvantages of using such large tows in filament winding.

P5.16. One common specimen used in testing the quality of materials in filament winding is the Naval Ordnance Laboratory (NOL) ring, which contains only circumferential fibers. The specimen dimensions are shown in the figure.



Develop a method of producing NOL ring specimens and the test techniques that can be used to measure the tensile, compressive, interlaminar shear, and in-plane shear strengths using such specimens. Discuss the advantages and disadvantages of NOL ring tests compared with the test methods presented in Chapter 4.

- P5.17. List material (both resin and preform), process, and tool design parameters that may influence the quality of a resin transfer molded part.
- P5.18. In an LCM process, liquid resin is injected under isothermal condition through a dry-fiber bed at a constant pressure  $P_{o}$ . Assuming that the flow is one-dimensional and is in the x direction, show that the fill time t is proportional to  $x^2$ , where x is the fill distance in time t.
- P5.19. RTM is used to mold 500 mm long  $\times$  50 mm wide  $\times$  2.5 mm thick E-glass fiber-reinforced epoxy plates. The following details are given.

$$v_f = 32\%$$
,  $\rho_f = 2.54 \text{ g/cm}^3$ ,  $\rho_m = 1.2 \text{ g/cm}^3$ ,  
Permeability (P) =  $4 \times 10^{-4} \text{ mm}^2$ .

The resin viscosity during mold filling =  $1.15 \times 10^{-6}$  MPa s.

The gate is located at one of the edges normal to 500 mm length of the flat plate mold.
- 1. How much resin (in kilograms) must be pumped to fill the cavity?
- 2. How much time will be needed to fill the cavity at a constant flow rate of  $130 \text{ mm}^3/\text{s}$ ?
- 3. What will be the maximum injection pressure needed to fill the cavity at this constant flow rate?
- P5.20. Suppose in Problem 5.19, it is decided to fill the cavity at constant pressure instead of constant fill rate. If the constant pressure is 1.5 MPa, how much time will be needed to fill the cavity?
- P5.21. Ultrasonic testing of an impact-tested quasi-isotropic composite panel containing carbon fibers in PEEK matrix shows the presence of local delaminations, even though there are no apparent damages on the outside. Propose, in as much detail as possible, a plan to repair the internal damage and recommend tests to validate the repair.
- P5.22. Eddy current technique has been used for nondestructively detecting cracks and inclusions in metals. Investigate how this technique can be used for fiber-reinforced composites and discuss its limitations.