3

Processing of Composite Laminates

3.1 Introduction

The processing of polymer matrix composite laminates has been the subject of considerable research during the last several decades (see Lee et al. 1982, Loos and Springer 1983, Bogetti and Gillespie 1991, and Khoun et al. 2010). Multiple physical and chemical phenomena must occur simultaneously and in the proper sequence to achieve desired laminate properties. There are several routes to achieve full consolidation and minimize void content of a polymeric matrix with a reinforcing fiber in volume fractions (50–65%) appropriate for structural applications. The most widely accepted approach is by impregnation of unidirectional fibers, textile fabrics, or random fiber arrays to create a thin sheet or tape. If the polymer is a thermoset, it is often advanced in its curing state to the “B” stage (a state of cure of the matrix that is incomplete but provides high room temperature viscosity). Known as prepreg in this form, it may be stored at low temperature (below freezing) to greatly reduce the rate of cure and thus increase the storage life. After being warmed to room temperature, these prepreg sheets or tapes may then be assembled into a laminate and subjected to a cure cycle.

It is also possible to assemble dry fibers into an appropriate geometric form and then impregnate the entire laminate in a single step. This approach is known as resin transfer molding (RTM) or resin infusion, and there are several variations, such as vacuum-assisted resin transfer molding (VARTM). The weaving of a fabric from reinforcing fibers is a widely accepted approach to creating the fiber preform, although there are other techniques designed to avoid fiber crimp and develop microstructures typical of that achieved with prepreg tape.

For prepreg, heat and pressure are first applied to the laminate to reduce the viscosity of the polymer matrix and achieve full densification of the laminate and coalescence of the laminae through matrix flow. The application of heat to the laminate is governed by the laws of heat transfer and is therefore a time-dependent phenomenon. Further, the pressure in the laminate is shared by the polymeric matrix and the fibers. For thermosetting polymers, the kinetic process to achieve gelation and vitrification is a thermochemical
process that is often exothermic. The decrease in polymer viscosity with
temperature and its increase with degree of cure for thermosets requires that
the necessary flow be achieved prior to gelation or vitrification. For thermoset
plastic polymers, the process involves both viscosity changes and changes in
the polymer morphology (degree of crystallinity). Thermoplastic crystalline
polymers will exhibit varying degrees of crystallinity depending on their
thermal history (Velisaris and Seferis 1986).

The instantaneous degree of cure of a thermoset polymer is measured by
the fraction of total heat generated at a given time divided by the total heat
of reaction. Thus, the degree of cure ranges from 0 to 1.0 and can be mea-
sured using differential scanning calorimetry (DSC), which determines the
heat of reaction as a function of time. As the reaction progresses and the
macromolecular network forms, the rate-controlling phenomenon changes
from kinetic to diffusion because of the reduction in polymer free volume
(a measure of the internal space available within a polymer). An accompa-
nying reduction in molecular mobility occurs because of molecular weight
increase and cross-link formation.

Uneven distribution of resin may result from nonuniform flow of the poly-
mer through the fiber reinforcement. This is particularly pronounced for
laminates with curvilinear geometry and tapered thickness, in which local
pressure gradients occur. The velocity of flow of a polymer through a porous
medium such as a fiber array has been shown to be proportional to the pres-
sure gradient and inversely proportional to the polymer viscosity. The pro-
portionality constant is known as the fiber array permeability.

3.2 Characterization of Thermoset Matrices

The characterization of thermoset matrices for polymer composites requires the
development of cure kinetic models to describe the state of cure within the
polymer after the composite system has been subjected to a thermal history.
Many of the performance and processing properties of the polymer matrix
depend directly on the state of resin cure, as indicated, for example, by glass
transition temperature, viscosity, cure shrinkage, stiffness, and thermal
expansion. In the following, models and processes for determining these
properties are discussed in the context of characterization. This is not to say
that the processing phenomena are not important in determining efficient and
effective means of manufacturing composite material systems, but the focus
of the current chapter is meant to give an understanding of those processing
conditions that can significantly affect the polymer composite properties.

Polymer matrices go through several phase transformations during the
curing cycle. The prepregging operation leaves the thermosetting matrix in
a state of cure that is appropriate to handling and to subsequent consolidation, but that is not significantly advanced. When the temperature of the thermoset matrix is raised to begin the curing cycle, the polymer assumes a fluid state with significantly reduced viscosity appropriate for flow necessary for complete penetration of the fiber array. As the cross-linking reaction advances, the physical characteristics of the thermoset resin change from a liquid to a rubbery state and then to a glassy state. Gelation is a term that defines the degree of cure wherein the polymer is transformed from the liquid state to the rubbery state by the presence of the cross-link network. Vitrification marks the transformation of this polymer gel to the glassy state after sufficient advance of the cure process. After vitrification and on subsequent heating, the polymer with a given extent of cure passes from the glassy back to the rubbery state at its glass transition temperature $T_g$. As will be discussed further, the glass transition temperature is a function of the extent of cure of the thermoset polymer and can be strongly influenced by the thermal curing history. Measurement of the glass transition temperature yields important information regarding the extent of cure as well as the upper use temperature of the composite system.

3.2.1 Phenomenological Cure Kinetic Coefficients

The curing reaction of a thermoset polymer transforms it into an infusible solid through formation of a cross-link network. To understand the properties of the solid, the cure kinetics must be established. Cure kinetics of a thermoset polymer such as the epoxies utilized in polymeric composites involve the determination of the extent of cure as measured by the amount of heat released by the exothermic reaction, $\Delta H_R$, divided by the total heat of reaction released for complete cure $\Delta H_T$. Thus, the degree of cure $\alpha$ varies between 1.0 (fully cured) and 0 (no cure). Composed of epoxide groups, these systems are typically cured with primary and secondary amines. When a common epoxy resin (bifunctional with two epoxide groups) reacts with a diamine (chemical compounds containing two amino groups), the network formation (cross-linking) can advance quickly. While there are many approaches to modeling the cure state in a thermoset polymer, a widely accepted approach utilizes an Arrhenius-type equation, which is a function of the temperature and the activation energy. The classic rate equation utilized in much of the phenomenological modeling of epoxies is given in the following, where the rate of the reaction is equal to the product of a function of temperature multiplied by 1 minus the extent of cure, raised to the $n$th power:

$$\frac{d\alpha}{dt} = K(T)(1 - \alpha)^n$$

(3.1)
When the temperature increases linearly over time, it is appropriate to express the rate equation as a function of temperature.

\[ T(t) = mt + T_0 \]  \hspace{1cm} (3.2a)

\[ \frac{dt}{dT} = \frac{1}{m} \]  \hspace{1cm} (3.2b)

Where \( m \) is the heating rate, Equation (3.1) can be rewritten in terms of temperature.

\[ \frac{d\alpha}{dT} = \frac{K(T)}{m} (1 - \alpha)^n \]  \hspace{1cm} (3.2c)

The objective of the experimental characterization of the cure kinetics of the thermosetting matrix is therefore the determination of the rate constants, \( K(T) \) and \( n \).

Equation (3.1) may be expressed in logarithmic form and plotted as \( \ln \left( \frac{da}{dt} \right) \) versus the \( \ln \) of the terms on the right-hand side. The linear relation in \( \ln-\ln \) space shows that the two constants \( n \) and \( \ln K \), respectively, are the slope and intercept of the line at \( \ln (1 - \alpha) = 0 \).

\[ \ln \left( \frac{d\alpha}{dt} \right) = n \ln (1 - \alpha) + \ln K(T) \]  \hspace{1cm} (3.3)

The second rate constant \( K(T) \) can be expressed in a typical Arrhenius form as shown in Equation (3.4), where \( T \) is expressed in Kelvin, \( R \) is the universal gas constant, \( R = 8.3145 \text{ J/K} \); and \( E_a \) is the activation energy (J/mol):

\[ K(T) = Ae^{-E_a/RT} \]  \hspace{1cm} (3.4)

By expressing this equation in \( \ln-\ln \) format, it is possible to determine the preexponential factor \( A \) and the activation energy \( E_a \) from the intercept and slope of the resulting linear relationship of \( \ln K \) versus \( 1/T \).

\[ \ln K = \ln A - \frac{E_a}{RT} \]  \hspace{1cm} (3.5)

Consider the following isothermal procedure for determining the parameters of the reaction. First, the residual heat of reaction is determined by DSC.
measurements after curing a resin sample for the given time and under a specific isothermal condition. This process is repeated for several isothermal conditions. To calculate the parameters with any graphical method, it is first necessary to determine conversion (degree of reaction) as a function of time. To accomplish this goal, it is necessary to construct a table with data of residual heat as a function of time and temperature and transform into conversion, $\alpha$ as a function of time and temperature. A typical set of results is shown in Table 3.1, where each value for the heat of reaction $\Delta H_R$ corresponds to an individual experiment.

After cure of a resin sample at 50°C for an hour, the residual heat determined by the DSC experiment performed afterward was 2.65 J/g. Therefore, all the possible heat of reaction from the sample, except the remaining 2.65 J/g, was evolved during the isothermal hold prior to the DSC analysis. The following equation is used to calculate the corresponding conversion of the resin after 1 h at 50°C:

$$\alpha = 1 - \frac{\Delta H_R}{\Delta H_T}$$

Note that in an earlier experiment the total heat of reaction $\Delta H_T$ for this material was determined as 220 J/g.
The reduction of the data in Table 3.1 is accomplished by approximating the time derivative with a forward difference approximation:

\[
\frac{d\alpha}{dt} \approx \frac{\alpha_2 - \alpha_1}{t_2 - t_1}
\]

(3.7)

As an example, for the previous 25°C data, Table 3.2 can be constructed. When isothermal cure is carried out at four temperatures (25, 50, 100, 150°C), the data can be plotted according to Equation (3.3) and presented as shown in Figure 3.1, where \(R^2\) is the measure of fit.

As shown in Equation (3.5), the Arrhenius rate constant \(A\) must also be determined from the data. From Figure 3.1, the values of \(K(T)\) extracted are given in Table 3.3.

![Figure 3.1](image)

**FIGURE 3.1**

Typical isothermal cure data.

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**TABLE 3.2**

Isothermal Reaction Data Reduction (25 °C)

<table>
<thead>
<tr>
<th>Time, s</th>
<th>(\alpha)</th>
<th>(\ln(1 - \alpha))</th>
<th>(\frac{d\alpha}{dt} \times 10^{-4})</th>
<th>(\ln(\frac{d\alpha}{dt}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>720</td>
<td>0.362</td>
<td>–0.449</td>
<td>2.45</td>
<td>–8.33</td>
</tr>
<tr>
<td>1800</td>
<td>0.624</td>
<td>–0.978</td>
<td>1.08</td>
<td>–9.13</td>
</tr>
<tr>
<td>3240</td>
<td>0.780</td>
<td>–1.514</td>
<td>0.527</td>
<td>–9.85</td>
</tr>
<tr>
<td>4680</td>
<td>0.856</td>
<td>–1.938</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The data in Table 3.3 are presented in Figure 3.2 for the determination of the rate constant \( A \) according to Equation (3.5) \((A = 0.564)\).

The cure kinetic parameters determined by the four isothermal test conditions are summarized in Table 3.4. The data in Table 3.4 completely define the reaction kinetics of the polymer system under study and can be used in Equations (3.1) and (3.2) to determine the polymer cure state resulting from a specified thermal history.

### 3.2.2 Gelation of the Thermoset Polymer

*Gelation* is the transformation of the polymer from the liquid to rubbery state, and it is important to relate the extent of cure that corresponds to the onset

#### TABLE 3.3

<table>
<thead>
<tr>
<th>Arrhenius Rate Constant Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T, \text{°C} )</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>150</td>
</tr>
</tbody>
</table>

#### FIGURE 3.2

Typical kinetic parameter data.

\[
y = -17537 \left(\frac{1}{RT}\right) - 0.5983
\]

#### TABLE 3.4

<table>
<thead>
<tr>
<th>Kinetic Parameters of the Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Term</strong></td>
</tr>
<tr>
<td>( n )</td>
</tr>
<tr>
<td>( E_a ) (kJ/mol)</td>
</tr>
<tr>
<td>( A ) (s(^{-1}))</td>
</tr>
</tbody>
</table>
of gelation during the curing process. Using the fundamentals of gelation theory, the relationship in Equation (3.8) has been developed, wherein the extent of cure at gelation $\alpha_g$ is related to the molar ratio of reacting groups $r$, the fraction of amine hydrogen $s$, and the functionality of cross-linking groups $f$ (Flory 1953).

$$\alpha_g = \frac{1}{[r + rs(f - 2)]^{1/2}}$$

(3.8)

When an epoxy resin is cured with an aromatic diamine, the number of cross-linking groups is four ($f = 4$) because each amine group can react with two epoxide groups. For equimolar conditions, $r = 1$, and for this functionality of cross-linking groups, $s = 1$. This leads to a prediction of a degree of cure at gelation of 0.58. The test method to determine gel time (time for a 120-ml sample at 23°C to reach the gel point) previously described in ASTM (American Society for Testing and Materials) D2471 (2008) was withdrawn and is currently under review.

As mentioned, the glass transition temperature of a thermosetting polymer matrix is a strong function of the extent of cure due to the continued growth of the cross-linking network with cure. The DiBenedetto equation (1987) gives a convenient relationship between the glass transition temperature at a given degree of cure $T_g$, the glass transition temperature of the un-cross-linked polymer $T_{g0}$, the ratio of lattice energies of cross-linked and partially cross-linked polymer $E_x/E_m$, and the ratio of segmental mobilities at the glass transition temperature $F_x/F_m$.

$$\frac{T_g - T_{g0}}{T_{g0}} = \left[\frac{E_x/E_m - F_x/F_m}{1 - (1 - F_x/F_m)}\right]^\circ \alpha$$

(3.9)

Expression (3.9) can be simplified by defining the glass transition temperature at full conversion as $T_{g\infty}$ to yield the following form:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\circ \alpha}{1 - (1 - \circ \alpha)}$$

(3.10)

where $\lambda$ is typically 0.4–0.5. The dependence of $T_g$ versus degree of cure is illustrated in Figure 3.3.

### 3.2.3 Viscosity and Cure Kinetics

The characterization of cure kinetics with rheological characteristics is based on the viscosity change of the thermosetting polymer as a function of its molecular weight and cross-link density. However, as the temperature of a thermoset resin is increased, two primary phenomena influence its viscosity. At first, the viscosity is reduced significantly by an increase in temperature,
but as the reaction progresses, the viscosity increases exponentially due to the cross-link network formation. Typical viscosity versus time for a linear increase in temperature is shown in Figure 3.4.

While a number of phenomenological models have been developed for the relationship between viscosity, extent of cure, and temperature, the Castro-Macosko model (1982) has been chosen here for its versatility. As shown in Equations (3.11) and (3.12), the viscosity \( \eta \) of the thermoset polymer of
incomplete cure is related to the degree of cure at gelation $\alpha_g$ and the degree of cure of the polymer $\alpha$.

$$\frac{\eta_c}{\eta_0(T)} = \left( \frac{\alpha_g}{\alpha} \right)^{(A+B')}$$  \hspace{1cm} (3.11)

The reference viscosity $\eta_0(T)$ follows an Arrhenius temperature dependence.

$$\eta_0(T) = C \exp \left( \frac{E_a}{R(T - T_0)} \right)$$  \hspace{1cm} (3.12)

where $E_a$ denotes the activation energy of the reaction, $R$ is the universal gas constant, $T$ is the absolute temperature of the system, and $T_0$ is the reference temperature.

Measurement of the viscosity of a thermoset presents challenges to the experimentalist because the material may pass from liquid to gel to vitrified states during the test. Some of the rheological equipment used in these measurements cannot accept these conditions, and care must be taken in the instrument choice. The ASTM D4473 (2008) test method specifies the use of a parallel plate rheometer. The system typically monitors the dynamic shear moduli of the polymer, consisting of the storage modulus and loss modulus of the system. Sweeps in frequency at constant temperature and temperature at constant frequency are the two testing options available. In the former, the change in viscosity under isothermal conditions can be determined through direct measurement, and in the latter, viscosity change with temperature can be observed. The typical frequency of the test ranges from quasi static to 100 Hz. The flat parallel plate geometry does not provide a uniform shear strain rate in the specimen, and for this reason, conical plate geometries are often utilized. By plotting the inverse of viscosity with time, it is possible to determine the point at which the viscosity approaches infinity and thereby gelation.

Consider the example viscosity data for an epoxy system in Table 3.5. Combining these data with the relationships given in Equations (3.11) and (3.12) provides guidance in determining the onset of gelation during the cure.

<table>
<thead>
<tr>
<th>Term</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$</td>
<td>76.5 kJ/gmol</td>
</tr>
<tr>
<td>$C$</td>
<td>$3.45 \times 10^{-10}$ Pa$^{-s}$</td>
</tr>
<tr>
<td>$A$</td>
<td>3.8</td>
</tr>
<tr>
<td>$B$</td>
<td>2.5</td>
</tr>
<tr>
<td>$\alpha_g$</td>
<td>0.47</td>
</tr>
</tbody>
</table>
of the resin when the thermal cure cycle is specified and thereby illustrates the need for the determination of these properties for a given resin system.

3.3 Processing of Thermoset Composites

The development of an interlocking network during the cure of a thermoset polymer is illustrated in Figure 3.5. As temperature and time increase, the network interconnectivity grows according to the steps illustrated: (a) The prepolymer and curing agents are interspersed; (b) polymer molecular weight (size) increases; (c) gelation occurs, and a continuous network is achieved; and (d) cure is complete (see the time–temperature transformation diagram, Figure 3.6). After the polymer approaches vitrification (i.e., the polymer changes from a rubbery to a glassy state), the rate of conversion decreases significantly. Should vitrification occur before completion of the cure reaction, polymer properties will not be fully achieved, and voids may form in the laminate. These phenomena must be considered in the development of an appropriate cure cycle.

Figure 3.7 illustrates the flow and compaction phenomena during the curing and consolidation steps. Initially, the increase in temperature serves to decrease the viscosity of the polymer, and the polymer carries the applied pressure. As the laminate is vented and flow begins, the fibers deform and act as an elastic spring in assuming a portion of the applied pressure (Figure 3.7). Volatiles produced in the chemical reaction or trapped gases will then escape from the laminate. Finally, the total pressure is carried by the fully consolidated composite panel.

Given that composite laminates are often processed in an autoclave, wherein heat transfer is achieved with a pressurizing medium (normally nitrogen, an inert gas), it is important to recognize that the instantaneous temperature within the laminate may not be equal to that of the autoclave.

![Figure 3.5](image)

**FIGURE 3.5**
Figure 3.8 illustrates a typical thermal cycle and shows that the temperature of the laminate can differ from top surface to interior (center) to tool surface. Thus, the dynamics of heat transfer must be considered when an appropriate cure cycle is developed.

Consider the typical cure cycle shown in Figure 3.9, where internal composite temperature lags autoclave temperature. Initially, the autoclave temperature is

**FIGURE 3.6**

**FIGURE 3.7**
Polymer and perform pressurization and flow. (From P. Hubert, Ph.D. thesis, University of British Columbia, 1996. With permission.)
increased at a constant rate of 2–3°C/min until it reaches 110°C, and then it is held constant for approximately 1 h. During this stage, the polymer is in the liquid state. Next, the autoclave temperature is increased to and held at approximately 180°C for 2 h. During this stage, the polymer passes through gelation at a degree of cure of 0.46 and then approaches vitrification. Vitrification occurs when the polymer passes from the rubbery or gel state to the glassy state. In Figure 3.8, the vitrification point occurs prematurely at approximately 190 min into the cycle. Because the rubbery-to-glass transition occurs at vitrification, stresses developed as a result of the shrinkage of the polymer with cure progression may not relax during the remainder of the curing cycle. For the

![Diagram](image_url)

**FIGURE 3.8**
Heat transfer through laminate thickness. (From P. Hubert, University of British Columbia Composites Group Report, 1994. With permission.)

![Diagram](image_url)

**FIGURE 3.9**
Cure cycle with premature vitrification. (From P. Hubert, University of British Columbia Composites Group Report, 1994. With permission.)
case in which vitrification is delayed until a point much later in the process close to cooling, much of this stress will be eliminated by completion of the cycle. Hence, the cure cycle can be tailored to the specific polymer to minimize residual stresses. Of course, thermal residual stresses will still develop in the laminate on cooling because of anisotropic thermal expansion, as discussed in Chapter 13.

3.3.1 Autoclave Molding

Figure 3.10 shows the vacuum bag layup sequence for a typical epoxy matrix prepreg composite. Different layup sequences can be used for other types of prepregs.

1. Thoroughly clean the aluminum plate (10) using acetone or a detergent. Then, apply mold release agent to the top surface of the aluminum plate twice.

2. Lay one sheet of Teflon film (1) and the peel-ply (2) (nonstick nylon cloth) on the aluminum plate. The Teflon film is used to release the layup from the aluminum plate, and the peel-ply is used to achieve the required surface finish on the laminate. Note: There should be no wrinkles or raised regions in the peel-ply, and its dimensions should be identical to those of the laminate.

![Diagram of vacuum bag layup sequence](image)

**FIGURE 3.10**
Vacuum bag preparation for autoclave cure of thermoset matrix composite.
3. Place the prepreg stack (3) on the plate, being sure to keep it at least 50 mm from each edge. Note: Do not cover up the vacuum connection in the plate.

4. Place a strip of the cork–rubber material (9) along each edge of the panel, making sure that no gaps exist and a complete dam is formed around the laminate. The dam around the layup prevents lateral motion of the panel and minimizes resin flow parallel to the aluminum plate and through the edges of the laminate (9).

5. Completely encircle the prepreg stack and dam with bagging adhesive, making sure that the adhesive material is adjacent to the dam. The purpose of the adhesive material is to form a vacuum seal.

6. Place a peel-ply (4) and a ply of Teflon-coated glass fabric (5) (with the same dimensions as the panel) on top of the prepreg stack. The purpose of the Teflon-coated glass fabric is to prevent the bleeder sheets (6) from sticking to the laminate.

7. Place the proper number of glass bleeder sheets (6) (e.g., style 181 glass cloth with the same dimensions as the prepreg stack) over the Teflon-coated fabric (5). The bleeder sheets absorb the excess resin from the laminate.

8. Place a sheet of perforated Teflon film (7) (0.025 mm thickness) over the bleeder material. The Teflon film, perforated on 50-mm centers, prevents excess resin from saturating the vent cloth (8).

9. Place a porous continuous vent cloth (8) (e.g., style 181 glass cloth) on top of the layup. Extend the cloth over the vacuum line attachment. Make sure that the vacuum line is completely covered by the vent cloth. The vent cloth provides a path for volatiles to escape when the vacuum is applied and promotes a uniform distribution of vacuum.

10. Place nylon bagging film over the entire plate, and seal it against the bagging adhesive. Allow enough material so that the film conforms to all contours without being punctured.

11. Place the plate in the autoclave and attach the vacuum line (Figure 3.11). An autoclave is generally a large pressure vessel equipped with a temperature and pressure control system. The elevated pressures and temperatures, required for processing of the laminate, are commonly achieved by electrically heating a pressurized inert gas (nitrogen). The use of an inert gas will reduce oxidizing reactions that otherwise may occur in the resin at elevated temperatures, and will prevent explosion of evolving volatiles.

12. Turn on the vacuum pump and check for leaks. Maintain a vacuum of 650 to 750 mm of mercury for 20 min and check again for leaks.
13. After closing the autoclave door, apply the pressure and initiate the appropriate cure cycle (see example shown in Figure 3.12). As the temperature is increased, the resin viscosity decreases rapidly, and the chemical reaction of the resin begins. At the end of the temperature hold, at 127°C in Figure 3.12, the resin viscosity is at a minimum, and pressure is applied to squeeze out excess resin. The temperature hold controls the rate of the chemical reaction and prevents degradation of the material by the exotherm. The pressure is held constant throughout the cure cycle to consolidate the plies until the resin in the laminate reaches its glassy state at the end of the cooling phase.

FIGURE 3.11
Vacuum bag sequence and tool plate placed in an autoclave.

FIGURE 3.12
Typical cure cycle for a carbon/epoxy prepreg.
The vacuum should be checked throughout the cure cycle. The vacuum is applied to achieve a uniform pressure on the laminate and draw out volatiles created during the cure. Loss of vacuum will result in a poorly consolidated laminate.

14. After the power is turned off to the autoclave, maintain pressure until the inside temperature has dropped to about 100°C.

15. Carefully remove the laminate from the aluminum plate. Gently lift it in a direction parallel to the main principal direction of the laminate.

16. Clean the aluminum plate and store it for future use.

### 3.3.2 Resin Transfer Molding of Thermoset Composites

Resin transfer molding of composite laminates is a process wherein the dry-fiber preform is infiltrated with a liquid polymeric resin, and the polymer is advanced to its final cure after the impregnation process is complete. An extensive review of the RTM process can be found in the work of Advani (1994). The process consists of four steps: fiber preform manufacture, mold filling, cure, and part removal. In the first step, textile technology is typically utilized to assemble the preform. For example, woven textile fabrics are often assembled into multilayer laminates that conform to the geometry of the tool. Braiding and stitching provide mechanisms for the creation of three-dimensional preform architectures.

Typically, a thermosetting polymer of relatively low viscosity is used in the RTM process. There have been applications for thermoplastic polymers, but they are rare. Pressure is applied to the fluid polymer to inject it into a mold containing the fiber preform, and the mold may have been preheated. The flow of the fluid through the fiber preform is governed by Darcy’s law (Advani 1994), wherein the velocity of the flow is equal to the product of the pressure gradient, the preform permeability, and the inverse of the polymer viscosity. Clearly, the lower the polymer viscosity, the greater the flow rate will be, and similarly, the greater the permeability, the greater the flow rate will be. Note also that because the fiber preforms typically exhibit different geometries in the three principal directions, permeability is a tensor and exhibits anisotropic characteristics. That is, for a given pressure gradient, the flow rates in three mutually orthogonal directions will differ. Flow through the thickness of a fiber preform that contains many layers of unidirectional fibers will be quite different from flow in the planar directions. In addition, the permeability of the preform depends on the fiber volume fraction of the preform. The greater the volume fraction, the lower the permeability is. It is important to vent the mold to the atmosphere to remove displaced gases from the fiber preform during the mold-filling process. Otherwise, trapped gases will lead to voids within the laminate.

After the polymer has fully impregnated the fiber preform, the third step occurs: cure. Cure begins immediately on injection of the polymer into the
mold and will occur more rapidly if the mold is at an elevated temperature. As the cure of the polymer advances to the creation of a cross-link network, it passes through a gelation phase wherein the polymer viscosity increases and transforms the polymer into a viscoelastic substance, where it possesses both viscous and elastic properties. As this process proceeds and the cross-link network continues to grow, the instantaneous glass transition temperature of the polymer increases. Finally, vitrification of the polymer occurs when its glass transition temperature exceeds the laminate temperature. Should gelation or vitrification (or both) occur prior to completion of mold filling and preform impregnation, the resulting laminate will not be fully impregnated.

The viscosity of most polymers is highly dependent on temperature, and polymer cure kinetics are controlled by temperature as well. Therefore, heat transfer phenomena must be managed for successful RTM processes. Heat transfer between the polymer and the fiber preform, and between tool, preform, and polymer, as well as exothermic heat generation during the cure of the polymer, are three such phenomena that influence the process (Lee et al. 1982).

### 3.3.2.1 Vacuum-Assisted Resin Transfer Molding

Both open-mold approaches, where one surface is bagged with a flexible film, and closed-mold approaches to RTM are practiced. An example of open-mold RTM, VARTM, is a common method employed as an alternative to autoclave use. The VARTM process is illustrated in Figure 3.13. In VARTM, atmospheric pressure is utilized to achieve consolidation and impregnation by vacuum bagging the laminate. An inlet for the polymer is located at one or
more points in the tool or bag, and vacuum outlets are located some distance away. The vacuum pump creates a pressure gradient of approximately 1 atm within the bag, which is sufficient for the impregnation of laminates large in size and complex in geometry. For processes in which final cure occurs after the mold is filled, completion of the cure may be carried out in an oven while atmospheric pressure is maintained on the impregnated laminate.

The VARTM procedure for a representative flat 61.0 × 30.5 × 0.64 cm panel (Figure 3.13) is described in the following steps:

1. Tool surface. The tool is a flat aluminum plate with planar dimensions sufficient to accommodate the composite panel. First, clean the metal tool surface using sandpaper and acetone. On the cleaned surface, create a 71 × 30.5 cm picture frame using masking tape. Apply several coats of release agent to the metal surface inside the masked frame. Remove the masking tape.

2. Bagging tape. In place of the masking tape, apply a 1.3 cm wide silicone bagging tape to the bare metal surface. The silicone tape should again form a 71 × 30.5 cm frame. Add a strip of the tape, 5 cm in length, to the outer edge of the length of the frame at either end. These two strips will provide an added adhesive surface for attachment of the inlet and outlet tubing. Leave the paper backing on the silicone tape to protect it during the remainder of the layup procedure.

3. Preform. Place the fiber preform stack on the coated tool, inside the tape frame. A 5.1-cm gap should exist between the silicone tape and both edges of the preform to allow room for tubing. No gap should exist between the silicone tape and fiber preform along the panel width to avoid providing a flow pathway outside the preform to the vacuum port.

4. Release cloth. Cut one layer of porous release film to 66 × 30.5 cm and place it on top of the preform. Place the cloth so that it completely covers the preform and allow 5.1 cm in length to overhang and contact the coated metal surface at the injection side of the layup. The release film will allow separation of the composite laminate from the distribution media. Cut a second piece of release cloth to 5.1 × 30.5 cm and place it on the tool surface at the vacuum side of the preform. This patch of cloth provides a clear path for the vacuum.

5. Distribution media. Cut one to six layers of highly permeable distribution media (e.g., biplanar nylon 6 mesh) to dimensions of 63.5 × 28.0 cm and stack them above the Armalon™ release cloth. Place the layers of media to leave a 2.5-cm gap on the top of the preform at the vacuum end. This gap will force the resin to fill through the thickness rather than be drawn directly into the vacuum port. The length of this gap will vary with the desired thickness of the composite panel. A 1.3-cm gap should exist between the media and the sides of the preform.
This will help prevent resin flow outside the preform. A 5-cm length of the media will overhang the preform at the resin inlet end of the layup.

6. **Distribution tubing.** Place a 28 cm length of distribution tubing across the width of the laminate at points 2.5 cm in front of the preform (inlet) and 2.5 cm away from the preform (vacuum). On the inlet side, place the tubing on top of the distribution media that overhangs the preform. At the vacuum side, place the tubing on the 5 × 30.5 cm piece of release cloth. Spiral wrap, 18-mm-diameter conduit is an ideal choice for the distribution tubing because it allows the resin to flow quickly into the distribution media and preform in a continuous line across the width. A plastic tube with holes at 2.5-cm intervals also works well. Attach a 13-mm portion of the spiral tubing to both the inlet–supply tubing and the vacuum tubing using Kapton™ tape (E.I. duPont de Nemours and Co.). Embed the free end of the spiral tubing in a 2.5-cm diameter roll of the silicone bagging tape and then affix it to the strip of bagging tape forming the frame of the laminate.

7. **Resin supply and vacuum tubing.** Use flexible plastic tubing (vinyl or Teflon, depending on temperature requirements) approximately 1.5 m in length to supply resin and draw vacuum on the laminate. Tape one end of the tube to the distribution tubing inside the bag. At a point just past this taped interface, wind one layer of silicone vacuum tape twice about the outer surface of the tubing. This 2.5-cm long sleeve of vacuum tape on the tube should match the tape frame and added strips that exist on the tool surface. Attach the taped tubes to the tool at these locations and place two more 7-cm long strips of tape on top of the tool and tape sealant to form a smooth, airtight joint when the bagging film is in place. Clamp the free end of the resin supply tubing to ensure a temporary airtight seal. Connect the free end of the vacuum tubing to a resin trap, which catches any resin that might be pulled into the tube on its way to the vacuum pump.

8. **Vacuum bag.** With the laminate complete and the tubing in place, the part can be bagged using an appropriate film. Take care to eliminate creases in the bag and ensure an airtight seal with the tool surface and silicone bagging tape. Once bagging is complete, the laminate should be fully evacuated to 762 mm Hg using the vacuum pump. Leaks can be detected by using either a listening device or by clamping the vacuum line and using a vacuum gage. Even a small leak in the system may result in voids and poor consolidation of the final composite part.

9. **Resin degassing.** Before infiltration can occur, the resin must be degassed to remove any air bubbles that were introduced during
mixing. Perform degassing separately in a vacuum chamber; degassing can typically require 1 to 4 h, depending on the resin viscosity. All air bubbles must be removed prior to infiltration. Contain the resin in a bucket.

10. **Resin infiltration.** With the bagged laminate under full vacuum, submerge the clamped end of the resin supply tubing in the degassed resin bucket. Remove the clamp while the tube end is submerged to prevent any air entering the tube and the part ahead of the resin. With the tube clamp removed, the resin flows through the supply tubing and into the distribution tubing. The spiral distribution tubing allows the resin to spread quickly across the width of the layup as it enters the distribution media. The distribution media provides the path for the resin to flow quickly down the length of the preform and then through the laminate thickness.

11. **Completion of infiltration.** The flow front of resin through the part can be viewed through the bagging film. Halt the flow of resin when the preform is fully infiltrated, as evidenced by resin beginning to enter the vacuum distribution tubing. Stop the resin flow by first clamping and severing the resin supply tubing and then clamping and severing the vacuum tubing. Again, these clamps must provide an airtight seal because any leaks during cure will result in poor consolidation of the part. It is recommended that a second envelope bag be used to pull vacuum on the part during cure. Finally, if elevated temperature cure is required, place the vacuum sealed part in an oven and heat it according to a cure cycle prescribed by the resin supplier.

### 3.4 Autoclave Processing of Thermoplastic Composites

Thermoplastic composites may be processed in a high-temperature autoclave. Figure 3.14 shows the autoclave layup sequence for a carbon/polyetheretherketone (PEEK) composite. Place Kapton film of slightly larger size than the panel, each side being coated with a release agent, on the tool plate. Place Kapton bagging film over the layup and seal the bag against the tool plate using A800 G3 (or equivalent) tacky tape. Place the tool plate and laminate in the autoclave and attach the vacuum line. The following processing cycle is recommended for a carbon/PEEK composite:

1. Maintain a vacuum of 650 to 750 mm Hg.
2. Apply a pressure of 0.5 MPa and simultaneously ramp the temperature as rapidly as possible to 390°C.
3. Apply a consolidation pressure of 1.4 MPa.
4. Hold the pressure at a temperature of 390°C for 5 min per 8 plies, but not for more than 30 min.
5. Cool the laminate rapidly to room temperature. The degree of crystallinity for crystalline polymers is influenced by cooling rate. Pressure can be released as the laminate temperature falls below the glass transition temperature of the matrix (≈140°C).

3.5 Determination of Volume Fractions of Fibers, Resin, and Voids

As discussed in Chapter 2, the stiffness and strength properties of composites are strongly dependent on the fiber volume fraction, and this parameter thus constitutes an important quality measure of such materials. This section details measurement of fiber volume fraction for polymer matrix composites reinforced with glass, carbon, or aramid fibers.

The fiber volume fraction of a composite may be determined by chemical matrix digestion, burn-off, or photomicrographic techniques. The matrix digestion method is standardized, ASTM D3171 (2011), and consists of dissolving the (polymer) matrix in a hot digestion medium (concentrated nitric acid for epoxy matrix composites or sulfuric acid followed by hydrogen...
peroxide for polyimides and PEEK). Care must be taken to select a medium that attacks the matrix but does not attack the fibers. After the matrix is dissolved, the fibers are weighed. The volume fractions are calculated from the weights and densities of the constituents. The resin burn-off method (ASTM D2584 2011) is sometimes used for glass fiber composites because glass fibers (as opposed to carbon and Kevlar [E.I. du Pont de Nemours and Company] fibers) are resistant to oxidation at the temperatures required to burn off the matrix (500–600°C). Similar to the chemical matrix digestion method, the fibers are weighed after the matrix has been removed to enable calculations of fiber volume fractions.

The photomicrographic method is not an ASTM standard, but it provides an independent estimate of the fiber volume fraction. The method requires a photograph of a polished cross section of a composite and many samples to produce reliable results because the area viewed is only about a hundredth of a square millimeter. On the other hand, it provides an image of the distribution of fibers and voids.

3.5.1 Chemical Matrix Digestion Method

Equipment needed for this procedure (Figure 3.15) includes

1. Fume hood with a vacuum system
2. Large flask that can be attached to the vacuum system
3. Buchner funnel with filter
4. A 400-ml beaker
5. Nitric acid
6. Glass stirring rod

FIGURE 3.15
Acid digestion procedure.
7. Bunsen burner or electric heater
8. Desiccator
9. Precision balance
10. Rubber gloves and goggles

3.5.1.1 Procedure

1. Take a 50 × 50 mm composite sample and weigh it. Also weigh the dry Buchner funnel with the filter.
2. Put on rubber gloves and goggles and activate a hood vent fan. Place the sample in the 400-ml beaker and pour in 200 ml of the nitric acid (use the glass stirring rod for controlled, slow pouring of the acid). Heat the beaker with the Bunsen burner until the acid fumes, but avoid boiling; stir occasionally. Continue heating until the matrix is dissolved and the sample disintegrates, leaving bare fibers.
3. Insert the funnel into the large flask attached to the vacuum system and transfer the acid and the fibers into the funnel. Turn on the vacuum pump and wash the fibers three times with 20 ml of nitric acid and then follow with a water wash.
4. Remove the funnel and the fibers and dry them in an oven at 100°C for at least 90 min. Break up the fiber flocks occasionally with a glass rod to facilitate drying. Remove the funnel and the fibers and let them cool in a desiccator. Weigh the funnel containing the fibers.

3.5.1.2 Calculation of Fiber Volume Fraction

From the weights of the fibers and matrix (\(W_f\) and \(W_m\), respectively) and their known densities (\(\rho_f\) and \(\rho_m\), respectively), the volume fraction of fibers \(V_f\) is determined from

\[
V_f = \frac{\rho_m W_f}{\rho_f W_f + \rho_m W_m}
\]  

(3.13)

where it is assumed that the void content of the composite is negligible.

As an example, consider the following data for a carbon/epoxy composite:

\[
W_f = 3.0671 \text{ g}; W_m = 1.2071 \text{ g (weight of composite minus } W_f)\]

Table 3.6 gives densities for some current fibers and matrix resins. Using the densities in Table 3.6, \(\rho_f = 1.73 \text{ g/cm}^3\) and \(\rho_m = 1.265 \text{ g/cm}^3\), Equation (3.13) gives \(V_f = 0.60\).
3.5.1.3 Determination of Void Content

Voids may form in the composite as a result of gases and volatiles evolved during processing becoming trapped in the matrix. Voids are generally undesired. For example, for autoclave-produced composite parts, a void content of less than 1% is commonly desired. The procedure for measurement of void content is given in ASTM Standard D2734 (2009). Void content requires an accurate measurement of the density of the composite:

\[ \rho = \frac{W}{V} \]  

(3.14)

where \( W \) and \( V \) are the weight and volume of the composite, respectively. Methods for density measurements are presented in ASTM D1505 (2010) and D3800M (2011). To obtain the void content, consider the following condition for the various volume fractions:

\[ V_f + V_m + V_v = 1 \]  

(3.15)

where subscripts \( f, m, \) and \( v \) represent fiber, matrix, and voids, respectively. From Equation (3.15), an expression for the void content can be obtained:

\[ V_v = 1 - \left( \frac{W_f}{\rho_f} + \frac{W_m}{\rho_m} \right) \frac{c}{W} \]  

(3.16)

in which \( W_f, W_m, \) and \( W \) represent the weights of fiber, matrix, and composite, respectively (\( W_f + W_m = W \)). This method enables verification that an acceptable void content (e.g., <1%) has been achieved.

3.5.2 Photomicrographic Method

Equipment needed for this procedure includes

1. Polishing table
2. Specimen mounted (embedded) in a specimen holder
3. Metallographic optical microscope (×400) with a camera

TABLE 3.6
Fiber and Resin Properties

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Carbon AS4</th>
<th>Carbon IM6</th>
<th>EGlass</th>
<th>Kevlar 49</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.80</td>
<td>1.73</td>
<td>2.60</td>
<td>1.44</td>
</tr>
<tr>
<td>Matrix Type</td>
<td>Epoxy N5208</td>
<td>Epoxy 3501-6</td>
<td>Polyimide</td>
<td>PEEK</td>
</tr>
<tr>
<td>Density</td>
<td>1.20</td>
<td>1.265</td>
<td>1.37</td>
<td>1.30(^a)</td>
</tr>
</tbody>
</table>

\(^a\) 30% crystallinity.

3.5.2.1 Procedure

1. Cut the specimen perpendicular to the fiber direction to expose the desired cross section.

2. Place the specimen inside a mounting cup (e.g., Buehler SampleKup) and pour a potting material (epoxy) into the cup. After the mounting material is cured, the specimen is ready for grinding and subsequent polishing.

3. Grind the specimen by working through four sandpaper grades (180, 240, 320, and 400). Then, proceed to polish the specimen on a polishing table (Figure 3.16) using 5-, 1-, and if necessary, 0.3-μm particles. Polishing is the final step to obtain a flat surface with a mirror-like finish. Choose any direction to start the polishing and maintain that direction for that step. When changing to finer paper grades, alter the polishing angle by 90° each time to remove scratches from the previous step. Rinse the specimen after each step to remove grit.

4. When the specimen is polished, it is ready to be examined in the optical microscope. Take a photograph of a polished cross section like the one shown in Figure 3.17.

3.5.2.2 Determination of Fiber Volume Fraction

The fiber volume fraction can be determined from the photomicrograph in two ways, as illustrated in Figure 3.18. One way is to determine the total area of the fibers in a given area of the micrograph. This can be done directly with
a quantitative image analyzer or by counting the number of fibers in the area and calculating the total fiber area from their average diameter. The fiber volume fraction is determined as

\[ V_f = \frac{A_f}{A} \quad (3.17) \]

where \( A_f \) and \( A \) are the total fiber area and the area of the selected region of the micrograph, respectively.

An alternative way, the line method (Figure 3.18), can also be used to determine the fiber volume fraction from the micrograph. In this method, a number of lines are randomly drawn on the micrograph. The fiber volume fraction is evaluated as the ratio of the cumulative length of fiber cross sections along the line to the length of the line. For a representative result, an average value should be determined from measurements along several lines.

![Figure 3.17](image1.png)

**FIGURE 3.17**
Photomicrograph of a polished cross section. (Courtesy of S. Nilsson, FOI, Stockholm, Sweden.)

![Figure 3.18](image2.png)

**FIGURE 3.18**
Illustration of area and line methods.
For a cross section of the carbon/epoxy composite discussed in the previous section, the results shown in Table 3.7 were obtained. From these data, an average fiber volume fraction was determined, $V_f = 0.62$, which can be compared with $V_f = 0.65$, determined with the acid digestion method. Differences between the two methods are likely due to the small region of the composite studied in the micrograph and to uncertainty in determining the length of the fiber cross sections. It is notable that the micrographic line method exhibits significant variability, as shown in Table 3.7, where the range is 0.54 to 0.72.

<table>
<thead>
<tr>
<th>Line</th>
<th>$L_f$ (mm)$^a$</th>
<th>$V_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.5</td>
<td>0.58</td>
</tr>
<tr>
<td>2</td>
<td>40.8</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>54.9</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>45.3</td>
<td>0.60</td>
</tr>
<tr>
<td>5</td>
<td>48.3</td>
<td>0.63</td>
</tr>
<tr>
<td>6</td>
<td>48.1</td>
<td>0.63</td>
</tr>
</tbody>
</table>

$^a L_f =$ cumulative length of fiber cross sections. Total length of each line was 76.2 mm.