

# 3

---

## *Processing of Composite Laminates*

---

The processing of polymer matrix composite laminates has been the subject of considerable research during the last two decades [1–11]. 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 to 60%) appropriate for structural applications. The most widely accepted approach is by impregnation of unidirectional fibers or textile fabrics 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 of the prepreg). 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), and there are several variations. 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 thermoplastic 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 upon their thermal history [5].

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. The degree of cure ranges from 0 to 1 and can be measured 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. An accompanying reduction in molecular mobility occurs because of molecular weight increase.

Uneven distribution of resin may result from nonuniform flow of the polymer 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 fiber mats has been shown to be proportional to the pressure gradient and inversely proportional to the polymer viscosity [12]. The proportionality constant is known as the permeability [12].

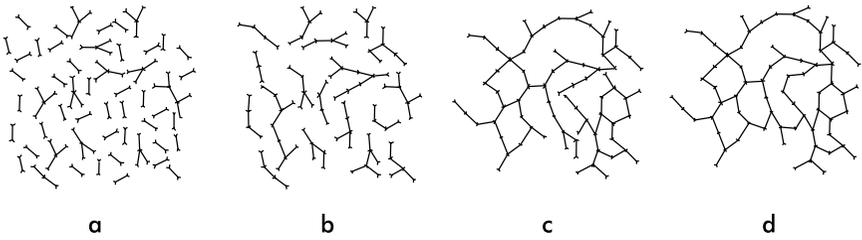
---

### 3.1 Processing of Thermoset Composites

The development of an interlocking network during the cure of a thermoset polymer is illustrated in [Figure 3.1](#). 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 3.2](#)). 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.

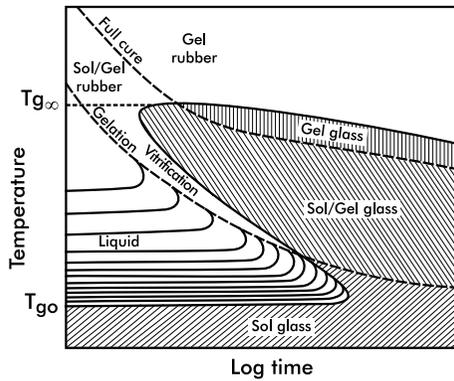
[Figure 3.3](#) illustrates the flow and compaction phenomena during the curing and consolidation steps. Initially, the increase in temperature serves to decrease the viscosity of the polymer and the polymer carries the applied pressure. As the laminate is vented and flow begins, the fibers deform and act as an elastic spring in assuming a portion of the applied pressure ([Figure 3.3](#)). 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



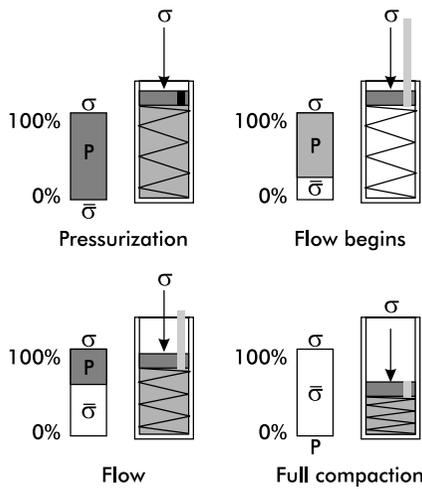
**FIGURE 3.1**

Dynamics of thermoset gelation and vitrification. (From L.A. Berglund and J.M. Kenny, *SAMPE J.*, 27(2), 1991. With permission.)



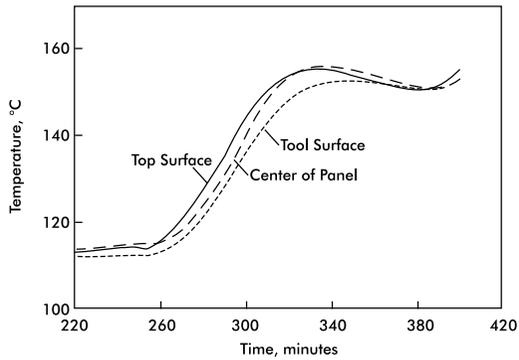
**FIGURE 3.2**

Time-temperature transformation diagram. (From L.A. Berglund and J.M. Kenny, *SAMPE J.*, 27(2), 1991. With permission.)



**FIGURE 3.3**

Polymer and perform pressurization and flow. (From P. Hubert, Ph.D. Thesis, University of British Columbia, 1996. With permission.)

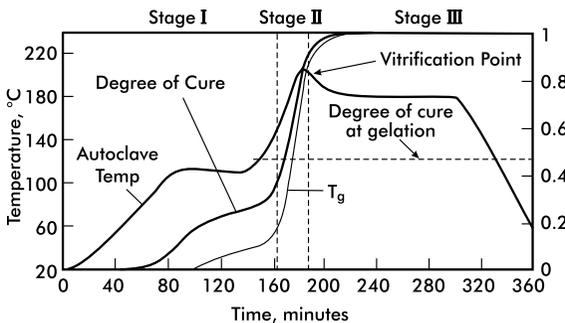


**FIGURE 3.4**

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

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 3.4](#) 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 3.5](#), where internal composite temperature lags autoclave temperature. Initially, the autoclave temperature is increased at a constant rate of 2 to 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 instantaneous glass transition temperature (defined as the temperature at which the polymer passes from the rubbery or gel state to the glassy state) of the polymer reaches the temperature of the laminate. In [Figure 3.5](#), the vitrification point occurs prematurely at



**FIGURE 3.5**

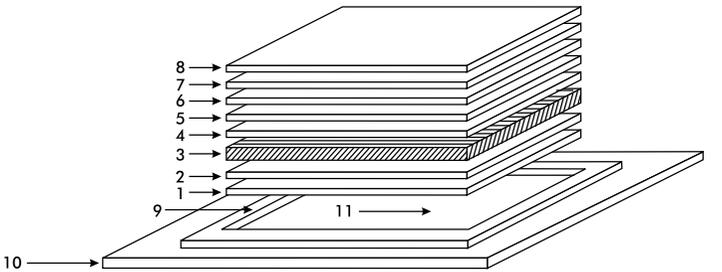
Cure cycle with premature vitrification. (From P. Hubert, University of British Columbia Composites Group Report, 1994. With permission.)

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 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 develop in the laminate upon cooling because of anisotropic thermal expansion, as discussed in Chapters 10 and 12.

### 3.1.1 Autoclave Molding

Figure 3.6 shows the vacuum bag lay-up sequence for a typical epoxy matrix prepreg composite. Different lay-up 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 lay-up 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.
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.

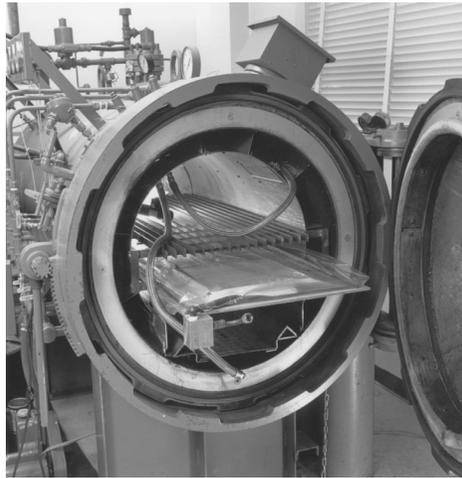


- |                                     |                                    |
|-------------------------------------|------------------------------------|
| 1. Teflon Film                      | 7. Teflon Film (holes every 50 mm) |
| 2. Peel Ply                         | 8. Vent Cloth                      |
| 3. Laminate (prepreg stack)         | 9. Cork or Rubber Dam              |
| 4. Peel Ply                         | 10. Aluminum Plate                 |
| 5. Teflon Coated Glass Fabric       | 11. Release Agent                  |
| 6. Glass Bleeders (1 per 3.5 plies) |                                    |

**FIGURE 3.6**

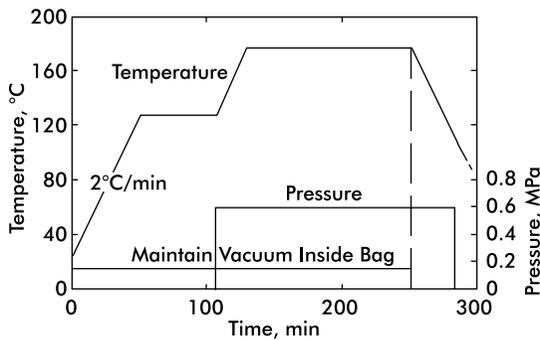
Vacuum bag preparation for autoclave cure of thermoset matrix composite.

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 lay-up 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) 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 lay-up. 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 achieves 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 3.7). 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 3.8). 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 3.8, the resin viscosity is at a minimum and pressure is applied to squeeze out excess resin. The



**FIGURE 3.7**

Vacuum bag sequence and tool plate placed in an autoclave.



**FIGURE 3.8**

Typical cure cycle for a carbon/epoxy prepreg.

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 is in its glassy state at the end of the cooling phase. 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.

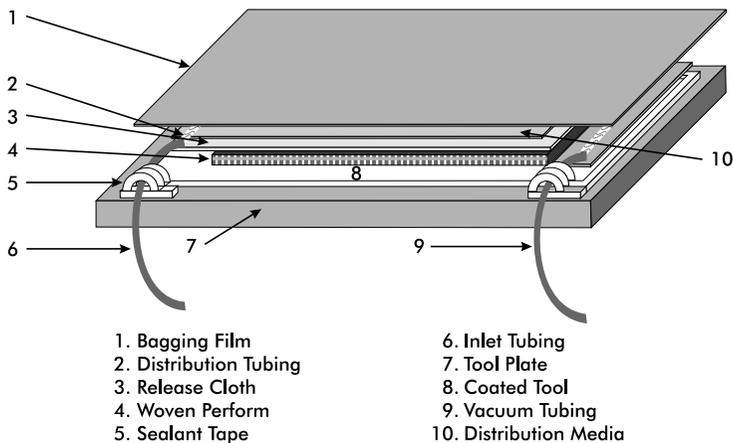
### 3.1.2 Resin Transfer Molding of Thermoset Composites

Resin transfer molding (RTM) 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 resin transfer molding process can be found in Reference [12]. 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 [12], 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, and the greater the permeability, the greater the flow rate. 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 than 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. 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. This step will begin immediately upon 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



**FIGURE 3.9**

VARTM process. (Courtesy of B. Grimsley, NASA Langley Research Center, 2001.)

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 [12].

### 3.1.2.1 Vacuum-Assisted Resin Transfer Molding (VARTM) Processing

Both open-mold approaches, where one surface is bagged with a flexible film, and closed-mold approaches to resin transfer molding are practiced. An example of open-mold RTM, vacuum-assisted resin transfer molding (VARTM) is a common method employed as an alternative to autoclave use. In VARTM, atmospheric pressure is utilized to achieve consolidation and impregnation by vacuum bagging the laminate in the same way as discussed in Section 3.1.1. 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 can be carried out in an oven while atmospheric pressure is maintained on the impregnated laminate.

The VARTM procedure for a representative flat  $61.0 \times 30.5 \times 0.64$  cm panel (Figure 3.9) is described in the following steps:

1. *Tool surface.* The tool is a flat aluminum plate with planar dimensions sufficient to accommodate the proposed composite panel. First, clean the metal tool surface using sandpaper and acetone. On the cleaned surface, create a  $71 \times 30.5$  cm picture frame using masking tape. Apply several coats of release agent to the metal surface inside of 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  $71 \times 30.5$  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 lay-up 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 silicon 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  $66 \times 30.5$  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 lay-up. The release film will allow the composite laminate to release from the distribution media. Cut a second piece of release cloth to  $5.1 \times 30.5$  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  $63.5 \times 28.0$  cm and stack them above the Armalon™ release cloth. Place the layers of media so that a 2.5-cm gap exists 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 lay-up.
6. *Distribution tubing.* Place a 28.0-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  $5 \times 30.5$  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

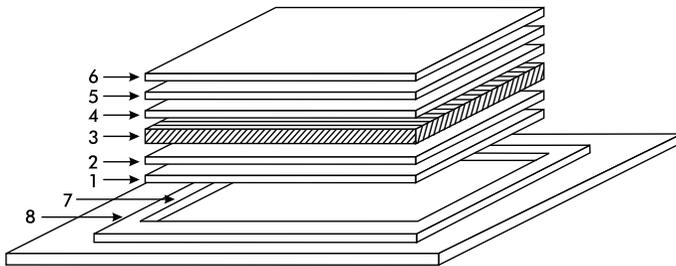
tubing using Kapton™ tape (E.I. duPont de Nemours and Co.). Embed the free end of the spiral tubing in a 2.5-cm-diameter roll of the silicone bagging tape, and then affix it to the strip of bagging tape forming the frame of the laminate.

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 of 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 mmHg using the vacuum pump. Leaks can be detected by using either a listening device or by clamping the vacuum line and using a vacuum gauge. 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 lay-up 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, place the vacuum-sealed part in an oven, and heat it according to a cure cycle prescribed by the resin supplier.

### 3.2 Autoclave Processing of Thermoplastic Composites

Thermoplastic composites may be processed in a high-temperature autoclave. Figure 3.10 shows the autoclave lay-up 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 lay-up 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. Kapton film coated with release agent on both sides | 5. Airweave breather plies (4) (high temperature capability) |
| 2. High temperature capability peel ply                | 6. High temperature bagging film (Kapton-no release)         |
| 3. Thermoplastic composite prelam stack                | 7. Tacky sealant tape (A800 G3 or equivalent)                |
| 4. High temperature capability peel ply                | 8. Tool plate  |

**FIGURE 3.10**

Vacuum bag preparation for autoclave processing of thermoplastic matrix composite.

1. Maintain a vacuum of 650 to 750 mmHg.
2. Apply a contact pressure of 0.5 MPa.
3. Simultaneously ramp the temperature as rapidly as possible to 390°C.
4. Apply a consolidation pressure of 1.4 MPa.
5. Hold the pressure at a temperature of 390°C for 5 min per 8 plies, but not for more than 30 min.
6. 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 ( $\approx 140^\circ\text{C}$ ).

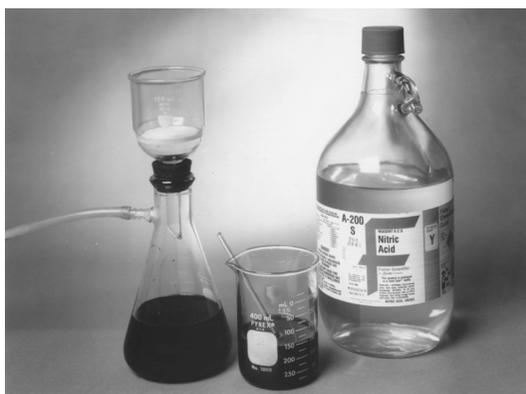
---

### 3.3 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, the burn-off technique, or by photomicrographic techniques. The matrix digestion method is standardized (ASTM D 3171 [13]) 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 or other digestion media (see ASTM D 3171 [13]). 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 D 2584 [14]) 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 to 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 is possible to obtain an image of the distribution of fibers and to detect voids.



**FIGURE 3.11**  
Acid digestion procedure.

### 3.3.1 Chemical Matrix Digestion Method

Equipment needed for this procedure (Figure 3.11) includes:

1. Fume hood with a vacuum system
2. Large flask which can be attached to the vacuum system
3. Buchner funnel with filter
4. A 400-ml beaker
5. Nitric acid
6. Glass stirring rod
7. Bunsen burner or electric heater
8. Desiccator
9. Precision balance
10. Rubber gloves and goggles

#### 3.3.1.1 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.

### 3.3.1.2 Calculation of Fiber Volume Fraction

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

$$V_f = \frac{\rho_m W_f}{\rho_f W_m + \rho_m W_f} \quad (3.1)$$

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 3.1 gives densities for some current fibers and matrix resins. Using the following densities in Table 3.1:  $\rho_f = 1.65 \text{ g/cm}^3$  and  $\rho_m = 1.265 \text{ g/cm}^3$ , Equation (3.1) gives  $V_f = 0.66$ .

**TABLE 3.1**

Fiber and Resin Properties

Fiber Type	Carbon AS4	Carbon IM6	E-Glass	Kevlar 49
Density	1.80	1.73	2.60	1.44
Matrix Type	Epoxy N5208	Epoxy 3501-6	K-Polymer	PEEK
Density	1.20	1.265	1.37	1.30 <sup>a</sup>

<sup>a</sup> 30% crystallinity.

### 3.3.1.3 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 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 D 2734 [15]. Void content requires an accurate measurement of the density of the composite

$$\rho_c = \frac{W}{V} \quad (3.2)$$

where  $W$  and  $V$  are the weight and volume of the composite, respectively. Methods for density measurements are presented in ASTM D 1505 [16] and D 3800 [17]. To obtain the void content, consider the following condition for the various volume fractions:

$$V_f + V_m + V_v = 1 \quad (3.3)$$

where subscripts  $f$ ,  $m$ , and  $v$  represent fiber, matrix, and voids, respectively. From Equation (3.3) an expression for the void content can be obtained

$$V_v = 1 - \frac{(W_f/\rho_f + W_m/\rho_m)\rho_c}{W} \quad (3.4)$$

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.

### 3.3.2 Photomicrographic Method

Equipment needed for this procedure includes:

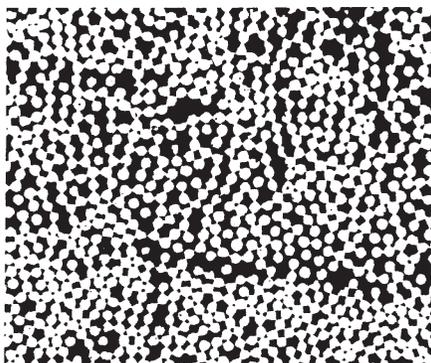
1. Polishing table
2. Specimen mounted (embedded) in a specimen holder [18]
3. Metallographic optical microscope (400×) with a camera

#### 3.3.2.1 Procedure

1. Cut the specimen perpendicular to the fiber direction to expose the desired cross section.
2. Place the specimen inside a mounting cup and pour a potting material (epoxy) into the cup [18]. 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 3.12) using the 5-, 1-, and, if necessary, use 0.3- $\mu\text{m}$  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.



**FIGURE 3.12**  
Polishing of the specimen embedded in mounting material.



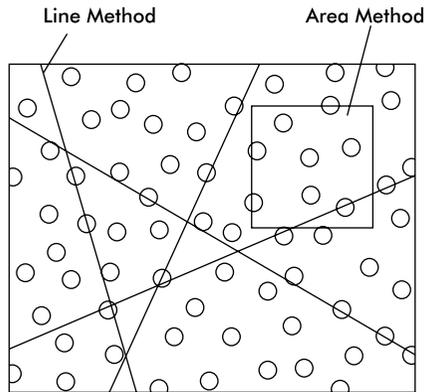
**FIGURE 3.13**  
Photomicrograph of a polished cross section. (Courtesy of S. Nilsson, FOI, Stockholm, Sweden.)

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 3.13](#).

### **3.3.2.2 Determination of Fiber Volume Fraction**

The fiber volume fraction can be determined from the photomicrograph in two ways, as illustrated in [Figure 3.14](#). 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

$$V_f = A_f/A \quad (3.5)$$



**FIGURE 3.14**  
Illustration of area and line methods.

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 3.14), 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.

For a cross section of the carbon/epoxy composite discussed in the previous section, the results shown in Table 3.2 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 smaller region of the composite which is studied in the micrograph and to uncertainty in determining the length of the fiber cross sections.

**TABLE 3.2**  
Determination of Fiber Volume Fraction  
with the Line Method

Line	$L_f$ (mm) <sup>a</sup>	$V_f$
1	44.5	0.58
2	40.8	0.54
3	54.9	0.72
4	45.3	0.60
5	48.3	0.63
6	48.1	0.63

<sup>a</sup>  $L_f$  = cumulative length of fiber cross sections.  
Total length of each line was 76.2 mm.

---

## References

1. W.I. Lee, A.C. Loos, and G.S. Springer, Heat of reaction, degree of cure, and viscosity of Hercules 3501-6 resin, *J. Compos. Mater.*, 16, 510–520, 1982.
2. A.C. Loos and G.S. Springer, Curing of epoxy matrix composites, *J. Compos. Mater.*, 17, 135–169, 1983.
3. J.L. Kardos, M.P. Dudukovic, E.L. McKague, and M.W. Lehman, Void formation and transport during composite laminate processing, *ASTM Spec. Tech. Publ.*, 797, 96–109, 1983.
4. S. Nilsson, L. Carlsson, and P. Bergmark, Influence of thickness on three-dimensional elastic properties of graphite/epoxy composites, *J. Reinf. Plast. Compos.*, 4, 383–395, 1985.
5. C.N. Velisaris and J.C. Seferis, Crystallization kinetics of polyetheretherkeytone (PEEK) matrices, *Polym. Sci. Eng.*, 26, 1574–1581, 1986.
6. R. Dave, J.L. Kardos, and M.P. Dudukovic, A model for resin flow during composite processing, *Polym. Compos.*, 8(1), 29–38, 1987.
7. M.R. Dusi, W.I. Lee, P.R. Ciriscioli, and G.S. Springer, Cure kinetics and viscosity of Fiberite 976 resin, *J. Compos. Mater.*, 21(3), 243–261, 1987.
8. M.V. Brusckke and S.G. Advani, A finite-element/control volume approach to mold filling in anisotropic porous media, *Polym. Compos.*, 11(6), 398–405, 1990.
9. L.A. Berglund and J.M. Kenny, Processing science for high performance thermoset composites, *SAMPE J.*, 27(2), 27–37, 1991.
10. T.A. Bogetti and J.W. Gillespie, Two-dimensional cure simulation of thick thermosetting composites, *J. Compos. Mater.*, 25(3), 239–273, 1991.
11. S.N. Lee, M.T. Chiu, and H.S. Lin, Kinetic model for the curing reaction of a tetraglycidyl diamino diphenyl methane/diamino diphenyl sulfone (TGDDM/DDS) epoxy resin system, *Polym. Eng. Sci.*, 32(15), 1037–1046, 1992.
12. S.G. Advani, *Flow and Rheology in Polymer Composites Manufacturing*, in the series, *Composite Materials*, R.B. Pipes, Ed., Elsevier, Amsterdam, 1994, pp. 465–511.
13. ASTM Standard D 3171-99, *Test Method for Constituent Content of Composite Materials*, American Society for Testing and Materials, West Conshohocken, PA, 2001.
14. ASTM Standard D 2584-94, *Test Method for Ignition Loss of Cured Reinforced Resins*, American Society for Testing and Materials, West Conshohocken, PA, 2001.
15. ASTM Standard D 2734-94, *Test Method for Void Content of Reinforced Plastics*, American Society for Testing and Materials, West Conshohocken, PA, 2001.
16. ASTM Standard D 1505-98, *Test Method for Density of Plastics by the Density-Gradient Technique*, American Society for Testing and Materials, West Conshohocken, PA, 2001.
17. ASTM Standard D 3800-99, *Test Method Standard Test Method for Density of High-Modulus Fibers*, American Society for Testing and Materials, West Conshohocken, PA, 2001.
18. *Buehler Sampl-Kup*, Buehler, Ltd., Evanston, IL.