

Long Fiber Thermoplastic Matrix Composites

1. INTRODUCTION

The techniques of autoclave, hand laminating, filament winding, pultrusion and liquid composite molding have been developed mainly using thermoset matrix composites. This does not mean that these techniques cannot be used for thermoplastic composites. An autoclave can be used to process thermoplastic composites provided that the temperature and pressure are high enough. Filament winding (or rather fiber placement process) can also be used and pultruded thermoplastic composites parts have also been made. Liquid composite molding can also be used provided that the viscosity of the resin is small enough. Recent development of low viscosity thermoplastic composites [1] facilitates this process.

The reason for a special chapter dedicated to discussion of thermoplastic composites is due to the high viscosity of the thermoplastic resin. This high viscosity demands the use of high temperature and high pressure to enable the resin to flow to the surface of the fibers, to wet and bond with them. This significance can be illustrated via the use of Darcy's law as:

$$u = \frac{K}{\mu} \frac{dp}{dx} \quad (8.1)$$

For the same fiber network, the permeability is the same, whether thermoset matrix or thermoplastic matrix is used. However, the viscosity of thermoset resin is about 500 cP at 20°C (Table 2.1, Chapter 2), whereas that of thermoplastic resin such as PEEK is 1,000,000 cp at 400°C. If the distance of flow dx is the same in both cases, then the pres-

sure required for processing PEEK at 400°C would be 2000 times more than that of the case of epoxy at 20°C. If a pressure of 689 kPa is required for the processing of epoxy at 20°C, then it would take a pressure of 1378 MPa to process PEEK at 400°C for the same processing time. This is not practical.

In the face of the above difficulties, it is desirable to find ways to manufacture thermoplastic matrix composites because they can offer many advantages, such as the following.

- a. Thermoplastic resin does not have the constraint of shelf life. To put it another way, thermoplastic composite preforms have infinite shelf life. This is because thermoplastic matrix solidifies upon cooling and there is no chemical reaction taking place to change its liquid state to solid state.
- b. Thermoplastic resins are more ductile than thermoset resins. Composites made of thermoplastic matrix composites therefore can have larger fracture toughness than those made of thermoset matrix composites. The strain energy release rate for carbon/epoxy is about 100 J/m² while that of carbon/PEEK is about 1000 J/m². This means that the thermoplastic matrix resin has large plastic deformation whereas thermoset matrix material does not. This is very important for structures that need to resist impact and fracture load.
- c. Thermoplastic resins can be recycled, i.e., they can be reheated to take a different form. This is also due to the same reason indicated above in which the material can be heated up to change the solid state to the melt state. At temperature close to the melt point, different shapes can be formed to make a new product. This behavior can also be used to heal the defects that may exist in the structure.
- d. The processing time can be fast. The heating and cooling of a thermoplastic composite material can take place within the order of minutes. This is in comparison with the order of hours for thermoset matrix material. The reason for the long processing time for the thermoset matrix resin is because of the time required for all the chemical bonds to take place. In the case of thermoplastic resin, cooling will solidify the material and this can take place very quickly.
- e. Thermoplastic matrix resin is weldable. This means that solid parts made of thermoplastic matrix composites may be welded together. For thermoset resins, because of the chemical bonding required for solidification, once the bond is formed, it cannot be used again to form another bond. The weldability of the thermoplastic resin en-

ables thermoplastic matrix composites to exhibit some degree of healing upon heating.

For the above reasons, special techniques need to be developed for thermoplastic composites manufacturing. The main focus of different strategies to handle thermoplastic matrix composites is to enhance the availability of the resin to the fiber surface. This can be seen in various approaches such as the formation of tapes, the use of fiber commingling, coating fibers with thermoplastic powder, and using fabrics with resin film sandwich. These techniques will be discussed in the subsequent sections of this chapter.

2. MATERIALS

As the name implies, thermoplastic matrix composites are materials made by the combination of fiber materials and thermoplastic matrix materials. Fibers are usually made of carbon, glass or Kevlar. Matrix materials can be made of engineering thermoplastic resins such as nylon, polypropylene or high performance thermoplastics such as polyetheretherketone (PEEK), polyetherketoneketone(PEKK), polyetherimide (PEI), polyphenylenesulfide (PPS) or polyethersulfone (PES). Table 8.1 (repeated from Table 2.6) shows the common high performance thermoplastic matrices along with their properties. A more comprehensive list of thermoplastic matrix that can be used to make composites can be found in Reference [2].

Among the semi-crystalline thermoplastic resins, PPS is the least expensive but has low fracture toughness. Both PEEK and PEKK have higher fracture toughness but have higher processing temperatures than PPS. PEEK has been used more than PEKK and has a larger database. PEKK has a lower processing temperature than PEEK and yet PEKK has a higher T_g and lower cost.

Cogswell [3] gave comprehensive information about the physical properties of PEEK. Table 8.2 shows the values.

Due to the high viscosity problem, the manufacturing strategies for thermoplastic matrix composites are different from those of thermosets. The objective of these strategies is mainly to compensate for this large viscosity and attempts to get the resin to the surface of the fibers and to wet the fibers.

The strategies of manufacturing using thermoplastic composites can be considered to consist of two stages. In the first stage, the preliminary material form is done, and in the final phase, the final product is made. At

TABLE 8.1 Commonly Used high Performance Thermoplastic Matrices (courtesy of CYTEC Engineered Materials).

	PEI	PPS	PEEK	PEKK (DS)
Morphology	Amorphous	Semi-crystalline	Semi-crystalline	Semi-crystalline
T_g (°C)	217	90	143	156
Process Temp (°C)	330	325	390	340
Comments: Pros	<ul style="list-style-type: none"> ✓ High T_g ✓ Moderate processing temperature 	<ul style="list-style-type: none"> ✓ Excellent environmental resistance ✓ Moderate processing temperature 	<ul style="list-style-type: none"> ✓ Extensive database ✓ Excellent environmental resistance ✓ High toughness 	<ul style="list-style-type: none"> ✓ Excellent environmental resistance ✓ High toughness ✓ Lower process temperature than PEEK ✓ Bonding and painting
Comments: Cons	<ul style="list-style-type: none"> ✓ Environmental resistance 	<ul style="list-style-type: none"> ✓ Low T_g ✓ Low toughness ✓ Low paint adhesion 	<ul style="list-style-type: none"> ✓ High process temperature ✓ High cost 	<ul style="list-style-type: none"> ✓ Limited database in composite form

TABLE 8.2 Physical Properties of PEEK [3].

	Resin	Composite	Resin in Composite
Cooling: crystallization temperature (°C)	300	294	
Cooling: latent heat (kJ/kg)	49	14	43
Heating: melting temperature (°C)	343	342	
Heating: Latent heat (kJ/kg)	44	12	39
Heat content at 400°C relative to 20°C (kJ/kg)		559	
Coefficient of thermal diffusivity across the fiber direction (cm ² /s)		3 × 10 ⁻³	
Coefficient of thermal diffusivity along the fiber direction (cm ² /s)		20 × 10 ⁻³	
Thermal expansion along fiber direction (10 ⁻⁶ /°C)		0.5 (23–143°C), 1.0 (143–343°C)	
Thermal expansion across fiber direction (10 ⁻⁶ /°C)		30 (23–143°C), 5 (143–343°C)	
Thermal expansion—quasi isotropic (10 ⁻⁶ /°C)		29 (23–143°C)	

the end of the preliminary phase, a preliminary combination of fiber and matrix is made. This combination can be in the form of a tape, fibers with clinging powder, reinforcing fibers commingled with filaments made from thermoplastic matrix, or fabric/film sandwich. Figure 8.1 shows the different preliminary material combinations (PMCs).

In the second (and final) stage, the preliminary material combinations (PMCs) are transformed into the final composite product. This transformation is usually done using either compression molding or by fiber placement process. Figure 8.2 shows the two processes as applicable to different material combinations.

3. PRELIMINARY MATERIAL COMBINATIONS (PMCs)

In the PMC, it is essential for the matrix to be in the vicinity of the fibers. This is important to reduce the time and pressure required to get the matrix to get to the fibers during the final product fabrication. Some of the approaches used will be discussed below.

3.1. Tape

A tape consists of unidirectional filaments bonded together by the ma-

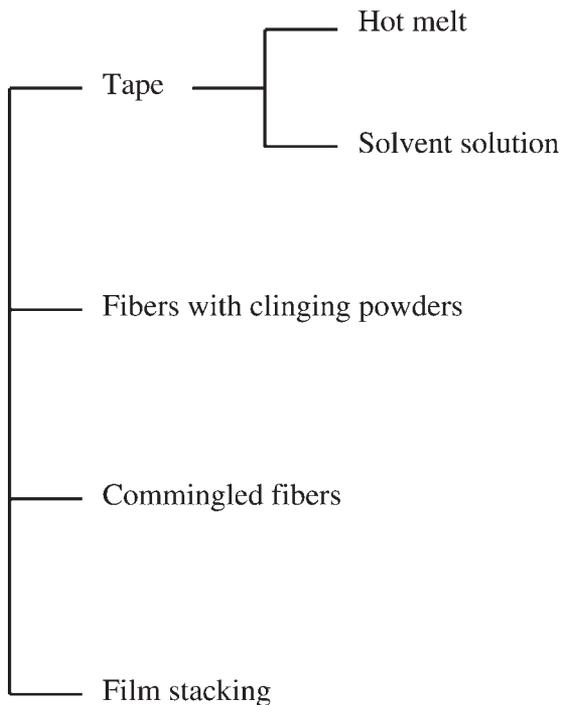


FIGURE 8.1 Preliminary material combinations (PMCs).

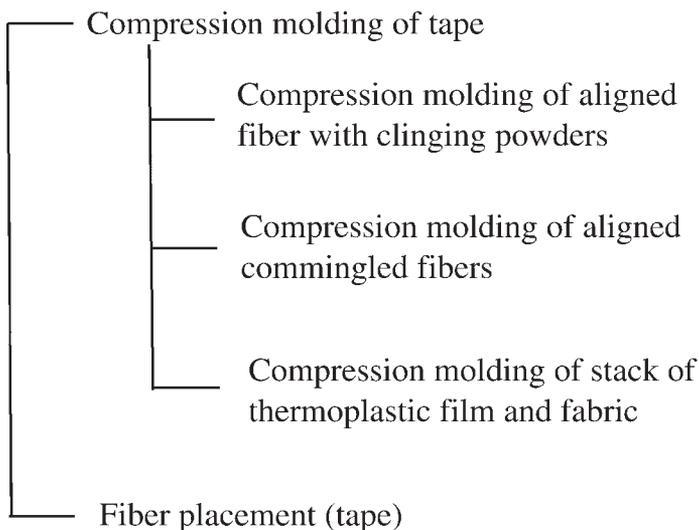


FIGURE 8.2 Processing the simple form into the final part.

trix resin. Resin needs to exist in liquid form to wet the fibers. This can be done by heating and melting the resin and running the fibers through the bath of liquid resin. Hot melt processes are probably most common. In the hot melt process, the matrix is heated until melting. Its viscosity should become low enough such that flow to the surface of the fiber is possible and wetting can take place. Figure 8.3 shows a schematic of the fibers running through a melt of resin. This can also be done by dissolving the matrix in a solvent and running the fibers through a bath of the solution. Solution processes are well established for thermosetting prepolymers. This process is used by Dupont to produce prepreg of Avimid K-III, a thermoplastic polyimide. The prepreg contains a substantial amount of residual solvent and must be cured. Therefore the production of Avimid K-III composite structures must be conducted in a manner similar to thermosetting composites. The complication in this technique is that solvent needs to be subsequently evaporated, which may give rise to voids and residual solvents.

Unidirectional tape is the most common form of thermoplastic ply. By convention, the tape is 0.127–0.152 mm (5–6 mils) and 7.62–30.48 cm (3–12 in) wide. To produce a 30.48 cm wide tape requires approximately 24 tows with 12,000 filaments each of 8 μm diameter to the combining process. Conversely, wide tape can be filament wound from a single tow using a large diameter mandrel. This latter approach is convenient for experimental ply production but may not be appropriate for low cost fabrication. Conversely, filament winding towpreg directly to produce a consolidated structure is potentially low in cost. This is due to process integration. Fabric plies are difficult to produce from thermoplastic towpreg due to the stiffness of most towpregs. Consolidated towpreg, typically from slit tape, can be braided into two dimensional fabrics, but

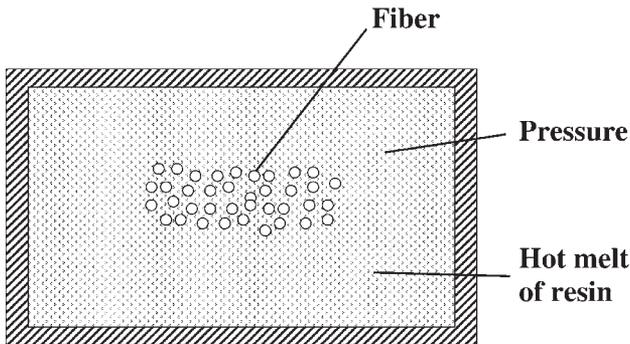


FIGURE 8.3 Impregnation of fibers by running fibers through a bath of melted resin.



FIGURE 8.4 Photo of a roll of unidirectional tape made of carbon/PEKK.

three dimensional fabrics are difficult to produce. Figure 8.4 shows a photograph of a roll of tape.

The speed of production of the hot melt process (meters per minute) depends on the viscosity of the melt, the thickness of the prepregs to be made and the applied pressure. Darcy's law can be used to estimate the rate of production as illustrated in the example below.

Example 8.1

A hot melt process is used to produce prepregs for carbon/PEEK 0.2 mm thick. The temperature of the process is 380°C giving rise to the viscosity of the resin of 1000 Pa(sec). A pressure of 1 MPa is applied to induce the flow across the thickness of the prepreg. Determine the maximum rate of production, if the length of the die is 50 cm and the permeability of the fiber preform is assumed to be 10^{-12} m².

Solution

The fastest rate of production occurs when the resin has sufficient time to flow across the thickness of the layer. Using Darcy's law, one has:

$$u = -\frac{K}{\mu} \frac{\Delta p}{\Delta x}$$

where,

u = the flow velocity across the thickness of the prepreg

K = the permeability of the fiber preform

Δp = the pressure gradient across the thickness of the prepreg

Δx = thickness of the laminate

Substituting in the values yields:

$$u = \frac{10^{-12} \text{ m}^2}{1000 \text{ Pa} \cdot \text{sec}} \frac{1 \text{ MPa}}{0.2 \text{ mm}} = 5 \times 10^{-3} \text{ mm / sec}$$

Time required to traverse the thickness of the preform:

$$t = \frac{h}{u} = \frac{0.2 \text{ mm}}{5 \times 10^{-3} \text{ mm / sec}} = 40 \text{ sec.}$$

For the length of the die of 50 cm, the maximum rate of production R would be:

$$R = \frac{L}{t} = \frac{50 \text{ cm}}{40 \text{ sec}} = 1.25 \text{ cm / sec} \quad \text{or} \quad 1.25 \text{ cm / sec}$$

3.2. Fibers with Clinging Powders

In the powder clinging process, the matrix powder is made to stick to the surface of the fibers. Figure 8.5 shows a schematic of the process. First, the dry fiber tow is fed from a creel to an air-conditioned spreader. The tow is spread to expose the fiber and grounded in order to pick up charge powder. By spreading a tow to expose virtually every fiber, it is easier to get the liquid resin to the surface of every fiber and it takes less pressure to force a polymer melt through a fiber bed. The fiber tow then enters into a heated chamber where matrix powder is electrified such that it carries an electrical charge, then it is fluidized. The powder is deposited on the band of fibers due to static electricity. At the next station of the

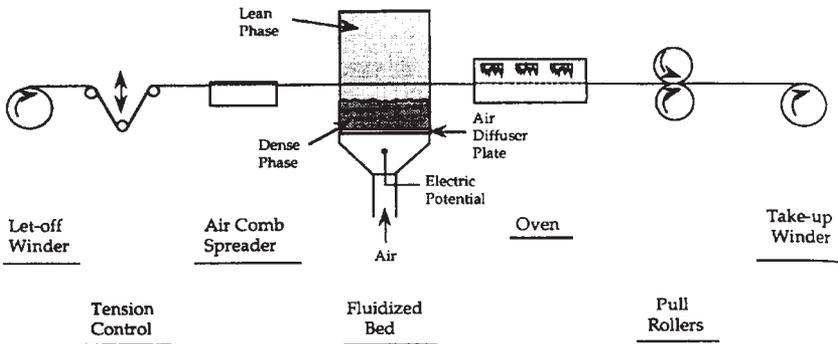


FIGURE 8.5 Process to get matrix powders to cling to fibers (reproduced from “The processing science of thermoplastic composites,” by J. D. Muzzy and J. S. Colton, in *Advanced Composites Manufacturing*, T. G. Gutowski, ed., with permission from Wiley Interscience).

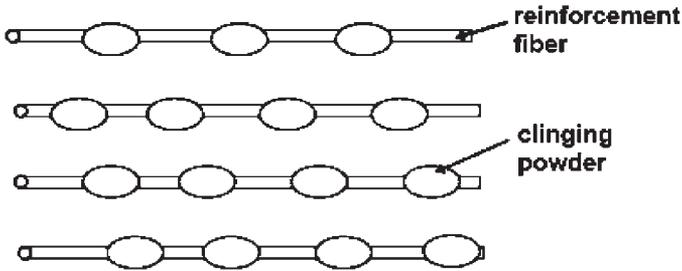


FIGURE 8.6 Fibers with clinging powders.

process, the material is heated. The resin melts, flows and then wets the fibers. After cooling, the powder is fused into the fibers. After passing through a fluidized bed, the tows enter a tunnel oven to melt the polymer onto the fiber. After cooling, the towpreg is wound onto a take-up roll.

There are advantages to the powder mixing process. By avoiding solvent or water in the combining operation, there is no need to remove volatiles. The extent of mixing between fiber and powder depends upon the extent to which the tow is spread. It is possible to spread the tow to expose virtually every fiber, thereby achieving good mixing. Spreading the tow and not collapsing it when the polymer is molten leads to a flexible tow that can be braided or woven. The coated tow can be heated and cooled rapidly to minimize polymer degradation. The tow is not exposed to high stress, which minimizes fiber damage. Since powder coating can be accomplished quickly and continuously, dry powder combining process is potentially inexpensive.

The production of towpregs using the electrostatic fluidized bed process has been demonstrated using numerous thermoplastics and thermosets as well as carbon, glass and aramid fibers. Good fiber wetting was obtained even when the particle size of the powder was substantially greater than the $8\ \mu\text{m}$ fiber diameter. In a commercial scale version of this process a line speed of $40\ \text{cm/s}$ has been achieved while attaining 40% vol polymer content. Figure 8.6 shows a schematic of the fibers with clinging powders.

3.2.1. Slurry and Foam

The above approaches appear to work particularly well for fine powders below $25\ \mu\text{m}$. Electrostatic cloud coating has worked successfully for powder well over $100\ \mu\text{m}$. Since many polymers are difficult to grind, the ability to accommodate large particles is a definite benefit. Slurries and foams are being explored as alternative combining methods.

3.3. Commingling/Bundling and Microbraiding

As long as the thermoplastic matrix can be spun into fiber form, it is possible to combine the thermoplastic matrix and reinforcing fibers by commingling (Figure 8.7). Wetting of the fiber in this case is deferred until the composite is consolidated. This approach leads to flexible preforms since the independence of the structural elements is maintained until the preform is consolidated. Because the matrix filament has not wetted out the reinforcing fiber until consolidation, more effort is required to complete consolidation compared to preconsolidated prepreg.

Another way of bundling the matrix filament together with the reinforcing fibers is to microbraid the matrix filaments with the reinforcing (Figure 8.8).

3.4. Fabric/Film Sandwich

Film stacking with dry fiber or commingled slit film and dry fiber are examples of combining processes where wetting is deferred until consol-

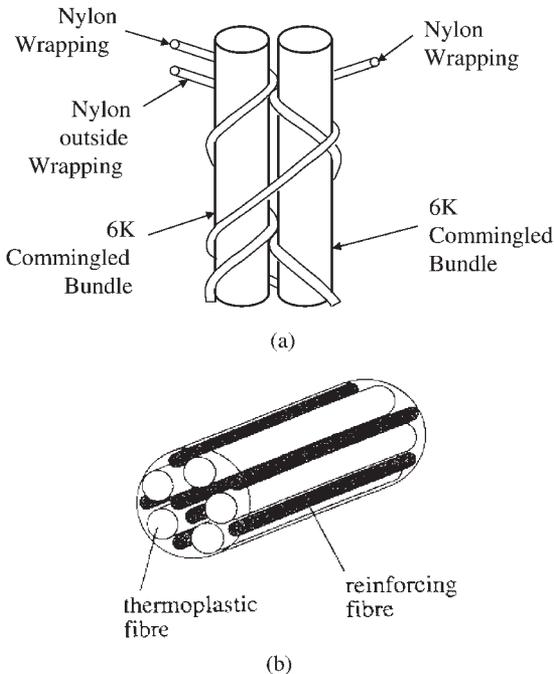


FIGURE 8.7 Commingling matrix filaments with reinforcing fibers.

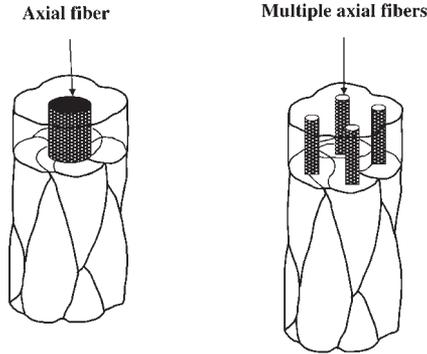


FIGURE 8.8 Microbraiding of matrix filaments with reinforcing fibers. The left shows one single reinforcement fiber tow at the center surrounded by matrix filaments. The right shows four reinforcement tows surrounded by matrix filaments (adapted from Reference [4], with permission from Canadian Association for Composite Structures and Materials).

idation (Figure 8.9). These options are less expensive than commingled fibers, but the degree of physical mixing is not as good as with commingled fibers.

3.5. Surface Polymerization

Surface polymerization of the polymer on the fiber consists of electro-polymerization on graphite fibers or vapor deposition polymeriza-

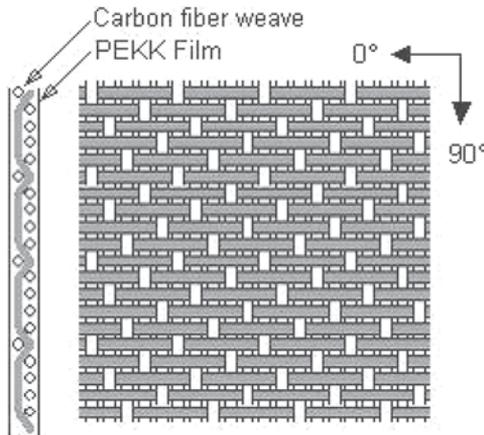


FIGURE 8.9 Fabric/film sandwich.

tion of paraxylene on graphite fibers, analogous to chemical vapor deposition. These approaches can produce individually coated fibers, hence the prepreg can have virtually the same flexibility as commingled fibers as well as complete fiber wetting.

4. FABRICATION OF THE FINAL PRODUCT

The transformation of the preliminary material combinations into the final thermoplastic composite product is mostly done using compression molding, and to a certain extent, fiber placement process.

4.1. Compression Molding

All of the PMCs (tape, tows with clinging powder, commingled tows, microbraided tows, tows with surface polymerization, or fabric/film sandwich) can be stacked up and compression molded to make the final composite product. The form of the PMC depends on the complexity of the configuration of the final product.

Thermoplastic tapes do not have sufficient drape and tack at room temperature to permit lay-up of complex shapes. Normally, flat pieces are made if tapes are to be used. Since cold thermoplastic tapes lack tack, they must be spot welded to the ply immediately below the ply being laid down. Either heat gun or ultrasonic gun is normally used for this task.

Tows with commingled matrix filaments, microbraided tows, tows with surface polymerization, or fabric/film sandwiches are more flexible than tapes and they can be arranged to make shapes other than flat plates. However, since the fibers in these configurations are not well constrained, alignment and tension need to be applied to the tows to assure proper fiber orientation control. For example, Figure 8.10 shows the ar-



FIGURE 8.10 Springs are used to align and tension commingled fiber tows.

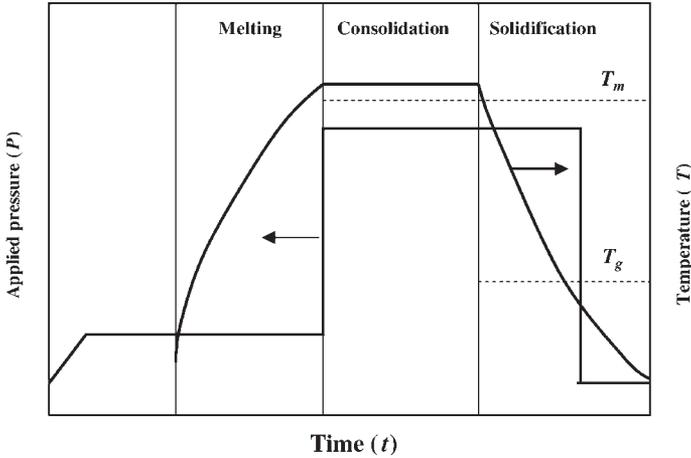


FIGURE 8.11 Heating and pressurizing cycles.

rangement where tension springs are used to tighten the commingled tows before being placed inside a compression molding press to make a flat plate.

Commingled tows, microbraided tows or tows with clinging powder can also be woven into fabrics, or braided into preforms before molding.

Subsequent to the preliminary assembly, the assembly of the dry fibers is placed in a compression molding machine for final molding. The molding parameters consist of application of heat and pressure for a certain amount of time. The general schedule for this application is shown in Figure 8.11, where the temperature needs to be increased before the pressure is applied. This allows the resin to be liquefied and to flow through the interstices to wet the fibers before the liquid resin is squeezed out for its minimization. The pressure is also maintained after the temperature is reduced from the maximum temperature. This prevents the fiber network from springing back before the resin solidifies.

There are two distinct approaches to making shapes from thermoplastic composite materials: preimpregnate the fibers with the resin and then mold into shape, or arrange the reinforcement and resin together in the mold and then consolidate and impregnate simultaneously.

- *Impregnation after shaping.* In film stacking technology, layers of reinforcement fiber are interleaved with layers of film and the whole is consolidated into simple shapes. The principal advantage of this approach, especially for drapable products such as co-woven or hybridized fiber is the potential for forming a

complex shape by hand and subsequently consolidating. The most obvious disadvantage of this approach is that it requires a relatively protracted molding cycle in order to carry out the impregnation stage and that impregnation stage contributes to product quality in two ways: by defining the microstructure of the molding, and by establishing the interface between the resin and the fiber on which the service properties of the composite depend.

- *Preimpregnated product forms.* Each product form has its own particular advantages: impregnated woven fabrics are most appropriate for thin skinned structures; woven single tow tapes, including tied uniaxial materials, offer modest drapability and can be made as very broad products. Uniaxial tapes are the most versatile product especially suitable for designing anisotropic composites.

Table 8.3 shows a comparison of strengths of samples made from the two types of products. It appears that the products relying on a post impregnation technology do not generate the full potential strength of the fiber reinforcement. Cogswell [3] attributed this difference to fiber attrition during the molding impregnation stage where the forces necessary to squeeze the resin into the spaces between the fibers also force the fibers together. By contrast, in preimpregnated products each fiber is lubricated by a protective coating of viscous polymer.

4.1.1. Heat Transfer-Melting

As discussed in Chapter 1, in order to make a composite, the resin has to wet the fibers. To do this, the resin has to have low viscosity (in liquid

TABLE 8.3 Properties as a Function of Impregnation Route [3].

	Axial Flexural Strength (MPa)	Short Beam Shear Strength (MPa)	Impact Energy 2 mm Sheet (J)
Preimpregnated products			
Cross plied uniaxial	907	76	23
Woven single tow	929	68	23
Woven fabric	1052	80	29
Impregnation after shaping			
Co-woven fibers	782	60	13
Film stacked	680	67	9
Powder coated fabric	545	54	

form). For PMC in the form of tapes, the resin has already wetted the fibers. As such the need for the resin to be liquid during the final fabrication stage is not essential as far as fiber wetting is concerned (liquefaction is still necessary to fill up all empty space inside the material to prevent voids).

For PMC in other forms, melting of the resin is necessary to wet the fibers. In order to determine the temperature and the energy required for melting the resin, differential scanning calorimeter (DSC) tests can be used. Figure 8.12 shows the DSC curve for amorphous PEEK. Figure 8.13 shows a typical DSC scan for a thermoplastic composite (PEKK).

The DSC curve contains a few features.

- First the ordinate shows the energy, positive is up and negative is down. Negative (endothermic) means that energy is entered into the material system, and positive (exothermic) means energy is released from the system. Along the curve, the positive and negative peaks can be interpreted along this way.
- Figure 8.13 contains two curves. The lower curve represents the heating and the upper curve represents the subsequent cooling.

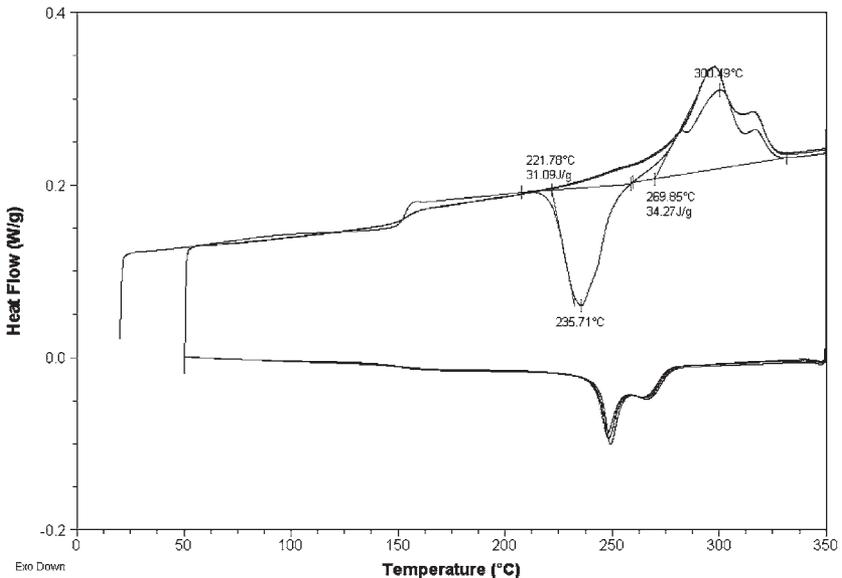


FIGURE 8.12 DSC curve for PEEK (DS) resin.

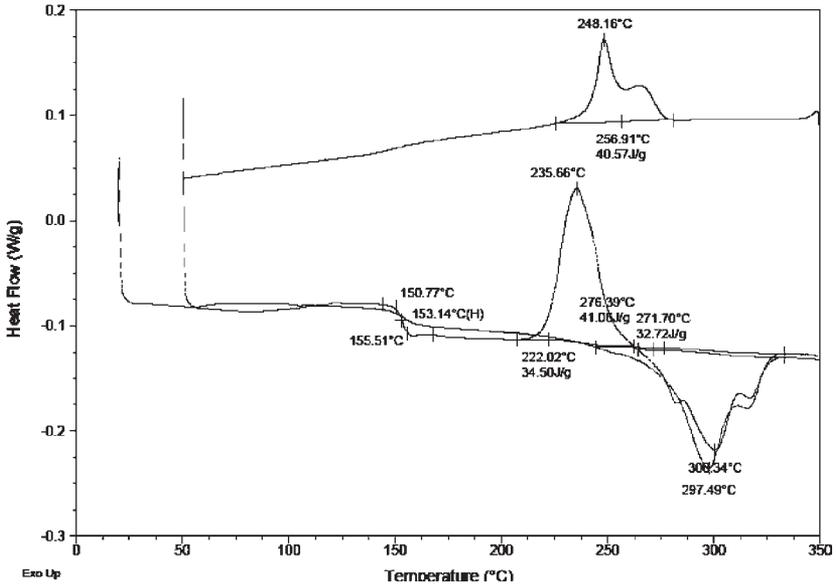


FIGURE 8.13 Typical DSC scan for carbon/PEKK composite.

- For the heating curve, as the temperature of the test is increased, there is some change in the slope of the curve indicating that energy is needed to be entered into the system to increase the temperature of the material. This is due to the heat capacity of the material according to the equation: $Q = mC_p\Delta T$ where m is the mass of the material, C_p is the heat capacity of the material and ΔT is the temperature change.
- There is a jump in the curve and a change in the slope of the curve at about 150°C. This change indicates a change in microstructure of the materials. The jump indicates that additional energy was entered into the system to make the change. The change in slope indicates that the heat capacity of the material has changed at that temperature. This temperature is called the glass transition temperature T_g , because upon heating past that temperature, the material changes from a glassy state to a viscous state. Each of these states has a different heat capacity. In this case, the glass transition temperature is determined to be 153°C. The material becomes soft above the glass transition temperature, and it is usually recommended to use the material at a temperature of about $T_g - 30^\circ\text{C}$.

- There is an exothermic peak beginning at about 222°C. Heat is coming out of the system. The reason for this emission of heat is due to crystallization of the material. When a material is crystallized, its microstructure becomes ordered. Some segments of the molecular structures of the thermoplastic polymer are ordered. Figure 8.14 shows the partially ordered molecular configuration. Ordering of the structure requires some degree of connection, similar to chemical bonding discussed in Chapter 2. When a bond or some arrangement is formed, heat is coming out of the system and we have an exothermic situation. The area under the curve corresponds to the heat of crystallization.
- There is an endothermic peak at about 300°C. This corresponds to the heat of melting. Energy is required to enter into the system to break the bonds between the molecules for melting to occur.
- The upper part of the curve represents the cooling of the sample after first heating. There is an exothermic peak at 245°C, which indicates that the material crystallizes around this temperature. Slow cooling facilitates crystallization.

It is noted that crystallization occurs during both heating and cooling. The reason for crystallization to occur during heating is because when the molecules are loose, they can be rearranged when the temperature is not too high. In order to bring the temperature of the material to the melting range, heat is normally used and conduction is the normal process for heat transfer.

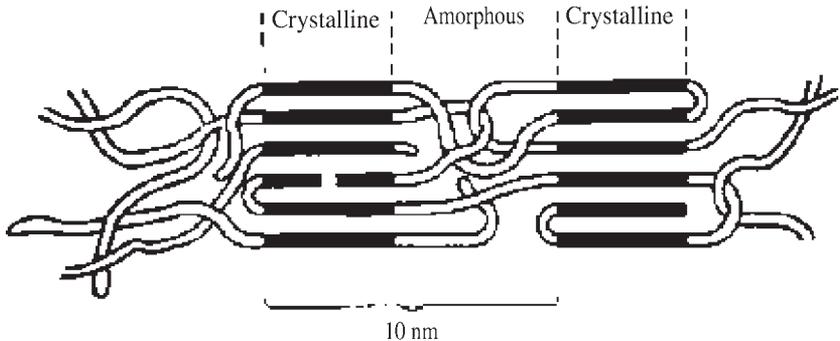


FIGURE 8.14 Configuration of partially ordered molecule.

4.1.1.1. Heat Transfer During Molding

Heat transfer is perhaps the most critical parameter in the processing of thermoplastic composites. Temperature distribution affects the quality and microstructure of the product in that flow, compaction, melting, and crystallization are thermally controlled processes.

Before consolidation, thermoplastic composites must be heated in order to melt the matrix resin and bond the surfaces. If the composite does not contain volatiles and solvents in its matrix, then rapid heating is preferred for short processing cycles. Several methods can be used to melt thermoplastic rapidly. Hot shoes, infrared heating, and focused laser heating are preferred in processes such as filament winding. Because of the high energy flux of a laser, the exposed surface can be melted in a few seconds, but it can be overheated and degraded if accurate control devices are not used. Resistance heating that utilizes the conductivity of carbon fibers, infrared radiation heating, and conduction heating by contacting hot rollers and shoes can be used to provide an adequate melting level for processing the composite.

The equation governing the heat transfer in a composite can be written as:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(K_{xx} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial T}{\partial z} \right) + H \quad (8.2)$$

where,

- ρ = the density of the composite material
- C_p = the specific heat of the composite material
- T = the temperature
- t = the time
- K_{ii} = coefficients of thermal conductivity
- H = the heat source

For the vast majority of commercial thermoplastic materials, no chemical reaction is involved during processing. Assume that the total heat of crystallization (H) of the polymer is negligible when compared to the heat energy released by the heating platens. Also assume that heat loss or gain through the thickness of the composite by convection and radiation is small since the thickness is much less than the length and width of the composite laminate. This reduces the problem to that of a one-dimensional heat conduction problem across the thickness of the composite as:

$$K_z \frac{\partial^2 T}{\partial z^2} = \rho C_p \frac{\partial T}{\partial t} \quad (8.3)$$

or

$$\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (8.4)$$

where

K_z = the heat conductivity along the thickness direction of the composite

ρ = the density of the composite

C_p = the heat capacity

α = heat diffusivity ($= K/\rho C_p$)

T = the temperature

t = the time

The thermal properties of PEEK and carbon fiber are shown in Table 8.4 [1]. Because heat is assumed to be conducted perpendicularly across the fibers, the value for transverse heat conductivity is shown. The axial conductivity is approximately 10 times as great as the transverse conductivity.

Thermal properties of the composite are obtained by averaging the values for the neat resin and carbon fiber as:

$$\frac{1}{K_c} = \frac{V_f}{K_f} + \frac{V_m}{K_m} \quad (8.5)$$

where

K_c = the thermal conductivity of the composite.

K_f = the thermal conductivity of the fiber.

K_m = the thermal conductivity of the matrix.

V_f, V_m = volume fraction of the fiber and matrix, respectively.

Similarly, the heat capacity of a composite can be obtained by mass averaged heat capacity of the matrix and fiber, as:

$$C_{pc} = C_{pf} m_f + C_{pm} m_m + C_{pf} m_f + C_{pm} (1 - m_f) \quad (8.6)$$

where

C_{pc} = the heat capacity of the composite.

C_{pm} = the heat capacity of the matrix.

C_{pf} = the heat capacity of the fiber.

m_f, m_m = mass fraction of the fiber and matrix, respectively.

TABLE 8.4 Physical Properties of PEEK, Carbon Fiber (transverse) and APC2 [1].

Material	Density (g/cm ³)	Resin Weight (%)	Resin (vol.%)	Heat Capacity J/(g·K)	Thermal Conductivity J/(m·K·s)	Thermal Diffusivity cm ² /sec
PEEK	1.26	100	100	1.339	0.251	1.49×10^{-3}
Carbon fiber (transverse)	1.79			1.255	0.427	1.9×10^{-3}
APC2	1.53	40	48	1.297	0.318	1.60×10^{-3}

Assuming a void-free composite, the density of a composite can be derived as the volume average of the respective densities of the matrix and fiber, as:

$$\rho_c = \rho_f V_f + \rho_m (1 - V_f) \quad (8.7)$$

where ρ_c , ρ_f , ρ_m are density of composite, fiber, and matrix, respectively.

Finally, the thermal diffusivity of the composite can be calculated from the heat conductivity, heat capacity and density of the composite as:

$$\alpha_c = \frac{K_c}{\rho_c C_{pc}} \quad (8.8)$$

Consider the case that a flat plate of composite is to be made. Both faces of the fiber beds are in contact with the surfaces of the mold. It is reasonable to assume that the temperatures at both surfaces of the sample are the same at all times. This can be considered as the case of a plate of thickness $2L$ with initial temperature T_o and is subject to a surface temperature of T_∞ for time $t > 0$. Figure 8.15 shows the schematic of the arrangement.

The temperature as a function of time and position for the situation where the plate's surfaces are heated at a constant rate, and the origin is

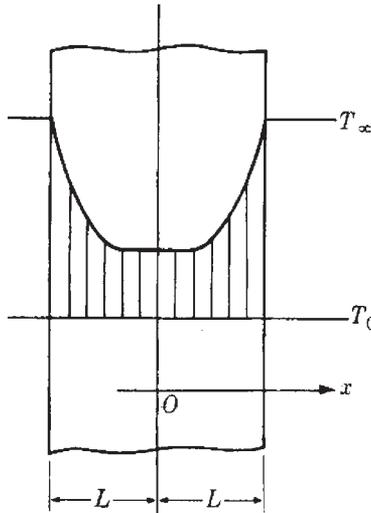


FIGURE 8.15 Schematic for the heat transfer of a flat plate.

defined at the lower surface of the plate with thickness $2L$ can be written as [5]

$$\frac{T(x,t) - T_{\infty}}{T_o - T_{\infty}} = 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left(-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right) \cos\left(\frac{(2n+1)\pi x}{2L}\right) \quad (8.9)$$

Equation (8.5) can be rearranged to be:

$$T(x,t) = T_{\infty} + 4(T_o - T_{\infty}) \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left(-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right) \cos\left(\frac{(2n+1)\pi x}{2L}\right) \quad (8.10)$$

In a situation where the temperature of the surrounding environment is a function of time, for example, the case where the surrounding liquid is being cooled, T_{∞} can be replaced by this temperature. For the case where $T_{\infty} = T_o + Kt$ where K is the heating rate, Equation (8.10) can be written as:

$$T(x,t) = T_o + Kt - 4Kt \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left(-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right) \cos\left(\frac{(2n+1)\pi x}{2L}\right)$$

or

$$T(x,t) = T_o - Kt \left\{ 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left[-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right] \cos\left[\frac{(2n+1)\pi x}{2L}\right] + 1 \right\} \quad (8.11)$$

where

K = heating rate ($^{\circ}\text{C/s}$)

L = plate half thickness (cm)

t = time (s)

T = temperature ($^{\circ}\text{C}$)

T_i = initial temperature ($^{\circ}\text{C}$)

x = position along the thickness direction (cm)

α = thermal diffusivity (cm^2/s)

At the center of the plate, $x = 0$ and the above equation simplifies to:

$$T(x, t) = T_o + Kt \left\{ 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp \left[-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2} \right] + 1 \right\} \quad (8.12)$$

The value of the thermal diffusivity of thermoplastic composites is about $1.5 \times 10^{-3} \text{ cm}^2/\text{sec}$ (Table 8.4). Figure 8.16 shows the variation of temperature as a function of space and time. Figure 8.17 shows the variation over time of the temperature at the center of the plate, for different laminate thicknesses.

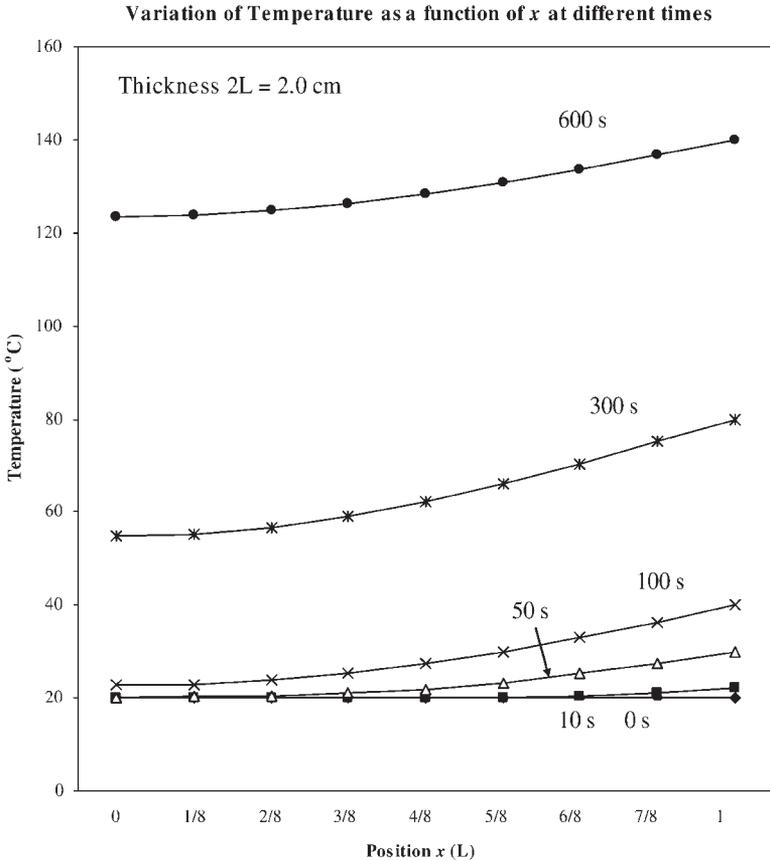


FIGURE 8.16 Variation of temperature as a function of space and time, ($T_i = 20^\circ\text{C}$, $K = 0.2^\circ\text{C}/\text{second}$, $\alpha = 1.5 \times 10^{-3} \text{ cm}^2/\text{sec}$).

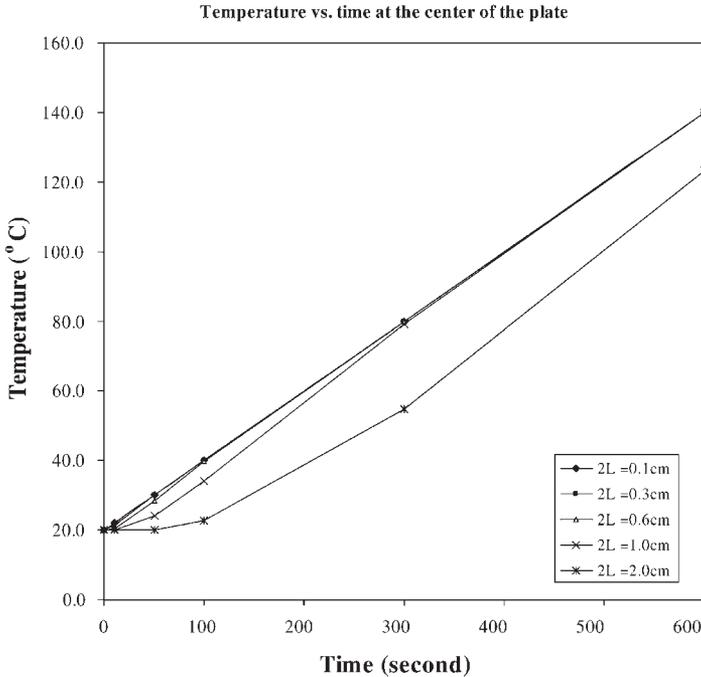


FIGURE 8.17 Variation versus time of temperature at the center of the plate for different plate thicknesses ($T_i = 20^\circ\text{C}$, $K = 0.2^\circ\text{C/second}$, $\alpha = 1.5 \times 10^{-3} \text{ cm}^2/\text{sec}$).

For thin plates, it is reasonable to assume that the temperature in the plate is independent of the space variable and the temperature can be expressed as:

$$T = T_i + Kt \quad (8.13)$$

It can be seen from Figure 8.17 that as the plate becomes thinner, the curve approaches the relation shown in Equation (8.13).

4.1.2. Bulk Consolidation

The consolidation of the fiber beds can be considered to consist of eliminating the empty space between the layers and eliminating the waviness of the fibers. Bulk consolidation is the phenomenon during which the individual layers in the plate are brought into intimate contact and the free space inside the composite is eliminated. The mechanism of bulk consolidation is different for each type of PCM. For tapes, the PCM is al-

ready fully impregnated, and during consolidation, spatial gaps only occur between plies because their surfaces are rough or uneven. An equation that can be used to model the bulk consolidation and analyze experimental data is:

$$P = B_y \ln \left(\frac{h_f}{h_i} \right) \quad (8.14)$$

where,

P = applied pressure

B_y = bulk modulus

h_i = composite height at beginning of resin permeation

h_o = final composite thickness

The range of bulk consolidation modulus was determined to be from approximately 1.21–8.58 MPa for APC2. The values depend on the number of layers, pressure, and temperature. The bulk consolidation of flexible towpregs is different from tapes. First, a flexible towpreg is not perfectly impregnated with the matrix. The flexibility of the towpreg makes intimate contact between the prepregs easy and immediate. Even though intimate contact is accomplished in this towpreg, the incomplete impregnation of the matrix plays a major role in bulk consolidation. Therefore, the bulk consolidation of flexible towpregs needs to include resin impregnation rather than intimate contact and can be explained by the resin flow model. One might say that bulk consolidation is the key concern when processing flexible towpregs and commingled tows.

During consolidation of the composite, the applied pressure decreases the thickness of the composite. Heat is applied, either simultaneously with the increase in pressure or shortly after bulk consolidation, to melt the resin. Resin melts and flows within the fiber network while consolidation continues through the second stage where fibers are straightened. Figure 8.18 illustrates the decrease in thickness as a function of consolidated time and indicates that several phenomena occur.

When the pressure is applied at the onset of consolidation, it is concentrated on developing intimate contact between the plies. Figure 8.19(a) shows the consolidation of a number of layers of a composite. Figure 8.19(b) shows the definition of A_{ic} (the blackened region) and how it increases as consolidation progresses. As consolidation continues, complete intimate contact is developed and A_{ic} approaches A_T . Eventually the resin is squeezed out of the plies and the fiber network carries a larger portion of the pressure.

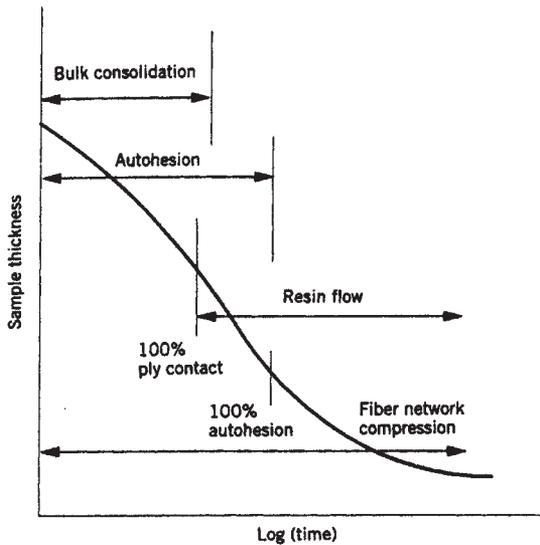


FIGURE 8.18 Decrease in thickness of a composite during consolidation (reproduced from “The processing science of thermoplastic composites,” by J. D. Muzzy and J. S. Colton, in *Advanced Composites Manufacturing*, T.G. Gutowski ed., with permission from Wiley Interscience).

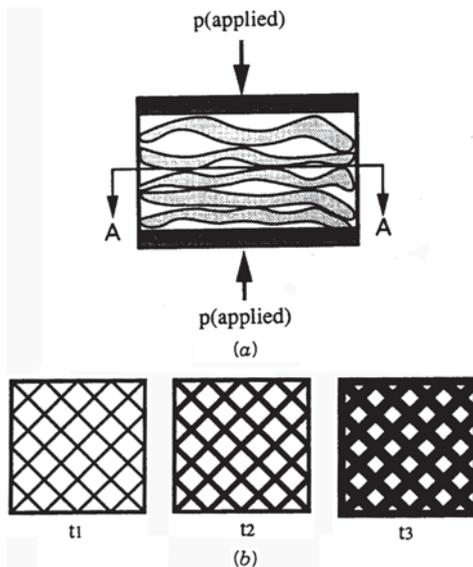


FIGURE 8.19 Different stages of fiber contact during compression (reproduced from “The processing science of thermoplastic composites,” by J. D. Muzzy and J. S. Colton, in *Advanced Composites Manufacturing* T.G. Gutowski ed., with permission from Wiley Interscience).

4.1.2.1. Elasticity of Fiber Networks

During consolidation, the fiber volume fraction increases and the fiber network begins to take up an increasing amount of applied load. In the extreme case, the fiber network carries all the load and the resin pressure drops to zero. Therefore, the elastic behavior of the network must be taken into account for a correct prediction of consolidation. The relation between the compression pressure and volume fraction was presented in Chapter 3, repeated here as:

$$\sigma = \frac{3\pi E}{\beta^4} \frac{1 - \sqrt{\frac{V_f}{V_o}}}{\left(\sqrt{\frac{V_a}{V_f}} - 1\right)^4} \quad (8.15)$$

where

E = Young's modulus of the fiber.

β = the geometric parameter (= L/a in Figure 3.19).

V_a, V_o, V_f = maximum allowable fiber volume fraction, initial fiber volume fraction, and current fiber volume fraction, respectively.

When a thermoplastic PMC lay-up is compressed at above its melting temperature, the pressure brings the PMCs into intimate contact and eliminates any free space between the plies. This is accomplished by the lateral squeezing flow of the resin on the prepreg material and is completed when the extent of spatial gaps between the plies is minimized.

4.1.3. Resin Flow

Four basic flow patterns have been identified during the processing of PCMs into product forms. These are: resin percolation through and along the fibers, transverse flow, intraply shearing flow along the fiber direction, and interply slip cooperative flow.

Percolation. Figure 8.20 shows the schematic for percolation. Percolation of resin through the reinforcing fibers plays an important role in all processing operations. Such resin flow heals any flaws in the structure and allows the bonding of different layers of preimpregnated tape.

As an approximate description of resin flow, a composite material is considered to be a porous medium and the resin flow can be described by

Darcy's law, which states that the flow rate per unit area in a certain direction q is directly proportional to the resin pressure gradient in that direction.

The permeability of the fiber network depends on the fiber diameter, the porosity, and the network geometry, as given by the Kozeny-Carman equation. Permeability is not a physical property and depends on fiber network geometry, fiber shape, and fiber properties. Therefore, the permeability is an empirical constant that is determined by measuring the pressure drop and the flow rate through the fiber network. The Kozeny-Carman relation, which is one of the most widely accepted derivations for calculating permeability as a function of fiber volume fraction, treats the porous medium as a bundle of parallel tubes. The Kozeny-Carman relation has an important limitation in its application to composite processing. It assumes that the porous medium is macroscopically isotropic and that the pore size and the fiber distribution are uniform. Of course, this is not true for aligned fiber composites. For example, any irregular packing of the fibers results in an increased flow rate and a decrease in the Kozeny constant in the fiber direction.

The nonuniform packing of the fibers results in favored, enlarged flow paths and increases the flow rate of the fiber beds. For high fiber volume fractions, there is only a small possibility that the fibers will be distributed in an irregular manner, while for low fiber volume fractions, nonuniform packing of the fiber bed is prevalent.

Transverse flow. One flow process that allows movement of the fibers is a simple transverse flow (Figure 8. 21). This flow mechanism allows

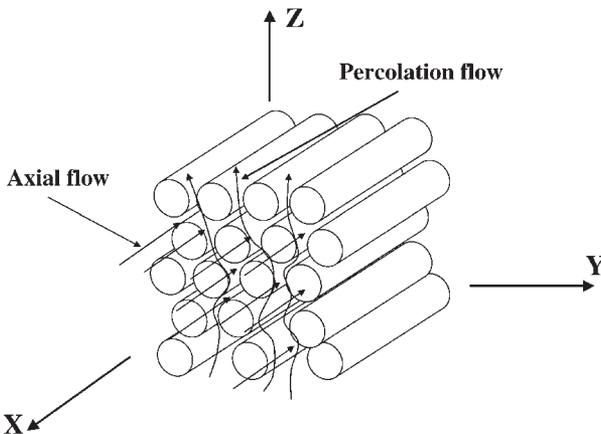


FIGURE 8.20 Flow by percolation.

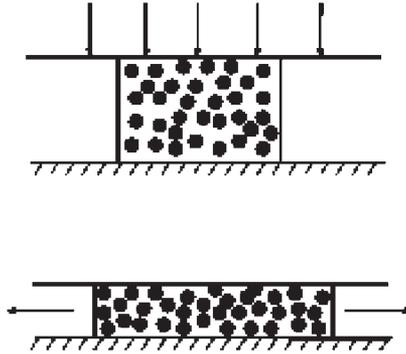


FIGURE 8.21 Transverse flow.

for healing of small gaps in the material, for example, those that occur in structures woven from impregnated single tows.

Axial shearing flow. In this flow, shearing along the fiber direction is observed in any flow process that alters the orientation of one layer of fibers relative to another.

Interply slip. Interply slip is the situation where layers of the fibers slide relative to each other. Figure 8.22 show the schematic of the two types of shearing flow.

Figure 8.23 shows the areas where the flows are applicable.

4.1.3.1. Resin Flow for Manufacturing Using Flexible Tows

For tapes, the resin has already wetted the fibers before compression molding takes place. The flow of resin during compression molding is required mainly to fill up the space between the tapes. For the case of flexi-

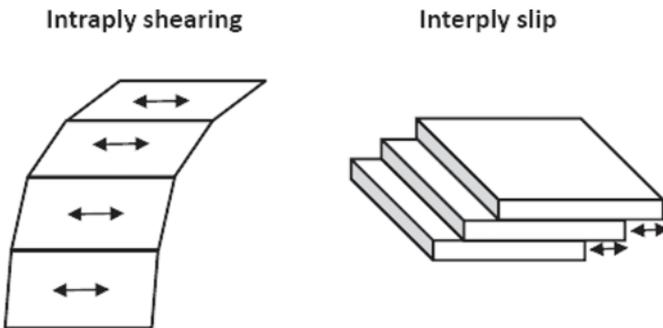


FIGURE 8.22 Shearing flows.

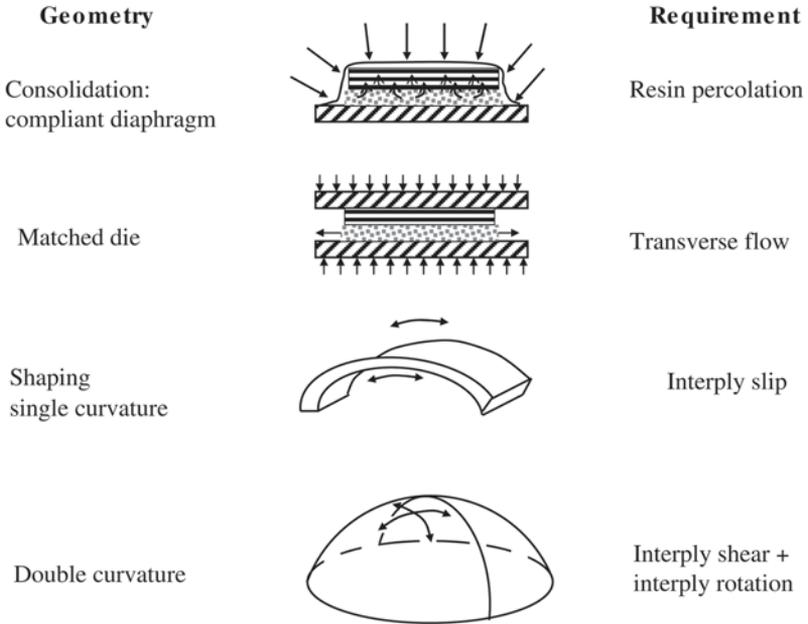


FIGURE 8.23 Deformation processes [4].

ble tows such as tows with clinging powder, commingled tows, or with fabric/film sandwich, apart from filling up the space between the tows, resin is also required to wet the fibers since the fibers are not wetted in the PMC form. An idealized configuration of a cross section of a commingled tow is shown in Figure 8.24. It can be seen that once the resin melts, it has to flow around the fibers to wet them, apart from the need to fill the empty space.

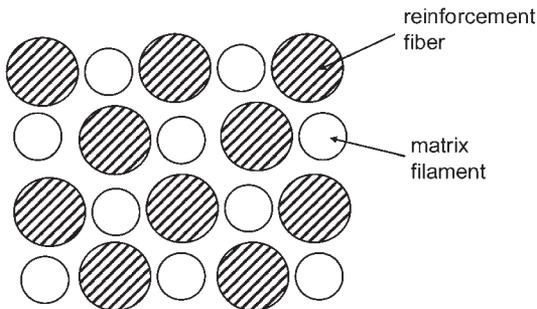


FIGURE 8.24 An ideal cross section of a commingled tow.



FIGURE 8.25 Cross section of a fabric/film sandwich.

Figure 8.6 shows an arrangement for the case of fiber tows with clinging powder. Again, the melted resin has to flow along the length of the fibers to wet them, in addition to the need to fill the empty space.

Figure 8.25 shows the cross section of a fabric/film sandwich. The arrangement in this figure is for the case of 5-harness satin, but the requirement for the melted resin to flow into the empty space applies to other types of weave also.

4.1.3.2. Resin Flow Analysis Model

For situations involving tapes, Loos and coworkers [6] developed an interplay intimate contact model by combining a prepreg surface roughness model with a resin flow analysis. A surface topology machine was used to measure the waviness or roughness of the resin rich prepreg surfaces. The measurements were taken across the width of the prepreg sheet, perpendicular to the fibers. From the topology measurements it appears that the surface waviness (roughness) of the prepreg is somewhat sinusoidal. For modeling purposes, the prepreg surface topology was represented by a series of rectangular elements of height h_o , with b_o and spacing w_o , as shown in Figure 8.26. The magnitudes of b_o and w_o are equal.

Application of the consolidation pressure resulted in deformation of the rectangular elements, the deformation of the rectangular elements

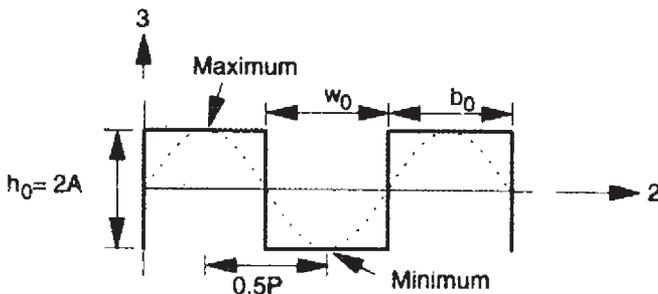


FIGURE 8.26 Prepreg surface roughness model. A and P are the amplitude and the period of the sinusoidal wave [6].

represented deformation and flow of the resin rich prepreg surfaces and was modeled as a squeezing flow between two rigid parallel plates. A formulation using the zero-shear-rate viscosity of the neat resin, which is a function of temperature, was derived to predict the interplay intimate contact achievement.

The degree of intimate contact (DIC) is defined as the ratio of the noncontact area over the total interface as:

$$DIC = \frac{b}{w + b} \quad (8.16)$$

The samples were processed at different combinations of temperature, pressure and time. Optical microscopy was used to take the degree of intimate contact from the unidirectional samples.

4.1.4. Autohesion [9]

After the prepregs coalesce, matrix interfaces can adhere to one another by the molecular diffusion of the matrix. This healing process is called autohesion. Autohesion is defined as the diffusion of chain segments across an interface, leading to the elimination of the interfaces. Conversely, adhesion is due to the chemical bonding of two dissimilar materials at an interface.

After the spatial gaps in the laminate are removed, the diffusion of polymer chains takes place at the contact surface. When two thermoplastic parts are brought in contact above the glass transition temperature of the resin, interdiffusion of polymer chains takes place at the contact surface that progressively heals the interface. The motion of a chain in an amorphous material has been modeled by reptation theory, which was developed by De Gennes [7]. This theory postulates that the motion of the polymer chains can be considered to be constrained in a tube that represents the steric effects applied by the other chains in close proximity. De Gennes made the following assumptions:

- The chain is moving in a fixed isothermal network and therefore is not allowed to cross any obstacles.
- The chain is able to move between obstacles by a snake-like motion.

Consequently the chain is confined in a tube of length L , which represents the steric constraints exerted by the network. As the chain moves in the tube because of Brownian motion, its extremities exit the tube. The chain ends are then free to move. The reptation theory predicts that the

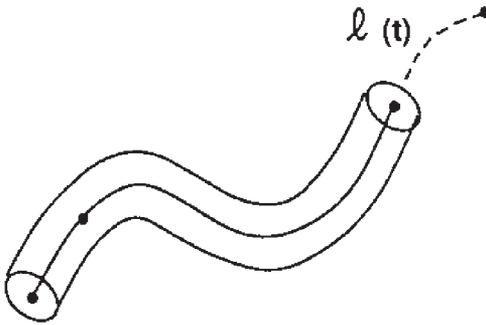


FIGURE 8.27 Minor chain length.

length, l , of the chain ends (called minor chains) varies with the square root of time (Figure 8.27). The reptation time T_r is defined as the time at which the chain has totally exited its original tube ($l = L$). Therefore, the following relation holds:

$$\frac{l}{L} = \left[\frac{t}{T_r} \right]^{0.5} \tag{8.17}$$

If one is interested in the interdiffusion of chain across an interface, it is possible to define the average interpenetration distance of the chain across the interface, y , which varies as the square root of the minor chain length (Figure 8.28). For the reptation time, $x = x_\infty$ which is equal to the radius of gyration of the chain. The following relation is derived:

$$\frac{x}{x_\infty} = \left[\frac{t}{T_r} \right]^{0.25} \tag{8.18}$$

As the chain motion grows, the penetration length of the chain across the interface increases and the fracture toughness and the tensile strength of the interface are enhanced. Kim and Wool [8] showed that mechanical properties such as stress, modulus and impact energy, are related to time,



FIGURE 8.28 Interpenetration distance of a chain across the interface.

temperature, and molecular weight, and developed the following relations:

$$\frac{S}{S_{\infty}} = \left(\frac{t}{T_r} \right)^{1/4} \quad (8.19)$$

$$\frac{G}{G_{\infty}} = \left(\frac{t}{T_r} \right)^{1/2} \quad (8.20)$$

where,

S_{∞} and G_{∞} = the tensile strength and fracture energy of the fully bonded interface.

T_r = the time to achieve a cohesive surface.

These relations are valid for the isothermal case and for a process time t less than T_r .

Dara and Loos defined the degree of autohesion by comparing the bonding strength of an interface to the strength of a completely bonded interface as:

$$D_{Au} = \frac{S}{S_{\infty}} \quad (8.21)$$

where D_{Au} is the degree of autohesion. Once D_{Au} reaches unity, there is no increase in the bond strength because any failure is entirely cohesive at this stage. For a reference temperature of 210°C and a zero shear rate viscosity of about 30 MPa·s, the contact time with $D_{Au} = 1$ can be estimated to be:

$$t_c = 22.9\eta \quad (8.22)$$

where η is viscosity in terms of MPa·s. Therefore, the contact time for perfect autohesion is directly proportional to the viscosity of the polymer.

The above equation shows that the required contact time for good autohesion is very short for PEEK at a normal processing temperature. The melt viscosity of PEEK above 360°C is much less than 1 kPa·s and the corresponding contact time is less than 1 second.

The autohesion time can be ignored for slow processes such as compression molding because the processing time is much greater than the autohesion time. For faster processes, such as filament winding, fiber placement, and pultrusion, the time of contact at high temperature and pressure is much shorter, and may be on the order of magnitude of the

time of complete autohesion. In this case, autohesion must be taken into account.

4.1.5. Cooling

After the consolidation or formation of a part, a thermoplastic matrix composite has to be cooled and solidified. The heat transfer during the cooling period can be examined by considering the thermoplastic composite plate as a plate of thickness $2L$ having a uniform initial temperature T_o (Figure 8.29). At time $t = 0$, the plate is plunged suddenly into a bath at the constant temperature T_∞ (similar to the case of quenching). Assuming that the surface temperature of the plaque remains at T_∞ during the whole process of cooling. If one assumes that the amount of heat generated due to crystallization during the cooling process is negligible, then the governing equation for heat transfer can be written as:

$$\frac{\partial \theta}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial z^2} \quad (8.23)$$

With the initial and boundary conditions:

$$\begin{aligned} \theta(x, 0) &= \theta_o = T_o - T_\infty \\ \frac{\partial \theta(0, t)}{\partial x} &= 0 \quad \theta(L, t) = 0 \end{aligned} \quad (8.24)$$

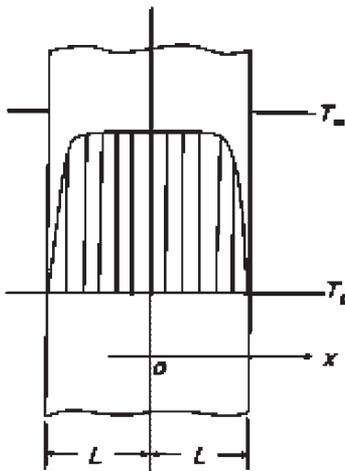


FIGURE 8.29 Plate exposed to constant surface temperature.

where

$$\theta = T - T_{\infty} \quad (8.25)$$

By using the method of separation of variables, it can be shown that the solution for the above problem can be written as [5]:

$$\frac{T(x,t) - T_{\infty}}{T_o - T_{\infty}} = 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left(-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right) \cos\left(\frac{(2n+1)\pi x}{2L}\right) \quad (8.26)$$

Equation (8.26) can be rearranged to be:

$$T(x,t) = T_{\infty} + 4(T_o - T_{\infty}) \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left(-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right) \cos\left(\frac{(2n+1)\pi x}{2L}\right) \quad (8.27)$$

In a situation where the temperature of the surrounding environment is a function of time, for example, the case where the surrounding liquid is being cooled, T_{∞} can be replaced by this temperature. For the case where $T_{\infty} = T_o - Kt$ where K is the cooling rate, Equation (8.23) can be written as:

$$T(x,t) = T_o - Kt + 4Kt \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left(-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right) \cos\left(\frac{(2n+1)\pi x}{2L}\right)$$

or

$$T(x,t) = T_o + Kt \left\{ 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi(2n+1)} \exp\left[-\frac{\alpha(2n+1)^2 \pi^2 t}{4L^2}\right] \cos\left[\frac{(2n+1)\pi x}{2L}\right] - 1 \right\} \quad (8.28)$$

Equations (8.26) to (8.28) are the solution for the case where the surface temperature of the plate is kept at a constant temperature T_{∞} throughout the cooling process. For the case where there is a convective coefficient h between the surface and the cooling liquid, the initial and boundary conditions Equations (8.24) are modified to be:

$$\theta(x,0) = \theta_o = T_o - T_\infty$$

$$\frac{\partial\theta(0,t)}{\partial x} = 0 \quad \frac{\partial q(L,t)}{\partial z} + \frac{h}{k}\theta(L,t) = 0 \quad (8.29)$$

The solution for the above problem can be shown to be [5]:

$$\frac{T(z,t) - T_\infty}{T_o - T_\infty} = 2 \sum_{n=1}^{\infty} \left(\frac{\sin \lambda_n L}{\lambda_n L + \sin \lambda_n L \cos \lambda_n L} \right) \exp(-\alpha \lambda_n^2 t) \cos \lambda_n z \quad (8.30)$$

where the zeros of the equation $(\lambda_n L) \sin(\lambda_n L) = (hL/K) \cos(\lambda_n L)$ are the characteristic values.

During the solidification, the maintenance of pressure is required until the temperature of the composite is below its matrix glass transition temperature. This restricts the nucleation of voids within the resin, suppresses the recovery of the fiber network, and enables the composite to maintain the desired dimensions.

Example 8.2

A thermoplastic composite plate mm thick was processed at 350°C. It is quenched in water at 2°C. Assume that the temperature at the surface of the plate remains at 20°C during the course of the cooling process. Plot the variation of the temperature in the plate across its thickness at $t = 5$ seconds, 10 seconds, 50 seconds, 100 and 150 seconds. $\alpha = 1.5 \times 10^{-3} \text{ cm}^2/\text{sec}$.

Equation (8.26) is used to determine the temperature as a function of time and space.

Figure 8.30 shows the temperature variations across the thickness of the laminate at different times for a thin plate (0.1 cm thick). Figure 8.31 shows the similar graphs for a thicker plate (2 cm thick). It can be seen that for a thicker plate, the temperature on the surface drops more quickly than at the center of the plate, even for a slow cooling rate of $-0.2^\circ\text{C}/\text{second}$. Figure 8.32 shows the variation of temperature at the center of the plates of different thicknesses. Figures 8.33–8.35 shows similar curves for a cooling rate of $-100^\circ\text{C}/\text{sec}$. It can be seen that at this fast cooling rate, the temperature drops quickly and there is a sharp temperature gradient across the thickness for thicker laminates.

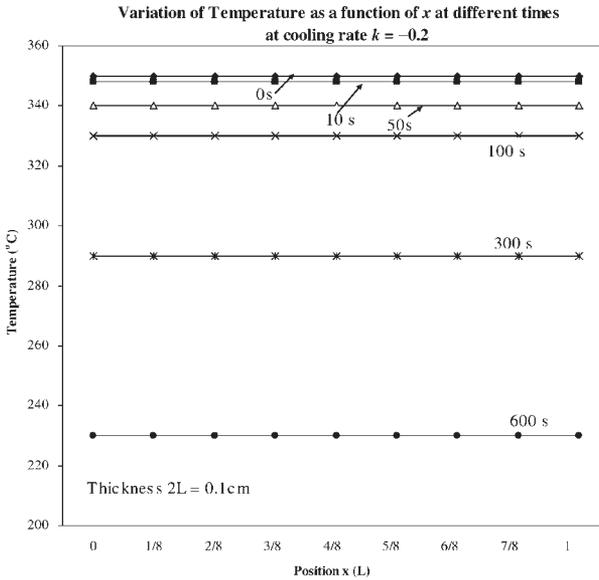


FIGURE 8.30 Temperature variation of a plate subject to cooling rate of $-0.2^\circ\text{C}/\text{sec}$, 0.1 cm thick.

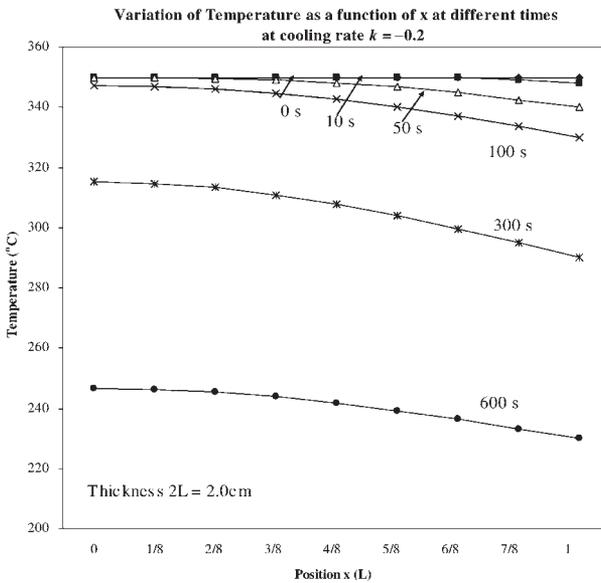


FIGURE 8.31 Temperature variation of a plate subject to cooling rate of $-0.2^\circ\text{C}/\text{sec}$, 2.0 cm thick.

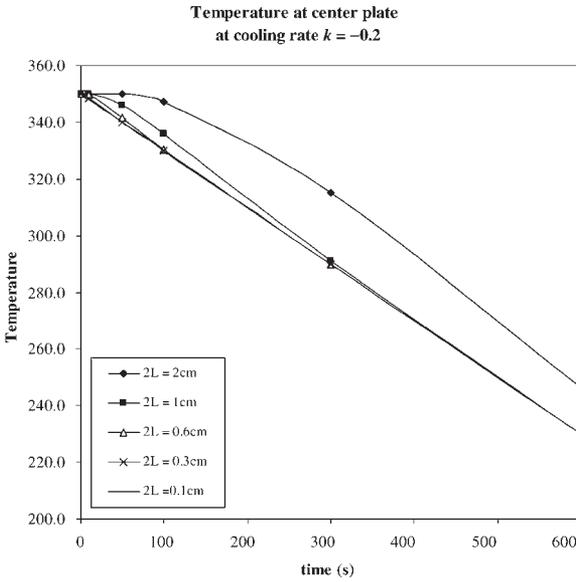


FIGURE 8.32 Temperature at center of laminate as a function of time for plates of different thicknesses. Cooling rate $-0.2^{\circ}\text{C}/\text{sec}$.

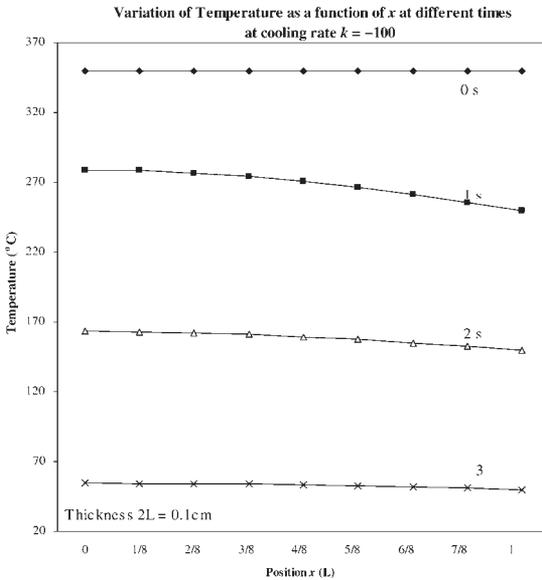


FIGURE 8.33 Temperature variation of a plate subject to cooling rate of $-100^{\circ}\text{C}/\text{sec}$, 0.1 cm thick.

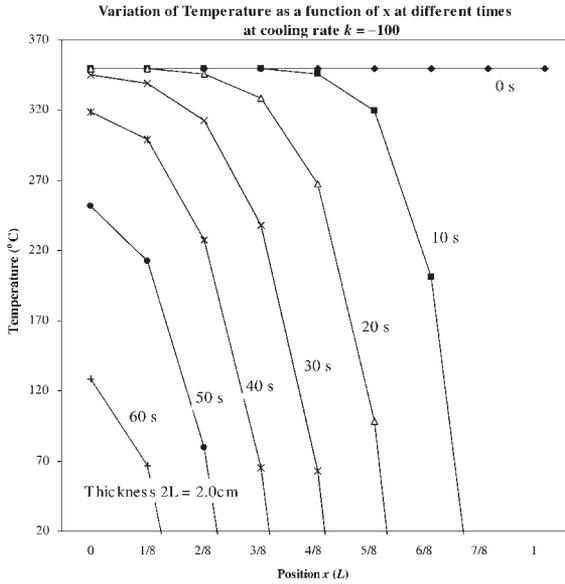


FIGURE 8.34 Temperature variation of a plate subject to cooling rate of $-100^{\circ}\text{C}/\text{sec}$, 2.0 cm thick.

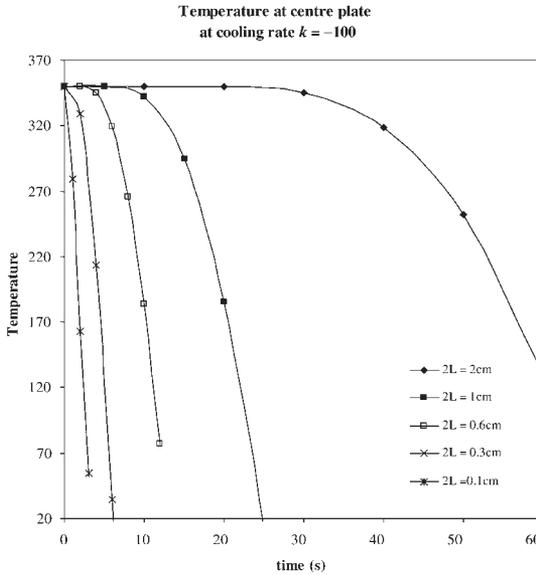


FIGURE 8.35 Temperature at center of laminate as a function of time for plates of different thicknesses. Cooling rate $-100^{\circ}\text{C}/\text{sec}$.

4.1.6. Crystallization

A semi-crystalline thermoplastic crystallizes when an appropriate cooling rate is applied. This crystallization has a significant effect on the mechanical properties and solvent resistance of the composites and results in crystallization shrinkage. In addition, the difference in thermal expansion coefficients between the fiber and the resin can lead to residual stresses and warping.

Fortunately, the residual stresses can be relieved partly during processing if the thermoplastic matrix is maintained near its glass transition temperature (annealed) or the cooling rate is controlled to provide an even temperature profile throughout the part. The degree of crystallinity drops as the cooling rate is increased. Figure 8.36 shows the crystallinity versus cooling rate using the spherulite growth model.

4.1.7. Solidification

If the applied pressure is reduced when the resin is still molten, the composite exhibits a significant elastic recovery. Figure 8.37 illustrates this elastic recovery in terms of thickness change. This recovery cannot be explained by the resin flow model alone. Therefore, it is necessary to introduce the elastic deformation of the fiber network in the model. In

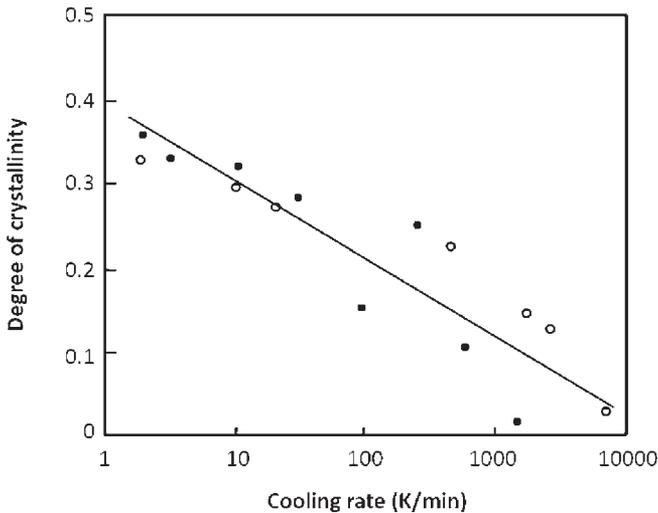


FIGURE 8.36 Variation of degree of crystallinity versus cooling rate for PEEK and APC (carbon/PEEK).

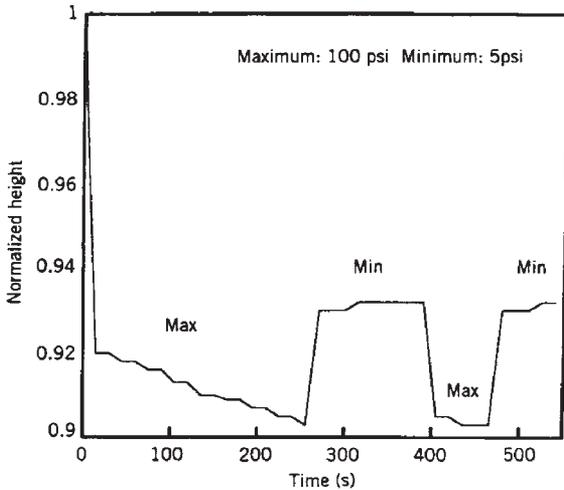


FIGURE 8.37 Elastic recovery of fiber network (reproduced from “The processing science of thermoplastic composites,” by J. D. Muzzy and J. S. Colton, in *Advanced Composites Manufacturing* T.G. Gutowski ed., with permission from Wiley Interscience).

many practical situations, the fiber network is compressed to the point that it starts to take up a significant portion of the applied load. This elastic behavior may be more significant if the fiber forms a woven mat or a flexible tow. From the reasoning above, the applied pressure during consolidation $P_{applied}$ can be divided into two components.

$$P_{applied} = P_f v_f \frac{A_{ic}}{A_T} + P_r v_r \frac{A_{ic}}{A_T} \quad (8.31)$$

where

- P_f = the pressure supported by the fiber network
- V_f = the volume fraction of fibers
- A_{ic} = the current area of intimate contact
- A_T = the total area of the part
- P_r = the pressure supported by the resin
- V_r = the volume fraction of the resin

4.1.8. Variation of Degree of Crystallinity Across the Thickness of the Part in the Case of Fast Cooling (Quenching)

It can be seen from the above discussion that the cooling rate has an effect on the crystallinity of the material. Faster cooling rate results in

smaller crystallinity. In cases where fast cooling rate is used (quenching), the temperature of the surface of the sample can go from about 350°C to room temperature (20°C) in the order of a few seconds. Assuming that the time involved is 3 secs, this gives a cooling rate of about 100°C/sec. Even though the temperature on the outer surface can be cooled quickly, due to the low thermal conductivity of the composite material, the inside of the material cools more slowly. The variation of the temperature as a function of location and time for a plate made of PEEK is shown in Figure 8.38.

The variation of temperature for a similar plate made of carbon/PEEK is shown in Figure 8.39.

The difference in cooling rate at different positions along the thickness of the plate gives rise to different degrees of crystallinity at these positions. Figure 8.40 shows the calculated volume fraction crystallinity for plates made of pure PEEK and carbon/PEEK for a 5-mm-thick plate cooled at 114°C/second.

Thermoplastic resins with higher crystallinity have higher stiffness. The variation in crystallinity along the thickness direction gives rise to changes in stiffness along this direction. Also the outer skin cools first

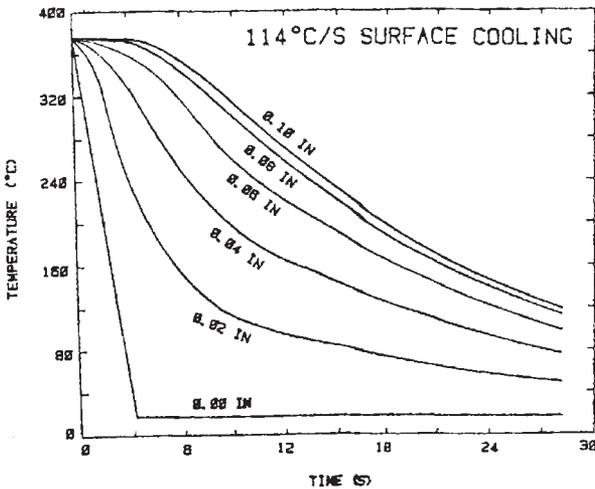


FIGURE 8.38 Predicted temperature as a function of time and position from the surface, for a 5-mm-thick neat PEEK plate with surface cooled at 114°C/second (reproduced from Velisaris C. N., and Seferis J. C. "Heat transfer effects on the processing-structure relationships of polyetheretherketone (PEEK) based composites," *J. Science and Engineering of Composite Materials*, Vol. 1, No. 1, 1988, pp. 13–22, with permission from Freund Publishing Ltd.).

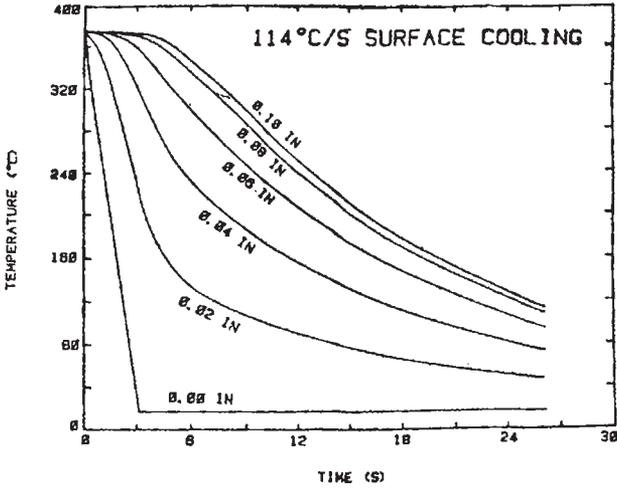


FIGURE 8.39 Predicted temperature as a function of time and position from the surface, for a 5-mm-thick neat carbon/PEEK plate with surface cooled at 114°C/second (reproduced from Velisaris C. N., and Seferis J. C. “Heat transfer effects on the processing-structure relationships of polyetheretherketone (PEEK) based composites,” *J. Science and Engineering of Composite Materials*, Vol. 1, No. 1, 1988, pp. 13–22, with permission from Freund Publishing Ltd.).

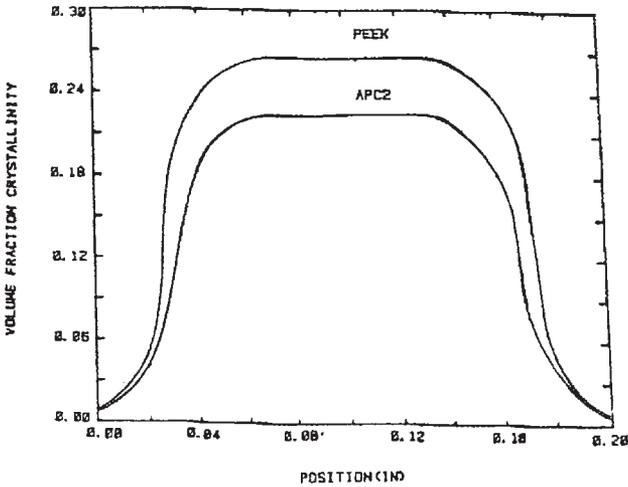


FIGURE 8.40 Calculated volume fraction crystallinity at different positions along the thickness for a 5-mm-thick neat PEEK and carbon/PEEK plates, with surfaces cooled at 114°C/second (reproduced from Chapman T. J., Gillespie J. W., Pipes R. B., Manson J. A. E., and Seferis J. C. “Prediction of process-induced residual stresses in thermoplastic composites,” *J. Composite Materials*, Vol. 24, June 1990, pp. 616–643, with permission from Sage Publications).

and therefore becomes solid first. The inner core cools later. Cooling also gives rise to shrinkage. The interaction between the shrinking core and the rigid outer skin gives rise to residual stresses. Figure 8.41 shows the influence of cooling rate on the transverse residual stresses in a 40-ply carbon/PEEK unidirectional laminate.

4.2. Fiber Placement Process

Figure 8.42 shows a schematic of the fiber placement process. The concept for fiber placement is a process that was started in the 1980s. Recently, with the development of new equipment with good control, the fiber placement process can be used to make good quality thermoplastic composite parts.

The process is similar to filament winding except that the prepregged tapes are pushed toward the mandrel. At the nip point, a heat source is directed toward the fiber to heat and melt the tape. A roller is used to apply pressure at the nip point to spread the fiber and also to apply compaction. As the material point is moved away from the nip point, the material should cool down at an appropriate rate to solidify.

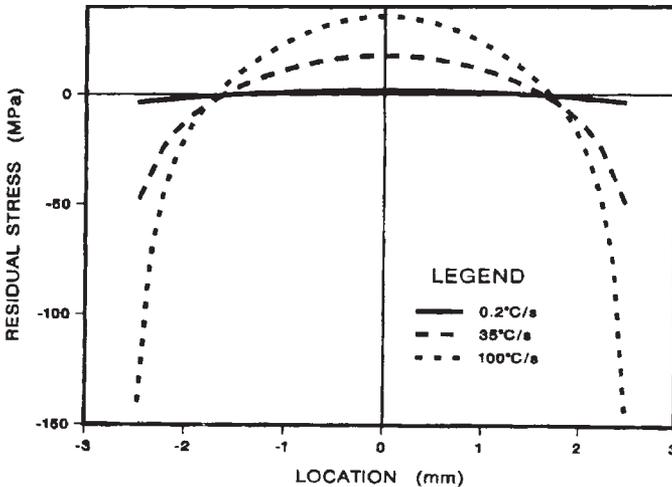


FIGURE 8.41 Predicted temperature as a function of time, and position from the surface, for a 5 mm (0.2 in) thick neat carbon/PEEK plaque with surface cooled at 114°C/second. Reproduced from Velisaris C.N., and Seferis J.C. "Heat transfer effects on the processing-structure relationships of polyetheretherketone (PEEK) based composites", *J. Science and Engineering of Composite Materials*, Vol. 1, No. 1, 1988, pp. 13–22, with permission from Freund Publishing Ltd.

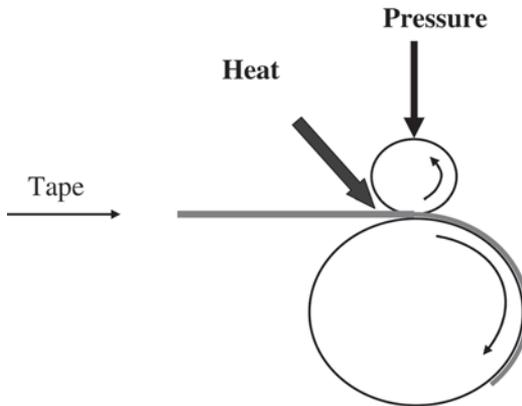


FIGURE 8.42 Schematic of the fiber placement process.

5. REFERENCES

1. Verrey J. et al. "Manufacturing cost comparison of thermoplastic and thermoset RTM for an automotive floor pan," *Composites. Part A*, 2006, Vol. 37, pp. 9–22.
2. Beland S. High performance thermoplastic resins and their composites, Noyes Data Corporation, 1990.
3. Cogswell F. N. "The processing science of thermoplastic structural composites," *International Journal of Polymer Processing*, 1987, Vol. 1, No. 4, pp. 157–165.
4. Lebel L. L. et al. "Processing and properties of carbon/nylon thermoplastic composites made by commingled tows and micro-braided tows," *Proc. of 5th Canada-Japan Workshop on Composites, Yonezawa, Japan, September 2004*, pp. 161–170.
5. Arpaci V. S., *Conduction Heat Transfer*, Addison Wesley, 1966.
6. Li M. C. and Loos A. C. "Modeling the consolidation process of thermoplastic composites," MD-Vol. 74, *Advanced Materials: Development, Characterization, Processing, and Mechanical Behaviour* (book of abstracts), ASME, 1996.
7. De Gennes P. G. *J. Chem. Phys.*, 1971, Vol. 55, p. 572.
8. Kim Y. H. and Wool R. P., *Macromolecules*, 1983, 16, p. 1115.
9. Muzzy J. D. and J. S. Colton, "The processing science of thermoplastic composites," in *Advanced Composites Manufacturing*, F. G. Gutowski ed., John Wiley and Sons, 1997.