PART 2

Techniques for Composites Manufacturing

Theoretically, manufacturing of composites can be broken down into the following items:

- Aligning of fibers
- Single filaments
- Tows
- Fabrics (mats, weaves, braids, knits)
- Bed consisting of many layers of fabrics
- Filling the interstices between filaments with liquid matrix
- Wetting the fibers
- Curing the resin

Filling interstices between the filaments with liquid resin can be done at the levels of single filaments, tows, fabrics, or a bed consisting of many layers of fabrics (refer to the list below). The arrangement of the fibers in different configurations was shown schematically in Figure 3.1. It is of no practical use to fill and wet single filaments with liquid resin so it is rarely done.

a. If resin filling happens at the level of many tows, preimpregnated tapes (for thermosets) or preimpregnated tow preg (for thermoplastics) is made.
b. If resin filling happens at the level of fabrics, preimpregnated fabrics are made. In order to make the final composite part, these preimpregnated tapes or fabrics need to be laid up on top of each other to form the thickness of the laminate.

c. If resin filling occurs at the bed of many layers of fabrics, then one can make the final composite part at the same manufacturing session with the liquid filling.

No matter which fiber level the liquid resin is introduced, it is essential that it wets the filaments to ensure good bonding between matrix and fibers. In the manufacturing process involving activities (*a*) and (*b*), the liquid resin has an opportunity to wet the fiber two times. First, when the preimpregnated tapes or fabrics are made, and second, when these layers are placed on top of each other and processed to make the final part. For processes involving activity (*c*), the liquid has only one opportunity to wet the fibers. Therefore it is necessary that sufficient time is allowed for the resin to properly wet the fibers.

The curing of resin is normally done after the resin has already filled all interstices and wet all filaments. However, due to the exothermic reaction, in order to avoid a peak in temperature rise, sometimes curing is done in stages (i.e. a thin layer may be cured first before additional layers are placed to add more thickness).

Above are the theoretical activities. For making a composite part, a manufacturer can combine or alternate these steps, depending on the requirements for quality and cost, as follows:

- For hand-lay-up in open mold for fiber glass/polyester, dry tows or dry fabrics are laid on a mold, liquid resin is then poured and spread onto the fiber beds. A few layers are wetted and left to cure in open air. After these layers are cured, more layers are added.
- For autoclave curing, pre-impregnated layers made from tows and fabrics are first manufactured by one group of people. The second group of people obtain these prepregs and lay them up to fit the the thickness and configuration of the part. These are placed inside an autoclave for curing.
- For filament winding, dry tows of fibers are run through a bath of resin to be wetted. These are then deposited onto the surface of a rotating mandrel. Many of these layers are deposited until the desired thickness is obtained. These layers are then left to cure either in room temperature or under some form of heat lamp.
- For pultrusion, the dry tows are run through a bath of resin to be wetted. These are then fed into a heated die. The fibers and resin are subjected to compaction and heating. When the assembly of fibers and resin exit the die, they are compacted and cured.

- For liquid composite molding, layers of dry fibers are stacked on top of each other in a mold. Liquid resin is then injected into the mold to wet the fibers. Heat is applied to cure.
- For thermoplastic composite processing, two different approaches are taken. In the first approach, the fiber tows are first impregnated with the liquid thermoplastic resin. It is then allowed to cool so that tow pregs of themoplastic resin and fiber are obtained. These tow pregs are then placed on top of each other to make up the thickness. The stack of tow pregs is compression molded to make the part. In the second approach, the thermoplastic resin is brought to the vicinity of the fibers. This can be done by drawing the thermoplastic resin into small filaments, calendering the liquid thermoplastic resin into thin sheets, or grinding the thermoplastic resin into powders. These forms of thermoplastic resin are placed close to the dry fibers. The whole assembly of dry fiber and thermoplastic resin is placed inside a mold. Compression molding is used to consolidate the final part.

The rule of thumb is that for good quality, the whole process should be broken down into small steps and each step done at a different time. For low cost manufacturing, many steps may be combined so the process can be done at one time or a lesser number of times. The selection of the process depends on weighing these two parameters: quality and cost. The following chapters present current techniques for manufacturing. By understanding the principles used for manufacturing, new techniques can also be developed.

CHAPTER 4

Hand Laminating (or Wet Lay-up) and the Autoclave Processing of Composites

1. HAND LAMINATING (OR WET LAY-UP)

The hand laminating or wet lay-up processing technique is presented in the same chapter with autoclave processing because these two processes have one thing in common: the depositing of the different layers is done by hand. (Initially the lay-up for autoclave has been done by hand; recently many large companies have adopted the automated fiber placement machine for laying laminates for autoclave curing.) Apart from that, the materials used, the components to be made and the quality of the parts are very different. The hand laminating or wet lay-up process is used to make low cost components such as boats and corrosion-resistant components in the chemical process industry, while the autoclave process is used to make components for the aircraft industry. Hand laminating or wet lay-up works with fiber glass and polyester (or vinyl ester) while the autoclave process mostly works with epoxy resins.

Hand laminating is a primitive but effective method that is still widely used for prototyping and small batch production. The most common materials are E glass fiber and polyester resin, although higher performance materials can also be used. The single sided mold is invariably operated at room temperature using an ambient curing resin. The reinforcement may be in the form of chopped strand mat or an aligned fabric such as woven rovings.

The usual feature of hand laminating is a single sided female mold, which is often itself made of glass fiber reinforced plastics (GRP), by taking a reversal from a male pattern. The GRP shell is often stiffened with local reinforcement, a wooden frame or light steel work to make it sufficiently stiff to withstand handling loads. The mold surface needs to be smooth enough to give an acceptable surface finish and release properties and this is provided by a tooling gel coat that is subsequently coated with a release agent. The latter prevents the matrix resin from bonding to the mold surface and facilitates the de-molding operation. It is common practice to use a surface tissue immediately after the gel coat to mask any reinforcement print-through on the outer surface.

Once the gel coat has hardened sufficiently, the reinforcement is laid in, one layer at a time. Catalyzed resin is then worked into the reinforcement using a brush or roller. This process is repeated for each layer of reinforcement until the required thickness is built up. For thick laminates, pauses need to be taken after a certain number of layers have been deposited to allow the exothermic heat to dissipate before additional layers are deposited. Local reinforcements can be used to provide stiffness in specific areas and lightweight formers such as foams or hollow sections can be laminated in for the same purpose. Figure 4.1 shows a schematic of the hand laminating process.

The major limitation of hand laminating is that the mold has only one smooth surface. The absence of direct control over part thickness, fiber content, void fraction and surface quality on the other surface means that the moldings are used in very low stress applications and in areas where dimension accuracy is noncritical. Although capital costs are low, production is labor intensive and quality control is relatively difficult. The quality of the final part is highly dependent on the skill of the operator.

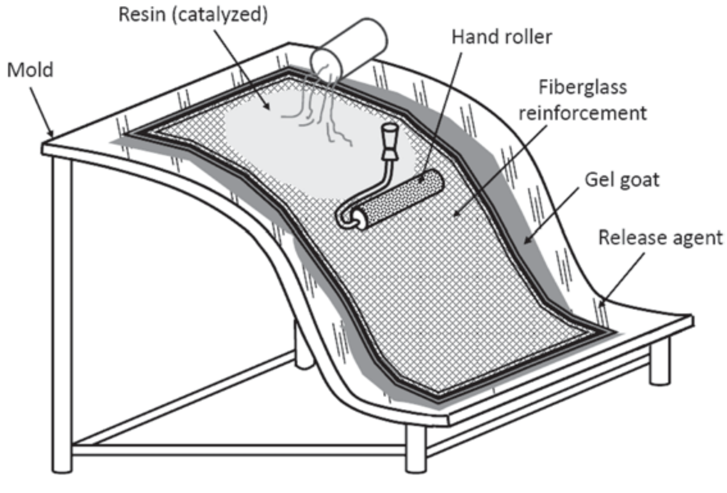


FIGURE 4.1 Schematic of the hand laminating process.

The process remains an important one for low volume manufacture, although increasingly stringent emission regulations are forcing several manufacturers to explore the use of closed mold alternatives. Hand laminating using open molds has traditionally been used for making structures out of fiberglass and polyester, but there are environmental concerns about evaporation of styrene into the atmosphere. There are new techniques of liquid composite molding that may produce similar parts with the closed mold, thus avoiding the environmental issue.

2. AUTOCLAVE PROCESSING

2.1. Introduction

Autoclave processing is commonly used for manufacturing composite components for the aerospace industry. The process produces composite components of high quality, but it requires a considerable amount of time. The main steps of the autoclave processing of composites are:

- Prepregs
- Tool preparation
- Laying up prepregs on the tool to make the part
- Curing of the part
- Removal of the part from the tool
- Inspection
- Finishing steps

In the Chapter 1, Figure 1.7(a) shows the different stages for the manufacturing of composites. For the manufacturing using autoclave, the stages involved are *a*, *b* and *c* or *a*, *b* and *d*. As one moves from stage *a* to *b*, the dry fibers and the liquid resin are combined to make a semi-finished form. This semi-finished form consists of both fibers that are uniformly spread out over a rectangular cross section area and partially cured matrix resin that holds the fibers in place. This semi-finished form is called *prepreg* (pre-impregnated). As one moves from stage *b* to stage *c* or from *b* to *d*, many layers of the prepregs are stacked on each other to form a sheet of sufficient thickness for practical use. Note that one does not move from stage *c* to stage *d*. In the case where the process involves stages *a*, *b* and *c*, flat plate laminates (as in stage *c*) are made. Flat plate laminates are usually made for the purpose of studying and characterizing the properties of the laminate. For real practical applications, normally laminates may have curvatures and more complex configuration such as those shown in stage *d*. For this latter case, the process goes di-

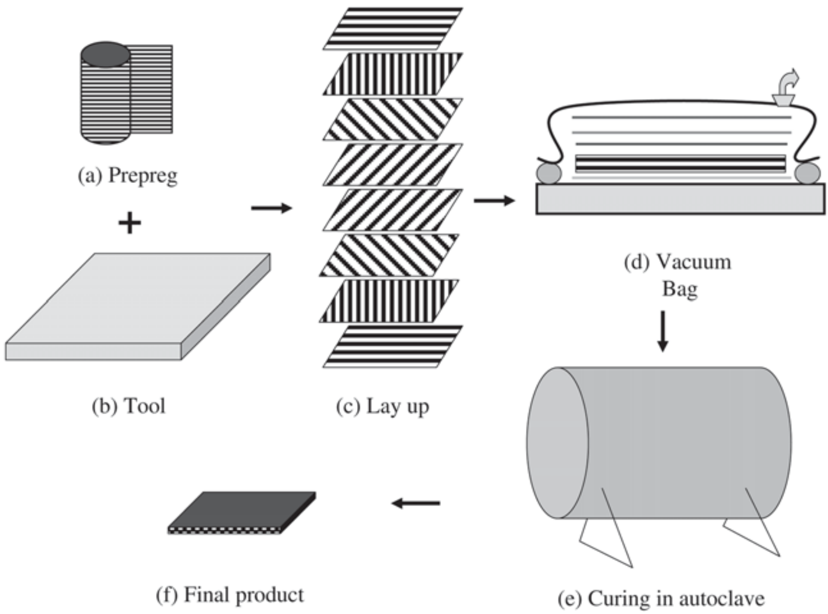


FIGURE 4.2 Main steps in the autoclave manufacturing process.

rectly from stage *b* to stage *d*. The properties of flat laminates can usually be applied to curved laminates with appropriate consideration for the change of the coordinate system. Figure 4.2 shows the main steps for autoclave manufacturing. These are described below:

2.2. Prepreg

2.2.1. *Prepreg Manufacturing and Handling*

Prepregging involves the incorporation of the partially cured resin with the fibers. Figure 4.3 shows a schematic of the prepregging machine. In the prepregging process,dry fibers are fed from creels through stations of combs where the fibers are spread out. The fibers then enter into a bath of wet resin where they are wetted. Subsequently the fiber/resin combination is heated to change the liquid resin into a partially cured state. The partially cured resin is viscous enough to help keep the fibers in the configuration of flat sheets. This fiber/viscous resin combination is called prepreg. Normally sheets of backing paper are placed on both sides of the prepreg for handing purposes. Then the prepregs are rolled up for storing and shipping.

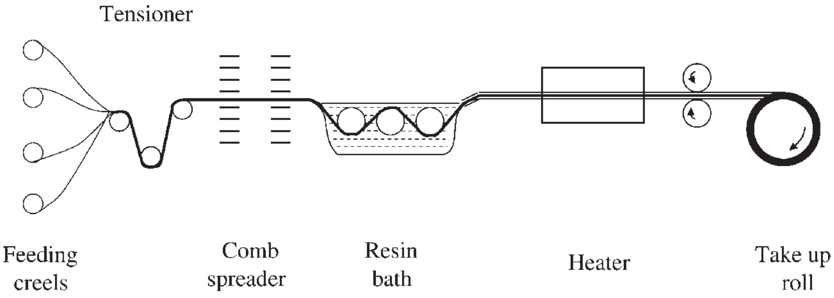


FIGURE 4.3 Schematic of a prepregging machine.

Resins are usually thermosets such as epoxies, although recently prepregs made of vinyl ester resins have also been available. The partially cured resin has about 30% of the crosslinks already formed. With the incorporation of fibers (such as carbon, glass or Kevlar at about 60% by volume), prepregs are flexible sheets of fibers about 150 mm thick. This is similar to a sheet of wallpaper except that it is sticky on both sides. Figure 4.4 shows a roll and a sheet of the carbon/epoxy prepreg.

FIGURE 4.4 A roll and a sheet of carbon/epoxy prepreg.

The thermoset resins (such as epoxy) inside the prepregs contain all of the curing agents necessary for the complete cure of the resin. Only a portion of the crosslinking, however. has taken place, due to the addition of certain amounts of inhibitors into the resin, and/or by allowing the reaction to take place at low temperature and within a limited amount of time. The time from the date of manufacturing of the prepregs to the time when the actual part is done may be several months. If the prepregs are left at room temperature on the shelf, the reaction in the resin may continue and the resin becomes hard (more crosslinking has already taken place). Once the resin is hard, it is no longer sticky and one cannot bond the prepregs together to make the composite component. Therefore it is essential to slow down the reaction of the resin until the prepregs are laid up to make the composite component. Slowing down is usually done by storing the prepregs at low temperature. Normally during shipping the prepregs are contained inside refrigerated bags. Once received, the prepregs need to be stored inside a freezer at about −5°C. Usually the supplier of the prepregs provides specifications as to the storage temperature and the maximum amount of time of storage (shelf life) at that temperature. This means that even at that low temperature, the resin in the prepregs may keep on with the process of crosslinking and become mostly cured at the end of the period.

Prepregs are available in the form of tapes (unidirectional fibers) or fabrics (woven). Widths of prepreg rolls vary from 25.4 mm (1 inch) to 305 mm (12 inches).

2.2.2. Prepreg Cutting

When one is ready to make the composite component, the prepregs are taken out of the freezer and left at room conditions for a few hours. This allows the prepregs to rise to room temperature, reducing viscosity of the resin. Since normal room conditions contain a certain amount of humidity, equilibrating between the prepregs and room conditions means that the prepreg may acquire a similar amount of moisture. This has implications for the formation of voids, which will be discussed later in this chapter.

Once the prepregs have become pliable (viscosity of the resin is low enough for the prepregs to be shaped to conform to the contour of the mold), they are cut into the desirable configuration. Cutting the fabrics of the prepregs is similar to cutting cloth fabrics to make a suit, except that here carbon fibers are involved, rather than textile fibers. This means that the contour of the cut depends on the configuration of the part to be made. For example, to make the nose cone of an airplane, the geometric configuration of the surface of the cone when it is opened up onto a flat surface needs to be worked out, in order to learn how the flat piece(s) of fabric will cover that surface. On surfaces with double curvatures, where several flat pieces of fabric are required, care should be taken to assure continuity of fiber orientation between adjacent pieces.

Cutting used to be done by hand. Recently, however, this work has been mechanized and computerized, not only to speed up the process but also to reduce waste, which ordinarily increases very significantly the cost of manufacturing a composite part. Waste occurs due to the requirement of cutting prepregs at an angle with the axis of the prepreg roll. By computerization, one may nest the different parts to minimize waste.

With the use of the prepregs, the availability issue mentioned in chapter 1 is not a concern. For the autoclave process this issue is already taken care of during manufacturing.

2.3. Tool Preparation

Manufacturing using autoclave is a molding process. As such, molds (also called tools) are required. The mold provides the shape and surface finish for the part. As such the size of the mold depends on the size of the part. Large parts require large molds and these can be very expensive. Advanced composites must be cured at about 180°C and at pressures of about 600 kPa; molds would be required to sustain these conditions for periods of several hours. In addition, there are many other considerations when designing and building tools. These include tool cost, life, accuracy, weight, machinability, strength, thermal expansion, dimensional stability, surface finish, and thermal mass and thermal conductivity.

Over a wide range of material systems and processing scenarios used for composites, there are many materials suitable for tooling. In general, the choices fall into three categories:

1. Reinforced polymers, for low to intermediate temperature ranges
2. Metals, for low to high temperatures
3. Ceramics and bulk graphite, for very high temperatures

In addition, one may use cast plaster and other inexpensive and relatively easy-to-process materials for small scale part runs like those needed for prototype verification.

For production tooling for advanced composites, the choice is usually made between metals, including aluminum, steel, nickel alloys (Invar), electroformed nickel, and graphite/epoxy tooling. Elastomeric tooling is often used as a pressure intensifier and to distribute the applied pressure over a part.

For high temperature applications, such as thermoplastic composites, much consideration has been given to bulk graphite and various ceramic systems, including a new material called "geopolymere."

2.3.1. Aluminum, Steel, and Invar Tool [1]

These materials are highly desirable for production tooling because of their good surface finish and ability to stand up to repeated production runs. In this respect, Invar is quite desirable because its hardness is similar to that of steel and greater than that of aluminum and its coefficient of thermal expansion (CTE) is below both aluminum and steel (on the order of 0.28×10^{-6} m/m °C). Conversely, aluminum is the least desirable because of its relative softness and high CTE (on the order of 26.2×10^{-6} m/m °C). On the other hand, aluminum tools can be significantly lighter than other tooling materials and therefore easier to move about on the factory floor. Table 4.1 gives the CTEs of various tooling materials relative to a $[45/0/{-45}/90]_s$ lay-up of the thermoplastic composite APC2/AS4. Aluminum has large thermal expansion coefficient which can result in large mismatch with that of the composite. In terms of ease of fabrication, however, aluminum is much easier to machine than is steel or Invar.

2.3.2. Electroformed Nickel [1]

Electroformed nickel tooling is produced by an electroplating process

TABLE 4.1 Coefficient of Thermal Expansion of Various Mold Materials (1) Lay-up $[45/0/{-45}/90]_{3s}$, (2) 0.2–0.5% Carbon Steel, (3) 18 Cr+9% Ni Steel.

Material	Coefficient of Thermal Expansion (10^{-6}/°C)
Composite APC2/AS4	3.8
Bulk graphite	3.0
Ceramic	0.7
Metal-ceramic	7.2
Polyimide	4.7
Aluminum	26.2
0.2–0.5% carbon steel	13.2
18Cr+9% Ni steel	17.8
Cast iron	11.1

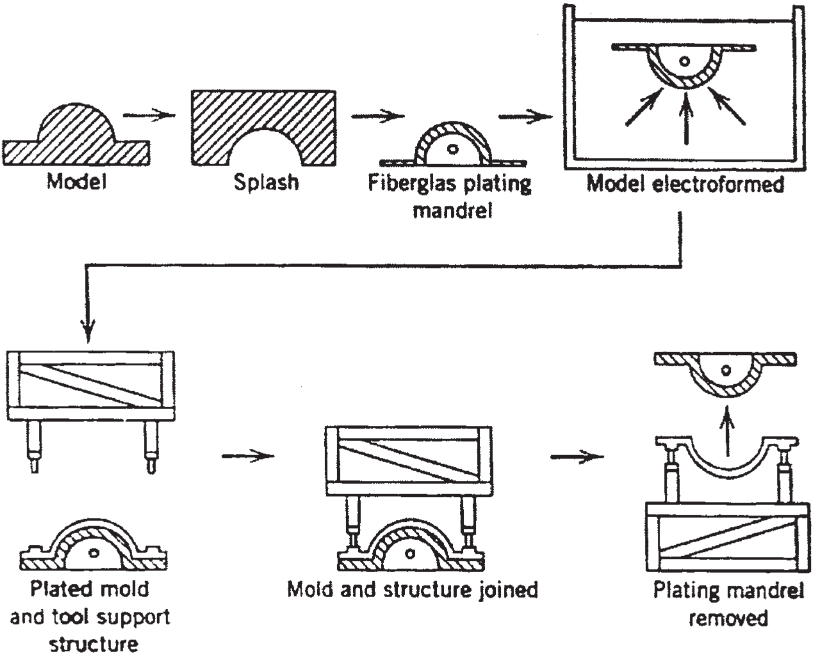


FIGURE 4.5 Stages in the production of electroformed nickel tooling (reproduced from *Advanced Composites Manufacturing* by T.G. Gutowski, 1997, with permission from John Wiley and Sons).

that deposits the material onto a master mold (made usually of plaster) which matches the dimensions of the final part (with perhaps some allowance for expected thermal distortions). The key requirement of the master mold is that it must remain dimensionally stable during the plating process. The basic stages of the process are shown in Figure 4.5.

Since the production of the master mold is the most time-consuming part of the process, one of major advantages of the technique is that duplication can be carried out at a relatively low cost and with great repeatability. Once the tool surface is produced, high polishes may be achieved using standard metal finishing techniques. The major drawback associated with electroformed nickel tooling is the high cost associated with the initial tool production.

Electroformed nickel tools are durable, scratch resistant, relatively easily repaired, and possesses good release properties from most commonly used composites. Perhaps the greatest advantage of this type of tooling is that the scale of the possible parts is limited by the size of the plating tank and the master production techniques.

2.3.3. Graphite/epoxy Tooling [1]

The problem of CTE mismatch with the use of metal tools has led to the increased popularity of graphite/epoxy tooling for autoclave molding processes. The tool making process is similar to that of electroforming of nickel in that it starts with the development of a master model that may, in some cases, be made from plaster or wood. This is then properly sealed and treated with mold release, and the carbon/epoxy material is laid up in the conventional manner. An autoclave curing cycle is applied to solidify the material. A high finish can be applied to the tooling by either polishing or applying a high-gloss gel coat to the master model.

Other than the ability to tailor CTE, additional advantages of graphite/epoxy tooling include lightness, ease of construction, and rapid response to heating profiles. The major limitation of the material is that it cannot be used when processing metals at temperatures greatly in excess of the glass transition temperature of the mold material, especially when high autoclave pressures are necessary. Since the surface is basically polymeric, graphite/epoxy tools tend to be somewhat less durable and resistant to scratches than conventional metallic tooling materials.

2.3.4 Elastomeric (or Rubber) Tooling [1]

Elastomeric tooling is employed to either intensify or redistribute pressure during a molding cycle. It is very useful in conditions where it is difficult to get a vacuum bag into the recesses of a complicated mold: for example, in the vertical elements of a stiffened panel. In such cases, the expansion of the elastomeric material generates high lateral loads as shown in Figure 4.6.

In its most basic form, elastomeric tooling may be applied as simply a rubber caul sheet between the vacuum bag and the part, or rubber pads that are used in areas of the part that are known to be difficult to consolidate. Elastomeric inserts are commonly used on parts where bridging or the composite or vacuum bag has caused problems of incomplete consolidations or bag rupture in tight radii.

The major disadvantages of elastomeric tooling are: low tool life?most elastomeric tools are seriously degraded after about 30 thermal pressurization cycles use for advanced composites; and low thermal conductivity, which slows the cure cycle and sometimes necessitates the redesign of the processing cycle. This may sometimes be alleviated by inserting metal plugs to reduce the rubber mass and increase conductivity.

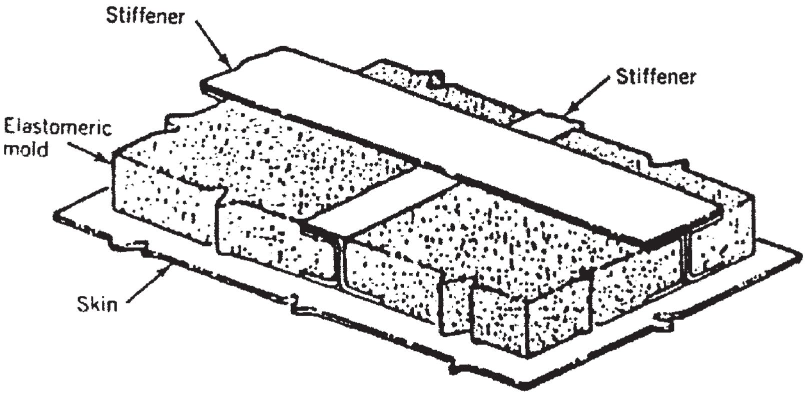


FIGURE 4.6 Example of elastomeric tooling for molding of stiffened panel (reproduced from "The autoclave processing of composites," by G. Dillon, P. Mallon and M. Monaghan, in *Advanced Composites Manufacturing,* by T. G. Gutowski, 1997, with permission from John Wiley and Sons).

2.3.5. Bulk Graphite and Ceramic Tooling [1]

The introduction of thermoplastic composites that must be processed considerably above their T_g has created the need for high temperature tooling. To date no thoroughly acceptable tooling material has been found. However, the need has sparked experimentation with various high temperature materials. Chief among them has been bulk or monolithic graphite and various ceramic tooling materials.

Bulk graphite tools have the advantages of low CTE, light weight, relatively easy fabrication, and high thermal conductivity and can be used to temperature as high as 2000°C. These tools are generally fabricated from blocks of monolithic graphite that are machined and joined together. The major drawback is that monolithic graphite tools tend to be extremely fragile, hence autoclave processing cycles can be quite low, perhaps less than 10.

2.4. Release Agent

Before the laying of the prepregs on the surface of the tool, a *release agent* needs to be applied. This is to facilitate the removal of the part after cure. Insufficient application of the release agent on the surface of the tool can result in the part sticking to the tool surface. Removal of the part that sticks to the tool may result in damage to both the tool surface and the part. Sometimes several coats of release agent may be required and baking of the release agent may be necessary. Release agents will be discussed further in the next section.

2.5. Lay-up of the Prepregs on the Tool to Make the Part

2.5.1. Determination of Number of Layers and Layer Orientation

Normally an engineering part requires a certain thickness to carry load. The thickness of composite laminates in aerospace applications is usually of several millimeters. Assuming that a part 3 mm thick is to be made, and assuming that a thickness of each layer after cure is 125 μm (thickness of a layer of prepreg of 150 μm was mentioned previously, some resin is bled out during the autoclaving process), one would require about 24 layers. The number of layers and the orientation of each of the layers can be tailored to meet the mechanical load requirement. (Discussion of the effects of different fiber orientation on the properties of the laminates can be found in Reference [2].) The order in which the layers are stacked on each other is called a stacking sequence. Figure 4.7 shows a typical stacking sequence. Normally the stacking sequence is written in a laminate code such as $[0/90/45/-45]_s$. This means that if one starts from the bottom, then the bottom layer has fibers that are oriented along the

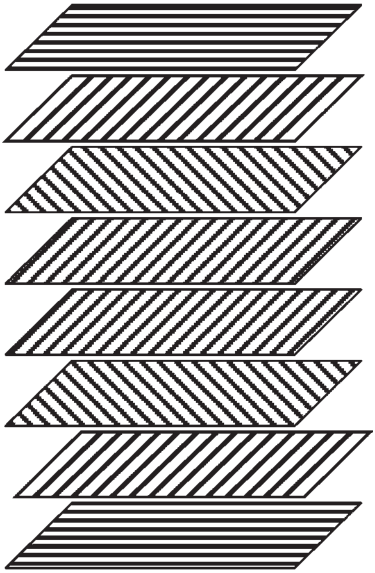


FIGURE 4.7 A typical lay-up sequence $[0/90/45/-45/]_s$.

axis of the part to be made, followed by a layer having fibers oriented at 90° with the axis of the part, then by a layer with fibers oriented at 45° etc. The subscript s indicates symmetry. In other words, the code can be written in full as [0/90/45/–45/–45/45/90/0].

After the prepregs are cut, they can either be laid on the tool to make the part right away or they can be kitted away for later laying up. Labeling of the kit is extremely important to avoid mix-up problems later on.

2.5.2. Laying Up

The laying up of the prepregs on the surface of the mold consists of not only the laying of the fiber prepregs on the mold, but also the placement of ancillary materials for the following purposes:

- To facilitate the removal of the part after cure (without the problem of the part sticking to the mold)
- To allow the compaction of the stack of prepregs using vacuum
- To prevent excess resin from running within the plane of the stack of fibers, which can distort the orientation of the fibers
- To provide an escape path for volatiles such as water vapor or gases that are generated during the curing process
- To provide materials that can absorb excess resins that ooze out of the laminate during the curing and molding process
- To obtain good surface finish on the part

The result of the laying up process is a stack of the prepregs along with many other layers within a vacuum bag as shown in Figure 4.8. The steps included in the laying up process are as follows.

2.5.2.1. Preparation of the Mold Surface

As discussed in Section 2.3 (Tool Preparation) of this chapter, the selection of the mold material depends on many factors. To assure good surface finish for the part, the mold surface needs to be well polished. Poor mold surface finish will result in poor surface finish for the part. Thermoset resins such as epoxies are basically glue. They will stick to the mold materials, which normally are made of metals, composites or ceramics. When the part sticks to the mold, removal of the part from the mold may result in damage to either the mold or the part. Molds are usually very expensive to prepare, therefore it is essential to prevent sticking. For this purpose, release agents are applied, either in liquid form that can be spread over the surface of the mold, or in the form of a release film.

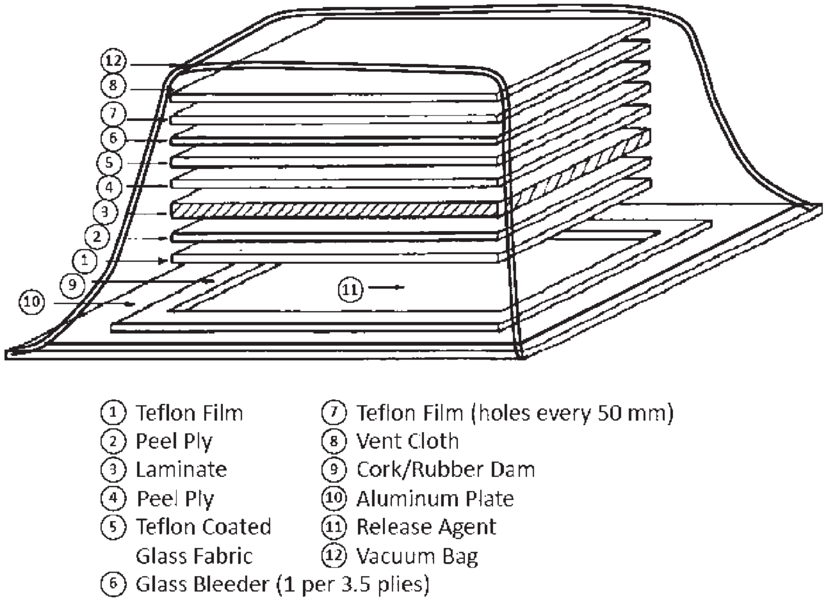


FIGURE 4.8 The lay-up assembly of different layers.

Usually several coats of the release agent are applied, each coat being allowed to dry before the next one is put on. Release films are usually made of low surface tension polymer such as Teflon. Sometimes the release film is applied on top of the liquid release agent. After the release film, a peel ply may be applied to add to the release action, and also to provide a texture for the surface of the part.

In order to prevent resins to flow out of the prepregs in the plane of the stack of prepregs, dams made of ceramic or metal blocks are placed along the periphery of the stack.

2.5.2.2. Laying Up the Stack of Prepregs

After the release agents and peel ply have been placed on the surface of the mold, stacks of the prepregs are positioned. This has been done by hand, thus the term hand lay-up (HLU). One may ask why such high tech parts as composite components for airplanes are made by such a rudimentary technique as HLU instead of by machines, which perform with greater consistency. The reason is the low volume production for aircraft components: airplanes are more or less custom-made for different customers, so aircraft companies do not mass produce them. Because parts that look similar may have differences in detailed configurations, it is not economical to build machines to do the laying up. This apparent disadvantage has an advantage in that the HLU process is so versatile that it can be used to build most, if not all, the composite parts for the aircraft industry. The exception is the manufacturing of tubes or other components having surfaces of revolution. Recently the development of fiber placement machines allow for automation of the hand lay-up process. These are virtually robots with many degrees of freedom (the Cincinnati Milatron, for example) which require huge capital investment, affordable only by large companies.

It is essential that the stack of prepregs is well packed. As discussed in Chapter 3, fibers in the prepregs may be wavy while one needs to make laminates with straight fibers. To assure good packing, the usual practice is to perform *debulking*. In this process, after about 3–5 layers of prepregs have been laid, a vacuum bag of thick film is placed around the mold and the stack of prepregs. Vacuum is then applied for about 10 minutes onto the partially laid prepregs for consolidation. The process is repeated after each stack of 3–5 layers are laid until the whole laminate is laid up. This is a time consuming process but it is essential to assure good quality laminates. After the laminate has been laid and debulked, another peel ply is applied on top for part removal purpose.

2.5.2.3. Placement of Bleeder Materials

Bleeder materials are used to absorb any resin that may ooze out during the curing and molding process. Usually prepregs contain more resin than what remains in the final laminate. Some of the resins in the prepregs will flow out and absorb into the bleeder material. The bleeder material is placed outside the release fabrics.

2.5.2.4. Placement of Breather Materials

Breather materials are perforated films of polymer of high temperature resistance. The holes allow volatiles such as water vapor or gases that are formed during the curing process to escape. The breather materials are placed outside the bleeder materials.

2.5.2.5. Placement of a Caul Plate

A caul plate is sometimes used to aid in the consolidation. The weight of the caul plate delivers some pressure to the laminate. The caul plate is placed outside the bagging assembly but inside the vacuum bag.

2.5.2.6. Placement of Vacuum Bag

The final layer that goes on top of the whole assembly is the vacuum bag. A hole is made in the vacuum bag to incorporate the vacuum valve. It is then sealed. The vacuum bag is used to compact the bed of prepregs, and also to aid in the removal of volatiles that may be produced during the curing process. Vacuum is kept on at all times during the autoclaving process.

The assembly of all layers is shown in Figure 4.9. The whole lay-up assembly is then placed inside the autoclave for curing. For making a small laminate such as that of coupons for testing, a plate of about 300 mm × 300 mm may be used and the whole assembly may not be too large or too heavy. However, the manufacturing of a large structure such as parts of a wing of an aircraft with dimensions on the order of tens of meters can require a whole bagging assembly (including the tool) of several tons in weight. The handling of such an assembly requires careful planning.

2.6. Curing and Consolidation of the Part

The resin in the stack of layers of composite in the bag mentioned in the previous section is a viscous liquid. This resin needs to be transformed into a solid to make a useful composite, which requires heat to activate the chemical reaction between the molecules (as discussed in Chapter 2). During this transformation of the resin, it is important to assure that the fibers maintain their orientation and that no resin rich area or

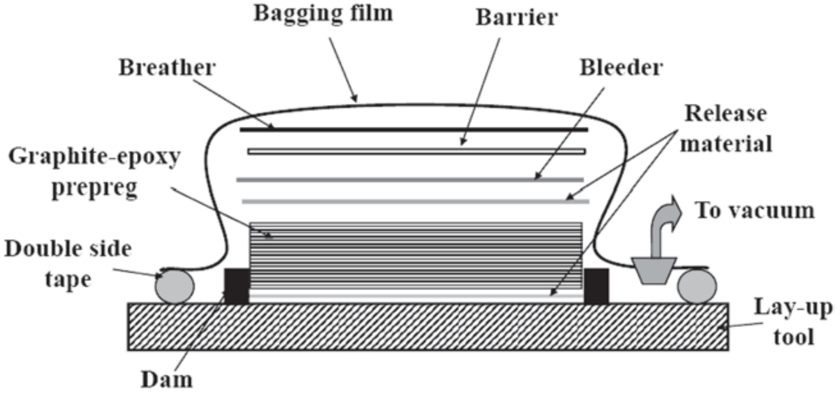


FIGURE 4.9 Assembly of the bagged composite.

other defects will exist. Sufficient amounts of pressure need to be applied for this purpose. Also, during the transformation of the resin from the liquid to solid state, volatiles such as water vapor or other gases may be generated. These need to be removed from the material in order to avoid the occurrence of voids after the resin has become solid.

Heating of the resin needs to follow a very carefully planned schedule. This is due to many phenomena that occur during the process:

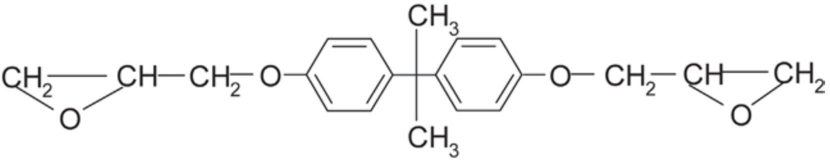
a. Heating will kick start the chemical reaction between the bonds that have not reacted. In the case of epoxy, these are the bonds between the epoxy molecules and the molecules of the curing agents (such as amines or anhydrides). The reaction between these bonds is exothermic, i.e. heat is generated as a result of the reaction. When this occurs, the temperature of the resin can increase. This increase in temperature can accelerate quickly. If not properly handled, the temperature of the resin can pass the degradation temperature of the resin and damage such as burning may occur.
b. The percentage of the amount of chemical bonds that have formed represents the degree of cure of the resin. At the beginning when no chemical bond has formed, the degree of cure is 0. When all chemical bonds have formed, the degree of cure is 1. When only a portion of the bonds have formed, the material is partially cured and the degree of cure is between 0 and 1.
c. The viscosity of the liquid resin depends on the temperature and also on the degree of cure. The greater the temperature, the smaller the viscosity of the liquid is (before curing becomes significant). At the same time, the greater the degree of cure, the higher the viscosity. Higher temperature does speed up the degree of cure. As such higher temperature provides two competing effects on the viscosity. The value of the viscosity has influence on the flow of the resin. Flow of resin is important for the squeezing of excess resin out of the laminate to assure high fiber volume fraction. Flow of resin is also essential for the squeezing out of bubbles of water vapor or volatiles. Therefore, it is important to apply pressure when the viscosity is low. At the same time, in order to reduce processing time, it is good to have the resin cure as quickly as possible. These two competing effects have influence on the determination of the heating and pressurizing schedule.

2.6.1. Resin Kinetics

As presented in Chapter 2, the curing of the resin happens due to the chemical reaction between the epoxy molecules and the curing agent molecules. This reaction is fairly complex and depends on the combination of the type of epoxy molecule and the type of curing agent molecule. For the purpose of illustration, DGEPBA epoxy and TETA amine curing agent are used. The chemical formulae for these molecules were presented in Figure 2.8 and Table 2.5 and are repeated for convenience in Figure 4.10.

For the epoxy-amine resin system, curing takes place due to the reaction between the epoxy group (the ring CH_2–O–CH at the end of the molecule) and the amine groups (segments of the molecule containing N atom) of the amine molecule. The amine groups are classified into two categories: primary amine and secondary amine. The reason for this is because it takes less energy to activate a reaction involving the primary amine than that of a secondary amine.

Refer now back to the presentation for the chemical reaction between the epoxy and amine curing agents in Section 3.2.2 of Chapter 2. In the DETA molecule shown above, the segment NH_2 is called the primary amine and the segment NH is called the secondary amine. Also when the primary amine has finished its reaction, one hydrogen atom leaves the segment and the remaining part of the segment contains NH. This remaining segment becomes a secondary amine. With the application of catalysts and/or heat, reaction between segments of the epoxy molecules may occur. This is called homopolymerization or Etherification. One group of researchers [3] proposed that the activation energies for the different amine reactions with an epoxy are: primary amine: 83 kJ/mole and secondary amine: 131 kJ/mole. From each of these reactions there are different amounts of heat that are generated. One group obtained the



DGEBPA epoxy molecule

$$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$$

Diethylenetriamine (DETA) molecule

FIGURE 4.10 Chemical formulae of epoxy and amine molecules.

amounts to be [4,5]: primary amine: 61.4 kJ/mole; secondary amine: 72 kJ/mole; and etherification: 101 kJ/mole.

Initially, some heating is required to get the reaction started and primary amines are normally the first involved. When some reactions have taken place, there will be heat generated from these reactions and the temperature of the material will increase. Apart from the involvement of the primary amines, secondary amines and even etherification may also participate into the reactions. This means that the reactions may not consume all of the primary amines before the secondary amines and etherification may get into the action. Besides this, the heat capacity of the material may change as it changes its state. This complicates determining the heat that may be generated during the course of the reaction. Too much heating from an external source may cause a runaway reaction which can become dangerous because the high temperature may cause burning. In the case where reaction takes place in an enclosed container, pressure may build up and this may lead to explosion.

In spite of the complexities involved, it is essential to control and quantify the process for engineering purposes. As mentioned in Chapter 2, the degree of cure of the resin is the percentage of the epoxy ends that have been consumed in the chemical reactions. This can be represented by the ratio of the amount of heat that has been generated over the total amount of heat that can be generated when the material is completely cured as:

$$\alpha = \frac{H_t}{H_T} \tag{4.1}$$

where,

α = the degree of cure
H_t = heat generated up to a certain time t
H_T = total heat generated at complete cure

The rate of cure is given as:

$$\frac{d\alpha}{dt} = \frac{1}{H_T}\frac{dH_t}{dt} \tag{4.2}$$

Differential scanning calorimeters have been used to measure the heat generated during curing of polymeric materials. Many efforts have been made to model the rate of cure of the resin. As can be seen the rate of cure depends on the temperature and the degree of cure. It also depends on the mechanism responsible for the curing reaction, such as whether primary amines, secondary amines, or etherification are involved. The general form for the rate of cure can be written as:

$$\frac{d\alpha}{dt} = f(\alpha, T) \tag{4.3}$$

Meticulous DSC measurements need to be carried out to determine the mathematical model for a particular resin system. One general form for the equation can be:

$$\frac{d\alpha}{dt} = K\alpha^{m}(1-\alpha)^{n} \tag{4.4}$$

where,

$K = Ae^{-E/RT}$
A = the frequency factor
E = activation energy
m, n = orders of the reactions

When $m = 0$, the model is called nth order and the reaction is fastest at the beginning when $\alpha = 0$. When $n = 0$, the model is called autocatalytic and the reaction is 0 at the beginning. Figure 4.11 shows the two extreme cases. The real case is when m and n have numerical values and the reaction is fastest after a certain amount of cure has already taken place.

Equation (4.4) shows the basic form for the model. The model can get

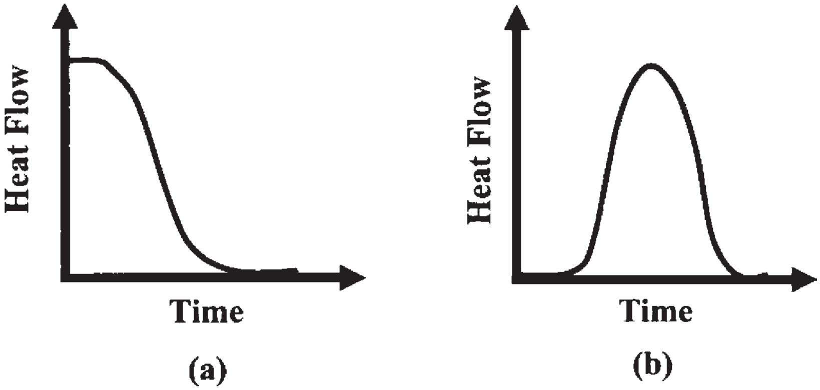


FIGURE 4.11 Two cases of cure rates: (a) nth order and (b) $m, n \neq 0$.

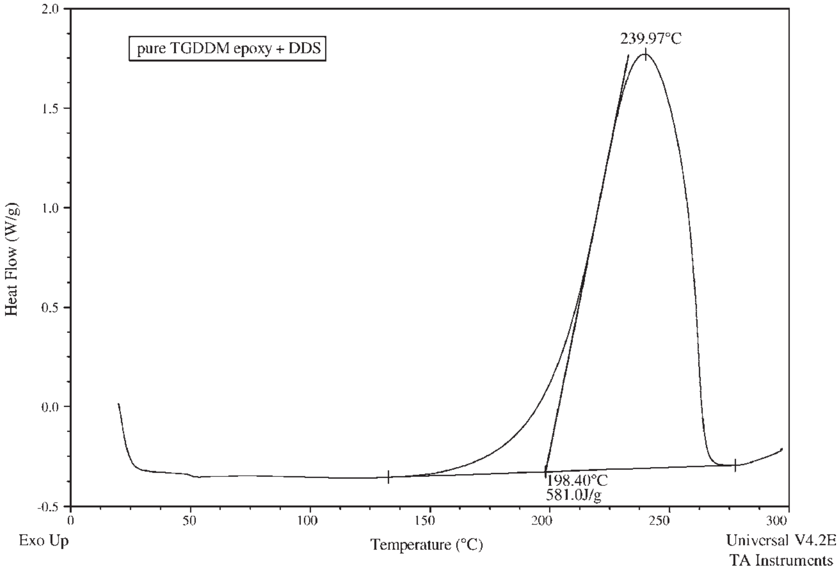


FIGURE 4.12 Heat flow versus time curve for TGDDM/DDS epoxy resin.

complicated where the mechanism of cure changes as curing progresses. One example would be:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1-\alpha)^{n1} + K_3(1-\alpha)^{n2} \tag{4.5}$$

In Equation (4.5), three activation energies E_1, E_2, E_3 (associated with K_1, K_2, K_3) are involved. Figure 4.12 shows an example of a more realistic heat flow versus time curve for an epoxy resin.

The above shows that the model for the rate of cure can get complicated. One needs to formulate a model for each resin system. The reason for this is because commercial resin systems usually contain blends of different resins. Also fillers such as accelerators or inhibitors are usually added to speed up or to retard the curing reaction, or only to kick up the curing reaction after a certain degree of cure.

2.6.2. Heat Transfer and Energy Balance

In order to determine the temperature of the composite material during the manufacturing process, a volume element of the material can be considered. For this volume element, there is heat transferred across the faces of the element and there is also heat generated due to chemical reaction. By neglecting energy transfer by convection as would be the case for a process such as autoclaving, the energy equation may be expressed as:

$$\frac{\partial(\rho C_p T)}{\partial t} = \frac{\partial}{\partial x}\left(K_x \frac{\partial T}{\partial X}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial T}{\partial Y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial T}{\partial Z}\right) + \frac{dH}{dt} \tag{4.6}$$

where,

ρ and C_p = the density and specific heat of the composite
K_x, K_y, K_z = the thermal conductivities in the x, y and z directions
T = the temperature of the composite

The coefficients of thermal conductivity of the material are usually determined to be those along the principal material direction. They need to be transformed into the coordinate system of the laminate. Figure 4.13 shows the relative orientation between the two coordinate systems. The relation between the coefficients of conductivity along the two coordinate system is given as:

$$\begin{bmatrix} k_{xx} \\ k_{zz} \\ k_{xz} \end{bmatrix} = \begin{bmatrix} m^2 & n^2 & mn \\ n^2 & m^2 & -mn \\ -mn & mn & m^2 - n^2 \end{bmatrix} \begin{bmatrix} k_{11} \\ k_{33} \\ k_{13} \end{bmatrix} \tag{4.7}$$

where,

k_{ij}, $i,j = x,z$ are the off-axis coefficients of thermal conductivity
k_{ij}, $i,j =$ 1,3 are the on-axis coefficients of thermal conductivity

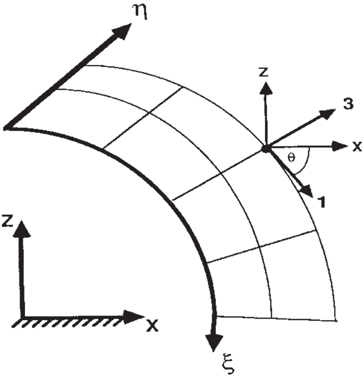


FIGURE 4.13 Coordinate systems for different coefficients of thermal conductivity.

TABLE 4.2 Thermal Properties for Glass/Polyester and Graphite/Epoxy [6].

	ρ (kg/m^3)	C_p (kJ/(W·°C)	k_{33} (kW/(m·°C)	k_{11}/k_{33}
Glass/polyester	1.89×10^3	1.26	2.16×10^{-4}	2
Graphite/epoxy	1.52×10^3	0.94	4.46×10^{-4}	5

The thermal properties of a few composite systems are given in Table 4.2 [6].

From Equation (4.2), the rate of heat generation by chemical reaction *dH*/*dt* can be written as:

$$\frac{dH}{dt} = \frac{d\alpha}{dt} H_T \tag{4.8}$$

where H_T is the total heat of reaction and α is the degree of cure predicted by the kinetic model.

The effective total heat of reaction for the composite, H_T, is based on the following rule of mixture: $H_T = w_r H_r + w_f H_f$, where H_r and H_f are the heats of reaction of the resin and fiber, respectively. w_r and w_f are the weight fractions of the resin and fiber, respectively. The fiber heat of reaction is assumed to be zero. Only the resin heat of reaction and the resin weight fraction are required. The total heat of reaction for two composite systems is shown in Table 4.3 [6]. The reaction rate for each material system is unique due to the inherent differences in the overall order of the reaction kinetics. The reaction rate for one glass/polyester is given by:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{\Delta E}{RT}\right)\alpha^m (1-\alpha)^n \tag{4.9}$$

where,

$A = 3.7 \times 10^{22}$ min^{-1}
$\Delta E = 1.674 \times 10^5$ J/mol
$m = 0.524$
$n = 1.476$

The reaction rate for graphite/epoxy (Hercules 3501-6 resin) follows the equation [8]:

$$\begin{aligned} \frac{d\alpha}{dt} &= (K_1 + K_2\alpha)(1-\alpha)(B-\alpha) \quad \alpha \le 0.3 \\ \frac{d\alpha}{dt} &= K_3(1-\alpha) \quad \alpha \succ 0.3 \end{aligned} \tag{4.10}$$

$$K_1 = A_1 \exp\left(-\frac{\Delta E_1}{RT}\right)$$

$$K_2 = A_2 \exp\left(-\frac{\Delta E_2}{RT}\right)$$

$$K_3 = A3 \exp\left(-\frac{\Delta E_3}{RT}\right)$$

$$A_1 = 2.101 \times 10^9 \ \text{min}^{-1}$$

$$A_2 = -2.014 \times 10^9 \ \text{min}^{-1}$$

$$A_3 = 1.960 \times 10^6 \ \text{min}^{-1}$$

$$\Delta E_1 = 8.07 \times 10^4 \ \text{J / mol}$$

$$\Delta E_2 = 7.78 \times 10^4 \ \text{J / mol}$$

$$\Delta E_3 = 5.66 \times 10^4 \ \text{J / mol}$$

For the case of autoclave manufacturing, it can be assumed that there are no variations of temperature along the in-plane directions (x and y) and Equation (4.6) can be written as:

$$\frac{\partial(\rho C_p T)}{\partial t} = \frac{\partial}{\partial z}\left(K_z \frac{\partial T}{\partial z}\right) + \frac{d\alpha}{dt} H_T \tag{4.11}$$

2.6.2.1. *Thin Laminates*

The solution for Equation (4.11) can be simplified when the laminate is thin. For thin laminates (thickness of about 3 mm or less), the tempera-

TABLE 4.3 Heat of Reaction for Two Composite Materials [6].

	Glass/polyester	Graphite/epoxy
w_r	46%	42%
w_f	54%	58%
H_{resin} (kJ/kg)	168.6	473.6
H_T (kJ/kg)	77.5	198.9

ture may be considered to be constant across the thickness of the laminate without large error. For that situation, Equation (4.11) can be simplified to be:

$$\frac{\partial(\rho C_p T)}{\partial t} = \frac{d\alpha}{dt} H_T \tag{4.12}$$

The determination of the development of the degree of cure and rate of cure for the case of thin laminates can be obtained using the incremental method and is illustrated in the following example.

Example 4.1

Consider a carbon/epoxy composite where the resin kinetic follows the equation:

$$\begin{aligned} \frac{d\alpha}{dt} &= K\alpha^m(1-\alpha)^n \\ K &= Ae^{-E/RT} \end{aligned} \tag{a}$$

with,

$A =$ 1.27×10^5 sec^{-1}
$E =$ 63400 J/mol
$m =$ 0.9
$n =$ 2.1

Values of the physical properties for many resins, fibers and composite systems are given in Reference [9].

Composite density: $\rho = 1580$ kg/m^3

Composite specific heat: $C_p = 870$ J/(kg·K)

$\rho C_p = 1.3746 \times 10^6$ J/(K·m^3)

Composite conductivity along the thickness direction: $K_z = 0.69$ W/m·K

$H_T = 150$ J/g (or 2.37×10^8 J/m^3)

R: Universal gas constant = 8.31 J/(mol·K)

It is desired to manufacture a laminate of eight layers with thickness of 0.150 mm per layer. The bottom of the laminate is an aluminum mold 12.7 mm thick and the top of the laminate has bagging materials (bleeder, breather layer, etc.). The whole assembly is placed inside an autoclave subject to a temperature cycle. Figure 4.14 shows the configuration.

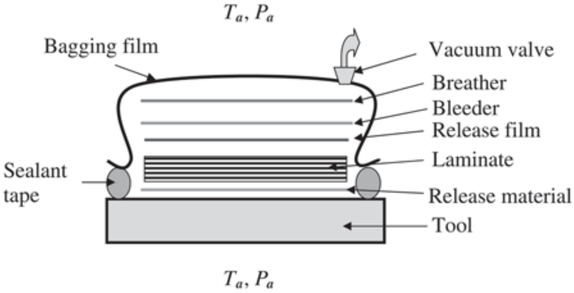


FIGURE 4.14 Configuration for the laminate curing.

Two schedules of temperature will be considered.

- *Linear increase in temperature:* In this schedule, the temperature of the autoclave is increased linearly from room temperature (20°C) at a rate of 5°C per minute.
- *Two-step temperature increase:* In this schedule, the autoclave temperature is increasing from room temperature (20°C) at a rate of 5°C per minute for 18 minutes. It is then held constant at 110°C for 10 minutes. Then it is increased by 5°C per minute for 14 minutes to a maximum of 180°C and held there for 60 minutes. (Figure 4.15 shows the temperature schedule.)

Determine the development of degree of cure and rate of cure as functions of time.

$K_{Al} =$ 237 W/K(m
$L =$ 1.2 mm (laminate thickness)
$t_1 =$ 12.7 mm (thickness of mold)
$t_2 =$ 1 mm (thickness of bagging material on top of laminate)
$\rho C_p L = 1.65 \times 10^3$ J/(K·m^2)
$K_{Al} =$ 237 W/m·K
$K_{\text{glass cloth}} =$ 0.26 W/m·K

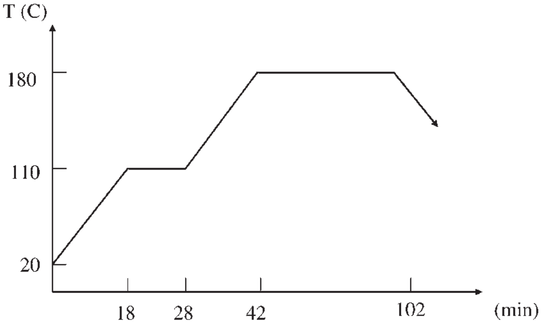


FIGURE 4.15 Schedule of boundary temperatures.

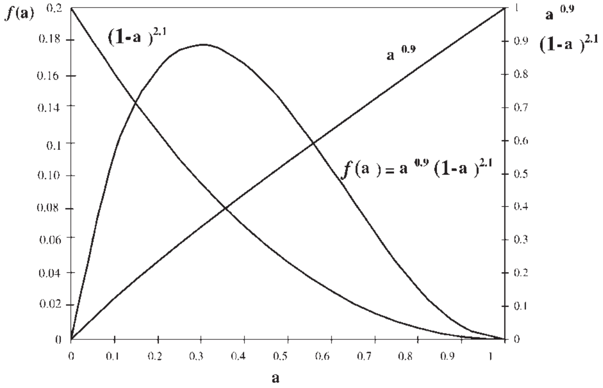


FIGURE 4.16 Function $f(\alpha)$ versus α.

Before proceeding to obtain the solution for this problem, it is informative to examine the influence of the curing order and the activation energy on the curing process. For this, we will examine the variation of the $f(\alpha)$ function and of the frequency factor K.

Define a function $f(\alpha) = \alpha^{0.9}(1 - \alpha)^{2.1}$. A plot of $f(\alpha)$ versus α is shown in Figure 4.16. In Figure 4.17, the portion $(1 - \alpha)^{2.1}$ represents the nth order of the reaction. It is maximum at the beginning and decreases to zero at full cure. This portion $\alpha^{0.9}$ may represent the segments involving primary amines, which are most active at the beginning but decrease in activity as curing proceeds. The portion may represent the autocatalytic segment of the reaction. It is zero at the beginning but increases as the curing proceeds. The combination of these two types of reactions gives rise to the curve of $f(\alpha)$, which has a local maximum with the fastest rate of reaction occurring at about 30% cure.

Denote another function $g(T) = e^{-E/RT} = e^{-63400/(8.31)T} = e^{-7629/T}$. A plot of $g(T)$ versus T is shown in Figure (4.17). Note that T has to be expressed in °K.

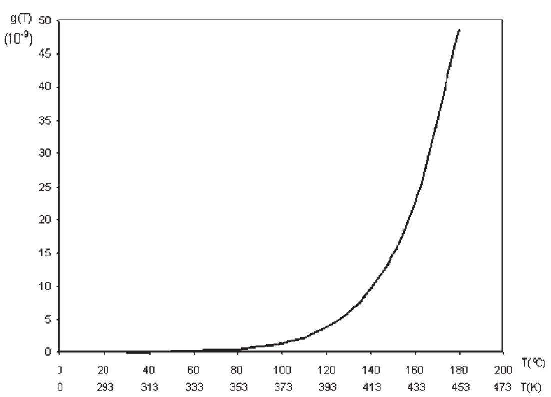


FIGURE 4.17 Plot of $g(T)$ versus T.

It can be seen that $g(T)$ increases very slowly with T at low T (less than 373 K or 100°C). Above 100°C, $g(T)$ increases sharply with T.

Solution

Assuming constant coefficients, Equation (4.12) can be written as:

$$\rho C_p \frac{\partial T}{\partial t} = H_T \frac{\partial \alpha}{\partial t} = H_T A e^{-E/RT} (\alpha)^{0.9} (1-\alpha)^{2.1} \qquad \text{(b)}$$

Equation (b) is a coupled equation and it takes numerical procedure to obtain a solution. However in order to examine the effect of different elements on the solution, an approximate procedure is used. In this procedure, the time scale is divided into small increments. For each time increment, the term on the right-hand side of Equation (b) will be calculated using the temperature of the material at the beginning of the increment. It will be treated as a constant during the increment of time. This term is the heat generated by the chemical reaction. It is the amount of heat per unit volume of the material. Instead of leaving this term in the governing Equation (b), this term will be considered as a heat flux entering into the element from one face (lower face). This equivalent heat flux Q_c is determined as:

$$Q_c = \frac{d\alpha}{dt} H_T L = A e^{-E/RT} \alpha^{0.9} (1-\alpha)^{2.1} H_T L \qquad \text{(c)}$$

In addition to this heat flux, there are also heat fluxes due to heat input from the autoclave through the aluminum mold, and the heat flux from the laminate across the bagging material on the top.

The problem can be formulated as shown in Figure 4.18 with heat flux Q_1 from the bottom face and Q_2 to the top.

The governing Equation (b) can then be written as:

$$\rho C_p L \frac{dT}{dt} = \text{ net heat flux to the sample } = Q_c + Q_1 + Q_2 \qquad \text{(d)}$$

where

Q_c is heat generated by the chemical reaction. Even though this is heat generated per unit volume, it was converted to an equivalent heat flux into the system. This is given by Equation (c) above. It can be seen that this is a function of temperature T. In the incremental procedure adopted below, this is calculated using the temperature at the end of the previous increment, and is considered as a constant during the time increment.

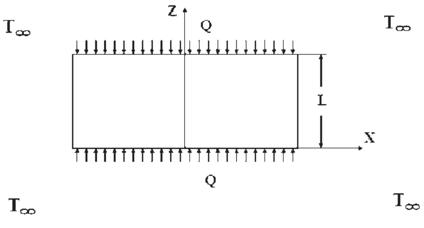


FIGURE 4.18 Equivalent heat transfer problem.

Q_1 is heat flux from the mold to the composite. This can obtained by the equation:

$$Q_1 = \frac{K_1}{t_1}(T_\infty - T) \tag{e}$$

where,

$K_1 =$ the thermal conductivity of the mold
$t_1 =$ the thickness of the mold
$T_\infty =$ the autoclave temperature

Q_2 is heat flux from the mold across the bagging material to the atmosphere in the autoclave on the top side of the laminate. This can be obtained by the equation:

$$Q_2 = \frac{K_2}{t_2}(T_\infty - T) \tag{f}$$

where,

$K_2 =$ the thermal conductivity of the bagging material
$t_2 =$ the thickness of the bagging materials

Substituting Equations (e) and (f) into Equation (d) yields:

$$\rho C_p L \frac{dT}{dt} = Q_c + \frac{K_1}{t_1}(T_\infty - T) + \frac{K_2}{t_2}(T_\infty - T) \tag{g}$$

which can be written as:

$$a\frac{dT}{dt} + bT + c = 0 \tag{h}$$

where,

$$a = \rho C_p L$$

$$b = \frac{K_1}{t_1} + \frac{K_2}{t_2} \tag{i}$$

$$+c = -\left[Q_c + T_\infty\left(\frac{K_1}{t_1} + \frac{K_2}{t_2}\right)\right]$$

Assume that the solution of Equation (h) takes the form:

$$T = c_1 e^{-mt} + c_2$$

Substituting this into Equation (h) yields:

$$-mc_1 a e^{-mt} + bc_1 e^{-mt} + bc_2 + c = 0$$

yielding:

$$m = \frac{b}{c} \qquad \text{and} \qquad c_2 = -\frac{c}{b}$$

Applying the initial condition: at $t = 0$, $T = T_o$, where T_o is the initial temperature of the lower surface of the laminate, we have:

$$T_o = c_1 + c_2$$

$$c_1 = T_o - c_2 = T_o + \frac{c}{b}$$

The solution is then:

$$T = \left(T_o + \frac{c}{b}\right)e^{-mt} - \frac{c}{b} \tag{j}$$

Substituting the expressions for a, b and c yields:

$$T = \left[T_o - \frac{Q_c + T_\infty\left(\frac{K_1}{t_1} + \frac{K_2}{t_2}\right)}{\frac{K_1}{t_1} + \frac{K_2}{t_2}} \right] e^{-mT} + \frac{Q_c + T_\infty\left(\frac{K_1}{t_1} + \frac{K_2}{t_2}\right)}{\frac{K_1}{t_1} + \frac{K_2}{t_2}} \tag{k}$$

and

$$m = \frac{\frac{K_1}{t_1} + \frac{K_2}{t_2}}{\rho C_p L} \tag{l}$$

For this problem, the following quantities have been determined:

$$Q_c = L\,H_T\,d\alpha/dt = [3.6 \times 10^{10}\ \text{J/(sec}\cdot\text{m}^2)]e^{-7629/T}\,\alpha^{0.9}(1 - \alpha)^{2.1} \tag{m}$$

$$\frac{K_1}{t_1} = \frac{K_{AL}}{t_1} = \frac{237\ \text{W / K.m}}{12.7\ \text{mm}} = 18661\ \text{W / (m}^2.K)$$

$$\frac{K_2}{t_2} = \frac{K_{glass\ cloth}}{1\ \text{mm}} = \frac{0.26\ \text{W / K.m}}{0.001\ \text{mm}} = 260\ \text{W / (m}^2.K)$$

$$\frac{K_1}{t_1} - \frac{K_2}{t_2} = 18921\ \text{W / (m}^2 K)$$

$$m = \frac{18921}{1.65\ \times\ 10^{+3}} = 11.47\ \text{sec}^{-1}$$

Rate of cure:

$$\frac{d\alpha}{dt} = (1.27\ \times\ 10^5\ /\ \text{sec})e^{-7629/T}(\alpha)^{0.9}(1 - \alpha)^{2.1} \tag{n}$$

Equation (k) can be written as:

$$T - T_\infty = \left[T_o - \frac{Q_c + 18401 T_\infty}{18401}\right]e^{-11.47t} + \frac{Q_c}{18401} \tag{o}$$

The determination of the degree of cure at a time increment ($n + 1$) is determined from the degree of cure at the previous step (n) following the equation:

$$\alpha^{n+1} = \alpha^n + \left(\frac{d\alpha}{dt}\right)^{n+1} \Delta t \tag{p}$$

Initial conditions:
$T_o =$ 273 K
$\alpha_o = 0.1$

Increment 1: Time increment from 0 to 5 minutes

During this time increment, the temperature of the surrounding T_∞ increases from 20°C to 45°C (293–318 K). An average temperature of 305.5 K for this increment is used for T_∞.

We have:

$T_\infty = 305.5°C$
$\alpha = 0.1$

Q_c is calculated based on the average temperature of the increment, which is 305.5 K. From Equation (m): $Q_c = 0.05$ W/m².

Temperature of the composite is calculated from Equation (o) as:

$$T - 305.5 = \left[273 - \frac{0.05 + 18921(305.5)}{18921}\right]e^{-(11.47)/(300)} + \frac{0.05}{18921} = 2\times10^{-6}$$

$$T = 305.5K$$

It can be seen that the increase in temperature due to heat generation by chemical reaction is very small and the temperature of the part is controlled mainly by the autoclave temperature for this case. The rate of cure as given by Equation (*n*) can be calculated as:

$$\frac{d\alpha}{dt} = (1.27\times10^5 / \text{sec})e^{-7629/3055}(0.1)^{0.9}(1-0.1)^{2.1} = 1.82\times10^{-7} / \text{sec}$$

The degree of cure at the end of this increment is:

$$\alpha_1 = 0.1 + (1.2\times10^{-7})(300) = 0.1$$

Increment 2: Time increment from 5 to 10 minutes

During this time increment, the temperature of the surrounding T_∞ increases from 45°C to 70°C (318–343 K). An average temperature of 330.5 K for this increment is used. In order to start the process, a degree of cure $\alpha_1 = 0.1$ is assumed. We have:

$T_\infty = 330.5°C$
$\alpha_1 = 0.1$
$Q_c = 0.34$ W/m²

The rate of cure as given by Equation (*n*) can be calculated as:

$$\frac{d\alpha}{dt} = (1.27\times10^5 / \text{sec})e^{-7629/3305}(0.1)^{0.9}(1-0.1)^{2.1} = 1.2\times10^{-6} / \text{sec}$$

The degree of cure at the end of this increment is:

$$\alpha_2 = 0.1 + (1.2\times10^{-6})(300) = 0.1$$

TABLE 4.4 Progression of Cure of the Example (linear increase in autoclave temperature).

Time (minutes)	T_a (°C)	T_∞ (°C)	T_∞ (K)	Q_c (W/m^2)	T (K)	Rate of Cure (sec^{-1})	Degree of Cure (α)
0	20	20	293	0	293	1.2×10^{-8}	0.1
5	45	32.5	305.5	0.05	305.5	1.2×10^{-7}	0.1
10	70	57.5	330.5	0.34	330.5	1.2×10^{-6}	0.1
15	95	82.5	355.5	1.72	355.5	6.1×10^{-6}	0.102
20	120	107.5	380.5	7.21	380.5	2.55×10^{-5}	0.110
25	145	132.5	405.5	26.1	405.5	9.17×10^{-5}	0.138
30	170	157.5	430.5	89.2	430.5	2.46×10^{-4}	0.211
35	180	175	448	217	448	7.64×10^{-4}	0.440
40	180	180	453	247	453	8.71×10^{-4}	0.702
45	180	180	453	99.8	453	3.70×10^{-4}	0.813
50	180	180	453	42.9	453	1.89×10^{-4}	0.941
55	180	180	453	4.33	453	1.53×10^{-5}	0.946
60	180	180	453	3.6	453	1.27×10^{-5}	0.950

Proceed with the same procedure for subsequent time increments. Tables 4.4 and 4.5 show the values of the temperature of the composite part and its degree of cure at different time points for linear increase and a two-step increase in temperatures of the autoclave.

TABLE 4.5 Progression of Cure of the Example (two-step increase in autoclave temperature).

Time (minutes)	T_a (°C)	T_∞ (°C)	T_∞ (K)	Q_c (W/m^2)	T (K)	Rate of Cure (sec^{-1})	Degree of Cure (α)
0	20	20	293	0	293	1.2×10^{-8}	0.1
5	45	32.5	305.5	0.05	305.5	1.2×10^{-7}	0.1
10	70	57.5	330.5	0.34	330.5	1.2×10^{-6}	0.1
15	95	82.5	355.5	1.72	355.5	6.1×10^{-6}	0.102
18	110	102.5	375.5	5.52	375.5	1.95×10^{-5}	0.106
23	110	110	383	8.39	383	2.96×10^{-5}	0.114
28	110	110	383	8.86	383	3.13×10^{-5}	0.123
33	110	110	383	9.27	383	3.27×10^{-5}	0.132
38	110	110	383	9.62	383	3.40×10^{-5}	0.142
40	120	115	388	13.0	388	4.6×10^{-4}	0.148
45	145	132.5	405.5	31.1	405.5	1.1×10^{-4}	0.181
50	170	157.5	430.5	102	430.5	3.6×10^{-4}	0.289
52	180	175	448	231	448	8.2×10^{-4}	0.387
60	180	180	453	265	453	9.4×10^{-4}	0.837
70	180	180	453	32.7	453	1.15×10^{-4}	0.906
80	180	180	453	11.1	453	3.92×10^{-5}	0.930
90	180	180	453	6.14	453	2.17×10^{-5}	0.942

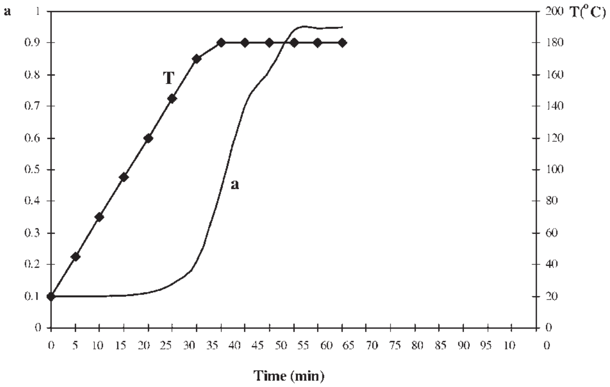


FIGURE 4.19 Variation of temperature and degree of cure as a function of time (linear increase in autoclave temperature).

Figures 4.19 and 4.20 show the variations of the temperatures and degrees of cure as functions of time for a linear increase and a two-step increase in temperature of the autoclave. It can be seen that the temperature of the part follows closely the temperature of the autoclave. The degree of cure reaches to 80% after 45 minutes but it takes a long time for it to reach full cure.

It can be seen that linear increase in temperature makes the resin cure very quickly (up to 30 minutes of low cure degree) while a two-step temperature increase allows more time for the resin to have a low degree of cure (up to 50 minutes of low-cured degree). Lower degree of cure ensures low viscosity, which is required for resin flow and for the elimination of voids as discussed in Section 2.6.5. Note that fairly coarse increments of time were used in the example for illustration purpose. Finer time increments should provide better results.

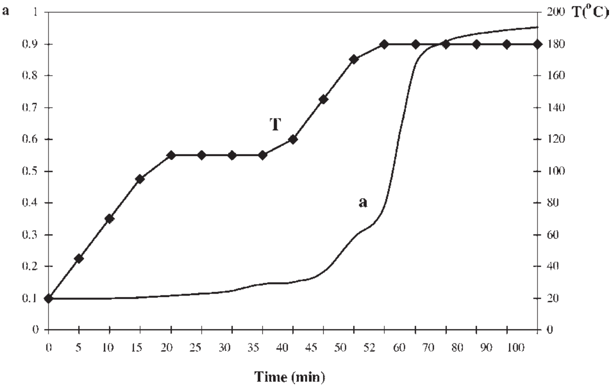


FIGURE 4.20 Variation of temperature and degree of cure as a function of time (two-step increase in autoclave temperature).

2.6.2.2. Thick Laminates

Thick laminates refer to laminates that are about 6 mm or more thick. For the thick laminates, the dependence on thickness of the temperature is significant and the simplification made for thin laminates does not apply. Equation (4.11) rather than (4.12) has to be solved. The solution procedure is complex and numerical method using a computer is necessary. Bogetti and Gillespie [7] have worked out the solution for a few thick composites. They examined thick laminates made of glass/polyester and graphite/epoxy. The variation of the modulus of the resin and resin shrinkage during cure were taken into account. The temperature distributions and stresses were calculated using a computer program. Figure 4.21 shows the temperature distribution across the thickness of laminates with different thicknesses. For laminates with thickness less than 2.54 cm, at 164 minutes into the curing process, the temperature at the mid-thickness region is larger than the temperature at the bottom and top of the laminate. However when the thickness is 5.08 cm, the temperature at the mid-thickness region is smaller than that on the surfaces. This is because for thinner laminates, heat flow from the mold can enter quickly into the mid-thickness area. This helps to kick-start the reaction in all parts of the laminate. Heat generated in the mid-thickness area cannot dissipate to the surrounding environment as quickly as heat generated

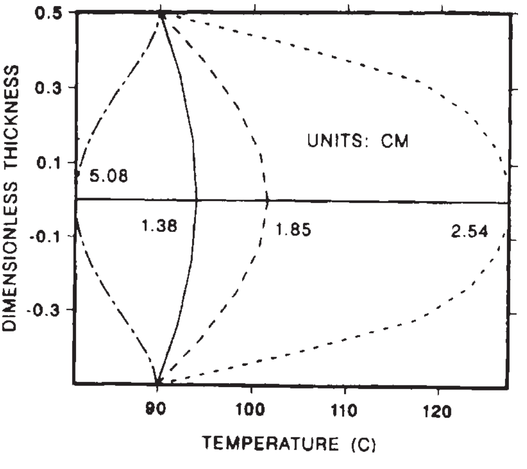


FIGURE 4.21 Temperature distribution in a thick laminate at 164 minutes (glass/polyester laminate) (reproduced from Bogetti T. A. and Gillespie J. W. "Process induced stress and deformation in thick section thermoset composite laminates," *J. Composite Materials,* Vol. 26, No. 5, 1992, pp. 626–660, with permission from Sage Publications).

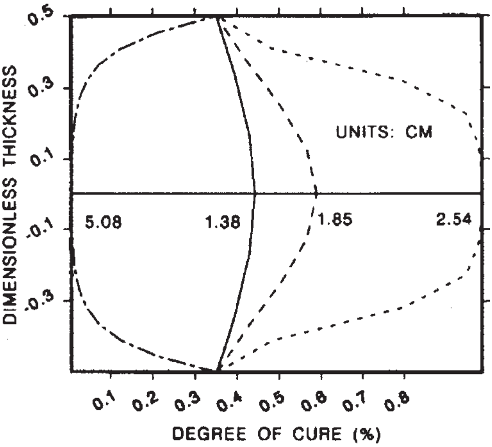


FIGURE 4.22 Degree of cure distribution in a thick laminate at 164 minutes (Glass/polyester laminate) (reproduced from Bogetti T. A. and Gillespie J.W. "Process induced stress and deformation in thick section thermoset composite laminates," *J. Composite Materials,* Vol. 26, No. 5, 1992, pp. 626–660,with permission from Sage Publications).

from areas close to the surface. As such, the mid-thickness region is hotter than regions close to the surface of the laminate.

On the other hand, for thicker laminates (5.08 cm thick), it takes longer for the heat from the tool to reach the mid-thickness region because the mid-thickness region has not had the chance for the reaction to take place at 164 minutes in to the cure. Temperature close to the surface of the laminate is therefore larger than that in the mid-thickness region.

Figure 4.22 shows the degree of cure development of the laminates studied by Bogetti and Gillespie [7]. The degree of cure follows the same distribution as the temperature distribution.

2.6.3. Viscosities

The viscosity of the resin as a function of time depends on the extent of the reaction of the components. An empirical relationship was used by Lee et al. in 1982 as [8]:

$$\mu = \mu_\infty \exp\left(\frac{U}{RT} + k\alpha\right) \tag{4.13}$$

where α is the degree of cure, μ_∞ is a constant, U is the activation energy for viscosity, and k is a constant that is dependent on the temperature. To

TABLE 4.6 Parameters for Equation (4.13).

Author	System	μ_o (Pa·s)	E (J/mol)	K (Pa·s)	Range of Validity
Lee et al. [8]	Hercules 3501-6	7.93×10^{-14}	9.08×10^{4}	14.1 ± 1.2	$\alpha < 0.5$
Dusi et al. [13]	Fiberite 976	1.06×10^{-6}	3.76×10^{4}	18.8 ± 1.2	$\alpha < 0.2$

characterize the viscosity as a function of temperature it is necessary to determine the value of *k* by fitting a least- squares curve to the μ versus α data. The degree and rate of cure can be determined from isothermal scans and, in general, the behavior is fit into an Arrhenius-type equation. This treatment is usually empirical, but the information is key to understanding the viscosity of the resin and thus the bleed-off and fiber volume fraction distribution that results from a given autoclave processing cycle. The values for these parameters for two resin systems are listed in Table 4.6.

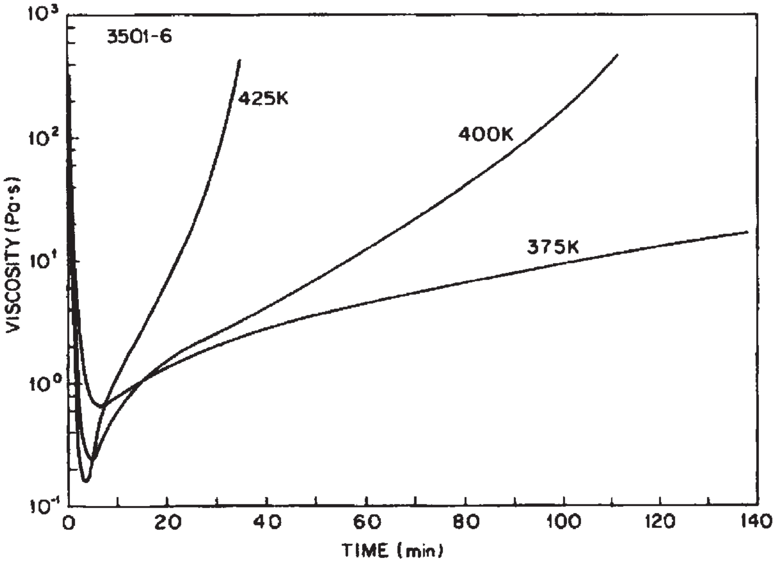


FIGURE 4.23 Isothermal viscosity for Hercules 3501-6 resin (reproduced from Lee W. I., Loos A. C. and Springer G. S., "Heat of reaction, degree of cure, and viscosity of Hercules 3501-6 resin," *Journal of Composite Materials,* Vol. 16, 1982, pp. 510–520, with permission from Sage Publications).

Substituting the values for Hercules 3501-6 into Equation (4.13) yields:

$$\mu = 7.93 \times 10^{-14} \exp\left(\frac{9.08 \times 10^{4}}{8.31T} + 14.1\alpha\right) \quad \text{in} \quad \text{Pa - sec} \qquad (4.14)$$

The variation of the degree of cure as a function of time at different temperatures for the above resin is shown in Figure 4.23.

Calado and Advani [9] gave a comprehensive table of many cure kinetic models for epoxies.

Example 4.2

Values of the temperature and degree of cure of example 4.1 are given in Tables 4.4 and 4.5 for two different schedules of heating. Using these values, determine the variation of the viscosity of the resin as a function of time, assuming that the viscosity follows Equation (4.14).

Table 4.7 shows the values of the viscosity for different times for a linear increase in temperature, and Table 4.8 shows the values for a two-step cure cycle.

Figure 4.24 shows the variation of viscosity for the two heating schedules. For the two- step heating schedule, long time at low viscosity allows more time to apply pressure. Note that after the dwell period at low viscosity, the viscosity increases rapidly.

TABLE 4.7 Viscosity for a linear increase in autoclave temperature.

Time (minutes)	T_a (°C)	T_∞ (°C)	T_∞ (K)	T (K)	Degree of Cure (sec^{-1})	Viscosity (Pa·s)
0	20	20	293	293	0.1	5138
5	45	32.5	305.5	305.5	0.1	1084
10	70	57.5	330.5	330.5	0.1	72.6
15	95	82.5	355.5	355.5	0.102	7.33
20	120	107.5	380.5	380.5	0.110	1.09
25	145	132.5	405.5	405.5	0.138	0.28
30	170	157.5	430.5	430.5	0.211	0.16
35	180	175	448	448	0.440	1.52
40	180	180	453	453	0.702	46.5
45	180	180	453	453	0.813	223
50	180	180	453	453	0.941	1356
55	180	180	453	453	0.946	1455
60	180	180	453	453	0.950	1540

TABLE 4.8 Viscosity for a Two-Step Temperature Cycle.

Time (minutes)	T_a (°C)	T_∞ (°C)	T_∞ (K)	T (K)	Degree of Cure (sec^{-1})	Viscosity (Pa·s)
0	20	20	293	293	0.1	5138
5	45	32.5	305.5	305.5	0.1	1084
10	70	57.5	330.5	330.5	0.1	72.6
15	95	82.5	355.5	355.5	0.102	7.33
18	110	102.5	375.5	375.5	0.106	1.50
23	110	110	383	383	0.114	0.95
28	110	110	383	383	0.123	1.08
33	110	110	383	383	0.132	1.22
38	110	110	383	383	0.142	1.42
40	120	115	388	388	0.148	1.06
45	145	132.5	405.5	405.5	0.181	0.50
50	170	157.5	430.5	430.5	0.289	0.48
52	180	175	448	448	0.387	0.71
60	180	180	453	453	0.837	310
70	180	180	453	453	0.906	820
80	180	180	453	453	0.930	1150
90	180	180	453	453	0.942	1362
100	180	189	453	453	0.951	1546

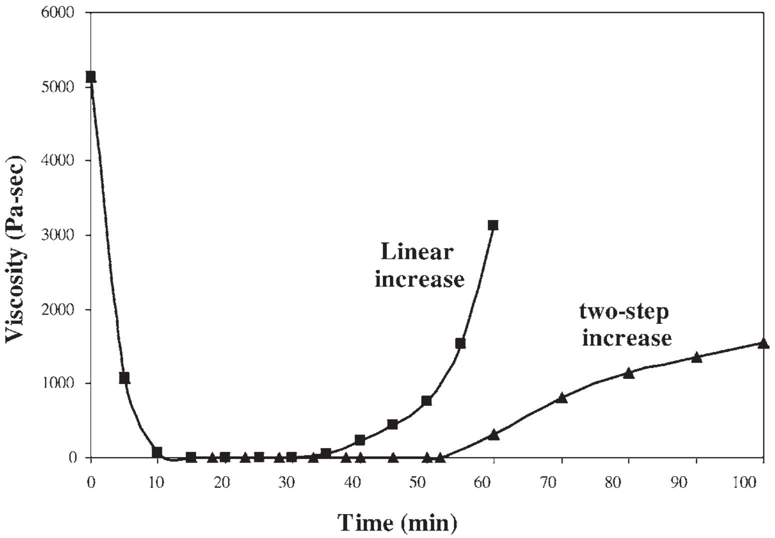


FIGURE 4.24 Variation of viscosity for two heating schedules.

2.6.4. Resin Flow and Consolidation

Usually the prepregs contain more resin than the final cured composite. During curing, the excess resin is oozed out. The excess resin flows from the bottom layers to the top layers. The bleeder materials absorb the excess resin. In order for the excess resin to flow from the mold side to the bleeder side, pressure needs to be applied. In addition, fibers are wavy and the fiber bed is similar to a springy network. It is necessary to flatten these fibers so that the composite layers are well consolidated. The combined springy fiber network and liquid resin is shown schematically in Figure 4.25.

This can be modeled as spring and dash pot as shown in Figure 4.26, where the stress P_a represents the pressure in the autoclave. The equilibrium condition can be written as:

$$P_a = P_r + P_f \tag{4.15}$$

In order to fully model the consolidation behavior of composites, both the resin flow and fiber deformation must be taken into account. The requirements for the resin pressure and the pressure required to consolidate the fibers are shown following.

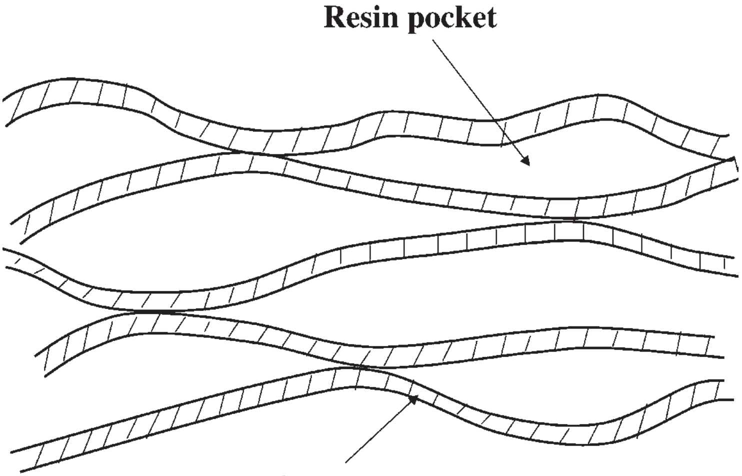


FIGURE 4.25 Springy fiber network surrounded by resin.

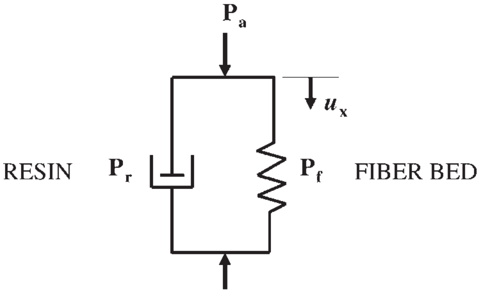


FIGURE 4.26 Model of fiber bed and resin.

2.6.4.1. Resin Flow

Flow through a fiber assembly is treated as flow through porous media, using the general form of Darcy's law, which states that the flow rate is dependent on the applied pressure, the fluid viscosity, and the permeability of the fiber network. Darcy's law can be written in vector form as:

$$\begin{bmatrix} u_x \\ u_y \\ u_z \end{bmatrix} = \frac{1}{\mu}\begin{bmatrix} K_{xx} & K_{xy} & K_{xz} \\ K_{yx} & K_{yy} & Kyz \\ K_{zx} & K_{zy} & K_{zz} \end{bmatrix}\begin{bmatrix} \dfrac{\partial p}{\partial x} \\ \dfrac{\partial p}{\partial y} \\ \dfrac{\partial p}{\partial z} \end{bmatrix} \tag{4.16}$$

where u_i are the components of the superficial velocity vector $\boldsymbol{u}$,K_{ij} are components of the permeability tensor K of the porous medium, $\partial p/\partial x$, $\partial p/\partial y$, $\partial p/\partial z$ are components of the pressure gradient vector $\Delta \mathbf{P}$, and μ is the fluid viscosity.

For the matrix of the coefficients of permeability, when the coordinate axes coincide with the principal material directions, only the diagonal values (K_{xx}, K_{yy}, K_{zz}) are non-zero. For a unidirectional ply, which is transversely isotropic, these directions correspond to the fiber axis and any two mutually perpendicular transverse axes. Generally the permeability is much higher in the direction along the fibers than transverse or through the thickness. The permeability is also a function of the fiber volume function V_f, fiber radius r_{fi} and fiber architecture. A number of studies have been carried out to determine the permeability of fibrous preforms. In general, the dependence of permeabilities on the material parameters mentioned above, and on the fiber volume fraction have been treated using the Kozeny-Carman equation, which can be written as:

$$K = \frac{r_f^2}{4k_o} \frac{(1 - v_f)^3}{v_f^2} \tag{4.17}$$

where k_o is the Kozeny constant. The value of k_o varies with the fiber architecture and the direction of the flow. For flow parallel to the fibers, values of 0.5–0.7 have been reported, while for transverse flow, values of $k_o = 11$–18 have been quoted. The measured values of the Kozeny constant show significant variation and are sensitive to experimental conditions. In practice, when the fiber volume fraction approaches its theoretical limit, lateral or through-the-thickness flow can shut off as the fibers are forced into contact with one another along their entire lengths.

Figure 4.27 shows a curve of axial permeability values for aligned AS4 fibers with the Kozeny-Carman equation. In this figure, the symbol S_{xx} is

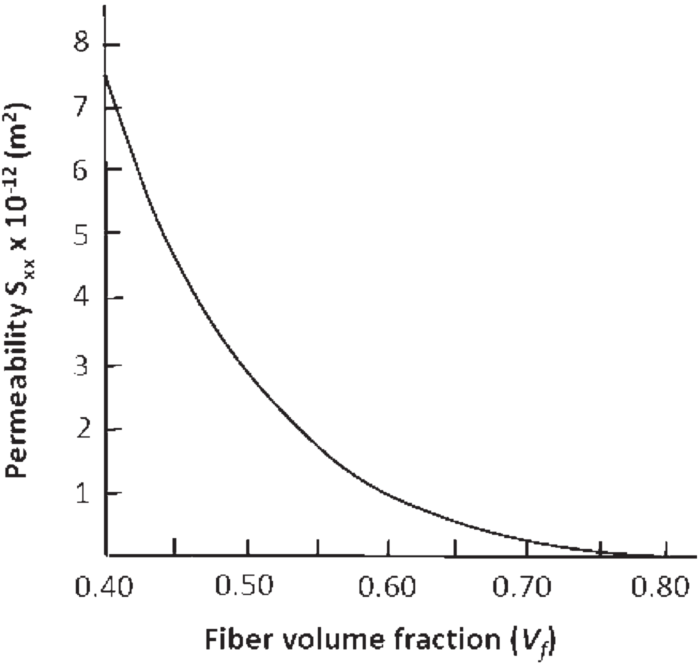


FIGURE 4.27 Axial permeability of aligned AS4 fibers with Kozeny-Carman equation ($k_{xx} = 0.7$) (corn oil and silicone liquid).

used to denote the permeability. This symbol has the same meaning as the symbol K_{xx}. Note that the permeability has the unit of length squared.

For most cases of practical importance, flow across the thickness of the laminate is considered. In this case, Equation (4.16) can be simplified to be:

$$u_z = \frac{K_{zz}}{\mu}\frac{dp}{dz} \tag{4.18}$$

The velocities in Equations (4.16) and (4.18) are dependent on viscosity, which varies greatly during an autoclave curing cycle. Most resins employed in aerospace material prepregs are in a B-staged or partly reacted condition. Their initial viscosities are therefore relatively high. As the material is heated, the viscosity drops dramatically and reaches a minimum at a temperature that is generally prescribed as a "hold" temperature in the autoclave curing cycle (Figure 4.23). This is to ensure that complete wet-out is achieved and that excess resin is effectively squeezed out of the plies and into the bleeder material.

This is also the temperature at which the resin is most susceptible to void formation (void formation is discussed in Section 5.5 later in this chapter). Thus the pressure developed in the resin at this time is absolutely critical. Continued heating leads to the initiation of cure and the resin viscosity increases progressively until the resin solidifies. The resin state changes during this process can be conveniently represented in a time-temperature-transformation (TTT) curve as shown in Figure 4.28.

In general, the resin in a typical epoxy prepreg system goes from the ungelled glass region (in the freezer) to a liquid (viscosity drops) through gelation (as the reaction proceeds) and into the vitrification regime (when solidification occurs). If the resin solidified before the voids are either compressed to negligible size or squeezed out of the laminate, then there will be holes in the solidified resin.

2.6.4.2. Consolidation

Consolidation involves the squeezing of the resin out of the laminate (into the bleeder materials) and also the flattening of the fiber network. Dave et al. [11] modeled the squeezing out of the resin by a system of water (representing the liquid resin) and spring (representing the fiber network) in a container (Figure 4.29). On top of the spring and water is a constant weight simulating the pressure applied by the autoclave, similar to the case of a piston in a cylinder. The piston has a relief valve which is

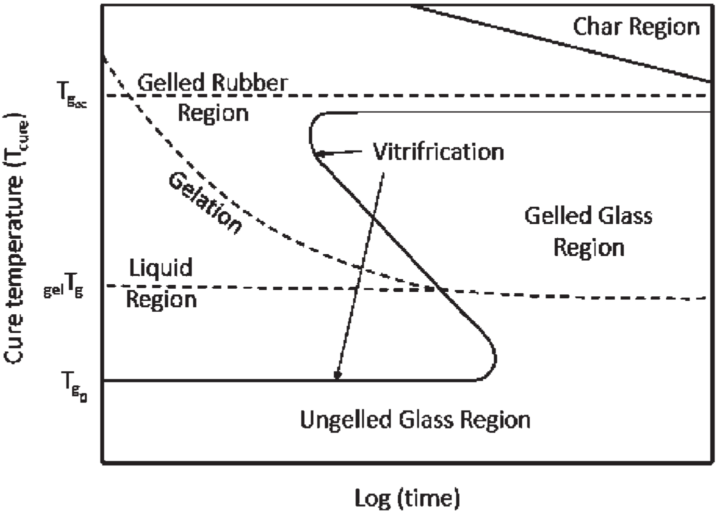


FIGURE 4.28 The time temperature transformation diagram for isothermal cure (reproduced from Enns J. B. and Gillham J. K., *Journal of Applied Polymer Science,* Vol. 28, 1983, pp. 2567–2591, with permission from Wiley Interscience).

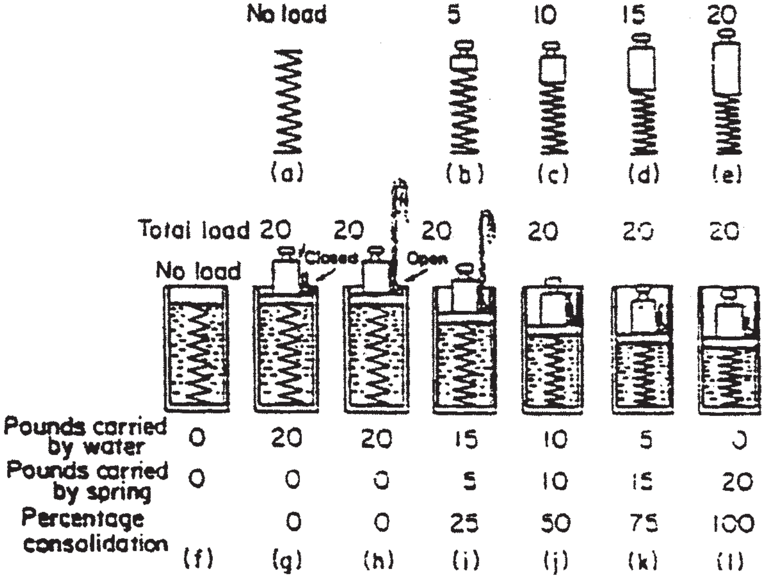


FIGURE 4.29 Conceptual representation of the consolidation of the fiber/resin system (reproduced from "A model for resin flow during composite processing. Part I: General mathematical development," by R. Dave, J. L. Kardos, and M. P. Dudukovic, *Polymer Composites,* Vol. 8, No. 1, 1987, 29–38, with permission from Society of Plastic Engineers).

closed at the beginning. The liquid (water) absorbs most of the load. At a certain instant of time during the curing process, the relief valve is opened. Liquid is allowed to leak out of the container. The spring is compressed and the spring takes up more and more of the load. At the end of the process, the spring takes up all of the load and the pressure in the liquid diminishes to almost nil.

Gutowski [1] proposed another model that considers the waviness of the fiber network. The formulation to calculate the stresses developed in the fiber network due to compression was presented in Chapter 3. As resin flows out of the composite, the fiber volume fraction increases. This decreases the spacing between the fibers to the point where significant fiber-fiber contact occurs. When significant contact exists, the fiber network becomes load-bearing and can have a significant effect on the overall flow behavior of the composite. One of the most important consequences of the chain of events is reduction in resin pressure, which can lead to voids in the matrix and a subsequent loss in the structural properties of the composite. This effect may be included in consolidation models by describing the load-carrying behavior of the fiber bundle. For transverse compression this relationship can be given as a function between the applied stress and the fiber volume fraction (repeated from Chapter 3).

$$\sigma_b = \frac{3\pi E}{\beta^4} \frac{1 - \sqrt{\dfrac{V_f}{V_o}}}{\left(\sqrt{\dfrac{V_a}{V_f}} - 1\right)^4} \tag{4.19}$$

where V_a is the maximum attainable fiber volume fraction, V_o is the initial fiber volume fraction corresponding to zero load, and β is a constant that describes the shape of the fiber.

Example 4.3

Continue from the case considered in Examples 4.1 and 4.2. Assuming that the pressure applied in the autoclave is 80 psi (547 kPa). Determine:

a. Stress absorbed by the fiber network.
b. Pressure in the resin.
c. Speed of flow of the resin out of the fiber network at the period of lowest viscosity (Figure 4.24).

d. Whether this speed is sufficient for the resin to flow out of the laminate before gelling.

The fiber volume fractions are:

Initial fiber volume fraction $V_o = 0.50$
Allowable fiber volume fraction: $V_a = 0.85$
Final volume fraction $V_f = 0.68$.
Fiber modulus: $E = 234$ GPa
Fiber aspect ratio: $\beta = 300$

Solution

a. Stress in the fiber bundle can be obtained using Equation (4.19):

$$\sigma_b = \frac{3\pi E}{\beta^4} \frac{1-\sqrt{\frac{V_f}{V_o}}}{\left(\sqrt{\frac{V_a}{V_f}}-1\right)^4} = \frac{3\pi(234\text{ GPa})}{300^4} \frac{1-\sqrt{\frac{0.68}{0.50}}}{\left(\sqrt{\frac{0.85}{0.68}}-1\right)^4} = 232.7\text{ kPa}$$

b. Pressure in the resin:

From Equation (4.15),

$$P_a = P_r + P_f$$

$$P_r = P_a - P_f = 547 - 232.7 = 314.3\text{ kPa}$$

c. Speed of flow of resin:

Using Equation (4.17) for permeability transverse to fiber direction with $r_f = 3.5$ µm and $k_o = 18$, we have:

$$K = \frac{r_f^2}{4k_o} \frac{(1-v_f)^3}{v_f^2} = \frac{(3.5\times10^{-6}m)^2}{4\times18} \frac{(-0.68)^3}{(0.68)^2} = 1.2\times10^{-14}\,m^2$$

Using Darcy's law, Equation (4.18)

$$u_z = \frac{K_{zz}}{\mu}\frac{dp}{dz}$$

The thickness of the laminate is 1.2 mm and the viscosity at the lowest point in Figure 4.23) is about 1 Pa·sec. We have:

$$u_z = \frac{1.2\times10^{-14}\,m^3}{1\text{ Pa - sec}} \frac{314.3\text{ kPa}}{1.2\text{ mm}} = 3.14\times10^{-3}\text{ mm / sec}$$

d. Is there sufficient time for resin to flow out of the laminate?

Time required for resin to flow out of the laminate:

$$t = \frac{\text{thickness}}{u_z} = \frac{1.2\text{ mm}}{3.14\times10^{-3}\text{ mm / sec}} = 382\text{ sec} = 6.37\text{ minutes}$$

Examining Figure 4.24, the duration where viscosity is low is about 25 minutes (from 10–35 minutes) for the linear increase in temperature and the duration is about 40 minutes (from 10–50 minutes) for the two-step increase. As such both heating schedules are adequate for the flow.

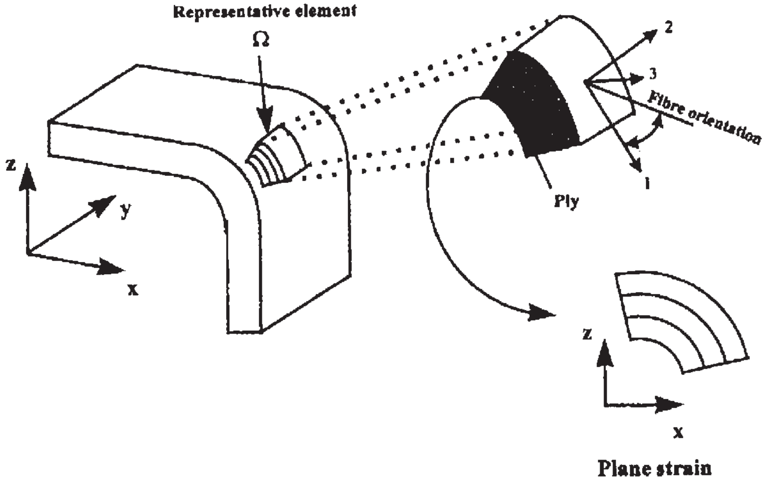


FIGURE 4.30 Angled piece (reproduced from Hubert P., Vaziri R. and A. Poursartip, "A two dimensional flow model for the process simulation of complex shape composite laminates," *Inter. J. for Numerical methods in Engineering,* Vol. 44, 1999, pp. 1–26, with permission from Wiley Interscience Publications.

For the manufacturing of curved pieces such as an angle piece, apart from the compression, there is also the possibility for shear flow. Figure 4.30 shows the configuration of an angled piece.

The stress-relation in this case needs to consider not only normal stresses but also shear stresses as shown in Figure 4.31.

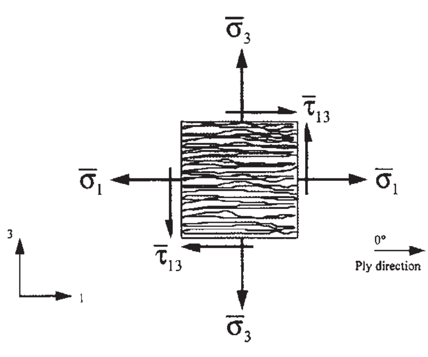


FIGURE 4.31 Fiber bundle subjected to three-directional loading (reproduced from Hubert P., Vaziri R. and A. Poursartip, "A two dimensional flow model for the process simulation of complex shape composite laminates," *Inter. J. for Numerical Methods in Engineering,* Vol. 44, 1999, pp. 1–26, with permission from Wiley Interscience Publications).

A simplified model was employed by Hubert et al. [12] to describe the stress-strain relation for the fiber bundle in Figure 4.31 as:

$$\begin{bmatrix} \bar{\sigma}_1 \\ \bar{\sigma}_3 \\ \bar{\tau}_{13} \end{bmatrix} = \begin{bmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & G_{13} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_3 \\ \gamma_{13} \end{bmatrix} \tag{4.20}$$

where E_1, E_2, G_{13} are the elastic constants describing the fiber bundle compaction behavior.

2.6.5. Void Suppression and/or Removal [16]

2.6.5.1. Void Formation

For autoclave processing, the prepregs are removed from the freezer and normally left at room condition for some time to thaw out. The resin in the prepreg may contain a certain amount of moisture, which may have diffused inside the resin material. During processing, upon initial heating, the resin first becomes a liquid. The vapor (or any other gases that may be contained within the resin) may grow to bubbles of a certain size, depending on the pressure in the resin. If the pressure in the resin (surrounding the bubble) is not high enough, these moisture or gas bubbles may grow to significant size. To avoid this there are two things that should happen. One is that if the pressure in the resin is high enough, then the moisture or gas may not be able to form bubbles of significant size. The other is that if the pressure in the resin is high enough, then whatever bubbles have already formed can be squeezed out of the material system while the resin is still a liquid. In either case, the pressure in the resin has to be sufficiently large to prevent large bubbles from remaining inside the resin after solidification has occurred. If bubbles do remain, they will appear as voids.

Let first consider the synergistic effect that water has on void stabilization. It is likely that a distribution of air voids occurs at ply interfaces because of pockets, wrinkles, ply ends, and particulate bridging. The pressure inside these voids is not sufficient to prevent their collapse on subsequent pressurization and compaction. However, as water vapor diffuses into the voids or when water vapor voids are nucleated, there will be, at any one temperature, an equilibrium water vapor pressure (and therefore partial pressure in the air-water void) that, under constant volume conditions, will cause the total pressure in the void to rise above that of a pure-air void. When the void equals or exceeds the surrounding resin hydrostatic pressure plus the surface tension forces, the void becomes stable and can even grow. Equation (4.21) expresses this relationship:

$$P_g - P_r = \frac{\gamma_{LV}}{m_{LV}} \tag{4.21}$$

where P_g and P_r are the gas and resin pressures, respectively, γ_{LV} is the liquid resin void surface tension, and m_{LV} is the ratio of volume to its surface area. Thus the difference in pressure is counterbalanced by the surface tension forces. When the temperature rises for a constant-volume system, P_g will rise faster than P_r, whereas γ_{LV} will decrease slightly. In addition to P_g increasing according to the perfect gas law, the partial pressure of water in the void can rise exponentially because of the temperature effect on the water vapor pressure.

In order to prevent the potential for pure water void growth by moisture diffusion in a laminate at all times and temperatures during the curing cycle, Kardos [14] developed a recommendation for minimum resin pressure at any point as:

$$P_{\min} \geq 4962 \exp\left(-\frac{4892}{T}\right)(RH)\% \tag{4.22}$$

where $P_{\min}(\text{atm})$ = minimum pressure in the resin required to prevent void growth by moisture diffusion at any time during cure. $(RH)_o(\%)$ = relative humidity to which the resin in the prepreg is equilibrated prior to processing, and $T(K)$ = temperature at any time during the curing cycle.

Equation (4.22) was derived from the requirement that void growth by moisture diffusion at any temperature cannot occur if the pressure within the void is greater than the saturated vapor pressure at that temperature. A plot of Equation (4.22) for two relative humidities (50% and 100%) yields a void stability map, which is shown in Figure 4.32. It is evident from this map that vacuum can be applied without encouraging void growth, if such application is coordinated with the temperature of the system.

At the same time, it is also clear that in order to prevent void formation, the resin pressure must be kept high as the temperature increases.

For a relative humidity of 52% and a temperature of 110°C (383 K), Equation (4.22) yields a minimum pressure of 0.732 atm (10.76 psi or 73.5 kPa). Considering the resin pressure of 340 kPa as determined in Example 4.3, the minimum pressure can be easily satisfied.

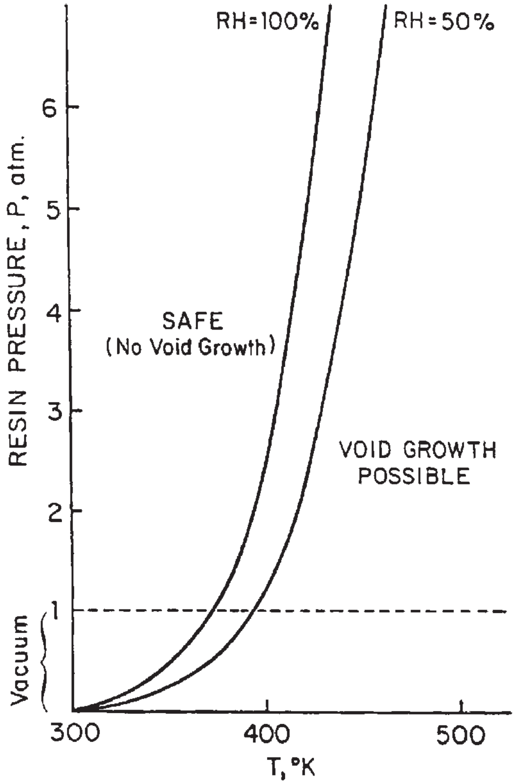


FIGURE 4.32 Void stability map for pure water void formation in Narmco 5208 epoxy matrix (reproduced from "The processing science of reactive polymer composites," by J. L. Kardos in *Advanced Composites Manufacturing,* T. G. Gutowski, ed. ,1997, with permission from Wiley Interscience Publications).

2.6.6. Curing Cycle

The above considerations (determination of temperature, degree of cure, rate of cure, viscosity, resin flow, void formation) can be taken into account to develop the curing cycle. Figure 4.33 shows a typical cure cycle for a carbon/epoxy composite laminate. The cure cycle consists of the temperature cycle, pressure cycle and vacuum. The cycle is called a two-step cure cycle since the temperature cycle has two holds (the horizontal parts of the cycle). Note that the first hold temperature is to allow sufficient time for the low viscosity period in which the resin can wet the fibers, and also to allow time for the resin to flow to the bleeders.

2.6.7. Autoclave [1]

An autoclave may be described as a large pressure vessel with an integral heating capacity. Figure 4.34 shows a typical configuration of an industrial autoclave.

For aerospace applications, the composite parts are quite large, and hence the autoclave has to be larger. For example, the dimensions shown in Figure 4.34 can be $D = 30$ m and $L = 50$ m.

Commonly used aerospace thermoset materials (e.g., high temperature cure epoxies) require cure temperature and pressure on the order of 175°C and 600 kPa (about 80 psi), respectively. Hence the autoclave must be strong at high temperatures. For some composite materials, the pressure and temperature requirements may be even higher. For example, thermoplastic composites (e.g., PEEK, PEI) and higher temperature

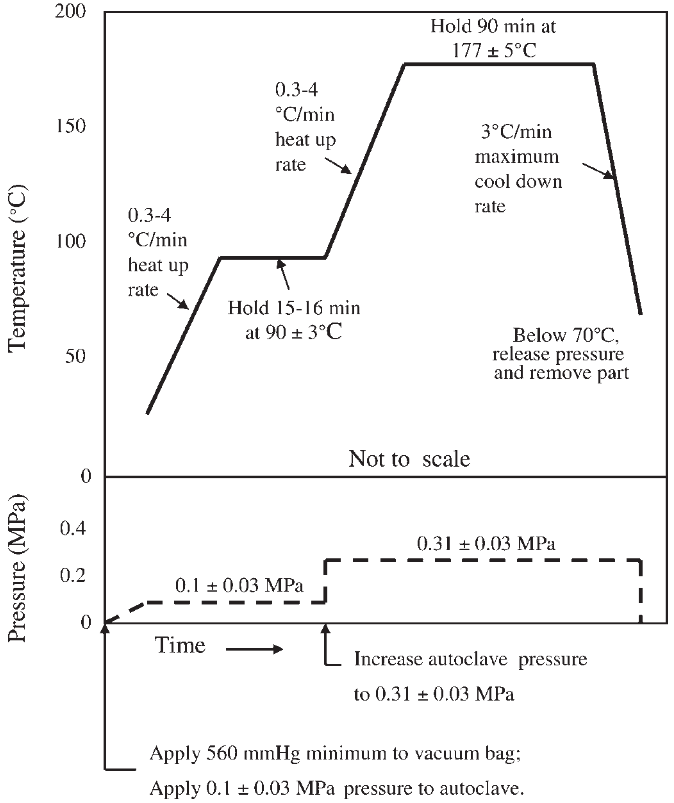


FIGURE 4.33 A typical cure cycle for epoxies.

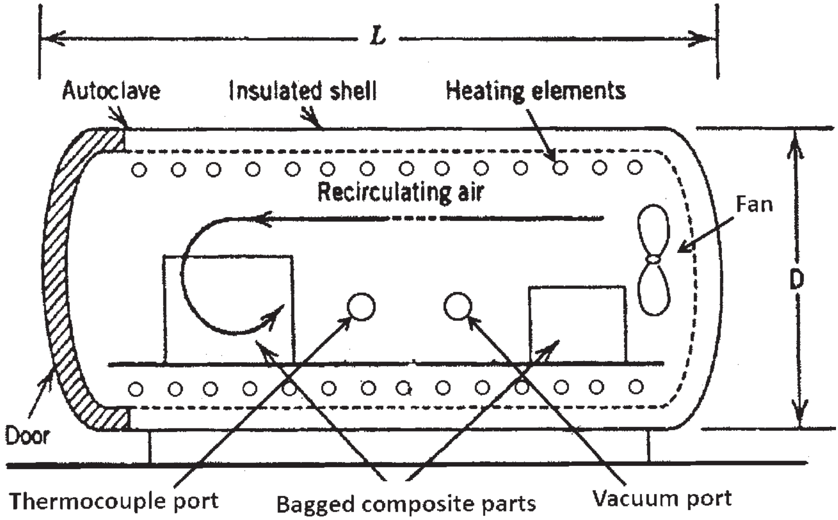


FIGURE 4.34 Schematic drawing of an aerospace autoclave.

thermoset materials (polyimides, PMR15) may require temperatures in the range of 300–400°C and pressures to 689 kPa (100 psi) or higher. For these applications, special autoclaves must be constructed to meet the special requirements but at a significantly higher cost. Fortunately from a cost point of view, most applications are at the mid-range in temperature and pressure.

2.6.7.1. Advantages of the Autoclave

One of the major advantages of the autoclave is its ability to process a wide variety of materials. In general, any polymeric material can be processed as long as its cure cycle falls within the temperature and pressure limitations for the autoclave. A typical cure cycle is shown in Figure 4.33. A second major advantage of the autoclave is that it represents an extremely flexible method to apply pressure to a part. Usually parts are laid-up on one-sided tooling and then wrapped in a plastic bagging material. Pressure is then applied onto the part, which presses it against the tool. The pressure on the part is further intensified by simultaneously pulling a vacuum in the bag. This technique allows the autoclave to be used for the processing of a variety of part shapes. Because of these advantages, the autoclave is used extensively for the production of aerospace advanced composite parts.

2.6.7.2. Disadvantages of the Autoclave [1]

Chief among the shortcomings are its sluggish temperature and pressure response, and relatively poor temperature control. To some extent, all of these problems are related to the large size of the autoclave and the methods of heating and pressurization. Note, however, that the cure cycles of many of the materials developed for aerospace applications are rather slow, on the order of hours. Hence the generally sluggish heating and cooling rates of a large autoclave and associated tooling do not severely limit the process for such materials. Temperature control can be addressed by an improved internal gas circulation system along with temperature sensing and control. Pressure buildup is related to temperature control since temperature is used to heat the gas and increases the pressure.

There are, however, basic fundamental limits to the performance of industrial autoclaves. For example, the time Δt to achieve a given adiabatic temperature rise ΔT for a given power is controlled by the mass M and heat capacity at constant pressure C_p as:

$$\Delta t \approx \frac{Mc_p \Delta T}{\text{power}} \tag{4.23}$$

In general, the Mc_p term for the autoclave and the tooling can be very large, much larger than that of the part. Thus the thermal inertia of the equipment and tooling represents a limitation on the heating and cooling rates for the process. As a result, large autoclaves are not suitable for the rapid processing of material with potentially short thermal cycles.

Currently the most popular pressurizing medium for autoclave is nitrogen. Although air is still sometimes used because of the risk of auto-ignition, its use is generally confined to low temperature cure systems. Either way, the pressurizing medium is compressible, while the volume of the autoclave is larger. Both of these result in relatively slow pressurization rates.

A primary concern for autoclave operators is safety. Autoclaves have to be built according to the ASME pressure vessel code. It is not an exaggeration to say that a heated autoclave is effectively a bomb, so safety procedures are rigorous. Industrial autoclaves are generally fitted with several relief valves, and inspections are carried out frequently to ensure that flaws have not developed in the structure. It is common practice in the aerospace industry to house only the door of the autoclave in the plant interior. Shell structures are on the outside.

Because of their size, temperature and pressure requirements, autoclaves are usually expensive. For example, even small lab scale autoclaves (approximately $D = 0$–5 m, $L = 1$ m) currently cost on the order of US $200,000. Peripheral equipment such as air or nitrogen lines, cooling elements, heaters, and monitoring equipment can also add to the cost. Large-scale industrial autoclaves and auxiliary equipment can cost in the range of US 1 million dollars.

2.7. Resin Shrinkage, Out-of-Dimensions and Residual Stresses

During the process of curing the resin, the part has to go through a temperature cycle. There are many phenomena that may affect the dimensions of the resin and of the part. These are as follows.

- There is shrinkage of the resin due to chemical reaction. The change of the state of the resin from liquid to solid is accompanied by some shrinkage of the resin.
- The increase and decrease in temperature during the cycle create thermal expansion and contraction in both resin and fibers.
- The combined chemical shrinkage and the thermal expansion (or contraction) will result in changes in dimensions of the part.
- Friction at the interface between the part and the mold and the mismatch between thermal expansion (or contraction) of the mold and deformation of the part can result in residual stresses in the part.

Figure 4.35 shows the schematic of the development of modulus and shrinkage of the resin during the curing process. This development can be divided into three stages. Stage 1 is from the liquid state until the degree of cure reaches the gel point where the modulus starts to be developed. Stage 2 extends from the gel point until the modulus is fully developed, and stage 3 is the solid phase. The shrinkage development can also be classified into three similar stages. However the limit of these stages may not coincide with the limits for the stages for the modulus.

2.7.1. Shrinkage and Modulus Development

Epoxy resins are known to exhibit shrinkage upon curing. The average shrinkage (percent change in volume in solid state as compared to liquid state of the same mass of resin) is about 5%–8%. The usual method to determine shrinkage is to measure the volume of the material in the liquid state and that in the solid state. One single number for the shrinkage is usually given. The PVT method [15] may be used to determine the de-

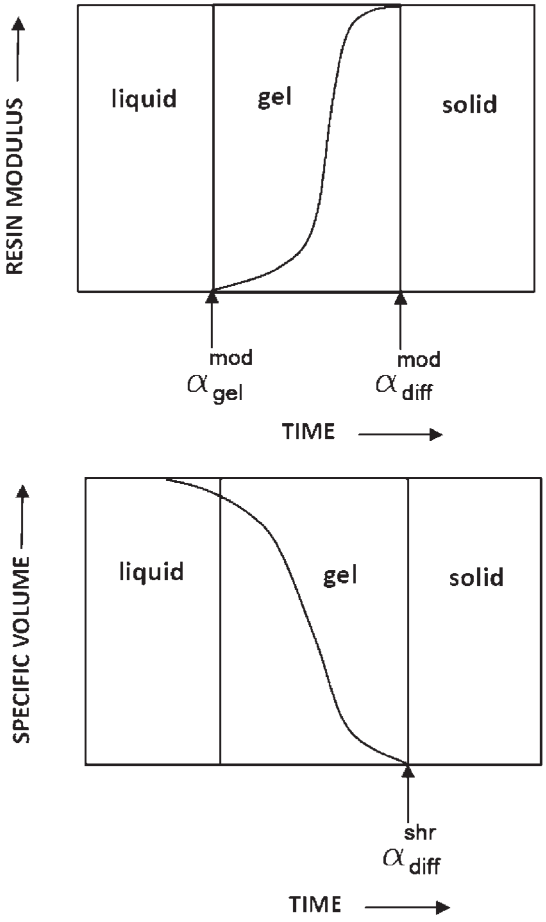


FIGURE 4.35 Shrinkage and modulus development.

gree of shrinkage as the resin changes state. Recently the ultrasonic method (PSM) developed at Concordia University [16] provides monitoring of the development of shrinkage and modulus of the resin during the curing process.

The history of shrinkage and modulus development for one epoxy system (Shell Epon 828 and Epicure 3046) determined using the PSM method is given in Figures 4.36 and 4.37. It can be seen that the shrinkage modulus developments of the resin depend on the amount of curing agent. There is a discontinuity in the modulus curve due to loss of the ultrasonic signal used for the detection of the development.

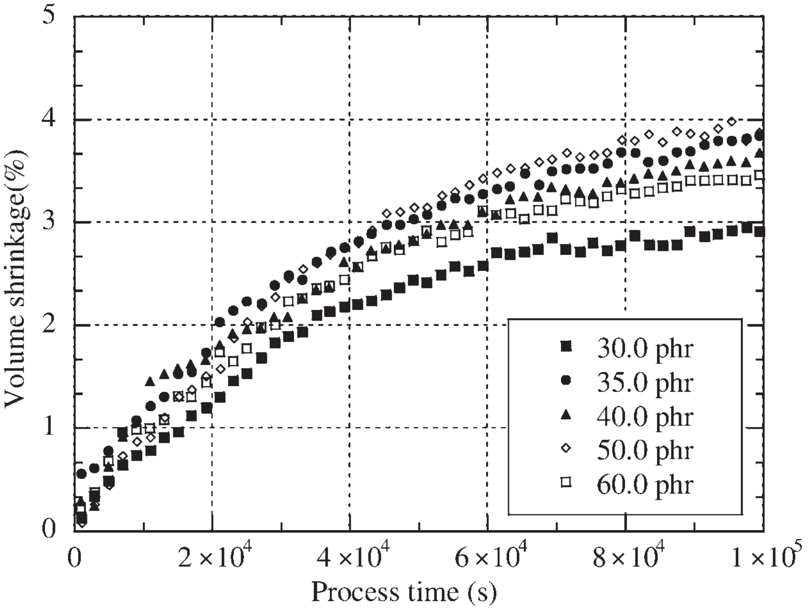


FIGURE 4.36 Shrinkage development in Shell Epon 828 and Epicure 3046 using the PSM method. Different curves show the effect of different amounts of curing agent [16].

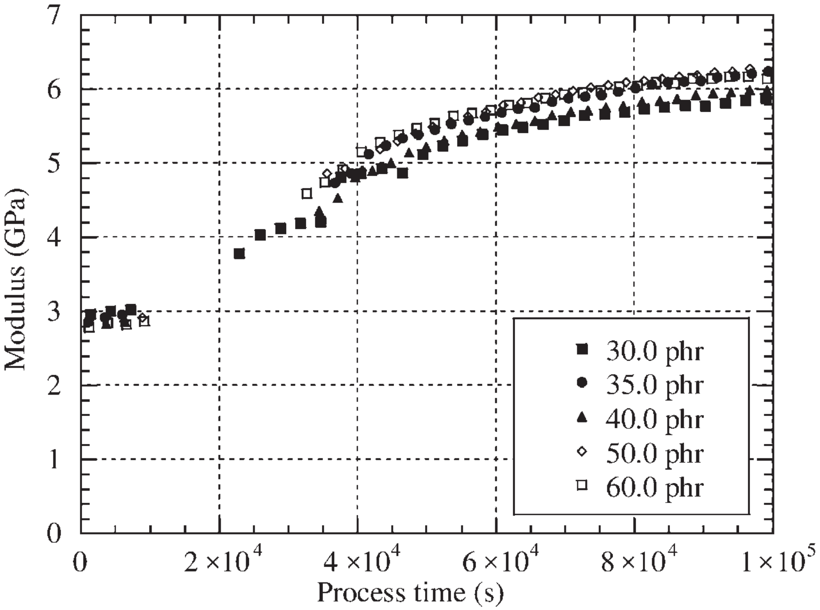


FIGURE 4.37 Modulus development of Shell Epon 828 and Epicure 3046 using the PSM method. Different curves show the effect of different amounts of curing agent [16].

Correlation between shrinkage and the degree of cure is shown in Figure 4.38. The shrinkage seems to follow the degree of conversion at the beginning of the process. After a certain amount of time, however, the conversion is faster than the shrinkage. Toward the latter part of the process, shrinkage catches up with the degree of conversion to reach full value at about the same time. The combined information on the shrinkage and modulus development can be used to determine the change in dimensions of the part and the residual stresses.

2.7.2. Determination of Changes in Dimensions of the Part and Residual Stresses

Due to resin shrinkage, coefficient of expansion (or contraction) of the part and of the tool, the dimensions of the final part may not follow the di-

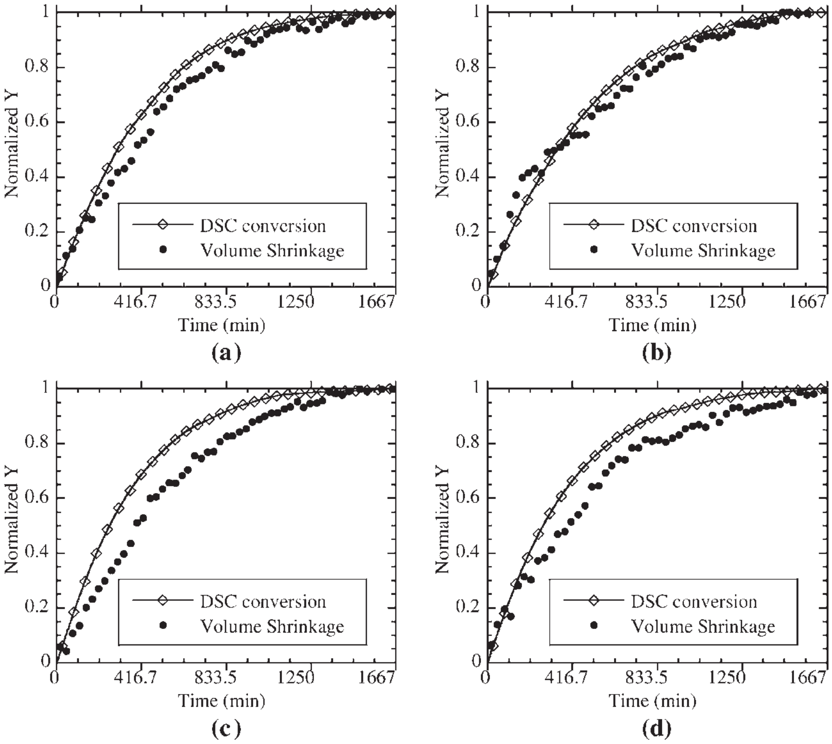


FIGURE 4.38 Correlation between degree of cure (DSC) and shrinkage development using the PSM method—Epon 828 and Epicure 3046: (a) 30 phr, (b) 40 phr, (c) 50 phr, and (d) 60 phr [16].

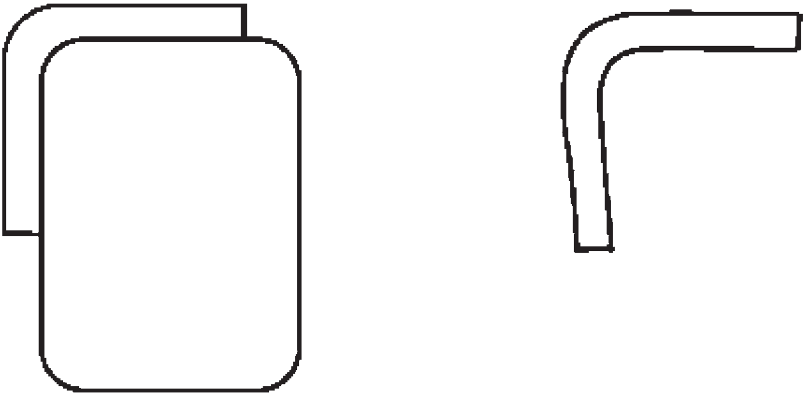


FIGURE 4.39 Out-of-dimensions due to shrinkage.

mensions of the tool. The result is a part with out-of-dimensions. Figure 4.39 shows an example of the spring-in phenomenon on parts with curved portions. This, together with possible friction between the part and the tool during the cool down cycle, may create residual stresses in the part. For large parts or for parts with complex geometry, this can present a very serious problem.

Numerical analysis (finite element analysis) is normally used to calculate the deformation of the part and its residual stresses, provided that information on the history of shrinkage and modulus development is available [6]. For the simple case of a flat plate, closed form solution is available. For this case, the situation can be represented as shown in Figure 4.40.

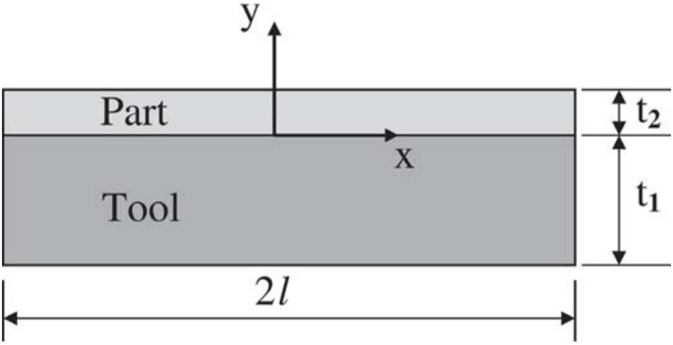


FIGURE 4.40 Flat composite part of a flat tool.

For the case of a flat part on a flat tool, the mismatch is due to thermal strain along the axial direction. For stress-free boundary conditions at the top surface of the part and at the bottom surface of the tool, the axial displacement and shear stress in the tool and part are given as [17]:

For the tool (denoted with subscript 1):

$$u_1 = \sum_{n=1}^{\infty} [\{D_{1n}^f \sin(k_n^f x) \cosh[\beta_{1n}^f (y + t_1)]\}] + \varepsilon_1^{ther} x \tag{4.24}$$

$$\tau_1 = \sum_{n=1}^{\infty} \{G_1 D_{1n}^f \beta_{1n}^f \sin(k_n^f x) \sinh[\beta_{1n}^f (y + t_1)]\} \tag{4.25}$$

For the part (denoted with subscript 2):

$$u_2 = \sum_{n=1}^{\infty} [\{D_{2n}^f \sin(k_n^f x) \cosh[\beta_{2n}^f (y - t_2)]\}] + \varepsilon_2^{ther} x \tag{4.26}$$

$$\tau_2 = \sum_{n=1}^{\infty} \{G_2 D_{2n}^f \beta_{2n}^f \sin(k_n^f x) \sinh[\beta_{2n}^f (y - t_2)]\} \tag{4.27}$$

where D_{1n}^f and D_{2n}^f can be found by applying the displacement and shear stress compatibility conditions at the interface (i.e., at $y = 0$), namely,

$$D_{1n}^f = (-1)^{(n+1)} \frac{2(\varepsilon_2^{theo} - \varepsilon_1^{theo})}{l(k_n^f)^2} \times \frac{G_2 \beta_{2n}^f \sinh[-B_{2n}^f t_2]}{\{G_2 \beta_{2n}^f \cosh[\beta_{1n}^f i_1] \sinh[-\beta_{2n}^f t_2] - G_1 \beta_{1n}^f \sinh[\beta_{1n}^f t_1] \cosh[-\beta_{2n}^f t_2]} \tag{4.28}$$

$$D_{2n}^f = (-1)^{(n+1)} \frac{2(\varepsilon_2^{theo} - \varepsilon_1^{theo})}{l(k_n^f)^2} \times \frac{G_1 \beta_{1n}^f \sinh[-B_{1n}^f t_1]}{\{G_2 \beta_{2n}^f \cosh[\beta_{1n}^f i_1] \sinh[-\beta_{2n}^f t_2] - G_1 \beta_{1n}^f \sinh[\beta_{1n}^f t_1] \cosh[-\beta_{2n}^f t_2]} \tag{4.29}$$

and

$$G = G_{xy}$$

$$\beta_n^f \sqrt{\frac{E_{xx}}{G_{xy}}} \frac{\pi(2n-1)}{2l}$$

$$k_n^f = 2n - 1$$

and ε^{ther} is the free thermal strain (due to CTE and cure shrinkage) in the axial direction.

Using the material properties for the tool and the part as given in Table 4.9, deformation and stresses were calculated by Arafath et al. [17]. One set of results on the variation of the residual stresses for different laminate lay-up and thicknesses is shown in Figure 4.41.

It can be seen that by assuming the development of the modulus as shown in Table 4.9, the residual stresses in the part first develop at the in-

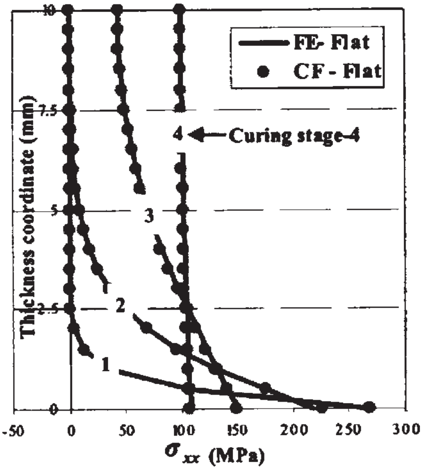


FIGURE 4.41 Variation of residual stresses for a flat composite plate across its thickness (reproduced from Arafath A. R. A., Vaziri R. and Poursartip A. "Closed form solutions for process induced stresses and deformations of flat and curved composite parts," *Proc. 6th Canadian International Conference on Composites, CANCOM 2007, Winnipeg, Canada, August 2007,* with permission from Canadian Association for Composite Structures and Materials).

TABLE 4.9 Thermo-mechanical Properties of Aluminum and Composite Materials [17].

Cure Stage	E_{11} (GPa)	E_{22}, E_{33} (MPa)	ν_{12}, ν_{13}	ν_{23}	G_{12}, G_{13} (MPa)	G_{23} (MPa)	CTE_1 $\mu\varepsilon/°C$	CTE_2, CTE_3 $\mu\varepsilon/°C$
Aluminum								
	69.00	69×10^3	0.0	0.0	2.6×10^4	2.6×10^4	23.6	23.6
Composite								
1	124.0	0.177	0.0	0.0	0.0665	0.058	3.74×10^2	29.5
2	124.0	1.77	0.0	0.0	0.665	0.58	3.74×10^2	29.5
3	124.0	17.7	0.0	0.0	6.64	5.8	3.74×10^2	29.5
4	124.0	175.0	0.0	0.0	66.3	57.6	3.74×10^2	29.5

terface between the part and the tool at stage 1. The stress then spreads toward the upper part of the laminate until the whole laminate feels the residual stress when the modulus is fully developed.

Bogetti and Gillespie [7] also obtained the residual stresses for glass/polyester. Figure 4.42 shows the residual stresses for laminates up to 2.54 cm thick. The transverse stress is compressive at the center of the laminate and tensile at regions close to the surface.

Figure 4.43 shows the residual stresses for laminates thicker than 2.54 cm. Thicker laminates show tensile residual stresses at the mid-thickness region and compressive stresses at regions closer to the surface of the laminate. This is the result of the temperature distributions as shown in Figures 4.21 and 4.22.

2.8. Out-of-Autoclave (OOA) Manufacturing Processes

Manufacturing of composites using the autoclave has been the workhorse for the composite industry for a long time. However, due to the large equipment required (large size autoclave) and the associated long heating time required to bring the environment in the autoclave to proper

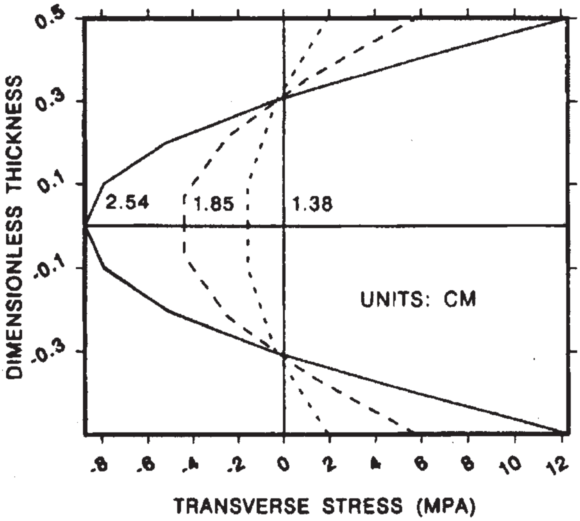


FIGURE 4.42 Residual process induced in-plane transverse stress distribution (t 2.54 cm) (reproduced from "Process induced stress and deformation in thick-section thermoset composite laminates," by Bogetti T. A. and Gillespie J. W., *Journal of Composite Materials,* Vol. 26, No. 5, 1992, pp. 626–660, with permission from Sage Publications).

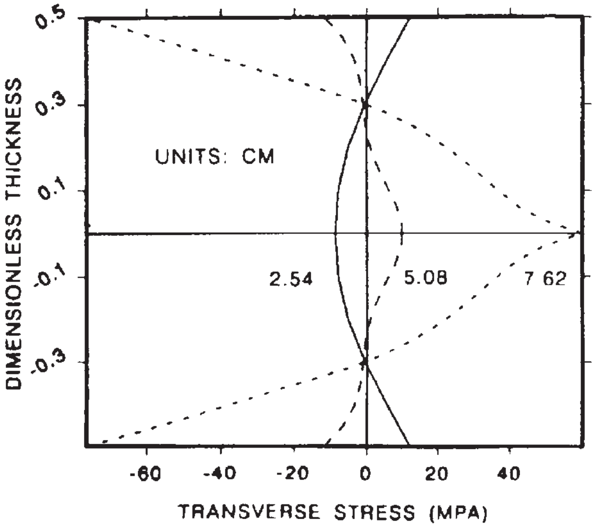


FIGURE 4.43 Residual process induced in-plane transverse stress distribution (t 2.54 cm) (reproduced from "Process induced stress and deformation in thick-section thermoset composite laminates," by Bogetti T. A. and Gillespie J. W., *Journal of Composite Materials,* Vol. 26, No. 5, 1992, pp. 626–660, with permission from Sage Publications).

temperature and the associated cost, there have been attempts to cure composites without using the autoclave. The term *out-of-autoclave manufacturing process* refers to those processes that do not require an autoclave. The main differences between OOA and autoclave processes are that the maximum compaction pressure for OOA is less than 1 atm (about 6 atm for autoclave processes) and that the curing temperature is typically less than 100°C for OOA (about 180°C for autoclave process). These processes are still in the experimental stage and have not yet reached widespread industrial applications.

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4. HOMEWORK

1. Determine the variation of the degree of cure for a carbon/epoxy laminate of Example 1 with the exception that the resin is 3501-6 with the kinetic equation given by the equation:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1-\alpha)(B-\alpha) \quad \alpha \leq 0.3$$

$$\frac{d\alpha}{dt} = K_3(1-\alpha) \quad \alpha \succ 0.3$$

$$K_1 = A_1 \exp\left(-\frac{\Delta E_1}{RT}\right)$$

$$K_2 = A_2 \exp\left(-\frac{\Delta E_2}{RT}\right)$$

$$K_3 = A3 \exp\left(-\frac{\Delta E_3}{RT}\right)$$

$$A_1 = 2.101 \times 10^9 \ \text{min}^{-1}$$

$$A_2 = -2.014 \times 10^9 \ \text{min}^{-1}$$

$$A_3 = 1.960 \times 10^6 \ \text{min}^{-1}$$

$$\Delta E_1 = 8.07 \times 10^4 \ \text{J / mol}$$

$$\Delta E_2 = 7.78 \times 10^4 \ \text{J / mol}$$

$$\Delta E_3 = 5.66 \times 10^4 \ \text{J / mol}$$

$$B = 0.47$$