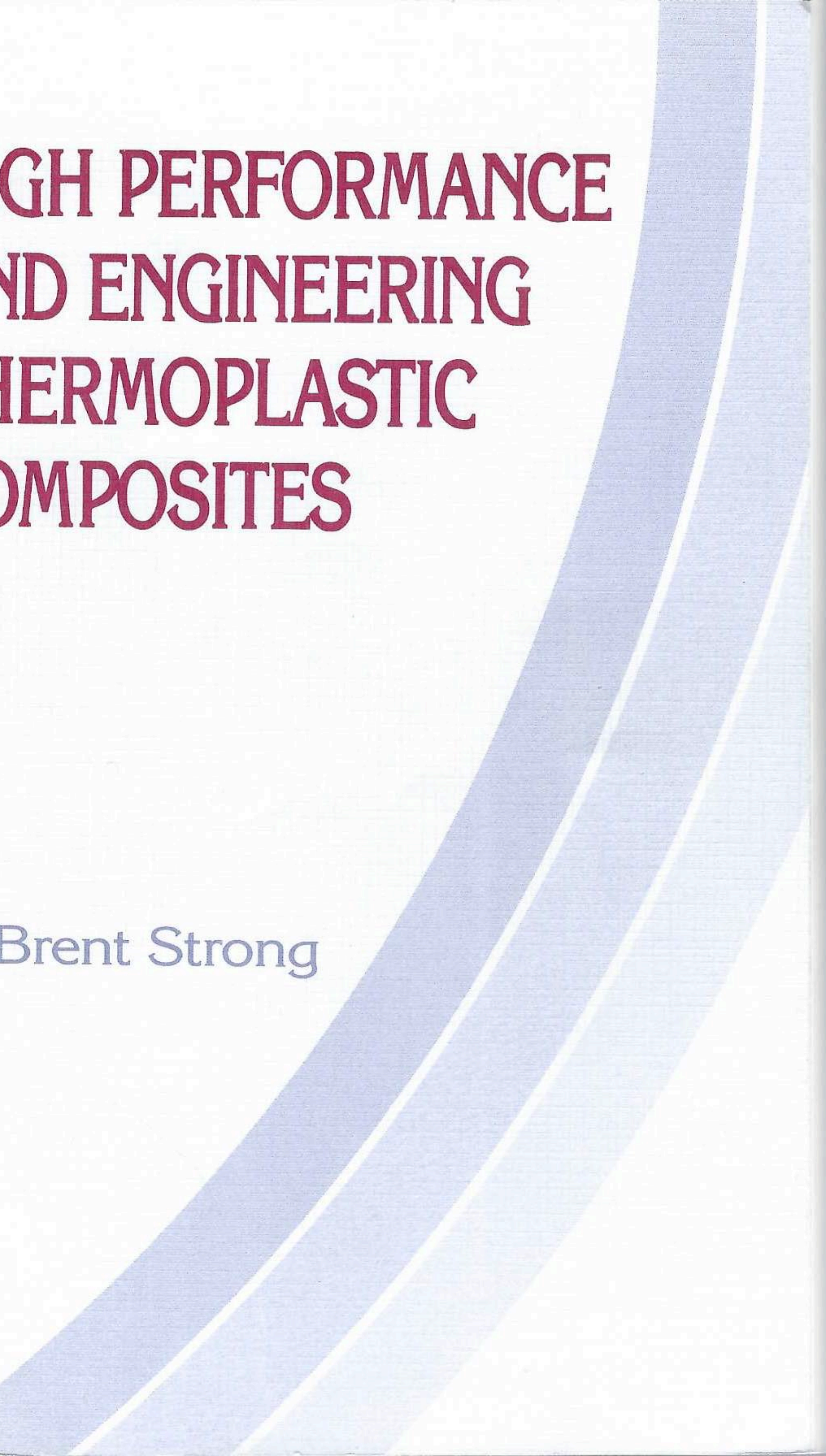
HIGH PERFORMANCE AND ENGINEERING THERMOPLASTIC COMPOSITES

A. Brent Strong



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To my parents,
Arthur and Nedra Strong,
for their love and example.

CONTENTS

PREFACE

This book is intended for several groups: engineers in industry who have little experience with thermoplastic composites or who may wish to increase their skills in a particular aspect of thermoplastic composites, managers in industry who need to develop an overview in the field of thermoplastic composites, and students of engineering who are interested in learning about this relatively new field within composites technology. Because of the diverse audience envisioned for this book, Chapter 1 is a review of composite principles and serves as a general introduction. Chapter 2 reviews resin properties, and emphasizes the unique position of thermoplastics.

In Chapter 3, the interactions of thermoplastic resins with the reinforcements are presented. The methods employed to combine the resin and the reinforcement are discussed in detail as is the resin/fiber interaction zone. These are key issues in understanding thermoplastic composites. Some of the special methods of improving the interactions between reinforcements and thermoplastic resins are also discussed. Chapter 4 examines the properties of the composite materials and relates directly to the interactions discussed in Chapter 3. The properties of most interest for thermoplastic composites are emphasized.

Chapters 5 to 8 are discussions of the methods used to manufacture thermoplastic composites. Chapter 5 is a general overview of manufacturing methods originally developed for thermoset composites and the modifications required to use those processes for thermoplastics. The processes discussed in Chapter 6 are the traditional processes used to manufacture nonreinforced thermoplastics and the changes made to run reinforced materials. In each case, the modifications are the major focus, but a general discussion of the process is also given. Chapters 7 and 8 examine composite manufacturing processes that are unique for thermoplastics. These chapters differ in the form of the raw material that is introduced into the process. Because of the many potential uses for molding of preconsolidated thermoplastic composite sheet, all of Chapter 7 examines the various methods used to form this sheet. Chapter 8 focuses on the forming of thermoplastics that are not sheets.

Chapters 9 through 11 examine the important auxiliary and support functions associated with the manufacture and use of composites. These chapters deal with molds and tooling, joining and repair, design, testing (including quality control), and costs.

The format of the book, with brief chapter overviews, is an attempt to allow the reader to quickly find the areas of the book that are of the most interest. Hopefully these features, along with the index, will allow the book to be used as a reference and research tool. To that purpose, the references are extensive.

ACKNOWLEDGEMENTS

I appreciate the help of my colleagues, especially Drs. William Pitt, Paul Eastman, and Christopher Rotz, who are co-directors of the Advanced Composite Manufacturing and Engineering Center at Brigham Young University. I also appreciate my family and their patience and support throughout the writing of this book.

CHAPTER 1

Introduction

This chapter will review the following concepts:

- Basic principles of composites
- Key uses of composites
- Differences between thermoplastics and thermosets
- Differences between advanced composites and industrial (or engineering) composites

BASIC CONCEPTS OF COMPOSITES

Composites can be broadly defined as any macroscopic combination of two or more solid materials in which the materials remain in separate phases. Common materials which are included in this definition include concrete, fiberglass reinforced plastic, and wood (where the two materials are cellulose and lignin). A narrower definition of composites is now becoming more common and is the definition that will be used herein. Under the new definition, composites are materials made from two different materials that remain as separate phases and where one of the materials is a binder or matrix and the other material is a reinforcement [1]. This definition is especially useful when discussing structural materials. Common materials that are included under this definition include the ancient building material – mud with straw bricks, and the more modern – fiberglass reinforced plastic (FRP).

The combination of dissimilar materials can have unique and very advantageous properties if the materials have appropriate characteristics, and can result in a material that is better in certain key properties than either of the materials alone. For instance, the straw-impregnated bricks were clearly a better building material than either the straw or the mud alone. In this case, the straw served to hold the mud together and prevented crumbling. We could say that the straw "reinforced" or "strengthened" the mud.

In much the same way, the fiberglass improves the performance of the plastic. With the fiberglass reinforcement the plastic is much stronger and stiffer, substantially increasing the load it can carry in a structural panel or increasing the pressure it could withstand if formed into a specific shape, such as a pipe. This fiberglass reinforced plastic pipe would compete favorably against other traditional pipe materials. For instance, the FRP pipe will be stronger and able to withstand more pressure than a traditional all-plastic irrigation pipe (such as the white PVC or black ABS pipes that are used for sprinkler systems or drain, waste, and vent pipes). FRP pipe can also compete effectively against concrete pipe, especially for high pressure applications, and against metal pipe because of corrosion resistance, lighter weight, and lower cost. The lower cost is simply because the plastic can be formed into the pipe shape more easily than can the metal, which is welded or extruded at very high temperatures.

The reinforcements and the matrix are usually very distinct types of materials with widely different physical properties. In the most modern types of composites, the reinforcements are often fibers with high stiffness, high strength, and small diameters. Other reinforcements can be whiskers (very short fibers) and particles (in which the length is not significantly longer than the width). Whiskers and particles have lower strength and stiffness properties (because of random orientations) but may be easier to process, especially in some matrices [2].

The matrix is less stiff and strong than the reinforcements but is easily formed into a complex shape. Typical matrix materials include polymers (the most common matrix), ceramics, and metals. In addition to giving the part its shape, the matrix also protects the fibers from environmental damage and transfers impressed loads onto the fibers. The choice of polymer, ceramic, or metal as a matrix material is complex but usually hinges on ease of fabrication, service conditions (especially temperature), and specific properties that might be required for a particular application such as wear.

The combinations of these materials, if done correctly, can utilize the stiffness and strength of the reinforcement and the ease of formability of the matrix to give a unique structural material – one that can withstand high loads but is easily shaped.

Another unique and very important characteristic of composite materials may not be readily apparent from this brief introductory discussion. That characteristic is high stiffness and/or strength with low weight. These properties are usually called specific stiffness or specific strength and are defined as the stiffness or strength of the material divided by its weight or density. The low specific stiffness and specific strengths of modern composites are principally due to the low density of the matrix material compared with other competitive materials. (A typical plastic matrix material would have a density of 0.9 – 1.5 g/cc compared with iron at 7.9 g/cc or aluminum at 2.7 g/cc [3].) Most low density materials would be weak, but in the case of composites, the reinforcement provides the structural attributes. The advantages of high specific stiffness and specific strength are most useful in applications where the part must be moved, such as in an airplane or rocket. In these weight-sensitive applications, composites provide equivalent strength to other materials but at substantially lower weight. Aluminum has traditionally been the material of choice in aircraft, but it does not have as high a specific stiffness or specific strength as composites, and, moreover, aluminum has limitations because of corrosion and fatigue that are far less severe in composites [4]. The ease of formability of composites can also be an advantage, especially if many separate aluminum parts are combined into a unitary composite replacement part.

The resistance to fatigue exhibited by composites is related to the advantage of thin fibrous materials over uniform bulk materials, such as aluminum. The composite materials have a much greater resistance to crack-initiated failure. In uniform bulk materials a crack, once initiated, will propagate with increasing ease throughout the material and will result in catastrophic failure. In fibrous materials, however, a crack in any one fiber would lead to failure of that fiber, but would not propagate throughout the structure. (This reasoning explains why a cable is stronger than a rod of equal weight [5].)

Many composite structures are built up from layers of fiber and matrix sheet materials. Each layer of fibers and matrix contains a carefully controlled ratio of matrix and fiber. Furthermore, the fibers in each layer are carefully oriented in specific directions. The fibers may all be in one direction (unidirectional), could be a cloth in which the fibers would cross, or could be randomly oriented. This method of construction (using layers of specifically oriented fibers) allows the fibers to be oriented in the direction or directions of load and results in a structure that is "tailored" to fit the application. Little material would be wasted in noncritical directions, in comparison with bulk materials which are usually uniform in all directions.

A major constraint on the acceptance of composites has been the difficulty of manufacture. To properly utilize all of the benefits of composites, the manufacturing methods have often been labor-intensive, slow, and difficult to control precisely. Some high volume production methods have been developed, but they are often limited to relatively simple shapes. The challenge of composites engineering is, to a large degree, the challenge of developing new manufacturing methods that are not limited by these restrictions but will maintain the advantages of composites (such as precise fiber directional control and content). Thermoplastic composites offer some important advantages in processing which might lead to even wider use of composites than at present. In spite of these limitations, the use of composites continues to grow rapidly, especially in the diversity of applications.

USES

The property advantages of composite materials have resulted in a rapid growth in the number of applications. A list of representative applications is given in Table 1.1.

Several factors are working together to increase the number of applications of composites. As indicated earlier, light weight combined with high strength and stiffness is a critical factor to the growth of composites, but the continued decrease in price, especially for the reinforcement materials, is also a positive factor. Furthermore, applications that depend on other unique composite properties are now being developed, such as the noncorrosive nature of many of the composite matrices, the transparency to radar waves and X-rays of some materials, the crashworthiness or ability to absorb impact, and the ability to dampen vibrations. Although the selection of both the reinforcement and the resin (matrix) is important in determining the applicability of composites for each of the uses, the focus of this book will be on the resin and the variations that can be expected from different resin materials.

TABLE 1.1 Typical Composite Applications.

Market	Typical Application
Aerospace	Radomes
	Rocket motor cases
	Space structures
	Aircraft skin sections, fuselage
	Aircraft cabin floors
	Helicopter rotor blades
Automotive	Leaf springs
	Drive shafts
	Body components
	Ducts, vents
Recreation	Boat hulls (motorboats, sailboats, canoes)
	Masts (boats, windsurfers)
	Golf club shafts and heads
	Racquets (tennis, racquetball, squash)
Industrial	Pipes
	Large tanks
	Water tank covers
Medical	Artificial legs
	Artificial joints
	X-ray tables

BASIC RESIN CONCEPTS

Resins are of the general class of materials called polymers. All polymers consist of long chains of atoms and are usually carbon based. The length of the chain determines a basic polymeric property known as the molecular weight and can range to several hundred units in length. As the molecular weight increases (that is, as the chains get longer), the mechanical properties (such as tensile strength and toughness) improve. This improvement in properties is thought to result from interchain forces, including entanglement of the chains, which are greater as the chains get longer, and the resulting resistance to movement, especially sliding of one chain past another [6]. The logical assumption would be, therefore, that polymers should be made with chains as long as possible in order to achieve the highest possible mechanical properties. Two factors tend to counter that apparent logic. First, the increase in mechanical properties is less rapid at high molecular weights. Second, since most polymers are shaped or processed in the liquid (molten) state, the ability to process the polymer diminishes rapidly as the molecular weight increases because the melting point and the viscosity also increase. The interaction or entanglement of nearby polymer chains is, therefore, a key characteristic in determining the nature of polymeric materials.

When the polymer chains in the entangled regions have no specific pattern in the solid phase and are random in nature, the polymer is said to be amorphous. When the chains fold next to each other into regular structures and develop strong interatomic attractions, the polymers are said to be crystalline. Crystalline polymers usually will have higher mechanical properties, such as stiffness, and higher physical properties, such as chemical resistance, than otherwise equivalent amorphous polymers. A typical crystalline polymer would have up to 90% of its atoms in crystalline structures and the remainder in amorphous regions [7].

Amorphous and crystalline polymers differ in ways other than mechanical strength, modulus, and chemical resistance. One of the most important differences is their response to elevated temperatures. Crystalline polymers tend to have a relatively sharp melting point, which is associated with the breakup of the crystalline regions and subsequent free movement of the polymer chains. Amorphous polymers, on the other hand, have no distinct melting point. They have a much more gradual onset of free movement, which is characterized by increasing vibrations and rotations within the polymer chain. These movements are largely absent in crystalline polymers because the chains are locked into the crystal structure. Some of these vibration and rotational modes in amorphous polymers can be detected by the absorption of energy and appear to be transitions, somewhat like a melting point, only smaller, much broader, and at lower temperatures. An especially important transition of this type is called the glass transition temperature (T_g) which is thought to be associated with a "crankshaft-like" rotation of the chain [8].

Two important properties of polymers are, therefore, molecular weight (polymer chain length) and crystallinity. Both of these affect mechanical properties and also thermal properties. Another key feature of polymers is the stiffness of the polymer chain. As the chain is stiffened, both mechanical and thermal properties increase. This stiffness is usually achieved by attaching large, stiff molecules to the polymer chain or by including these large, stiff molecules directly into the chain backbone. The most common of these large, stiff molecules (but not the only one) is benzene. Polymers with benzene in them are said to be "aromatic." Therefore, a polymer with many benzene rings is said to be "highly aromatic." Another method of increasing the stiffness of polymer chains is to increase the interaction between adjacent chains. This interaction is usually achieved by causing an attraction to occur between the chains. When the attraction is a formal bond, the basic nature of the material is significantly altered. Polymers with bonds between chains are called thermosets. Polymers without these bonds between chains are called thermoplastics.

THERMOPLASTIC AND THERMOSET RESIN COMPARISONS

The bonds between chains in thermoset resins are usually created by chemical reactions and are called crosslinks. In polyester thermosets, the crosslinks are between carbon–carbon double bonds in the backbone of the polymers. A "bridge molecule," usually styrene, is also employed to assist in linking the polymers together. This crosslinking is illustrated in Figure 1.1.

Crosslinks can join many polymers together, so that the entire polymer network will become a single unitary structure. This process of forming the crosslinks is called curing. When curing is extensive, that is, when many polymers are crosslinked together, the effect is to increase the molecular weight dramatically, to an almost unmeasurable value. Therefore, the mechanical properties of a crosslinked polymer network will be much higher than that same polymer without crosslinking. Likewise, the thermal properties, both the melting point and the glass transition temperature, will be raised. In most highly crosslinked polymers, the melting point is raised so much that it is higher than the temperature required to decompose the polymer. In these cases, the polymer cannot be melted but will decompose at high temperatures instead. The processing consequences of crosslinking are that any shaping of the resin must be done before curing takes place. However, the noncrosslinked resin need not be extremely high in molecular weight because the molecular weight can be increased during the cure.

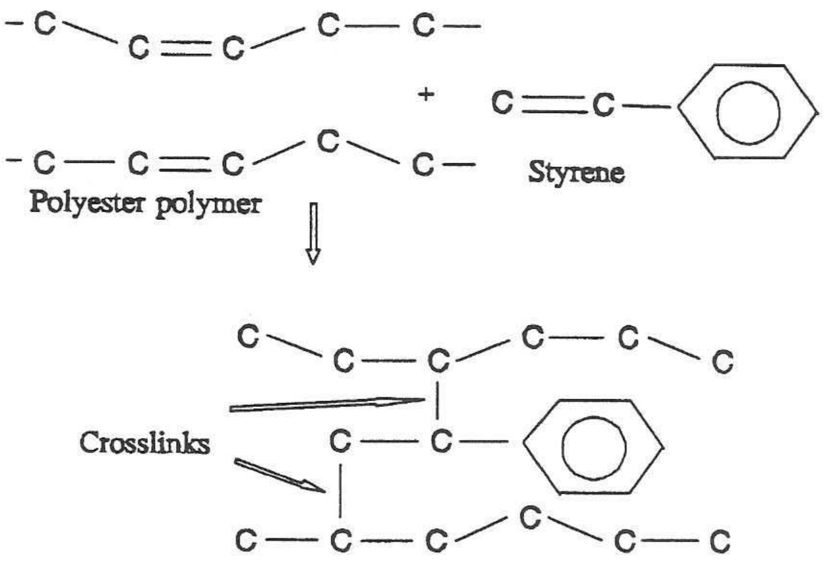

FIGURE 1.1. Illustration of polyester crosslinking.

While the chemistry of crosslinking in other thermoset resins is different in some respects, the basic concept of linking adjacent polymer chains to eventually form a unitary structure is the same. The changes in mechanical and thermal properties are also similar.

The basic differences between thermosets and thermoplastics depend, therefore, on the presence or absence of crosslinks. Because thermosets are cured and form crosslinks, the resins can have a low molecular weight, low viscosity, and easy processability before curing, and high mechanical and thermal properties after curing. Curing, however, can be a rather long and difficult process to accomplish, as it usually requires considerable heat and pressure. Thermoplastics, in contrast, are not crosslinked, so the polymers must have an inherently high molecular weight in order to achieve the high mechanical properties desired for most applications. The high molecular weight will also mean that the initial thermal properties and viscosity will be high, thus complicating the processing of the thermoplastics. A compromise in molecular weight and processability is usually sought so that the minimum acceptable mechanical and thermal properties are obtained. The advantage of processing thermoplastics is that once melted, they can be shaped easily and returned to a solid form simply by cooling. This process takes far less time than curing.

Several other important considerations and differences arise from the basic nature of thermoset and thermoplastic resins. For instance, because of the increase in rigidity that accompanies the formation of the crosslinks, thermoset materials will generally have lower elongation than thermoplastics and will therefore have little resistance to impact. Or, in other words, thermoplastics are tougher.

Another consideration is the ability of the thermoplastic material to be reheated and reshaped should the initial processing be incorrect. This reprocessing, if done, is usually minor but even that small amount is more than can be done with thermosets. This ability to reshape may be especially important in repair of thermoplastic composites.

Because thermoset curing is a chemical reaction (rather than just melting and cooling, as with thermoplastics), at least two components need to be mixed to initiate the curing. This mixing requires attention to proper proportions and often has the added problem of vapor and dangerous chemical control. Furthermore, as soon as the chemicals are mixed, the reaction starts and so shelf life is limited, even when the mixture is kept at low temperatures. As a result of these chemically related problems, many manufacturers of composite parts using thermosets have opted to purchase prepreg material in which the resin has already been mixed and coated onto the fibers. These prepregs are usually sold as rolls of either coated unidirectional fibers or coated fabric. In many cases, the viscosity of the uncured thermoset resin is so low that it drains off the fibers. To prevent this, many prepregs are partially cured to increase the viscosity but still allow for full molding and shaping. This intermediate curing is often called "B-staging" the resin. (The A-stage is no cure and the C-stage is fully cured.) This intermediate prepregging step will, of course, add to the material's cost.

Some other differences between thermosets and thermoplastics are not directly related to the crosslinking of thermosets, but to other properties. One example is the generally improved solvent resistance and low moisture absorptivity of many thermoplastics as compared to polyesters and epoxies, the most common thermosets. Some of the newer thermoplastic materials also have a significant reduction in flammability as compared to polyesters and epoxies.

Some disadvantages of thermosets would, therefore, be

- required mixing of chemicals to effect the cure
- potentially harmful vapors and chemical handling

- limited shelf life
- multistep processing
- longer times for solidifying the part (cure time)
- inability to be reprocessed
- poor toughness
- potential higher overall costs
- poor solvent and moisture resistance (polyesters and epoxies)
- poor flame retardance (polyesters and epoxies)

Over 80% of the 23 billion kilograms of plastic produced in the United States in 1986 were thermoplastics and the other 20% were thermosets [9]. In spite of the disadvantages for thermosets, the resins most often used in composites are thermosets, nearly reversing the percentages of the total resin market, with most of the thermoplastic composites in short fiber compounds. This is partly historical, because the reinforcement fibers could be wetted out by the low viscosity thermoset resins more easily than by the thermoplastics. Also, the mechanical properties required could be obtained more easily with the thermosets. Finally, the use temperatures of many applications required the higher thermal properties obtainable with thermoset resins. However, advances in thermoplastic resins have improved their mechanical and thermal properties so that they can now be competitive in many of the traditional thermoset applications. Therefore, the general increase in composite usage has also increased the use of thermoplastic composites in many of the applications already listed. In addition, the unique properties of thermoplastics (which will be described in detail in later chapters) have led to some preferred applications for thermoplastics. Because the composites market was and to a large extent is still dominated by thermoset matrix materials, the original uses of thermoplastics were largely because of obvious deficiencies of thermosets. Such uses are shown in Table 1.2.

Although the advantages of thermoplastics have opened some markets, thermoplastic resins are not without their disadvantages. Many of these disadvantages result directly from the basic nature of thermoplastic materials. For instance, because of the need to have high molecular weight to obtain good mechanical properties, the polymer chains must be very long. (In thermoplastics, the chains must be inherently long since their length cannot be increased through curing, as is done with thermosets.) These long polymer chains will be highly entangled and will result in increased viscosity in the melt phase. This high viscosity makes the wet-out of the reinforcement fibers difficult.

The high molecular weight of the thermoplastics also increases the melting temperature. The high crystallinity of many thermoplastics (also needed for good mechanical properties) further increases the melt temperature. A further factor in increasing the melt temperature is the high aromatic

TABLE 1.2 Typical Thermoplastic Composite Applications.

Market	Typical Application
Aircraft	Wing leading edges
	Wing ribs
	Access doors
	Vertical stabilizers
	Interior panels
Automotive	Alternator end cap
	Door frames
	Body panels
Wear resistant	Bearings
	Gears
	Bushings
	Rollers
	Seals
Personal	Attaché cases
Medical	Knee brace orthotic
Industrial	Filter housings
	Electronic equipment housings
Recreation	Tennis racquets
	Rifle stocks
	Golf club heads
	Ski poles

character (again to increase mechanical properties) of many thermoplastics. The combined result of these effects is a melt temperature that is so high, at least for the thermoplastics with the highest mechanical properties, that most traditional plastics manufacturing equipment cannot be used for processing them.

The dilemma in processing high performance thermoplastics is, therefore, that both the viscosity and melt temperatures are very high. In most polymers the viscosity could be lowered by simply raising the temperature. In the case of the high performance thermoplastics, however, the high melt temperature is so close to the polymer decomposition temperature that temperature increases much above the melt temperature are not possible without degradation.

Another processing disadvantage of thermoplastics is the lack of tack in thermoplastic prepregs. Tack is a stickiness that is common to thermoset prepregs. This stickiness facilitates the layup of the prepreg sheets. Without the tack, the sheets tend to slide and change orientation, thus reducing the quality of the laminate. The standard procedure in thermoplastic prepreg layups is to melt selected spots of the thermoplastic prepreg with a soldering iron, thus sticking one layer to another and anchoring the entire laminate structure. The problem is not severe, but it can be a nuisance.

HIGH PERFORMANCE VERSUS ENGINEERING RESINS

Some of the applications, especially aerospace, require high temperature capabilities or other high physical properties. The reinforcements for these applications would typically be high strength and high modulus fibers such as carbon (graphite), aramid, or high strength fiberglass. The composites made from these high performance materials are called high performance or advanced composites, and the resins for these applications would be high performance or advanced thermosets or thermoplastics. The most common high performance thermoset resins are epoxies, phenolics, and polyimides.

The number of high performance thermoplastic resins is quite limited. These resins, which have physical and thermal properties that can compete with the thermosets, have only been developed in the last few years. Examples of high performance thermoplastic resins are PEEK and PPS. The properties of these and other high performance thermoplastic resins will be discussed in Chapter 2.

Many composite applications do not require the properties obtained with the advanced composites. Some examples are boats, automobile parts, electrical circuit boards, and plastic gears. The resins used in these applications are called engineering resins. The most common thermoset engineering resins are polyesters, vinyl esters, and polyurethanes. In the case of thermoplastics, many resins fall into the engineering resin category. Typical examples would be nylon, ABS, polycarbonate, acetal, PET, acrylic, and polypropylene. Generally, however, these engineering thermoplastics have been used without reinforcements or with only very short fiberglass reinforcements, so that they could be processed by traditional thermoplastic methods such as injection molding and extrusion. Some recent advances in processing have, however, suggested methods for processing these engineering thermoplastics with longer fibers. The objective is to achieve improved physical properties while still utilizing inexpensive processing methods. Because the engineering resins are relatively low cost, the overall costs of the parts made with these resins should be low. A major challenge in composites is to continue to expand the capability of engineering thermoplastic processes and allow the use of long fibers so that the range of parts that can be made from these materials is increased.

SUMMARY

The use of composite materials in which the matrix is a polymer and the reinforcements are high strength, high stiffness fibers continues to grow in their traditional markets of aerospace, automobiles, and recreation. Several new applications for these materials such as medical devices, industrial structures and pipes, and personal consumer goods also show good growth.

The predominant matrix materials in current use are thermoset resins. These materials depend upon a chemical crosslinking reaction (curing) to bond the polymer chains together and thus increase the molecular weight. This high molecular weight results in excellent mechanical and thermal properties. Before curing, the resins have a low viscosity which facilitates the wetting out of the fiber reinforcements and thus simplifies this processing step in making composites. Thermosets, however, have several inherent problems such as the need to mix chemicals (some of which may be dangerous) to effect the cure, limited shelf life after mixing, the need for multistep processing, poor toughness and impact damage resistance, and long cure cycles with expensive equipment which leads to high manufacturing costs.

Thermoplastic resins effectively avoid many of the problems of thermosets, although, of course, other new problems are encountered. Some of these problems include the high viscosity of the melted resin which complicates the wet-out of the fiber reinforcements, high processing temperatures that are required, and the high cost of advanced performance resins.

A potential method of reducing the costs of the thermoplastic resins is to utilize engineering thermoplastics in applications that have traditionally been reserved for advanced composites. This use will require careful identification of the performance requirements for each application and a comparison with the resin or composite properties available with the engineering thermoplastics. Current information shows that many applications do not need the high performance properties and the engineering resins would be appropriate. Further use of these engineering resins also depends upon the development of low-cost manufacturing methods that will allow the engineering resins to be applied to long fiber reinforcements. The mechanical performance of composites has been shown to be dependent upon the length of the fiber reinforcement, and so the ability to merge long fibers with the engineering resins is a key to their wide applicability.

The remainder of this work will focus on thermoplastic resins as they are used in composites. In many cases the subjects have not been fully explored and may not be commercially utilized. However, the hope is that ideas will be planted which will prove to be fruitful.

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CHAPTER 2

Thermoplastic Resin Properties

This chapter will review the following concepts:

- Chemical structures
- Mechanical properties
- Thermal properties
- Environmental resistance (water, solvents, flammability)

CHEMICAL STRUCTURES

The matrix in a fiber reinforced, resin-matrix composite has several functions. It transfers the impressed loads to the fibers, so it must have a good bond with the fibers. It gives shape to the part, and so must be readily formable, and it must retain that shape and other mechanical properties throughout the temperature range of use. The matrix protects the fibers from environmental damage, so it must have toughness and impact resistance, and it must resist other potential damages from environments unique to the application such as solvents and water, ultraviolet light and other forms of radiation, and atomic oxygen.

Some applications, such as aerospace, emphasize the mechanical and thermal properties imparted by the matrix and are less concerned about costs of materials and production. Others, such as automotive, are just the opposite. Those matrices that tend to favor performance over cost are called advanced or high performance, and they generally have higher mechanical and thermal properties than the matrices that favor cost, the engineering resins. Despite the disparity of focus of these resins, their properties will be examined jointly in the hope that by considering the polymers together

TABLE 2.1 High Performance Thermoplastics.

Generic Name	Manufacturer	Trade Name [1]
Polyaryletherketone (PAEK)	ICI	Victorex® (PEEK)
	DuPont	PEKK
	BASF	Ultrapek®
	Amoco	Kadel®
Polyphenylene sulfide (PPS)	Phillips	Ryton®
Polysulfone (PSU)	Union Carbide	Udel® P-1700
Polyarylsulfone (PAS)	Union Carbide	Radel®
Polyetherimide (PEI)	General Electric	Ultem®
Polyamideimide (PAI)	Amoco	Torlon®
Thermoplastic polyimide (TPI)	DuPont	Avimid K®
	Mitsui Toatsui	LARC-TPI
Liquid crystal polymer (LCP)	Dartco	Xydar®
	Hoechst Celanese	Vectra®

as potential matrix materials, some innovative selections might be stimulated. Some separations will be necessary because of the differences in some properties and the differences in availability. For instance, the high performance thermoplastics are generally proprietary and have a single source. On the other hand, the engineering thermoplastics are usually generic and can be obtained from several suppliers in a wide variety of grades and performance options. While the number of high performance thermoplastics is rather limited, the number of engineering thermoplastics is very large. Therefore, only a representative number of engineering thermoplastics will be discussed in general, with occasional reference to some of the others as the data and use dictate.

A list of the major types of high performance thermoplastic resins and their principal suppliers and trade names is given in Table 2.1. A list of selected engineering thermoplastics, as well as some of their suppliers and trade names, is given in Table 2.2. A wide range of engineering thermoplastics are listed. All are used as matrices for composites.

Other high performance thermoplastics have been formulated but have not received widespread commercial acceptance [2–5]. In addition, some blending of the common thermoplastics to obtain specific properties has been successfully accomplished [6]. The number of engineering thermoplastics and suppliers is very large, and has been characterized elsewhere [7,8].

The chemical structures of several high performance and engineering thermoplastics are given in Table 2.3.

The molecular structures of these polymers are generally highly aromatic, especially the high performance thermoplastics. This high aromatic content leads to stiffened polymer chains, higher strength and higher thermal properties. The engineering thermoplastics are generally less aromatic and would have correspondingly lower strength and thermal properties (although some intermolecular hydrogen bonding increases the strength and thermal properties, as is seen in nylon).

Another important factor in determining the properties of a polymer is the molecular weight. This property is rarely reported for the high performance thermoplastics, but can be important in determining the properties and the processing conditions. In engineering plastics, the molecular weight is so important that it is usually reported with each shipment of material and

TABLE 2.2 Engineering Thermoplastics.

Generic Name	Manufacturer	Trade Name
Polyamide (nylon)	DuPont	Zytel®, Minlon®
	Monsanto	Vydyne®
	Allied Signal	Capron®, Nypel®
	BASF	Ultramid®
Polyethylene terephthalate (PET)	Allied Signal	Petra®
	BASF	Ultradur®
	Eastman	Ekdar®, Kodar®
	GE	Valox®
Acetal	Hoechst Celanese	Celcon®
	DuPont	Delrin®
	BASF	Ultraform®
	Akzo	Formaldafil®
Polycarbonate	GE	Lexan®
	Dow Plastics	Calibre®
	Mobay	Makrolon®
	Akzo	Polycarbafil®
	ICI	Thermocomp®
ABS	Akzo	Absafil®
	GE	Cycolac®
	Dow	Magnum®
	Monsanto	Lustran®
Polyphenylene ethers (PPO)	GE	Noryl®
	Akzo	Fiberfil®
	ICI	Thermocomp®
	Thermofil	Thermofil®
Polypropylene (PP)	Exxon	Escorene®
	Eastman	Tenite®
	Polycom Huntsman	Huntsman PP®
	Phillips	Marlex®
	Akzo	Profil®
	Schulman	Polyfort®

TABLE 2.3 Chemical Structures of Thermoplastic Polymers.

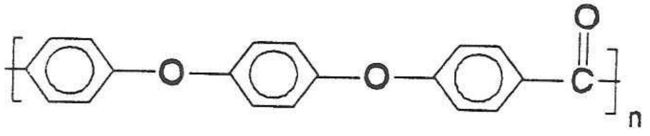
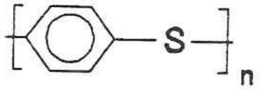
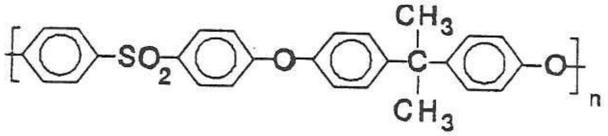
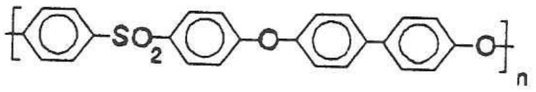
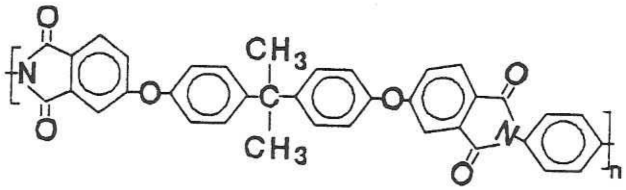
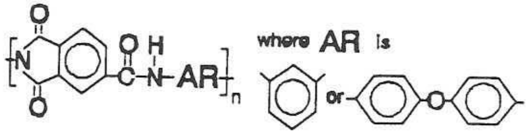
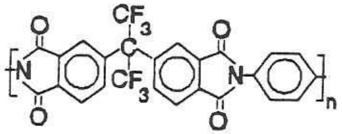
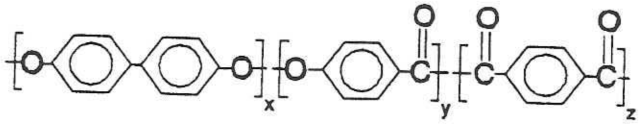
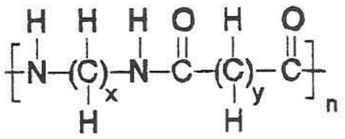
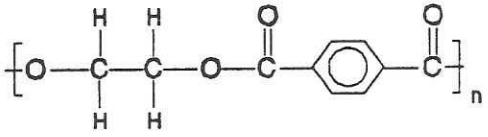
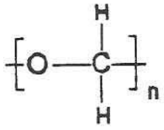
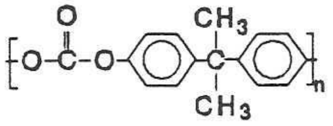
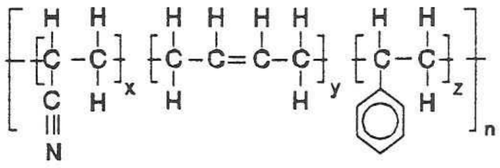
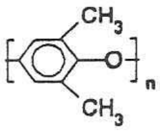
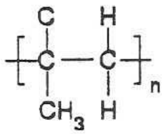
Polymer	Chemical Structure
PEEK	
PPS	
Polysulfone	
Polyarylsulfone	
Polyetherimide	
Polyamideimide	
TP polyimide	
Xydar	

TABLE 2.3 (continued).

Polymer	Chemical Structure
Nylon	
PET	
Acetal	
Polycarbonate	
ABS	
PPO	
PP	

is determined as a routine quality control procedure. The molecular weights of several high performance thermoplastics have been determined by several standard techniques and the results from the various techniques seem to be complementary [9].

Some caution must be exercised in comparing the mechanical and thermal properties of thermoplastic materials with thermoset materials. While aromatic content, intermolecular forces, and molecular weight are also important in thermoset materials, their effects are often secondary to the effects arising from crosslinking. Crosslinking inherently stiffens, strengthens, and increases the thermal properties of the molecules. On the other hand, elongation is generally significantly reduced because of crosslinking. Therefore, in applications where elongation is a benefit, such as resisting impact damage, the thermoplastics would have an inherent advantage over thermosets. (Some thermoset materials have been formulated with decreased aromatic content or are blended with thermoplastics to increase the toughness of the polymer.)

The pattern of mechanical and thermal properties that emerges is an overlap of the high performance thermoplastics with the mid-range (generally epoxy) thermosets as illustrated in Figure 2.1. The higher performance thermosets (such as polyimides) exceed the strength, stiffness, and thermal properties of the high performance thermoplastics. The lower performance thermosets (such as the polyesters) are generally in the same range of performance as the stiffer and stronger engineering thermoplastics.

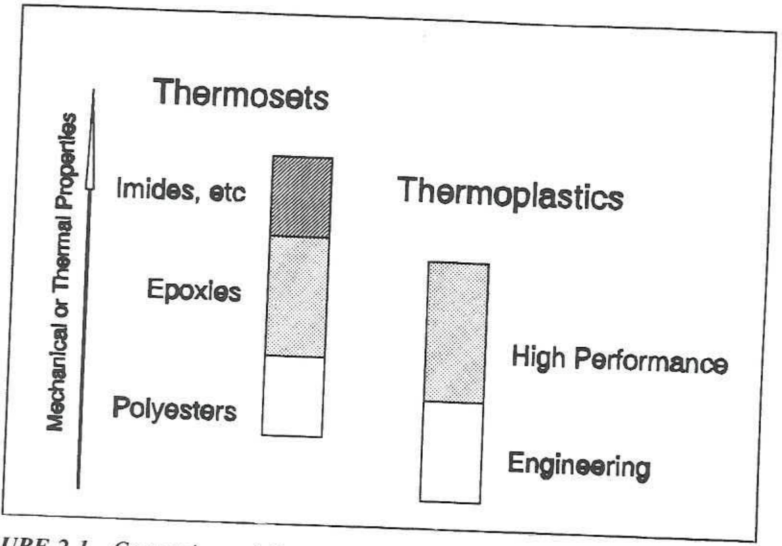


FIGURE 2.1. Comparison of thermoset and thermoplastic mechanical and thermal properties.

The flexible engineering thermoplastics are much more flexible than any thermoset material.

Crystallinity

Another important factor affecting mechanical and thermal properties, as well as chemical and environmental resistance properties, is the crystallinity of the polymers. Many of the polymers shown, especially the high performance thermoplastics, are crystalline or semicrystalline materials. The higher intermolecular forces associated with crystallinity increase the energy required to cause the molecules to move. Therefore, the strength is somewhat increased, stiffness is much higher, the use temperature is increased and solvent resistance is increased over comparable amorphous polymers [10]. Some authors have suggested that the use of amorphous polymers can be advantageous for some applications where the ultimate strength or temperature capability are not needed but improved processability through solvent thinning would be useful [11]. Increased crystallinity also results in lower elongation. The toughness of the material is a function of the ability of the material to absorb energy and can be related to the total area under the stress-strain curve. Logically the lower elongation (strain) would lead to lower toughness unless this lower elongation is compensated for with a higher strength. This compensation may be occurring in some cases as toughness as a function of crystallinity has been reported to increase in some cases and decrease in others [12,13]. These effects also arise from other factors such as differences in fracture mechanisms and fiber-resin bond strengths. Thermal expansion has also been reported to be a function of crystallinity with a change in the direction of the expansion at higher temperatures [14].

Several methods for determining the crystallinity of the thermoplastic resins have been discussed. Ching-Ling Ong et al., reported success in determining the amount of crystallinity of PEEK and PPS using differential scanning calorimetry (DSC), Fourier transform infrared spectrometry (FTIR), and X-ray diffraction [15]. Some differences in the crystallinity using the three methods were noted. The crystallinity as determined using FTIR was highest, the DSC determined value next, and the X-ray value lowest, although the authors note that the amount of crystallinity is strongly dependent on the time and temperature to which the samples have been exposed. Ostberg and Seferis [16] also report large differences in crystallinity, this time between measurements using DSC and density gradient techniques. Wolf and Bornmann [17] comment that X-ray crystallography may be the preferred method for obtaining unambiguous values, but it is a difficult determination in the presence of carbon fibers and usually requires a highly skilled operator. Wolf and Bornmann also note that crystallinity can be determined by density measurements but this method requires precise knowledge of both the matrix-to-fiber ratio and the void content of the sample. They conclude that although DSC is probably the most straightforward method, substantial errors can arise in the measurements if the nature of the amorphous-to-crystalline transition is not fully appreciated, as was also mentioned by Ching-Ling Ong et al., and Ostberg and Seferis. Wolf and Bornmann suggest that the DSC method not be used for samples having a crystallinity greater than 21%. D'Amore et al. used dynamic mechanical and dielectric characterization to investigate crystallization. They found that dielectric test methods are as sensitive as DSC in determining the morphology of PEEK [18].

To further complicate the determination of crystallinity, Ostberg and Seferis pointed out that the heating rate had some effect on the overall crystallinity. Deslandes et al. [19] examined a PEEK film which was heated above the melt temperature for various periods of time and concluded that "both nucleation and crystal growth are influenced by the temperature at which the polymer is heated and the time it is kept there. Destruction of existing polymer nuclei, formation of new nuclei, chain branching, crosslinking and chain degradation are all believed to take place at different times and to a different extent during the process." A wide variety of factors that influence crystallinity was investigated by Day et al. [20]. They reaffirmed that melt history plays an important part in crystallinity and further pointed out that the presence of oxygen, molecular weight, nucleating agents, and perhaps carbon fibers play an important role in crystallinity. They concluded that for maximum crystallinity "the material should be processed in the absence of air, with the melt temperature and hold time in the melt being kept as low and short as is practical." They observed that although the crystallinity decreases rapidly with increasing molecular weight, commercial samples often contain nucleating agents which have a greater influence on the crystallization behavior than does the molecular weight. They also concluded that the presence of silicon mold release and the nature of the metallic mold surface had little effect on the crystallinity. Not surprisingly, variations in crystal lattice have also been related to changes in the sequence and proportion of various bond types along the polymer backbone [21].

An etching technique was described by Peacock et al., which was applied to PEEK and allowed the matrix morphology to be examined directly[22]. They studied PEEK/carbon fiber composites that had been cooled at two widely differing rates and found that the crystalline structure was spherulitic with the origin of the spherulites predominantly occurring at the carbon fiber surfaces. At the higher cooling rate, only a marginal increase in bulk-initiated spherulites and a slight decrease in spherulite size were observed. The bulk-initiated spherulites are typically of a different pattern. They nucleate perpendicular to the reinforcing fibers and are called transcrystalline.

A model for the formation of crystals in semicrystalline polymers is the Avrami model [23]. The Avrami expression, in its most simple form, is:

$$X(t) = e^{-(kt^{n})} \tag{2.1}$$

where:

$X(t)$ = total mass fraction of crystallinity at time t
k = material constant
n = Avrami constant

As indicated by Arnold Lustiger [24], the Avrami constant, n, lends an insight into the nature of the crystallization process. This parameter will be a function of three conditions controlling crystallization: (1) how the crystalline phase nucleates (initiated by some surface or homogeneous initiation); (2) the growth geometry of the crystallizing entity (one-dimensional rods, two-dimensional disks, or the most common three-dimensional spherulites); and (3) the rate limiting step in crystallization (diffusion to form the crystals or attachment of the molecules to a surface). Although some qualitative information using the Avrami equation is certainly helpful, the quantitative aspects of the agreement with theory are not completely satisfactory [25].

In one important group of polymers the crystallinity of the polymer persists even in the liquid (solvated) phase. These polymers are called liquid crystals and the property is called *lyotropic*. Some newer liquid crystal polymers have been shown to be oriented in the melt and these are called *thermotropic*. (The thermotropic polymers generally have more flexible bonds than the lyotropic polymers [26].) All of these polymers are strong, stiff, rod-like materials which exhibit a grouping together into domains when in the liquid phase. Typical examples of thermoplastic polymers in the lyotropic group would be DuPont's Nomex and Kevlar – resins used for making honeycomb or for fibers but not available for matrix materials. A typical thermotropic material would be Xydar (Dartco) or Vectra (Hoechst Celanese).

An interesting application of liquid crystal polymers has been the use of these materials as reinforcements in traditional matrix materials. Crevecoeur and Groeninckx report that they were able to spin fibers from Vectra and use it for reinforcement in engineering resin matrices. The Vectra fibers showed both macroscopic and microscopic orientation [27].

The crystallinity of several of the most important thermoplastic resins is given in Table 2.4.

TABLE 2.4 Properties of Neat Thermoplastic Polymers [28 – 37].

Polymer	Crystallinity	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
PEEK	semi	92 – 103	3.1 – 3.8	11 – 50
PPS	semi	65.5 – 82.8	3.91 – 4.3	3 – 20
Polysulfone	amorphous	68.9 – 76	2.14 – 2.48	60 – 76
Polyarylsulfone	amorphous	70 – 82	2.14 – 2.66	30 – 60
Polyetherimide	amorphous	95 – 105	2.96 – 4.5	7 – 60
Polyamideimide	amorphous	89 – 186	2.8 – 4.8	9.7 – 30
TP polyimide	amorphous	102	3.8	14
Xydar	liquid crystal	110 – 138	8.3 – 16.6	1.1 – 5
Nylon 6/6	crystalline	75.8 – 94.5	1.59 – 3.79	15 – 60
PET	crystalline	48.2 – 72.3	2.76 – 4.13	30 – 300
Acetal	semi	66.8 – 68.9	3.10 – 3.58	25 – 75
Polycarbonate	crystalline	62.7 – 69.0	2.37	110 – 135
ABS	amorphous	22.7 – 55.1	1.86 – 2.76	1.5 – 80
PPO	amorphous	66.1	2.45 – 2.62	60 – 82
PP	semi	31.0 – 41.3	1.14 – 1.55	100 – 600

Note: The ranges of values reflect the various data sources listed as endnotes and the various grades of materials available.

The use of liquid crystal polymers has been limited because of the very high melting points and process difficulties of these polymers. One approach to easing these problems has been to blend the liquid crystal polymers (LCP) with lower melting resins such as PET and PP [38]. Careful analysis of the material indicated that the LCP formed continuous reinforcing fibrils in the respective matrix material.

MECHANICAL PROPERTIES

Key mechanical properties for several important thermoplastic matrices are also given in Table 2.4. A comparison of the crystallinity and the mechanical properties in Table 2.4 illustrates the complexity of their interrelationship and suggests that other factors besides crystallinity are important in determining the mechanical properties (such as molecular weight). Some observations relating crystallinity and mechanical properties are, however, relevant. The highest crystallinity of the materials listed would be in the liquid crystal molecule Xydar. This material is also seen to have the highest tensile modulus and among the highest tensile strengths of the materials listed. Although the semicrystalline materials generally have high tensile moduli, some amorphous materials are in the same range. These same amorphous materials (polyetherimide, polyamideimide, and TP polyimide) also have high tensile strengths. The high stiffness of the imide group and the associated stiffness of the polymeric chain seem to be manifest in the higher tensile properties. Other polymers known to have stiff polymeric chains, such as those with high aromatic content, are also generally higher in modulus and strength than the largely aliphatic (non-aromatic) materials.

Ultimately, the discussion of mechanical properties of resins used for matrix materials in composites must consider the effect of the reinforcement material. A detailed discussion of composite properties will be given in Chapter 4. The tensile properties and compressive properties are especially fiber dominated, although the fiber-matrix bond is also very important and is discussed in Chapter 3.

One mechanical property of composites that is highly dependent on the matrix is toughness. Toughness is a measure of the ability of the material to absorb energy and, therefore, resist the deformations and shear that would lead to failure. This energy can be related to the area under the tensile stress-strain curve. Therefore, the toughness is related to the product of the ultimate tensile strength and the elongation at failure. The relationship is complicated, however, because the performances of stress and strain are not linear, the time dependence is not adequately characterized (most polymers are viscoelastic and therefore the rate of deformation is important), and many brittle materials are sensitive to surface defects which significantly alter the toughness. A further problem associated with the determination of toughness by tensile measurements is that tension is rarely the failure mode of interest for toughness related failures.

In an effort to overcome these problems, toughness has usually been measured by impact. The most common impact tests are pendulum types (Izod, Charpy and Tensile Impact) or falling weight (Gardner and Dart Drop). The specimens used in the pendulum tests are often notched to induce, and therefore control, the sensitivity of the material to surface cracks. The pendulum tests do not, however, reflect the failure mode of most composite materials. The falling weight tests more closely match the typical failure mode but they have a wide variation in the results and are hard to determine the failure point. Although these tests have many problems, they are reliable enough that they are widely used and reported. Table 2.5 lists the notched Izod data for several high performance and engineering thermoplastic resins (neat).

Even though toughness and shear are difficult to measure, they are critically important properties in some applications, such as those where minor damage might seriously affect performance. In these cases, the residual compressive strength as a function of the impact energy can be measured. A plot of these properties for various materials gives the materials' resistance to impact damage as can be seen in Figure 2.2.

TABLE 2.5 *Matrix Dominated Mechanical Properties* [28 – 37].*

Polymer	Izod, Notched (J/m)
PEEK	86–115
PPS	18–23
Polysulfone	64–77
Polyarylsulfone	95–64
Polyetherimide	33–59
Polyamideimide	161
TP polyimide	47
Liquid crystals	123–273
Nylon 6/6	32–59
PET	14–41
Acetal	48–137
Polycarbonate	714–948
ABS	178–301
PPO	119–417
PP	23–84

*Unidirectional laminates with nominal 60% fiber volume (AS-4 or equivalent).

Thermoplastic resins, in general, have higher toughness than thermosets and are, therefore, preferred for these toughness-critical applications. Thermoplastics are seen to be tougher (more impact resistant) than even toughened epoxies at moderate to high impact energies. The lower impact toughness of the thermosets is undoubtedly due to the crosslinking which increases brittleness and decreases elongation.

THERMAL PROPERTIES

As previously mentioned, an important function of the matrix is to give shape to the composite structure and to retain that shape and other mechanical properties throughout the temperature range of use. As the temperature of the composite is increased, more and more energy is imparted to the polymer. This energy is converted into molecular motion. At lower temperatures, the motion is largely vibrational because vibration is relatively unrestricted motion. At higher temperatures the molecules gain sufficient energy to flex and rotate and at even higher temperatures the molecules begin to translate. When these molecular motions become unimpeded by the surrounding molecules, the polymer is considered a liquid because it then flows freely. In highly crystalline polymers the crystal lattice energies are strong resulting in tightly held molecules. These crystalline molecules have very little rotation and almost no translation until the imposed energy is sufficient to overcome the crystal lattice energies. When the energy reaches that threshold value, the crystal lattice breaks apart and the molecules are free to rotate and translate. This phenomenon is called the crystalline melting point for the polymer.

In totally amorphous polymers there is no crystalline structure and therefore no crystal lattice energy. In these amorphous polymers the transition from solid to melt is more gradual with only small indications of the increased mobility of the molecules. One of these indications is, however, useful in characterizing the thermal nature of the polymer. This transition, called the glass transition temperature, T_g, is associated with a particular rotational movement that can be readily identified by analyzing the thermal transitions of the polymer. If the polymer is tightly bonded between molecular chains, it is extremely stiff, or if its molecular motions are highly restricted in some other way, T_g will be high indicating that considerable energy must be imparted in order to induce the characteristic rotational movement identified with T_g. In thermoset resins the crosslinking of the polymer molecules is a restriction of movement. Therefore, as the number of crosslinks (crosslink density) increases, T_g will increase. This phenomenon has been used to follow the crosslinking reaction and to predict the crosslink density of thermosets.

Amorphous polymers are, therefore, characterized by T_g, whereas crys-

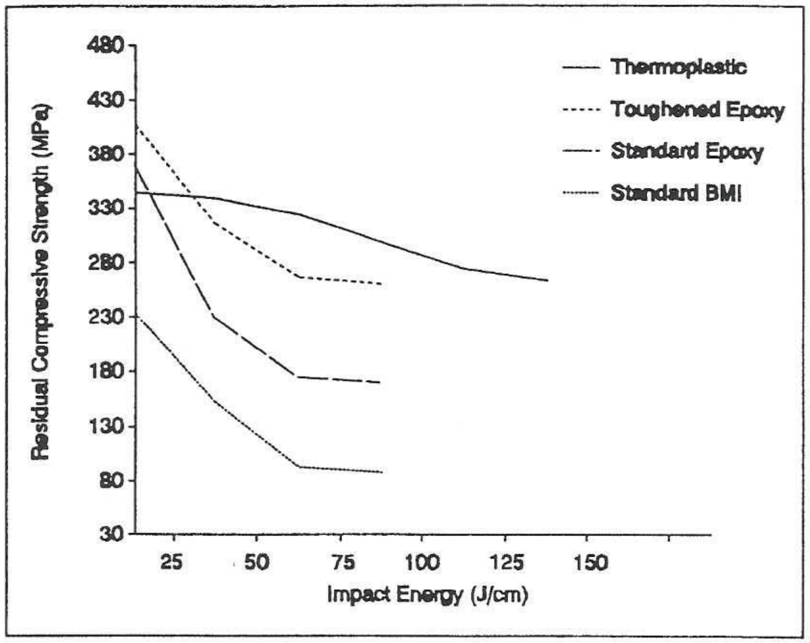


FIGURE 2.2. Comparison of various resins in damage toughness.

talline polymers are characterized by the melting point, T_m. Polymers that have some amorphous and some crystalline regions may have both T_g and T_m, although the magnitude of the temperature transitions in the thermal analysis of the polymer are generally less pronounced than in pure amorphous or pure crystalline materials and may, in fact, merge into one signal. The values for T_g and T_m are reported in Table 2.6. Aging of the polymers (annealing) at temperatures below T_g has been reported to increase T_g and mechanical properties, probably due to the change in crystallinity of the polymers [39].

As with most polymeric materials, the thermoplastic matrix materials have a significant reduction in mechanical properties with increasing temperature. This reduction in properties has been well characterized for several of the polymers listed in Table 2.6, especially for the high performance resins since these are the resins most likely to be used in high temperature applications [40–44]. A test that is often used to characterize this reduction in properties is the heat distortion temperature (HDT) which is also reported in Table 2.6. The HDT value has often been considered to be a maximum use temperature for the polymer for continuous service. The maximum use temperature of the polymer can also be related to the T_g or T_m. Although not as accurate as the HDT, in its absence a rule of thumb that has been suggested is that the maximum use temperature should be no more than 75% T_m or 75% T_g.

TABLE 2.6 Matrix Dominated Thermal Properties [28 – 37].

Polymer	Glass Transition T_g (°C)	Melting Point T_m (°C)	Processing Temperature (°C)	Heat Distortion Temp, HDT (°C)
PEEK	140–145	334–343	370–400	152–160
PPS	85–90	275–290	315–343	115–260
Polysulfone	180–220	–	300–399	174–175
Polyarylsulfone	189–225	–	330–388	182–204
Polyetherimide	215–217	–	340–400	197–200
Polyamideimide	275–288	–	330–400	274–278
TP polyimide	251–330	–	280–360	–
Liquid crystals	350	358–421	360–430	337–355
Nylon 6/6	47–80	255–265	260–327	190–243
PET	69–80	245–265	265–285	158–207
Acetal	−75	163–175	193–243	160–173
Polycarbonate	149–150	220–230	293	138–149
ABS	88–120	–	325–500	95–100
PPO	90–220	262–484	400–600	96–215
PP	−27	163–176	71–80	45–120

The high T_m and T_g of the high performance polymers are reflected in the relatively high processing temperatures (see Table 2.4) of these polymers when compared with the processing temperatures for engineering plastics or for thermoset materials which are usually limited to 177°C (350°F). The elevated processing temperatures for high performance thermoplastics cause several complications in processing. For instance, much of the traditional composites manufacturing equipment such as autoclaves and compression presses will not reach 300°C without significant modifications in heating elements, gaskets, and other components. The materials used for some of the processing methods, such as vacuum bagging film, bleeder cloth, and sealant, will often degrade or melt above 300°C and alternate materials must be found.

Low temperature properties also have importance for some composite applications. In general, the thermoplastic polymers showed no decrease in tensile strength, Izod impact strength, or compressive strength that would indicate brittleness or a breakdown between the resin and the reinforcement in the −56.6°C temperature range [45].

ENVIRONMENTAL RESISTANCE

Resistance to water and organic solvents is another property of thermoplastics, especially high performance thermoplastics, that is better than with the common thermoset matrix materials. Some of the high performance thermoplastics (PPS, PEEK, PAI, and LCP are some of the polymers that fit in this category) show almost no solvent sensitivity to entire groups of common solvents such as aromatic hydrocarbons, aliphatic hydrocarbons, esters and ketones, alcohols, amines, weak bases and salts, strong bases, strong acids, strong oxidants, or water. Other high performance resins, such as PSU, TPI, PAS, and PEI show good resistance except for one or two of the solvent groups [46–48]. The resistance to various liquids commonly encountered in the normal composite material environment is also important. Some of these liquids would include motor oil, transmission oil, gasoline, brake fluid, ethylene glycol, trichloroethylene, jet fuel, hydraulic fluid, methyl ethyl ketone (MEK), and methylene chloride. The resistance of the high performance thermoplastics to these liquids is excellent [49,50]. One study, however, indicates that when subjected to stress, the solvent resistance of the sulfone-related high performance thermoplastics is significantly degraded, although methods for correcting this deficiency were demonstrated [51]. The engineering thermoplastics are generally much more sensitive to solvent attack and would perform at roughly the same solvent resistance level as the common thermoset materials.

This excellent solvent resistance of the high performance thermoplastics is obviously an advantage in hostile environments where these solvents may be encountered. The resistance to solvation can, however, be a problem in cases where the matrix needs to be dissolved, such as in testing for fiber content or in applying the matrix to the fibers by the solution impregnation method. The problem of fiber impregnation by other methods makes this inability to dissolve the matrix material especially troublesome. Some of the methods which have been developed to achieve improved fiber impregnation are discussed in Chapter 3.

Another important environmental consideration is the flame retardance of the polymers. Highly aromatic polymers (including most of the high performance thermoplastics) are inherently flame retardant because of their tendency to char. Char forms a protective boundary (layer) between the flame front and the combustible material. The more aliphatic polymers, such as nylon, polypropylene, and acetal, will burn readily if they are not precompounded with chemical flame retardants [52]. Flame retardance is very important in the use of composites in mass transport vehicles such as trains, planes, and buses.

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CHAPTER 3

Fiber/Matrix Interactions

This chapter will review the following concepts:

- Fiber/matrix adhesion
- Characterization of the resin-matrix interphase
- Resin properties affecting impregnation and fiber-reinforcement bond strengths
- Impregnation methods
  - Solution impregnation
  - Hot melt coating
  - Film stacking

FIBER/MATRIX ADHESION

The unique properties of a composite material depend upon the simultaneous and cooperative interaction between the matrix and the reinforcement. When a force is applied to the composite material, the lower modulus and lower strength material (matrix) deforms first and distributes the load to the higher strength reinforcement material. Furthermore, when an individual fiber fails, the load is redistributed by interaction with the matrix to all the other fibers [1]. In this way the strength of the combined (composite) material is higher than the strength of either of the constituent parts. The success of this cooperative interaction between matrix and reinforcement depends to a significant degree on the nature of the region where the fiber and matrix touch. This contiguous region is called the interphase and is illustrated in Figure 3.1.

The current theory of reinforcement-matrix interactions involves the recognition of a flexible, three-dimensional interphase which is thought to

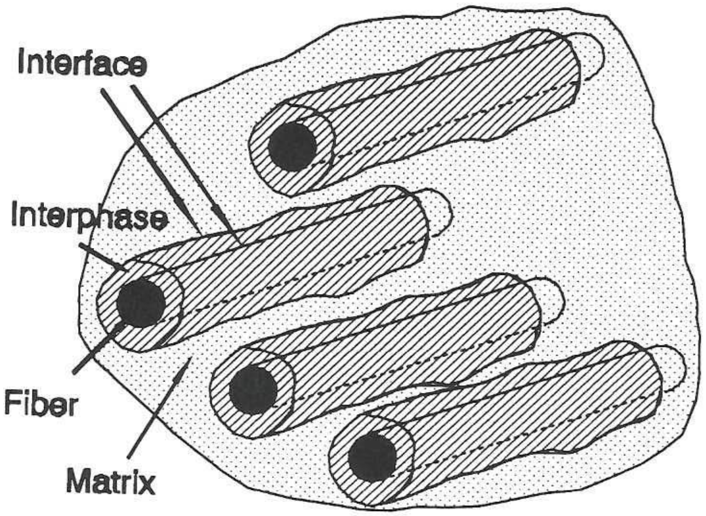

FIGURE 3.1. *Interphase region and interfaces.*

exist between the matrix and the reinforcement [2]. This interphase is formed by the interpenetration of the matrix lattice (polymer structure) with the polymer lattice of the fiber such that each entity has entered the other's domain. In this theory the planes of maximum extent of the matrix and the fiber are called the interfaces [3]. This interphase or interpenetrating polymer network theory has also been postulated for blends of polymers to explain some of the synergistic effects [4]. Many of the high performance thermoplastics have been blended with other resins because of the difficulty of processing the high performance thermoplastics.

In many cases the reinforcement fibers will be coated with a polymeric material (called a size or sizing) which serves as a protective layer to prevent mechanical damage before they are combined with the matrix. For glass fibers the sizing is often an easily removed polymer such as polyvinyl alcohol to which a silane coupling agent has been added to improve the adhesion of the glass fibers to the matrix. (The coupling agent molecule has one end that is chemically similar to the glass and the other end that is chemically similar to the matrix, thus promoting the interpenetration of the matrix and fiber lattices.) The sizing on carbon fibers is usually an epoxy that is added after the fibers have been passed through an oxidative bath to clean the surface of debris created during the fiber formation operation and to implant surface groups (such as hydroxyl or amine groups) that can react with the sizing. When the carbon fibers are to be combined with a thermoplastic matrix instead of the more common epoxy, the use of a thermoplastic size (usually the same resin as the matrix) has been shown to increase mechanical properties [5]. Aramid fibers are often used without a sizing but when present, an epoxy is used most often.

When the fibers are coated with a sizing, two interphase regions exist—one between the fiber and the sizing and the other between the sizing and the matrix. The concepts of interphase and interface are not changed in essence, therefore, when either a sizing or coupling agent is present on the reinforcement. This model of interfaces and interphase between the matrix and the reinforcements is simply a way of envisioning the mechanisms which contribute to adhesion between the matrix and the fiber.

Although the focus in this book is on the matrix properties, the properties of the fiber surface in determining adhesion are also important. For instance, a study of carbon fibers in liquid crystal polymers showed that the fiber surfaces influenced the orientation and orientational dynamics of the liquid crystal matrix and, therefore, affected the adhesive bonding [6]. The interaction of polymer matrices with various filler surfaces also gives valuable insights into the nature of the interphase area [7].

To take full advantage of the mechanical properties of both fiber and matrix, the interfacial shear strength resulting from the fiber/matrix adhesion must be greater than the shear strength of the matrix or of the fiber. This adhesion determines the strength of the interfacial (or interphasial) bond and can be attributed to a combination of the following mechanisms [8–10].

Adsorption and Wetting

It is essential that the fibers be wetted by the matrix in order to form a continuous interphase region. The phenomena of wetting can be described by applying the general principles of surface chemistry. The work (energy) required to separate two surfaces can be defined in terms of the surface free energies of two particles, *A* and *B*, by the equation

$$W_{\text{adhesion}} = \gamma_A + \gamma_B - \gamma_{AB} \tag{3.1}$$

that is, the work needed to separate particle *A* from particle *B* is equal to the surface free energy of *A* plus the surface free energy of *B* minus the surface free energy of the interaction between *A* and *B*. The summation of the work of adhesion for all of the particles on the surface gives the total work of adhesion of the surface. The surface free energies can be approximated by making surface tension measurements and so the work of adhesion can be determined experimentally. However, the work of adhesion should not be equated to the adhesive bond strength since the bond strength also contains the energy of dissipative processes such as viscoelastic deformation, plastic deformation, local microcracking, etc. But, under certain conditions (low temperature and high peel rate) the work of adhesion W_{adhesion}, approximates the bond strength W_{bond} [11]. Therefore, surface adhesion is essentially a surface energy phenomenon and can be enhanced by altering the surface energies of the fiber or the matrix.

One study has indicated that the absorption of the polymer onto the surface can be increased by annealing [12]. The annealing also improves crystallinity of the matrix in the vicinity of the fiber which can further improve interphase penetration and thereby improve the interface bond strength.

Chemical Bonding

Chemical bonding between the matrix and the reinforcement is one of the most effective methods of increasing the interfacial bond strength. Some fibers have chemically active surfaces which react directly with active groups in the matrix. The high strength and high modulus fibers that are most commonly used for composites (fiberglass, carbon, aramid) do not, however, have these active groups unless the active group is specifically added by some special process. Instead, coupling agents, described previously, have long been used, especially with glass fibers to obtain chemical bonding. The presence of the coupling agent may increase the interphase stiffness as postulated for nylon/fiberglass systems [13].

Several studies have investigated the use of plasma gas as a novel technique to improve interfacial adhesion [14–21]. Significant improvement in the interfacial bonding has been demonstrated using plasma as an activation medium. The plasma extracts atoms from the fiber surface and promotes attachment of reactive groups which can then bond with appropriate chemical groups on the thermoplastic. The use of corona has also shown some ability to improve bonding between thermoplastics and fibers.

Mechanical Adhesion

Bonding of the matrix to the irregularities of the fiber surface takes place through mechanical interlocking. Fiber surface roughening usually enhances this mechanical adhesion because surface craters and other defects can serve as sites for mechanical interlocking.

Interdiffusion

The interactions present in the formation of the interphase such as molecular intertwining can increase the strength of the adhesive bond. The mutual solubility of the two materials is a first approximation to the amount of interdiffusion [22]. Highly crystalline materials have relatively poor interdiffusion below their T_g.

Crystallization of the Matrix on the Fiber

Moderate crystallization creates an inherently strong interphase region because of the intimacy of the crystal growth pattern on the fiber surface. Therefore, crystallization can either decrease or increase adhesion depending on the relative effects of interdiffusion and crystalline intimacy.

Electrostatic Attraction

Adhesion between fiber and resin may be promoted, at least initially, by a difference in electrostatic charge between the two materials.

For the high performance and some of the engineering thermoplastics, all of the mechanisms of adhesion and matrix-reinforcement bonding are poor. Adhesion between thermoplastic resins and reinforcement fibers is usually weak because of the poor adsorption and wetting, chemical bonding, mechanical adhesion, interdiffusion and electrostatic attraction. The surface free energies, γ, for thermoplastics are usually much lower than for conventional thermoset resins resulting in a low $W_{adhesion}$. Wetting of fibers by thermoplastics is also poor because of the high viscosity of many thermoplastics. This high viscosity, low solubility, and high crystallinity of some materials also limit the interpenetration of the interphase regions. The thermoplastic resins have few active sites, especially in the highly aromatic resins, that can form chemical bonds with the surfaces of the reinforcements. Mechanical bonding is complicated by the need to create a smooth and crack-free reinforcement surface and by the difficulty of getting the viscous thermoplastic resin to flow into the small surface pockets to effect good mechanical bonding. Generally no electrostatic bonding is present in thermoplastics.

In order to achieve good bonding between the thermoplastic matrices and fiber reinforcements, several studies have focused on techniques such as electrodeposition of polymers on the fiber surface [23], improvements in coupling agents [24,25], improved surface oxidation treatments [26–28], matching of mechanical properties (modulus) of the fiber outer surface and the matrix to lower the stress concentrations which occur at the surface during loading [29–31], and use of a ductile material in the interphase to provide a conformational layer to reduce interfacial stress concentrations [32].

CHARACTERIZATION OF THE MATRIX AND FIBER INTERPHASE

The fiber and matrix surfaces have been characterized by wetting studies, including Wilhelmy balance techniques [33,34], X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Fourier transform infrared (FTIR), secondary-ion mass spectroscopy (SIMS), H^1 and C^{13} nuclear magnetic resonance (NMR) [35], and differential scanning calorimetry (DSC) [36,37]. Mechanical tests have also been used to characterize the strength of the interfacial bond. The most common are the short beam shear, transverse tensile test, single filament pullout (or microdroplet pulloff), and embedded single filament tests [38]. These tests are illustrated in Figure 3.2.

The short beam shear test is widely used because of its simplicity and the ease of performing the test. This test is similar to a flexural strength test of unidirectional fibers except that the sample length (span) is very short with respect to its thickness which promotes failure by shear. The short beam shear test has been criticized, however, because the results have been found to be dependent upon fiber volume which is not accounted for in the calculation and the samples have shown some evidence of compression which would indicate a mixed failure of both shear and compression [39].

The transverse tensile test is also simple to perform. This test is like a standard unidirectional tensile test except that the fibers are oriented perpendicular to the direction of load. Failure is, therefore, controlled by the resin and by the resin/reinforcement bond strength. This method, however, is very sensitive to internal defects such as voids or crossed fibers and should be considered as a "weakest link" test [40].

The single fiber pullout test is the oldest of the single fiber tests and is simple in concept but is highly sensitive to fiber damage and, therefore, premature sample failure. Because the test is so dependent upon the characteristics of the fiber, the method is tedious and subject to large data scatter, but has yielded sensitive results which agree well with other test methods

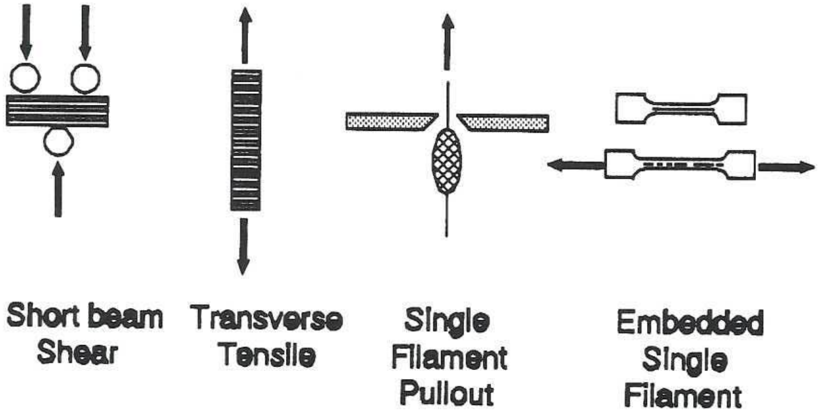

FIGURE 3.2. Tests to determine interfacial bond strength.

[41,42]. Using this test, the interfacial bond strength, τ, is calculated by the following equation:

$$\tau = \frac{\sigma_m d}{4L} \qquad (3.2)$$

where:

σ_m is the maximum stress applied to the fiber.
d is the fiber diameter.
L is the embedded fiber length.

The embedded fiber test utilizes the determination of the critical fiber length to determine the interfacial bond strength. This critical fiber length is determined by embedding a single fiber in a matrix which has been shaped to a tensile-like dogbone pattern (except much smaller). This tensile specimen is then subjected to tensile loading. The fiber will fracture into smaller and smaller lengths until a length is reached which will no longer transfer loads. This smallest length is the critical fiber length, l_c. The equation relating the interfacial bond strength and the critical fiber length is:

$$\tau = \frac{\sigma_u d}{2l_c} \qquad (3.3)$$

where:

τ is the interfacial shear strength.
σ_u is the ultimate fiber tensile strength.
d is the fiber diameter.
l_c is the critical length.

This test requires a special tensile device and a microscope to observe the fibers. In practice the critical length is usually determined by observing the fibers through polarized light and noting the point where the light ceases to have a nodal pattern (which corresponds to the point where the stresses are uniformly distributed). Use of this test also requires that the fiber diameter and ultimate tensile strength be carefully characterized, usually statistically. In spite of the difficulties associated with this test, it has gained wide support [43].

Other tests are the longitudinal tensile strength [44], longitudinal compressive strength, longitudinal flexural strength, impact toughness, and *in* *situ* fracture processes. These are less widely used but have some adherents, especially for unique situations.

RESIN PROPERTIES AFFECTING FIBER-MATRIX BOND STRENGTHS

The thorough wetting of the fibers by the matrix is the fundamental process affecting the fiber-matrix bond strengths. All of the matrix-reinforcement interactions affecting the bond strength—chemical bonding, mechanical adhesion, interdiffusion, etc.—depend upon the resin penetration of the fiber bundle and complete coating of each filament. Otherwise the bond cannot form. In order to achieve this wetting, the resin must flow. Four types of flow behavior have been identified [45,46]: (1) resin percolation through and along the fibers, (2) transverse fiber flow (squeezing flow consisting of resin shear within the ply in the transverse direction), (3) intraply shear along the fiber direction, and (4) interply slip (cooperative flow among the layers with the layers in the same or different orientations). Of these four types of flow behavior, the resin percolation is the most important in achieving good bonding between the fiber and the matrix. This percolation heals flaws, allows bonding of layers, and is the process of interphase interpenetration that has already been discussed.

Generally this percolation is easiest along the direction of the fibers, especially at high fiber volume fractions. However, the flow path in the fiber direction is often quite long compared to the path length perpendicular to the fibers. As a result, the apparent flow path is in the transverse direction. This flow results in a penetration of the fibers that can be modeled using Darcy's one-dimensional law of flow through porous media [47]. By integrating the Darcy equation over the media thickness with time, the following relation for the one-dimensional penetration is obtained [48]:

$$x = \left(\frac{2kPt}{\mu}\right)^{1/2} \tag{3.4}$$

where:

x = penetration depth
k = media permeability coefficient
P = pressure
t = time under pressure
μ = media viscosity

Equation (3.4) shows that high viscosities will reduce the penetration depth unless porosity of the fiber bundle, pressure, or time are increased accordingly.

This penetration is more difficult in thermoplastics than in thermosets because the thermoplastics have inherently higher molecular weights and, therefore, higher viscosities at the time the fibers and resin are mixed. (The thermosets develop the high molecular weight during the cure operation which is after the fibers have been coated.) The higher viscosities simply mean that the mixing and coating are more difficult to achieve. Viscosities for thermoplastic resins at their processing temperatures are typically 10^3 to 10^5 Pa·s for high performance thermoplastics and from 10^{-2} to 10^4 Pa·s for engineering thermoplastics. The viscosities are very sensitive to molecular weight but the range of molecular weights is fairly narrow for the high performance thermoplastics. The viscosities of the engineering thermoplastics will typically have a broader range because the applications and methods of processing are much more varied for the engineering thermoplastics. For comparison, the viscosity of a typical uncured epoxy material is 0.5–1 Pa·s; the viscosity of molasses is 10^2 Pa·s.

The width of the molecular weight distribution also plays a part in determining the ease of fiber wet-out. If the molecular weight distribution is narrow, the polymer will melt over a narrow range and wetting of the fiber will be easier. Likewise, crystallinity affects the ease of fiber wet-out. A highly crystalline polymer would have a narrow melting range resulting in an easier fiber wet-out than totally amorphous polymers.

A process for improving the ability of selected high viscosity thermoplastics to penetrate and coat fibers is based on the chemical technology known as "cyclics." In this developing technology the thermoplastic resin is initially formulated in a cyclical, short chain structure which has an inherently lower viscosity than the normal linear structure of the polymer. Then, after penetration of the fiber, the polymer cyclic structure (ring) is opened which converts it to the linear structure and the molecular weight is simultaneously increased by heating the resin in the presence of an anionic catalyst. This ring opening and polymerization can usually be accomplished during the normal shaping or molding step [49].

METHODS FOR COATING FIBERS WITH THERMOPLASTIC RESINS

Because of the difficulties associated with fiber wet-out for thermoplastic resins, several techniques have been used to obtain uniform and integral coatings of the fibers by the resin and to give good processability of the resulting material. These methods include the following: solution impregnation, hot melt coating, film stacking, commingled fibers, powder coating, and *in situ* polymerization. In principle all of these methods could be employed to coat the fibers with thermoplastic resins during final product forming or in a preliminary operation wherein a prepreg material is made. In practice some of the methods are better suited for making prepregs and others for final forming; but the objectives of obtaining a good coating of the fiber surface and good adhesion are the same in either case [50].

Solution Impregnation

This process, which is well established for thermoset resins, entails the solvating of a resin, coating the fibers with the solution, and evaporating the solvent [51]. Solution impregnation has the inherent advantage that the solution is almost always low viscosity and can, therefore, readily penetrate the fiber bundles and coat the fibers easily. Another advantage is that it may be possible to choose a solvent that enhances the wetting of the fiber. One inherent disadvantage of solution impregnation for both thermosets and thermoplastics is that the solvent must be removed, usually as part of the prepregging operation. For thermosets, because of their incomplete cure, the prepreg will usually be slightly sticky and pliable (that is, it will have good tack and drape). For thermoplastics, because the polymers are solids at room temperature, the prepreg will be stiff and boardy. To impart some measure of tack and drape to the thermoplastic, some solvent might be left in the prepreg. This would then require that the solvent be removed during the final forming process which has often proven to be difficult. The presence of solvent during final forming can cause blisters, surface imperfections, and internal voids which substantially weaken the composite part. Should the resin not all be removed during final forming, the solvent will have a plasticizing effect on the resin and the mechanical properties will be much lower than those of the resin without the solvent. This effect was demonstrated by Leeser and Banister by tracking the decrease in T_g with residual volatiles in a PEEK laminate. They showed that the T_g decreased from 400°F to 250°F with a change in residual volatiles of 0 to 3.7% [52].

Another major difficulty with solution impregnation of thermoplastic resins, especially advanced thermoplastics, is the resistance of these materials to solvation. Some of the materials have no known solvents at room temperature and most are highly solvent resistant. Therefore, solution impregnation would not be possible for many of the high performance thermoplastics and would be impractical for many of the other thermoplastics.

Hot Melt Coating

The basic nature of thermoplastic resins means that they can be melted by increasing the temperature. Further increases in temperature above the melting point will reduce the viscosity of the melt and allow easier fiber coating. This process is, therefore, the most commonly used for fiber impregnation. The technology for coating fibers with a thermoplastic is much like the fiber impregnation technology for thermosets except that the resin is heated. For both thermosets and thermoplastics the process for making prepreg usually involves the pulling of the fiber tows through a comb device to align the fibers if tape is being made or simply off an aligned roll of fabric if prepreg fabric is to be made. The fibers or fabric are then pulled through a bath resin (heated in the case of thermoplastics) or over a roll onto which resin (heated) has been doctored and then onto a roll of backing paper with additional backing paper added on the top. Alternately the aligned fibers or fabric could be pulled onto backing paper that has already been uniformly coated with resin (and heated continuously in the case of thermoplastics). In all cases the paper/resin/fiber/paper sandwich would then be squeezed to enhance fiber wet-out and then rolled up for storage and shipment. Note that in some cases where the molecular weight of the thermoset resin is high, the thermoset resin must be heated to form a melt so that the fibers can be coated. In these cases the impregnation process is similar to the thermoplastic process except that the degree of heating is much less for the thermoset than for the thermoplastic because of the very high melting point of the thermoplastic resin.

Although the prepreg process is simple in concept, a complication arises with many of the high performance thermoplastic resins because they have decomposition temperatures (that is, temperatures at which the polymeric structure begins to break down) that are only slightly higher than the melting point. This results in a narrow range of acceptable temperatures for the melt. In many cases the viscosity cannot be reduced sufficiently within this operating temperature range to give good wet-out of the fibers.

An alternate method to achieve lower viscosity resins is by shear thinning at relatively high temperatures, but below the decomposition temperatures. This shear thinning, which occurs because the resins are non-Newtonian, can reduce the viscosity of the resin several orders of magnitude. The method usually involves the forcing of the heated resin through a die under conditions that create high shear. Although the lower viscosity resin created by this shear will successfully coat the fibers, the resin molecules will be highly oriented in the direction of the fibers and may, therefore, have lower adhesive bonding with the fibers [53].

For on-line impregnation processes, such as filament winding, the coating of fibers is usually different for thermoset matrices and thermoplastic matrices. In the case of thermosets, the fibers are often simply pulled through a resin bath or over a doctored roll much like the process of making prepreg. In the case of thermoplastics, the materials are usually too viscous and the times too short to effectively coat the fibers on-line. Therefore for thermoplastics, prepreg tows (that is, tows which have already been coated with resin) are the most commonly used materials. The implications of this process will be discussed in more detail in Chapter 5.

Film Stacking

The inherent nature of thermoplastic resins allows them to be shaped into one form and then reshaped into another by heating and molding. Therefore, if the thermoplastic matrix is shaped into a film, two or more of these film layers can be interleaved with layers of reinforcement fibers in either tape or cloth form and then heated and pressed to form a laminate structure. The pressing is often done with nip rollers or platens. This method is, therefore, a modification of hot melt coating except that the thermoplastic is heated after the fibers are placed rather than before. Many of the problems associated with hot melt coating still exist with film stacking (such as poor wetting and lack of tack and drape).

An advantage of film stacking over hot melt coating is that the processing temperature for film stacking can be lower than the melting point of the resin because the resin need only soften and flow under pressure rather than melt completely. This lower processing temperature decreases the potential for resin degradation. The film stacking process can also allow additional time for resin migration which might improve the uniformity and fiber wetting. A further advantage is that the heating and pressing can occur at the time of final part shaping so the extra step to make a prepreg may not always be necessary. A difficulty with hot melt coating that can be solved with film stacking is the variability of the weights of resin and fiber in the prepreg. This variability is minimized if a constant-thickness layer of resin is applied to the paper, but is still greater than can be achieved with known weights of film and fiber in the film stacking process.

A disadvantage of film stacking is that the process requires more steps than hot melt coating and probably more processing time. Furthermore, if done in platens, the continuous nature of the hot melt process is lost.

Commingled Fibers

The thermoplastic matrix could also be shaped into the form of continuous fibers which can be intermixed with the reinforcement fibers (on the individual fiber level) to form a hybrid fiber bundle which can then be heated above the softening or melting point of the thermoplastic and molded to cause the thermoplastic fibers to flow and coat the reinforcement fibers. This process is a modification of hot melt coating and has the following potential advantages: the fiber volume fractions can be precisely controlled and high fiber contents can be achieved; temperatures may not need to be as high as the melt temperature; the heating is done after the matrix and reinforcement have been combined, giving more processing time; matrix and reinforcement consolidation can be done at the time of final forming; and the variability of weights of matrix and reinforcement can be carefully controlled [54].

The commingling process has the further advantage over film stacking in that the resultant hybrid material is inherently flexible and therefore will conform easily to complex contours. Furthermore, the hybrid yarns can be woven into complex shapes, even three-dimensional, that are conformable and drapeable.

A disadvantage of commingling is the difficulty of opening up the reinforcement fiber bundle to intermix the matrix fibers. This is especially difficult because of the stiffness and brittleness of most reinforcement fibers and is further complicated because the thermoplastic fibers are often much larger in diameter than are the reinforcement fibers. This problem can be alleviated to some extent by wrapping the bundle of reinforcement fibers with the thermoplastic fibers (a process called serving). The wrapped fibers would then be formed into tapes, woven into cloths, or used in on-line processes much like prepreg tow. Alternately, separate reinforcement yarns and resin tows can be woven into hybrid fabrics which can then be laid up easily into complex shapes. The successful use of these latter configurations (wrapped tows and hybrid cloth) depends, however, on the ability of the thermoplastic fibers to flow into the bundles of reinforcement fibers and wet them thoroughly. This usually requires very long consolidation times compared to simple commingled fibers. Even then, the wetting is usually not as complete and the physical and mechanical properties of the resultant composite are lower than the commingled which are themselves lower than hot melt coated prepreg tape [55]. These lower properties are attributed to fiber breakage during the weaving process, poor fiber/matrix distribution and poor fiber/matrix adhesion [56].

Another disadvantage to commingled fibers (and wrapped fibers as well) is that the commingled product is difficult to use in on-line processes such as filament winding because of the lack of bundle integrity. Chang and Lees [57] observed that during filament winding with PEEK fibers commingled with carbon fibers, a separation of the two fiber types occurred as tension was applied during normal processing. The resulting part (a tube) showed a low torque strength with a high level of voids after postconsolidation via autoclave. In contrast, a melt impregnated carbon/PEEK tow with good bundle integrity was successfully processed with a resulting torque strength that was 66% higher.

Powder Impregnation

A method which retains many of the advantages of commingling but alleviates some of the problems is powder impregnation. This variation of the commingling process intermingles finely powdered thermoplastic resin with the fiber tows. Several methods to achieve this intermingling have been reported. In one method the fiber tows are passed through a chamber of charged and fluidized powdered resin and then through an oven to permanently adhere the polymer to the fiber [58–61]. This technology could be used to coat fiber tows or woven cloth, although reliable methods for spreading the fibers in cloth for best impregnation must still be developed.

Another method involves impregnation of the fiber tows by passing the fibers through a fluidized bed and then encapsulating the resin powder in the fiber bundle with a sheath of thermoplastic resin that is melted (extruded) onto the tow [62,63]. Preferably the extruded thermoplastic resin is the same as the impregnation resin.

The fibers can also be impregnated by passing the fibers through a slurry of the resin powder in water [64]. The slurry impregnated method has the additional advantage that the material is tacky because of the retention of some of the water. The water is driven off during the forming process which can be a problem but generally is not because of the long times required to ensure full wetting of the fibers by the resin.

In all of these cases the commingled resin and fibers are flexible and can therefore be formed easily into complex shapes. One inherent difficulty with powder impregnation is that the fiber bundle must be spread to achieve good intermingling of resin and fibers. Also, best impregnation is obtained if the size of the resin granules is approximately the same as the diameter of the fibers. All of these processes require the additional step of granulating the resin unless the resin is produced as a powder, as are many of the engineering thermoplastics.

An obvious potential problem with the powder impregnated materials is that the powder could be knocked off the fibers during handling. Thus, the fibers require careful handling and may not be capable of being woven, especially into tight weaves. Another potential problem is the presence of excess resin used to hold the resin granules in place. This resin may result in lower mechanical properties, especially shear and other matrix dominated properties.

In situ Polymerization

A logical method of reducing the viscosity of the thermoplastic matrix material is to utilize monomers or solvated prepolymers of the thermoplastic to coat the fibers and then to polymerize the thermoplastic *in situ*. Only a few of the thermoplastic matrix materials can be processed by this method (chiefly thermoplastic polyimides), but for those, the method has great promise [65]. The presence of low molecular weight materials or solvents imparts good drape and tack to the material.

A disadvantage of this method is that the processing times are long, even when compared to thermosets, thus eliminating one of the major advantages of thermoplastics – rapid processing.

In situ polymerization has also been recommended as a method of improving the adhesion between the polymer and the fiber because of the improvements in the interphase that are possible [66]. In this method the surface of the fiber is activated by heating the carbon fibers in oxygen or nitric acid and then polymerizing in the presence of these activated fibers. The result is a fiber on which the polymer has been grafted. Adhesion is improved by this technique.

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CHAPTER 4

Composite Properties

This chapter will review the following concepts:

- Mechanical properties of thermoplastic composites
- Fiber length and resin property considerations
- Impact toughness
- Fatigue
- Environmental resistance

COMPOSITE MECHANICAL PROPERTIES

The composite structure is the combination of the matrix and the reinforcement. While the mechanical properties of the neat resin which were discussed in Chapter 2 are certainly important, many mechanical properties of the matrix are overshadowed by the mechanical properties of the reinforcement in any reasonable composite structure. For example, the modulus of elasticity of the composite (E_c) in which the fibers are all oriented in the direction of tension is found by the following equation called the rule of mixtures:

$$E_c = E_f \nu_f + E_m \nu_m \qquad (4.1)$$

where:

E_f and E_m are the moduli of the reinforcement and matrix.
ν_f and ν_m are the volume fraction of the reinforcement and matrix.

In a typical case the modulus of the reinforcement would be 85 to 300

GPa and the modulus of the reinforcement would be 2 to 5 GPa. Clearly, the reinforcement will dominate the composite modulus at volume fractions that are commonly used for commercial composites (10% to 65%). Under these conditions the modulus of the matrix will have little effect on the modulus of the composite.

These same arguments (domination of composite properties by the reinforcement) are also true of many other properties such as tensile strength, flexural strength, and thermal expansion when these are measured in the direction of the fibers. The tensile relationships are illustrated in Figure 4.1 which can serve as a model for the reinforcement dominated properties. The composite strength will be chiefly dependent upon the fiber strength, provided that the matrix can effectively transfer the load onto the fibers. This load transfer is dependent upon the strength of the fiber-matrix bond. The role of this bond has been discussed in more detail in Chapter 3.

Because the mechanical properties of composites (and many other properties as well) are fiber dominated, comparisons of properties in which different resins are involved can be misleading. For instance, the tensile strength differences between two composites with two different resins may be due to differences in fibers, layup, manufacturing method, or some other property that might not be readily apparent, in addition to the obvious different resins. (The differences could also be due to resin differences that are not readily apparent such as molecular weight or amount of crystallinity.) Care must be taken, therefore, to insure that the same fiber type, fiber content, fiber length, fiber treatment, or thermal history, among others, are used. Data with the degree of standardization necessary to make these comparisons are not generally available. Therefore, the data presented herein will be normalized, as much as possible, to standard conditions. When this cannot be done, the comparisons will be made narrowly with the focus on the specific property being analyzed; and in those cases, comparisons beyond the narrow scope indicated should not be made.

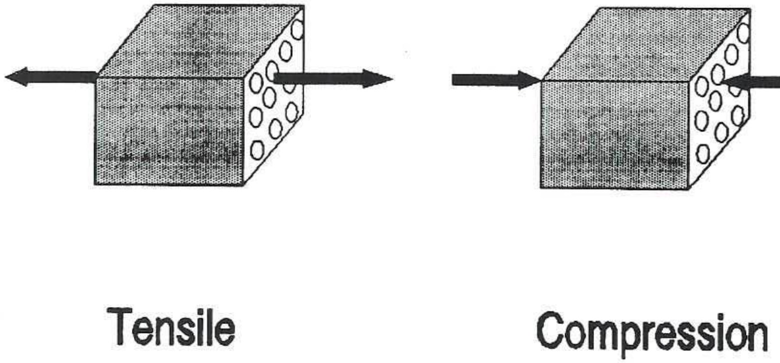


FIGURE 4.1. Fiber dominated loading mechanisms in composites.

TABLE 4.1 Mechanical Properties of High Performance Thermoplastics [1 – 6].

Polymer	Tensile Strength (MPa)*	Tensile Modulus (GPa)*	Compressive Str. (MPa)*
PEEK	1869 – 2452	125 – 141	1033 – 1469
PPS	1345 – 1929	120 – 145	654 – 960
Polysulfone	1069 – 1331	129 – 141	1041
Polyarylsulfone	–	–	–
Polyetherimide	–	136	820
Polyamideimide	1379	142	1379
TP polyimide	–	117	993
Liquid crystals	1492	143	862

*Unidirectional laminates normalized to nominal 60% fiber volume (AS-4 or equivalent), continuous fibers.

In spite of the difficulties mentioned above, mechanical properties remain the primary properties for design. Most composite applications are driven by tensile modulus and tensile strength and these will, therefore, be discussed herein. Other properties (such as impact toughness, compression, thermal and other environmental properties) are important for some specialized applications and will also be discussed.

The most important mechanical properties for composites are listed in Table 4.1 for many thermoplastic resins. The properties have been normalized to 60% fiber volume fraction.

The tensile strength values for the thermoplastic materials are in the same range as values for typical thermoset materials. For instance, epoxy-carbon composites typically have tensile strength values of 1276 – 1482 from one study [7] and 1654 – 2819 in another study [8]. These data again emphasize the dependence of the tensile data on fiber properties. The wide range in the data from these sources further reinforces the difficulties in giving tabular information regarding composite materials.

Typical epoxy or other high performance thermoset materials generally have compressive strengths that are in the range of 1500 to 2000 MPa which are significantly higher than the compressive strengths of the high performance thermoplastic materials. The rationale for this difference in compressive strengths is not clear. Some believe that poor fiber alignment and poor fiber interfacial adhesion are the cause [9]. Explanations for why the thermoplastic materials would have more misalignment than the thermosets are not given. Other investigators believe that the lower thermoplastic compressive strengths likely arise from a lower stability in shear [10]. In any case, comparisons of compressive strength against neat resin tensile modulus indicate that the relationship for thermoplastics is fundamentally different from the relationship for thermosets in such a way as to suggest that thermoplastics are not as efficient in increasing compressive strength with resin modulus as are thermosets [11,12]. Attempts to increase the compressive strength might result in reductions of the fracture toughness of the thermosets, indicating that the higher elongation of the thermoplastics compared to the thermosets might be the underlying property controlling the difference.

The complex failure mechanisms might be further understood by examining the compression strength after impact (CAI) or open-hole compression (OHC) tests. The failure mechanisms in these tests are different from normal 0° compression (compression is dominated by fiber buckling and the CAI by delamination), but the combination of the tests gives a broad view of the failure process. The CAI values are much greater for thermoplastics than for thermosets, whereas the OHC results are comparable.

If composite values for different fibers are compared, the broad range is again evident. Turner and Cogswell [13] give tensile strengths in MPa of PEEK on various fibers as follows (adjusted to 60% fiber content): Quartz = 1313, E glass = 1107, S glass = 1055, Aramid = 976, HS Carbon = 2095, and IM Carbon = 2657. They report on a technique using scanning electron microscopy and etching to examine the fiber-matrix interphase region and determine the nature of the crystallization in that zone.

In a similar vein, comparisons of laminates made from prepreg tape and from prepreg cloth show that the tape-based laminates have higher strengths. This difference has been related to the fiber kinks and bends that are inherent in fabric-based composites [14].

Tensile properties for the engineering thermoplastics are given in Table 4.2.

TABLE 4.2 Mechanical Properties of Engineering Thermoplastics [15,16].

Polymer	Tensile Strength (MPa)*	Tensile Modulus (GPa)*	Compressive Str. (MPa)*
Nylon	172–193	90–103	155–276
PET	139–165	90–99	172
Acetal	90–153	100–116	89–351
Polycarbonate	127–154	86–117	124–139
ABS	89–110	69–83	100–117
PPO	103–128	69–90	123
PP	45–90	48–69	45–58

*Fiber laminates normalized to normal 30% fiber volume fiberglass, short random fibers.

The tensile strength values of the high performance thermoplastics and the engineering thermoplastics are difficult to compare because little data of continuous fibers, especially carbon, are available for the engineering thermoplastics. Likewise, little short glass fiber data are available for the high performance thermoplastics. However, in the case of nylon, continuous carbon fiber data are available and the range of tensile strengths and moduli are approximately the same as with the high performance thermoplastics (1493–1517 MPa) [17]. The similarity of the tensile data for high performance and engineering thermoplastics suggests that the main application differences between the resins is probably due to properties other than tensile strength, tensile modulus and compressive strength. Some of the properties that may be important to distinguish these two resin groups could be toughness or resistance to environmental factors. These properties will be examined in more detail.

A brief review by John Therberge [18] of the availability of reinforced engineering thermoplastics indicates the following:

- *Nylons* are available in grades with glass content from 10 to 60% in resin types 6, 6/6, 6/10, 6/12, 11 and 12. Each glass/nylon material is available with a heat stabilizer added for reduction of brittleness during long-term use in high temperature environments. Flame-retardant grades are available with a UL-94 listing of V-0. Other reinforced nylons are available with additives to promote flow. Special formulations offer hydrolysis resistance when exposed to hot water.
- *PET* resins are available with 20, 30 and 40% glass fiber contents. Tensile, toughness and flexural properties are improved significantly over the unreinforced resin.
- *Polycarbonate* compounds are available with 10, 20, 30 and 40% glass fiber loadings. Mechanical properties are greatly improved by the addition of fiberglass. Thermal stability is also significantly improved.

EFFECTS OF FIBER LENGTH, ORIENTATION, AND CONTENT

One of the obvious differences between high performance and engineering thermoplastics is the fiber content and fiber length that are commonly available with each category of resin. The traditional uses of high performance thermoplastics are in the aerospace field and so the fibers are usually continuous carbon or aramid at high (60%) fiber volumes. The processing methods most common for these materials are those commonly associated with thermoset composites (layup, filament winding, pultrusion, RTM, etc.). These will be discussed in Chapter 5.

Engineering thermoplastics are typically used in commercial applications and are most often reinforced with short glass fibers at about 30% fiber volume. The shorter fibers and lower content in the engineering thermoplastics allows the use of traditional thermoplastic processing such as injection molding and extrusion. These processes will be examined in detail in Chapter 6.

Even though the processing methods will be discussed later, some discussion of fiber length and content on the properties of thermoplastic composites is appropriately considered here. The properties of short fiber composites are generally intermediate between continuous fiber composites and nonreinforced polymers. Any skew of the properties toward one of the boundary materials depends, generally, on the length, orientation, and the amount of the fibers. Ideally, the fiber parameters would be chosen so that the key properties approach that of the continuous fiber analog but the processing would approach the nonreinforced polymer. These short fiber materials would fit nicely, therefore, as secondary materials where mechanical or some other physical properties were less important than in primary structures but cost (processing ease) was more important.

The theory of short fiber composites is explained well by others [19–21] and will not be examined in detail herein. From theoretical considerations, it is clear that the stiffness and dimensional stability of the composite increase with increases in the following factors: fiber aspect ratio (l/d – ratio of fiber length to diameter), volume fraction of fibers (v_F), and fiber-to-matrix modulus ratio (E_F/E_M). The increase in mechanical properties with an increase in fiber aspect ratio has been attributed to the decrease in the number of fiber ends which can serve as crack initiation sites [22].

The composite stiffness is also dependent on the fiber orientation distribution but, as yet, there is no direct and efficient calculation format to handle the relationship. Lavengood and Goettler [23] have developed a rule-of-thumb expression for the modulus of a structure with three-dimensionally random fiber orientation:

$$E_1 = \frac{1}{5}E_{11} + \frac{4}{5}E_{22} \tag{4.2}$$

where E_{11} and E_{22} are the longitudinal and transverse engineering stiffnesses for a unidirectionally oriented ply. The degree of adhesion at the interface does not affect stiffness and dimensional stability. All that is required of a good system is that there be good material contact, that is, no voids at the interface [24]. In theory, therefore, the stiffness of a short fiber composite can approach the stiffness of a continuous fiber composite if the fiber aspect ratio is high enough although at high aspect ratios the fibers often suffer from brittleness due to the large number of flaws [25]. (Fiber volume fraction and fiber-to-matrix modulus ratio cannot be varied above certain physical constraints.)

The strength of a composite with short fibers depends on the same parameters considered for stiffness plus the following additional parameters: strength of the interface bond, orientation of the fiber, and strength of the fiber. Unlike stiffness, however, the strength of continuous fiber composites cannot be attained in short fiber composites. (The upper boundary for strength in short fiber composites appears to be about 70% of the continuous fiber composite strength.) The concept of using a strength reduction factor (SRF) has been suggested by Halpin and Kardos [26] as a convenient method of predicting short fiber composite strengths. The SRF is defined as the uniaxially aligned short fiber composite strength divided by the strength of an aligned continuous fiber system with the same volume fraction fibers. This SRF value (which is the ratio of a short fiber laminate to a continuous fiber laminate) is then applied to the strength of each layer in a continuous fiber multilayered laminate by calculating the strain level of each ply and noting the stress at each ply failure level and then summing up all of the stresses for the various layers.

An alternate formulation for the strength of short fiber composites has been suggested [27] which uses a modified rule of mixtures as its basis:

$$\sigma_c = \sigma_m v_m + \sigma_f v_f \epsilon_1 \epsilon_0 \tag{4.3}$$

where:

σ_c is the tensile strength of the composite.
σ_m is the tensile strength of the matrix.
σ_f is the tensile strength of the fiber.
v_m is the volume fraction of the matrix.
v_f is the volume fraction of the fiber.
ϵ_0 is an efficiency factor related to the orientation of the fibers in the composite.
ϵ_1 is an efficiency factor related to the effectiveness of the fiber-matrix bond.

The efficiency factor, ϵ_0 varies from 1.0 (unidirectionally oriented fibers) to 0.33 (randomly dispersed in a plane) to 0.162 (random in three dimensions). The efficiency factor ϵ_1 is not well defined from a theoretical standpoint and is determined empirically, but has been shown to be dependent upon the critical aspect ratio, as was seen in the previous formulation involving the strength reduction factor (SRF).

An interesting product, marketed as Verton® (ICI) or Fiberod® (ICI) Vari-Cut, has been introduced that is intermediate between short fibers and continuous fibers. This product is made by pultruding small rods of continuous fibers in a thermoplastic matrix and then chopping the rods to the length of traditional thermoplastic injection molding pellets. In this manner the fibers are the entire length of the pellet and are much longer than the fibers that are in traditional reinforced thermoplastic pellets. These pultruded and chopped fibers are often called "long" fibers to distinguish them from short or continuous fibers. The mechanical properties of composites containing Verton increase significantly. For instance, the tensile strength of an injection-molded nylon sample containing 50% short glass fibers was 220 MPa and was increased to 255 MPa with long glass fibers. (The comparable value for continuous fibers was determined to be 565 MPa in a compression molded sample.) The flexural modulus increase was 15 to 16 to 21 GPa. Impact strength (toughness) as measured by notched Izod increased from 139 to 320 to >4270 J/m [28]. Other properties, including the effects of temperature, have similar increases with the use of long fibers in a variety of resins [29].

Another interesting fiber form that is intermediate between short and continuous fibers is discontinuous fibers. These are made into a prepreg tape much like continuous fibers but have random breaks in the fibers. These breaks allow the prepreg to be formed beyond the ultimate strain of the fibers because the fibers separate at the breaks and continue to conform to the mold. Because the breaks are random, the apparent fiber length is similar to continuous fibers.

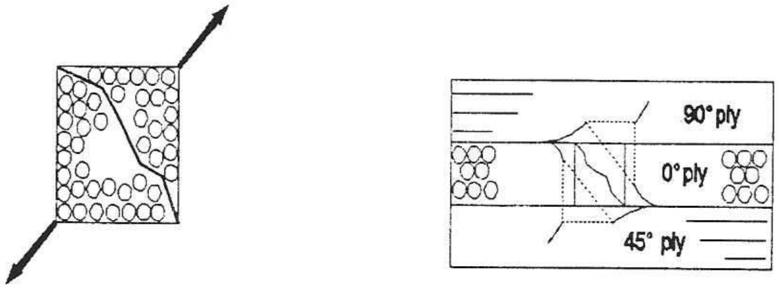
The effects of fiber length, orientation and content on other properties have been less well defined. Toughness has a complex relationship with these fiber properties and may have different trends in short fiber composites than in continuous fiber composites. Creep, HDT, wear and other environmentally dependent properties are also complex. In some of the cases the performance of the short fiber composite is similar to the continuous fiber analog.

COMPOSITE DAMAGE TOLERANCE

Composites are generally much more brittle (lower elongation or ductility) than either neat plastic materials or metals. Therefore, the composite materials have relatively poor ability to resist impact damage without some internal fracture. These impact loads are generally normal to the planes of the fiber laminates, a situation that is quite different from the damage that occurs from tensile and compression loading. Failure from impact is no longer dominated by the fibers because the fibers have little strength in the direction perpendicular to their length. The matrix is then the component that dominates the failure along with the strength of the resin-matrix interface bond, although within the similar matrix systems, the fiber direction and other fiber properties have a secondary effect upon the impact damage characteristics. If the impact is of low velocity, the failure mode is shear through the matrix and between the fibers as indicated in Figure 4.2(a) with little actual fiber damage. After the shear has propagated through the layer, the crack is skewed in the direction of the principal strain as indicated in Figure 4.2(b) [30].

This movement often initiates a delamination between the layers, especially when the layers have different fiber orientation directions. This delamination is a critical property for composites. Careful analysis of the delamination pattern for various resins has resulted in pattern recognition systems and design optimization to minimize delamination by the appropriate selection of laminate orientation sequences [31–33].

The propagation of the crack through the matrix and around the fibers is, of course, a shear phenomenon. Shear-related properties such as toughness are difficult to characterize. They are dependent upon the fiber direction, as has already been shown, and are also dependent upon the type of failure induced in the determination (testing) of the shear. In attempts to understand the shear failure mechanisms, interlaminar shear test methods based on classical linear elastic fracture mechanics have been developed. In these methods the critical strain energy release rate is used as the characterizing parameter and the test procedures attempt to isolate failure by one of the classical modes. These strain-energy failure modes are represented in Figure 4.3.



(a) **Single layer shear**

(b) **Multilayer shear leading to delamination**

FIGURE 4.2. *Transverse crack initiation and subsequent delamination.*

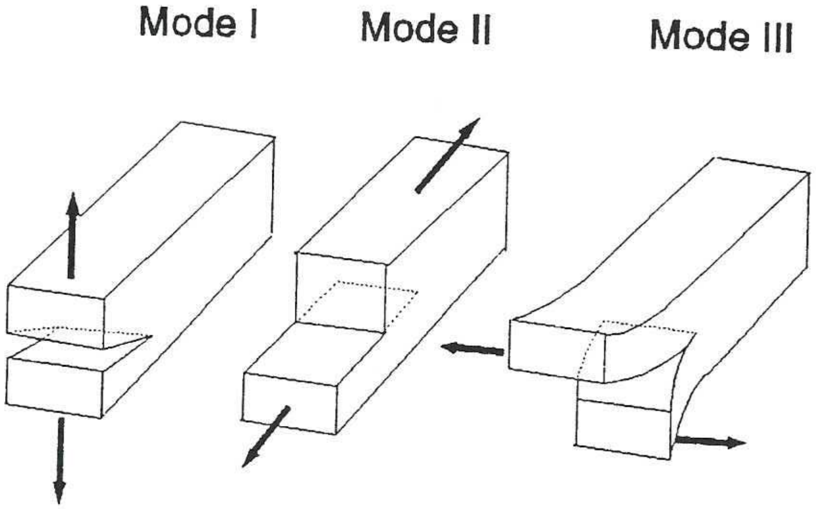


FIGURE 4.3. Strain-energy release rate failure modes.

The methods to determine shear strain-energy release rates are the following [34,35]:

- *Double Cantilever Beam Test*—The test closely approximates the geometry of the mode I in Figure 4.3 and is used to determine pure mode I failures.
- *Edge Delamination Test* (mode I)
- *End Notch Flexure Test* (mode II)
- *Cracked Lap Shear* (mode II)
- *Short Beam Shear*—This test is much like a three-point flexural test except that the specimen has a short span compared to its thickness. By decreasing the span, the major failure mode becomes interlaminar shear rather than the compression and tension of traditional flexural tests. However, some compression and tension failure still occurs which compromises the short beam shear results from a theoretical view. This test is the oldest of the shear tests and is still popular because of the wealth of data available for comparison and because of the ease of performing the test.

Another method of determining composite toughness is based upon the concept that the composite should be damaged and then some physical property tested to determine the difference from a predamage state. (An alternate view of these tests is to simply measure the after-damage property and determine if that residual value is sufficient for the particular use.) These tests assume that even though the fibers may not be damaged by a low velocity impact, the matrix may be seriously degraded. Therefore, traditional tensile tests, which cause the fibers to bridge over the damaged areas in the matrix, are not appropriate analysis test methods. Compressive tests or specialized tensile tests are far more important in assessing after-damage strength. The most common tests to determine after-impact properties are the following [36]:

- *Compression after impact*—In this test the specimen is impacted (usually with a falling dart) and then tested in compression. A special compression fixture is used so that the relatively large specimen (4 inches × 6 inches) can be used. The problem with this test is the unreliability of the impact.
- *Open-hole compression*—In an attempt to standardize the damage to the specimen, the open-hole compression test uses a specimen in which a hole has been drilled.
- *Open-hole tension*—This test concept is much like the open-hole compression. Normally tension would not be a good test to evaluate toughness failure, as has been previously discussed, but in this case, the fibers cannot bridge the damage zone and so reliable data is obtained.

Shear and impact toughness data for several key high performance thermoplastic materials are given in Table 4.3.

Toughness values (from the same references as listed for Table 4.3) for a thermoset epoxy material range from an interlaminar shear toughness of 80–250 J/m^2, a compression after impact of 130–275 MPa, and a short

TABLE 4.3 High Performance Toughness Properties [37–40].

Polymer	Interlaminar Shear Toughness G_{Ic} (J/m^2)*	Compression after Impact, CAI (MPa)**	Short Beam Shear (MPa)
PEEK	1500–3000	310–331	105–117
PPS	530–1400	179	69
Polysulfone	1175–3200	–	–
Polyarylsulfone	5500	–	–
Polyetherimide	950–3700	–	94
Polyamideimide	1050–3400	345	110
TP polyimide	1300–14,000	274–276	98
Liquid crystals	–	–	–

*Interlaminar shear toughness determined by the Double Cantilever Beam Test.
**Compression after impact measured after impact of 67 J/cm.
These values have been normalized to 60% carbon fiber content.

beam shear of 121 MPa. These values are, in general, much lower than the comparable values for the thermoplastics, attesting to the higher toughness of the thermoplastic matrix composites.

The high fracture release energies may contribute significantly to high crashworthiness because the crashworthy behavior of composites has been shown to depend on the fracture release energy [41]. Other investigators have found that the failure mode of fiber and matrix is dependent on the fracture rate, with the higher rates favoring matrix failure rather than fiber or interface failure [42]. The viscoelastic behavior (including the degree of crystallinity) of the matrix also has an important determining effect.

The nature of thermoplastics to flow if heated has given rise to a concept in fracture toughness called healing. In this technique, if the part is impacted without damage to the fibers, the part could then be reheated with the idea that the resin would flow to fill in or remove the cracks. Experimental tests of this concept using the double cantilever beam test to measure the amount of toughness that could be recovered after healing have indicated that 80 to 90% of the original toughness can be restored [43].

The toughness of engineering plastics is usually measured by methods that are more traditional for neat resins such as the pendulum impact tests (Izod, Charpy, and Tensile Impact) and the falling impact tests (Falling Dart and Gardner). This practice arises from the concept within the plastics and composites industries that fiber reinforced engineering thermoplastics should be viewed as strengthened and stiffened neat plastics. The toughness data for the engineering thermoplastics are given in Table 4.4.

Because the testing methods are often different, comparisons between the toughness of high performance and engineering thermoplastics are difficult to make. Some studies [46,47] have, however, conducted similar tests on the two materials and these indicate that the toughness values are in the same general range for the materials. That is, there is as much spread in data between the engineering thermoplastics (or the high performance thermoplastics) as there is between the two groups. Therefore, the use of engineering thermoplastics for toughness applications should be considered, even in applications where continuous fibers are required, unless some other property (such as thermal stability) dictates otherwise.

TABLE 4.4 Toughness Properties of Engineering Thermoplastics [44,45].

Polymer	Izod, Notched (J/m)
Nylon	85–240
PET	85–117
Acetal	43–80
Polycarbonate	91–198
ABS	64–75
PPO	91–123
PP	53–117

These data have been normalized to 30% fiberglass content.

FATIGUE

A property that is closely related to toughness is fatigue. Fatigue measures the time-dependent change in mechanical properties as the sample is repeatedly loaded and unloaded. In general, several studies have indicated that thermoplastic composites have better fatigue resistance than thermoset materials. This improved fatigue performance is attributed to the resistance to the initiation and growth of fatigue damages (cracks) due to the matrix. (The number of cracks per inch in epoxy systems are reported to be in the 40 to 80 range after 30,000 cycles; whereas for PEEK, the number of cracks per inch is in the 5 to 20 range after 1,000,000 cycles [48].) In another study tensile strengths were found to fall to roughly 60% of their initial value in PEEK after 1 million cycles and to fall to 50% of their initial value in epoxy [49].

An important property of fatigue is the fatigue limit. This is the minimum value to which property will degrade at an infinite number of cycles. PPS is reported to have a fatigue limit of 7 ksi [50]. This property is very advantageous because it gives the designer an ultimate decay factor for properties, regardless of the time of service.

The fatigue performance of thermoplastics was seen to depend on the frequency of the fatigue loading in an opposite manner from thermosets. For thermoplastics, an increase in the frequency of loading decreased the overall fatigue performance, presumably because the thermoplastic could not recover fully in the shorter cycle interval. It was, therefore, more like the thermoset materials at higher frequencies [51].

Of particular interest in the engineering thermoplastics is the effect of fiber length on fatigue properties. Nylon samples loaded with 50% short fibers and 50% long fibers were compared in fatigue. The short fiber sample was found to decrease from 89 MPa after 10^4 cycles to 79 MPa after 10^7 cycles or an 11% decrease. The long fiber sample was found to decrease from 120 MPa to 108 MPa or a 10% decrease over the same cycle range. Therefore, not only are the mechanical properties higher for the long fibers, but the retention of properties after fatigue testing is also higher [52].

ENVIRONMENTAL RESISTANCE

Because of the inherent temperature sensitivity of thermoplastics, the retention of key mechanical and physical properties of thermoplastic matrix composites at elevated temperatures has been an important consideration in composites design and use. Because of the diversity of the crystalline and other chemical properties of the thermoplastics, broad generalizations are difficult to make except that the mechanical properties of all thermoplastics will decrease with increasing temperature [53,54]. The sensitivity of this temperature dependence can be estimated from the heat distortion temperatures of the fiber reinforced composites. Some representative values of resins reinforced with carbon fiber are nylon 6 HDT = 174 – 184°C; ABS HDT = 100°C; PPS HDT = >260°C; thermoset polyester HDT = 200 – 260°C; and phenolic HDT = >280°C [55].

PEEK composites with carbon fiber have been shown to vary only slightly in tensile properties up to the glass transition temperature [56,57], although the performance of the material is definitely strain rate sensitive, as would be expected with a viscoelastic material [58]. Matrix materials which are similar to PEEK but formulated for higher temperature performance gave improved behavior for 40 to 50°C beyond the normal PEEK T_g [58]. PEEK was much more sensitive to compression loading at high temperatures, presumably because the matrix allowed fiber buckling [60]. Loading in directions or with composite layups that emphasized the matrix were more sensitive to temperature than those which emphasized the fibers [61].

The high temperature performance of the engineering thermoplastics was similar in trend to the high performance thermoplastics. For instance, the tensile properties of nylon were found to decrease 10 to 12% with an increase in temperature from 23°C (room temperature) to 120°C. The fatigue resistance was found to be proportionately worse as elevated temperatures, going from a 10% loss in strength over 10^3 cycles at 20°C to a 32% loss in properties at 120°C [62]. Similar decreases in mechanical properties with increasing temperature were reported by the ASM Committee on Forms and Properties of Composite Materials [63] for nylons, PET, and polysulfone.

An important thermal property of materials is the heat transfer capability. The presence of carbon fibers greatly enhances the heat transfer capabilities of most resins. For instance, the coefficient of thermal diffusion across the fiber direction has been reported to be 3×10^{-7} m²/s whereas the coefficient in the fiber direction (where the effect of the fibers is much stronger) was 29×10^{-7} m²/s [64]. For carbon fiber systems the coefficient of thermal diffusion across the fiber is typically three times that of conventional thermoplastic systems, while that along the fiber direction is ten times greater still. With other fibers, such as glass, the advantage will not be as great.

The coefficient of thermal expansion is also an important thermal consideration in composites. In any heating process there will be dimensional change. In the case of composites, the dimensional change follows the rule of mixtures (discussed previously in this chapter). Therefore, the property will be dominated by one of the constituents if the property values for the constituents are vastly different. They are in this case. The coefficient of thermal expansion for the fibers is typically much less than for the matrix. (A typical value for a unidirectional composite in the fiber direction is 0.5×10^{-6} cm/cm/°C, but in the direction across the fibers would be 30×10^{-6} cm/cm/°C. In a quasi-isotropic composite the coefficient of thermal expansion would be 2.9×10^{-6} cm/cm/°C [65].)

The fatigue properties at high temperature have been reported to be complex in their trends and are different from the room temperature behavior. Initially the fatigue degradation is small but increases near the end of the product's performance life, presumably due to the increasing rate of deformation at that point [66].

The ability of a composite to resist water (moisture) or other solvent absorption is also an important property. Because of the superior solvent resistance, especially to water, of many of the thermoplastics, they have been investigated extensively for this property. Generally the initial assumption of the good resistance has been verified. An important implication of the low moisture absorption is that the mechanical properties are degraded very little in moist or solvent environments [67–70].

The ideal environmental resistance behavior is to have high retention of original properties after impact and simultaneously high retention of properties in hot/wet conditions. Thermoplastic matrix composites generally possess this desired combination of properties. As is reflected in Figure 4.4, the thermoplastics are superior to the other common matrix material types.

This combination of properties, along with others, has been suggested as an excellent criterion for the selection of space materials [71], although many other applications in both aerospace and industry have similar requirements.

One other important environmental property is the resistance to mechanical erosion or wear resistance. Thermoplastic composites have shown an excellent wear resistance, especially when the reinforcing material is an aramid or with an improved compatibility in fiber sizing [72–75]. This improvement in wear has been demonstrated in reinforced nylon 6/6, acetal, and PPS. A further improvement in wear has been demonstrated in liquid crystal polymer composites by adding 15% polytetrafluoroethylene-filled compound. Coefficients of static and dynamic friction are reported to be two orders of magnitude less than the base resin [76].

The use of conductive fibers in PEEK, PPS, and liquid crystal matrices has proven to be a convenient method of obtaining low-cost, easily formable conductive composite materials for use as EMI shielding. These matrices were shown to be compatible with carbon fibers, stainless steel fibers, nickel flakes, and nickel plated graphite fibers [77].

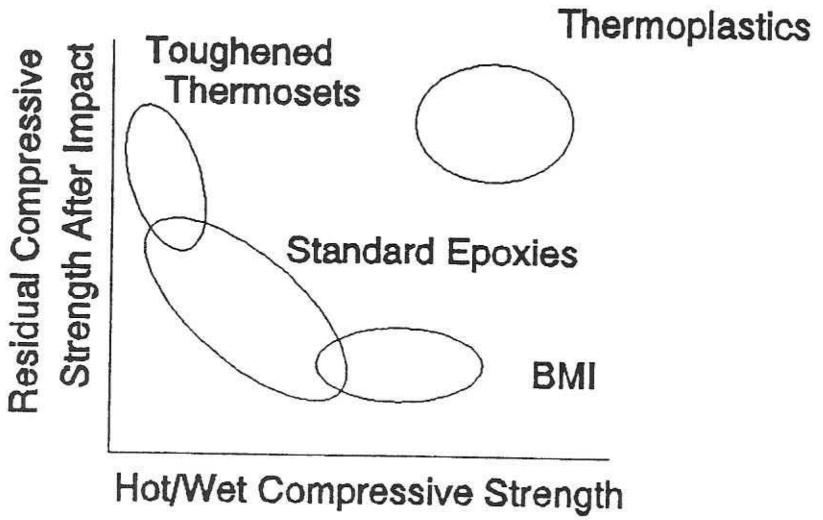


FIGURE 4.4. Schematic representation of residual compression after impact vs. hot/wet compressive strength of different matrix materials.

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CHAPTER 5

Manufacturing by Traditional Thermoset Methods

This chapter will review the following concepts:

- Layup (manual and automated)
- Filament winding and fiber placement
- Pultrusion
- Matched-die molding
- Liquid composites molding (RTM/RIM)
- Consolidation or "curing"

MANUFACTURING OVERVIEW

Because the use of composites has generally been driven by the excellent properties available with these materials, composites manufacturing has focused on maintaining these excellent properties, even at the expense of efficient manufacturing. However, as composites are considered for a wider range of applications and as cost considerations become more important, the manufacturing method will be scrutinized as a potential area for efficiency improvement. In some of the applications of composites the ultimate optimization of properties may not be important and a slightly lower level of performance can be accepted in order to accommodate improved manufacturing. This investigation is now underway, but has chiefly focused on modifications in the traditional thermoset manufacturing methods which have been developed to maximize properties. These traditional thermoset processes will be examined in detail in this chapter with special attention on the modifications to those processes that have been made to accommodate thermoplastics. Traditional thermoplastic manufacturing methods have also been used to manufacture reinforced thermoplastic materials. Chapter 6 will examine these processes in detail. Then, in Chapters 7 and 8, the manufacture of thermoplastic composites by some processes which are nontraditional for either thermosets or thermoplastics will be examined.

The shift from thermoset materials to thermoplastic materials requires a change in thinking about the basic nature of the manufacturing process. With thermosets the manufacturing process focuses on control of the chemistry of the crosslinking reaction, whereas with thermoplastics the focus is on control of the rheology of the resin. The rheology is important in the way the resin flows to coat the fibers, but is also important in the flow of the resin into the final part shape. Two overall strategies have been developed for the coating of the fibers. These strategies are (1) preimpregnate the fibers and then, in a separate step, mold or shape the part; and (2) consolidate the fibers and resin at the same time as impregnation. Generally the first strategy has been the widely followed and has led to the extensive use of prepreg materials. These materials were discussed in some detail in Chapter 3. The second strategy has been less widely used, but will be discussed in this chapter and Chapters 6 and 7 as each manufacturing method is examined as an option to the more popular prepreg method. One of the problems with the second strategy is that the properties of the composite material seem to be lower when the consolidation and wet-out are done simultaneously. Cogswell reported the data shown in Table 5.1 [1].

The causes of the differences in these are not fully understood, perhaps because of the complexity of the fiber wetting process as described in Chapter 3, and the strong coupling of the microstructure of the resin and its processing history. The basic nature of the melting, flow, and resolidification is not simple, and involves heat diffusion, a change of phase in the material, and motion of the liquidic state. Many properties can be affected by this process sequence. For instance, the degree of crystallization can affect shear strengths, resin-fiber bond strengths, and resistance to environmental factors. Other examples of factors which complicate the fabrication of thermoplastic composites are the thermal stresses that can be induced in the part because of the changes in temperature and volume throughout the process, the changes in local fiber distribution that can come from the pressures involved in the molding, and the effects of voids or other imperfections on final properties. Therefore, the manufacturing of thermoplastic composites is a fruitful area of research both from the standpoint of theory and modeling and from the viewpoint of practical demonstration and part fabrication.

TABLE 5.1 Effect of Impregnating Fibers before or after Shaping.

	Axial Flexural Strength (MN/m^2)	Short Beam Shear Strength (MN/m^2)	Impact Energy 2 mm (J) Sheet
Preimpregnated fabric	1052	80	29
Simultaneous impregnation/ shaping fabric (film stacked)	680	67	9

Models of general thermoplastic composite manufacturing have been developed [2,3]. These models generally envision three major processing steps – introduction of the matrix between the fibers, consolidation of the individual plies, and heating and cooling such that the properties of the matrix are controlled. These models and others that have been and may be proposed [4,5] will, hopefully, give additional insight into the manufacturing processes.

LAYUP

This is the most basic of the manufacturing processes used with composites and was developed for thermosets, but has been modified for thermoplastics. The basic process as applied to thermosets consists of placing multiple layers of fibers and resin, either by hand or by machine, into a mold until the desired thickness is reached and then applying pressure and heat to cause the part to consolidate and, in the case of thermosets, to cure. If the resin is applied to the fibers in process, that is, at the time the fibers are laid into the mold, the process is called wet layup. A somewhat superior product can be made, with less resin and fiber handling difficulty, by using a reinforcement that has been preimpregnated with resin and then cured slightly to increase the viscosity. This material is called a prepreg and was discussed in Chapter 3. Because of the difficulty of controlling the viscosity of thermoplastic resins and the high temperatures required to melt them, wet layup with thermoplastics is not generally done. Therefore, the layup discussion will focus on the use of prepreg materials.

Manual prepreg layup gives more flexibility and control in orienting the fibers and therefore in controlling the physical properties, especially for complex three-dimensional parts, than any other composite manufacturing process. In addition, the high cost of materials motivates manufacturers to minimize the amount of scrap created in producing composite structures and this process allows layup of near net-shape parts [6].

Thermoset prepregs are leathery and have a slight tackiness (tack) so that the layers do not slide over each other during layup and will stick or maintain their location in the mold. The prepreg is also conformable to the mold so that complex shapes can be made. This ability to conform is called drape. Drape and tack are often associated with each other and are chiefly dependent on the resin type and amount as well as any solvent that may have been added. Because thermoset resins have already been initiated when the prepreg is made, these prepregs have a limited shelf life before they turn into a dry and board-like material that is difficult or impossible to use. The shelf life is usually several days to weeks at room temperature, but it can be extended by keeping the prepreg cold. In many prepregs the resin content is higher than is desired in the finished part. This improves tack and drape, but the excess resin must be removed at some point in the manufacturing process. The removal of this excess resin assists in the removal of entrapped air and volatiles, which will flow out with the excess resin. It is essential to remove the volatiles and entrapped air, since voids within a laminate have a negative effect on the interlaminar shear strength. As a guide, the interlaminar shear strength is reduced by about 7% for each 1% of voids present up to a maximum of about 4% voids. A reasonable goal for void content in the finished laminate is 0.5% or less [7].

Most high performance thermoplastics are available in prepregs with most normal reinforcement fibers and in many fiber forms (unidirectional and fabrics). As discussed in Chapter 3, the most common method of impregnation is by melting the matrix resin and applying it to the fibers from a hot-melt bath. An alternate method might be solvent impregnation, but the most high performance thermoplastics have limited solubility and so this method is rare. Because thermoplastic resins are high molecular weight solids at room temperature, they differ from thermoset prepregs in several important ways. The most obvious difference is that thermoplastic prepregs are stiff and boardy (no drape) and have no tack. The lack of drape and tack presents some problems in layup because the thermoplastic prepregs are much more difficult to lay into complex shapes and they tend to shift or slide over one another. The most common method of alleviating this problem is to soften (slightly melt) the thermoplastic prepreg so that the drape and tack can be improved. This softening is usually done with an air gun or direct heating tool, such as a soldering iron. In one processing guide [8] the following recommendation is given: "The use of a pencil type soldering iron with a 650°F–700°F tip temperature is recommended. A 1/4 inch spade type tip has been found to be most convenient. Note that the above tip temperature may require an iron rating in excess of 700°F to achieve the correct working temperature at the laminate."

As discussed previously in Chapter 3, thermoplastic prepregs have been made in several forms other than the traditional hot-melt or solvent processes, some of which substantially eliminate the drape problem. For instance, the reinforcement fibers have been combined as either commingled yarns or cowoven to make a fabric with fibers made from the thermoplastic matrix resin. In this way the prepreg behaves like a woven fabric which obviously has good drape. In order to use this commingled material, however, molding should be done at temperatures high enough to destroy the previous thermal history of the matrix (PEEK). If not done, the fiber/matrix adhesion is not optimal. However, at temperatures just above these high temperatures, some matrix degradation occurs and the properties are again reduced. A narrow temperature range exists for processing hybrid commingled fibers [9].

Another of the methods to prepare thermoplastic prepreg materials involves coating the reinforcement fibers with powdered matrix. The powder-coated material has much more drape than the traditional prepreg and has been shown to result in parts with equivalent mechanical properties [10]. In some methods of applying the powder thermoplastic a solvent is used (usually water) which acts as a plasticizer for the resin and increases the tack of the prepreg. This residual water must, of course, be withdrawn when the part is consolidated, but that has been reported to be done easily with little detectable deterioration of many mechanical properties although shear or transverse strength remains a problem [11,12].

An advantage of thermoplastic prepreg in any of its forms over thermoset prepreg is that thermoplastics have infinite shelf life. Refrigeration is not necessary and no precautions are needed to ensure usefulness over a long period of time. This property is advantageous because of reduced storage costs, elimination of out-of-date waste products, the need to certify and requalify outdated material, and the elimination of several nuisances associated with handling and thawing the frozen thermoset prepreg material.

An important new development in layup of composites is the introduction of automated layup machines. These machines hold the promise of increasing the productivity of the layup method by reducing labor and by producing a more repeatable and better quality and larger product. The drawbacks of automatic tape laying machines are limitations in the complexity of the part that can be fabricated, economic limitations on making small parts because of the long head turnaround times, and requirements for considerable programming time.

Automatic tape laying machines were first introduced for thermosets and proved to be valuable for relatively flat parts made in high volume. With the introduction and acceptance of thermoplastic matrix resin materials, the development of automated tape laying machines for thermoplastics seemed a logical step. With the development of tape laying machines for thermoplastics, a new concept emerged—the simultaneous laying of the tape and consolidation of the layers together which could conceivably eliminate the need to further consolidate the laminate. This process has been called "*in situ* consolidation." *In situ* consolidation was demonstrated on laboratory scale equipment [13,14] and in some full-size parts. The current best technology, however, seems to suggest a postfabrication consolidation step, although this consolidation is much faster and more uniform than panels from non-consolidated prepreg sheets [15]. Disadvantages noted in

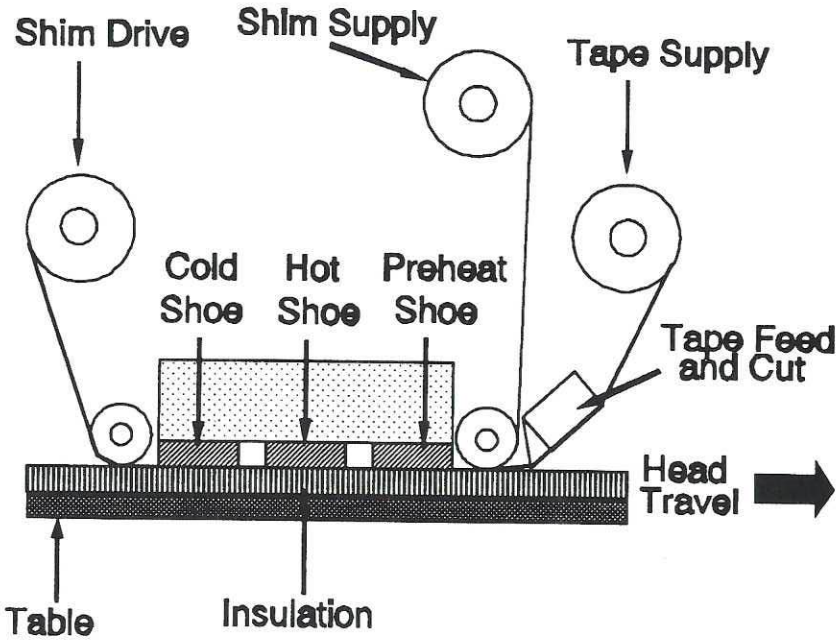

FIGURE 5.1. Thermoplastic tape laying machine.

thermoplastic tape laying that do not exist in thermosets is the tendency of the panels to warp due to the uneven localized heating from the tape laying head and the tendency of some resins to be oxygen sensitive at high temperatures, thus requiring a nitrogen blanket during the tape laying process.

Thermoplastic tape laying machines differ from thermoset machines in that the tape must be heated just before contact with the mold or with the other plies already laid onto the mold and then pressed to the other layers while still molten so that the layer will stay in place. Therefore, three variables must be considered—temperature, pressure, and time (speed). Secondary variables include back tension, tape feed, cutting force, and tape edge placement [16]. The tape laying process has been modeled and found to predict many experimentally determined variables [17], although many correlations are yet to be determined [18]. Early laboratory and later commercial investigations of heating methods, compaction materials and forces, laydown surfaces and techniques, and machine control seem to have resulted in commercially viable tape laying machines for both thermosets and thermoplastics. These experiments clearly pointed out the need to preheat the material that had already been laid down, to heat the tape to the melting point, and to hold the materials together while cooling. Figure 5.1 is a schematic of a thermoplastic tape laying machine that illustrates the three-shoe head that has been adopted commercially that uses these principles.

In this design, the shim is used to remove any relative motion from the tape surface by resolving the forward reaction force into the shim rather than into the tape. Cutting is done automatically. The consolidation from this type of machine is reported to be 80–90%.

After layup of the prepreg materials, all thermosets and most thermoplastics are covered with various types of release and absorbent materials and then placed inside an airtight bag and subjected to heat and vacuum. A typical vacuum bag assembly is illustrated in Figure 5.2.

These various bagging materials allow the resin to flow uniformly from all areas of the part and the excess resin to be absorbed and not sucked into the vacuum pump. The release allows the bagging materials to be removed from the part after consolidation and cure.

Some complications in bagging arise with thermoplastics, chiefly because of the much higher temperatures required to process the thermoplastic layup and achieve the liquid state. Whereas with thermosets the processing temperature rarely goes higher than 232°C, with thermoplastics the temperatures often exceed 370°C. Very high melting or nonmelting materials are available for many of the components of the bagging assembly, but in a few materials special care must be taken. The bagging material used most often with thermosets is nylon film. That material will not work for thermoplastics because of its low T_m. Therefore, a polyimide film (such as DuPont's Kapton®) or hardened aluminum foil are suggested [19]. Other materials for which a high temperature alternate to the regular thermoset

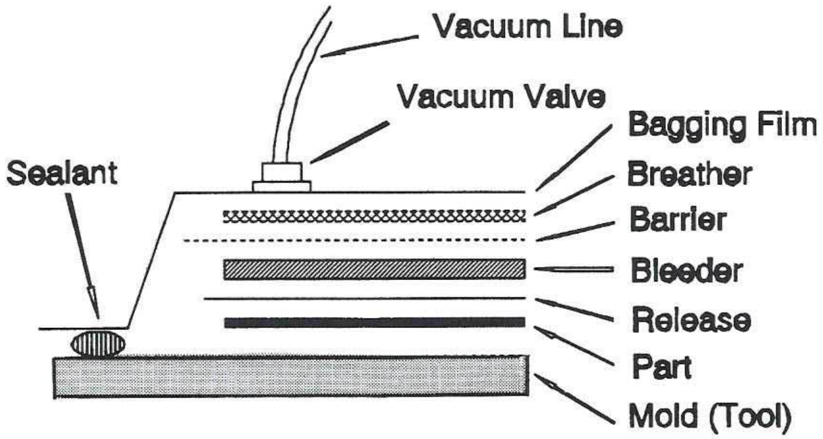

FIGURE 5.2. Vacuum bag assembly.

materials must be used are the sealant tape, the mold release material, and the release cloth (Teflon® coated fabric should be avoided because Teflon degrades at the high processing temperatures).

The layup of thermoplastic parts has been proven to be successful in several instances. At Northrop Corporation an aluminum landing gear door was redesigned for PEEK/IM6 (carbon fiber). The outer skin consisted of several deep drawn pockets and reliefs. The part was 49 plies and built up using prepreg tape that had previously been cut to length. Each layer was tacked in place using a soldering iron. The part was bagged using a fluorosilicone vacuum bag and high temperature vacuum bag sealant tape. The forming temperature and pressure were approximately 385°C and 1378 kPa. The door was proof-tested for both the closed and open door configuration with no apparent damage detected using ultrasonic C-scan inspection [20].

FILAMENT WINDING AND FIBER PLACEMENT

The traditional filament winding and related process of fiber placement were developed for thermoset resins but have been successfully modified for thermoplastics. In the basic filament winding process, a continuous tape of resin-impregnated fibers is wrapped over a mandrel to form the part. Successive layers are added at the same or different winding angles until the required thickness is reached. Either the mandrel or the application head can rotate to give the fiber coverage over the mandrel, although the rotating mandrel is far more common. The fiber placement process is similar except that in fiber placement the fibers are pressed onto the mandrel by compaction of the head (much like in automated tape laying) rather than being pulled onto the mandrel and held in place by tension as is the case with filament winding. When using thermosets, the most common method of winding (called wet winding) passes the uncoated fibers through a bath of liquid resin and then directly onto the mandrel. These wet or soaked fibers are usually passed through a roller between the bath and the mandrel to control the resin-fiber content, but this control is not precise and the ratio of resin to fiber would only be approximate, even under the best conditions. An alternate winding system (dry winding) uses fibers which have already been impregnated (prepreg tow) and winds that onto the mandrel. The wet winding system is less expensive, but the dry system avoids the problems of environmental vapor control and fluctuations in resin-fiber content.

Usually the dry winding method (prepreg tow) would be used with thermoplastics because of the difficulty of achieving good wet-out in the short time available in wet winding, although one report has utilized matrix powder to coat the fibers after which the fibers are passed through a small pultrusion die to melt the powder and form a well-defined rectangular cross section. The matrix is kept in a molten state until it reaches the contact point on the mandrel. The process is quite slow and parts have high void contents. Nevertheless, on-line impregnation, if controllable, offers many advantages over prepreg tow [21].

Because thermoplastic tows (in the traditional form) lack tack and drape, they must be heated before they are applied to the mandrel and the layers already on the mandrel. However, the short time interval between the heating and laydown have caused some limitations in the speed of thermoplastic filament winding. This heating and laydown process has been the subject of several research projects. In one method a hot gas torch was used to melt the resin in the prepreg tow which then passed to a compression wheel for consolidation on the mandrel [22]. In another system a split shell infrared oven encapsulated the mandrel while an infrared preheated tow was run through the split shell heater and applied to the mandrel. The same study also reported the use of infrared heated tows and a quartz lamp heated mandrel [23]. A third heating method used a laser. The laser was directed at the contact point between the prepreg tow and the mandrel and some heating occurred in both materials [24,25]. All of these heating methods have some problems [26]. The hot gas method is typical of gas convection heating with relatively poor heat transfer because of the low heat capacity of gases. This poor heat transfer tends to limit both the maximum obtainable tow temperature as well as the total heat capacity available. The gas may be air, nitrogen, or many others. This method has the advantage of being a uniform heat source and a potentially inert environment. Radiant heating in the form of infrared or quartz heaters is a convenient, readily adjustable, noncontact heat source. High heat capacity can be concentrated into a small area. However, these heaters are unforgiving with respect to material speeds and will not heat materials that are transparent to the infrared light frequencies. Laser heating can concentrate a large amount of heat into a small area but requires constant refocusing of the light as the winding progresses. The cost of the laser may also be an impediment to the use of this method.

In the most effective heating methods both the material already laid onto the mandrel and the prepreg tow are heated and then compressed, either by tension or a compression device (such as a roller or a shoe) or by both. The heating control is critical since the melting point of many of the thermoplastic resins is near the decomposition temperature.

The problem of consolidation and the question of whether consolidation can be done at the time of layup *(in situ)* or whether postlayup consolidation is required is another question that has received considerable attention. The problem of *in situ* consolidation is difficult to evaluate in general because it seems to depend upon the thickness and shape of the part. Some cases of acceptable parts made by *in situ* consolidation have been reported [27,28] but other researchers are skeptical, at least for some parts. These researchers report that *in situ* consolidation must be considered separately for each part with consideration of its shape and use [29]. For instance, if the part is small, thin, and uniformly round so that the tension of the filament winding process is uniform, the part can likely be consolidated *in situ.* In this respect, parts made by filament placement may be more likely to be consolidated *in situ,* but work to support that supposition has not been reported.

The use of powdered or commingled prepreg tape is an obvious alternative to the heating of the fibers prior to pressing them onto the mandrel. However, the use of powdered or commingled materials will eventually require heating and consolidating so no real savings are realized except that the winding process might be less troublesome.

The automated nature of filament winding suggests improved efficiencies over layup methods. Therefore, the use of less expensive, engineering resins in this automated process may result in low-cost parts that have excellent properties from the continuous fibers. ICI reports a range of preimpregnated fibers (Plytron®) using the following engineering resins: polycarbonate, nylon, and polypropylene [30].

The use of filament winding with engineering thermoplastic matrices has been demonstrated in the automotive market. A specially adapted computer winding system with a proprietary delivery head and using a thermoplastic polyester system has shown great promise. Also noted are pipe systems, oxygen bottles, and acetylene tanks that all have great potential for thermoplastic composite materials [31].

PULTRUSION

In the pultrusion process, continuous reinforcement fibers are impregnated with resin and shaped, consolidated, and cured or solidified by drawing them through a die. This process is analogous to the extrusion of metals or of nonreinforced thermoplastics with the obvious exception that pultrusion incorporates fibers and, in the traditional method, involves thermoset resins. (One pultruder has actually used metal pultrusion equipment for thermoplastic composite parts and operated the equipment at approximately half the temperature needed to process titanium [32].) Pultrusion is a continuous processing method and, therefore, has great potential for high throughput and reduced manufacturing costs. The major limitation of pultrusion, as with the extrusion process too, is that the cross section of the part normally must be constant, although both solid and hollow parts as well as many profiles can be made. Compliant dies that permit a change in thickness have been designed for special applications and permit some variation in cross section, but these are the exception in this process.

Manufacturers of thermoplastic resins and independent pultruders have demonstrated the capability of modifying the pultrusion process to accommodate the use of thermoplastic resins. Shapes such as channels and rods have been tested and found to have excellent properties, especially impact toughness, compared with similar thermoset parts [33,34]. These resin manufacturers and producers have revealed some of the details regarding the methods for manufacturing these pultruded parts, but also indicate that some proprietary technology is involved [35].

Several investigators have modeled the thermoplastic pultrusion process in an effort to identify and optimize the key segments of the traditional thermoset pultrusion process which should be modified to permit thermoplastic composite pultrusion [36–40]. These models also reduce the number of experiments needed to define the operating conditions of the process. The models have dealt with the following considerations: fiber continuity, resin continuity, flow, resin viscosity, fiber deformation, heat transfer, and thermal expansion. The solutions to the equations covering these aspects of the process define the pressure, resin flow, temperature, pulling force, and cooling rate. Agreement with lab experiments have been reasonably accurate and give encouragement that the one-dimensional models proposed should be expanded to three-dimensions and other simplifying assumptions treated more completely.

Researchers have performed experimental studies to characterize the operating parameters of thermoplastic pultrusion and, sometimes coincidentally, to verify the models [41–44]. In at least one case, the verification of the operating parameters involved the construction of a special pultrusion line just for thermoplastics [45]. In these theoretical and experimental studies, some of the key components and operating conditions are as follows:

- *Impregnation*—The most common method of testing was to use prepreg material. As has already been described, this method vastly simplifies the impregnation process because impregnation can be done as a separate step, without the time constraints of downstream equipment. However, in-line impregnation has also been successfully demonstrated with all of the common methods of impregnation used in prepregging, that is, hot melt, solution, powder coating, and commingling.
- *Preheating*—All of the impregnation methods require heating prior to or during the consolidation in the die. This heating must melt the thermoplastic resin, whether in the prepreg, powder, or commingled form so that the shape can be given in the die. In the

case of the solvent impregnation, an additional purpose of the preheater is to evaporate the solvent. The major methods of preheating are with infrared lamps, resistance heaters, radio frequency, and heated air. No comparative studies on these different methods have been reported so the relative effectiveness of the methods is difficult, at present, to assess. Great care must be taken to uniformly heat all areas of the product, especially in the case of large cross sections. There is no exothermic reaction with thermoplastics so all of the heat must be supplied externally and it must be sufficient to melt the resin so that good consolidation can occur. A lack of proper heating in the preheat section may limit the amount of heat that can be added within the die and thus may limit the amount of consolidation and forming that takes place within the die. It is doubtful that the heat from the die can overcome problems associated with improper preheating [46].

- *Die*—In both the thermoset and thermoplastic pultrusion processes, one important purpose of the die is to shape the wetted fiber strands into the final part shape. For thermosets, this shaping can be done merely with the application of pressure. With thermoplastics, the pressure must be accompanied with heat to insure that the resin is melted. Other functions of the die are quite different between the thermoset and thermoplastic processes. In the thermoset process the die heats the resin so that cure will occur. In the thermoplastic process the die cools the resin so that solidification will occur. For thermoplastics, therefore, the die might be divided into two sections. In the first section the part is formed while under heat to insure that the resin is melted and good consolidation and shaping occurs. In the second section the part is retained in the desired shape but is cooled to give it final rigidity. Some thermoplastic pultrusion lines have only one die section which is for shaping and cooling; these rely entirely on the preheater to melt the resin. In either case, the thermal expansion and contraction of the resin must be recognized or proper consolidation may not occur.
- *Pulling mechanism and cut-off saw*—These components are not substantially different for thermoplastic pultrusion from those used for thermosets with the solitary precaution that the pulling forces are higher for thermoplastics and, therefore, the equipment must be able to exert these higher forces.

One of the key issues in achieving improved properties seems to be improving the resin/fiber interface and that is strongly affected by the crystallinity of the resin. Improved polymer grades can increase the crystallinity in pultruded parts from the 10–15% range to the 40–50% range and thereby improve the mechanical properties significantly [47].

A modification of the thermoplastic pultrusion operation is the use of ultrasonic vibrations just prior to entry into the die to increase the resin flow and, therefore, improve the fiber wet-out and reduce processing time [48].

A concept that is gaining favor in the composites industry is manufacturing standard shapes (rods, channels, I-beams, hat structures, plates) by pultrusion and then postforming them to give some minor shape changes appropriate for a specific use. One example was the pultrusion of a graphite-reinforced thermoplastic cable which was postformed by thermoforming for use as a marine mooring cable [49]. This concept of pultrusion followed by postforming will be explored in detail in Chapter 8.

One application of extrusion deserves special consideration. In this application tows of fibers are pulled through a thermoplastic melt and through the die but the tows are kept separate. All of the consolidation occurs with individual tows. The tows, which are shaped into thin rods (roughly like spaghetti) are then chopped into short pellets (about 10–12 mm long). These pellets can then be used for injection molding or extrusion. The advantage of these pellets is that the fiber length is much longer than the fiber length in traditional short fiber reinforced plastics for injection molding and extrusion. These fibers will be discussed in more detail in Chapter 6.

MATCHED-DIE MOLDING

This process, also called compression molding, involves the placement of the resin and fiber mix into a mold which has been mounted in a platen press. The press is closed and the material flows to fill the mold. With thermosets the molds are heated so that cure occurs within the mold. The most common thermoset materials used in this process are bulk molding compound (BMC), sheet molding compound (SMC) and preform molding. BMC and SMC, sometimes called premix, are partially cured thermoset resins to which chopped fiber reinforcement and filler have been added. The viscosity of these materials is carefully controlled so that the resin and fiber flow evenly throughout the mold. The flow characteristics are often adjusted by varying the amounts of resin, fiber and filler as well as the extent of cure of the resin and the length of the fiber. This process is very important in fiberglass-polyester molding for the automotive industry and other high production volume parts. The mechanics of the resin and fiber movement are important in determining the properties of the part and have been studied extensively [50]. Preform molding is accomplished by placing a dry fibrous preform into the mold and then adding liquid thermoset resin which flows to coat all the fibers during the molding cycle.

In a broad view of the process, the use of matched-die molding for thermoplastics could take two forms. In the first, a laminate of thermoplastic composite materials which had already been consolidated would be heated and then placed into a matched-die mold and formed. This process is, however, much more analogous to traditional thermoplastic thermoforming than to thermoset compression (matched-die) molding. In the thermoforming case the material would be preformed into a shape, the material would be heated external to the mold, and the mold pressures would be very low; whereas with compression molding the input material would be in a nonfinished, shapeless condition and would be heated within the mold at high pressures to give the part its shape. Because this thermoplastic process is so analogous to thermoforming, it will be discussed in detail in Chapter 7.

The second method of using matched-die molding for thermoplastics is much closer to thermoset compression molding. In this method the unformed prepreg materials are placed into a heated matched-die mold and formed and consolidated in one step. This process is, therefore, a competitive process to layup wherein the pressure from the press is used to consolidate rather than the pressure from the vacuum or the autoclave.

The input materials for this process can, theoretically, be any of the prepreg materials already discussed for thermoplastics—melt impregnated, solvent impregnated, powder coated, or commingled—although the problems with solvent removal in a closed press essentially eliminate this option. In addition, sheets of nonimpregnated reinforcement fiber and sheets of thermoplastic (as either cloth or film) can be interleaved in the mold and consolidated and shaped simultaneously. These processes have been applied to both high performance and engineering thermoplastics with good results [51].

The transfer of heat into the resin is an especially important part of the thermoplastic compression molding process. A model has been developed [52] that has been applied to a 64-layer composite with good preliminary agreement between the theory and experimental results.

The most common shape that is made by this process is the flat sheets that could later be used in the thermoforming process mentioned above or could serve as raw stock for punched parts or other sheet metal-like processes. Shaping to a flat sheet avoids many of the inherent problems associated with matched-die molding of thermoplastics such as the simultaneous movement of the fibers and the heating of the resin. Because of the rigidity of the resin prior to melting, a shaped mold cannot be closed faster than the resin is melted or the fibers will break. In a flat laminate, this problem does not arise. (The problem can also be avoided by using powder coated or commingled prepreg.)

LIQUID COMPOSITE MOLDING (RTM/RIM)

Liquid composite molding is a term that encompasses both resin transfer molding (RTM) and reaction injection molding (RIM). In resin transfer molding or the closely related process, reaction injection molding, a mold is loaded with reinforcement material, the mold is closed, and resin is then slowly injected into the mold. The mold with the preform in it is often put under vacuum to facilitate the movement of the resin through the fibers. The reinforcement material is wetted out by the pressure of the injection but depends upon fiber surface characteristics, resin properties, temperature, geometry and several other parameters [53]. This method has some similarities to other composite and nonreinforced plastic manufacturing methods. For example, the method of loading the reinforcement is similar to that of preform molding with matched dies, but in preform molding the resin is introduced into an open mold and with RTM and RIM the mold is closed. Because the mold is closed, the processes of transfer molding (for thermosets) and injection molding (for thermoplastics) are similar. (In fact, it is the similarity to transfer molding that gives RTM its name.) However, in neither of these processes is the mold precharged with a reinforcement material.

Although this process was developed for thermosets, the use of thermoplastic materials might be possible, although very few instances of thermoplastic RTM have been reported. The obvious problem with the use of thermoplastics in this application is the high viscosity and poor fiber wet-out of the thermoplastic resins. The temperatures required to melt the resins, especially high performance thermoplastics, and the tendency to degrade at these temperatures makes the RTM process a difficult one. However, in one reported application [54] a process was used that is analogous to RIM. In this process the thermoplastic monomers (nylon monomers in this case) were mixed and injected into the mold. Because these injected materials had not polymerized, they had low viscosities and coated the fibers readily. The polymerization took place within the mold, much like a thermoset crosslinking reaction. (In RIM the monomers that are usually injected produce polyurethane.) The nylon tennis racquet made by this process compared favorably in mechanical properties and in processing time to an RTM-made epoxy racquet.

CONSOLIDATION OR "CURING"

All of the thermoplastic and thermoset processes which use sheets of material laid up to form a laminated part require consolidation of the layers. Without this consolidation, the layers would not be bonded together and the laminate would have a high void content and resulting poor properties. This consolidation requires pressure, either from a press, vacuum, or an autoclave, and simultaneous imposition of heat. In the case of thermoplastics, the heat is to cause the resin to melt and flow between the layers and, in some cases, to wet the fibers. In the case of thermosets, the heat is to cause the resin to crosslink. For thermoplastics, the heating step must be followed by a cooling step to resolidify the resin in its new shape, whereas with thermosets, the crosslinking reaction results in a solid part without specific cooling, although cooling is done simply to allow handling of the part. Because of its importance in achieving good properties, consolidation has been extensively studied [55–62]. For thermoplastics, the analyses are similar to those for fiber impregnation, except for the complication of multiple fiber layers, the consideration of three-dimensional shaping and of fiber movement perpendicular between the prepreg layers. Some studies treat specific aspects of the consolidation process such as void formation [63,64], cooling rate [65], part irregularities [66], and measurement of the processing variables [67].

In some situations, such as in a pultrusion die, the consolidation process is slightly different because of the unique imposition of the pressure and the high viscosity and drag of the movement of the material. This situation has also been studied and the process was divided into four main areas: (1) frictional forces (fiber friction against the die wall), (2) viscous forces (shear viscous flow in a thin resin layer), (3) back flow forces (drag resistance on fibers), and (4) temperature-induced forces (increasing viscosity and resin thermal expansion) [68].

Some studies have focused on the improvement of properties with post-consolidation annealing [69]. Flexural properties were improved by this method, probably because the crystallinity increased. While this method is effective, other efforts to improve the crystallinity by controlling the resin properties and the nucleation parameters hold better possibilities from a long-term productivity viewpoint.

Another postforming technique that holds some promise for property improvements in thermoplastics is the bombardment of the formed material with electron irradiation to induce crosslinking. The use of electron irradiation to induce crosslinking in thermoset materials has been reported for several polymers [70–72] and has been adopted commercially [73]. The use of electron beam irradiation to crosslink thermoplastics has also been well known for nonreinforced thermoplastics in order to improve key physical properties, especially environmental stress crack resistance [74,75]. However, the use of electron beam irradiation to improve thermoplastic composite properties has only been recently studied [76]. Results from this study indicate that mechanical properties can be improved about 10% by electron beam crosslinking. Other studies are underway to investigate this property improvement further.

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CHAPTER 6

Injection Molding and Extrusion

This chapter will review the following concepts:

- Extrusion
  - Process overview
  - Compounding
  - Finished part formation
- Injection molding
  - Process overview
  - Reinforced fiber molding
  - Process modeling
  - Fiber orientation
  - Fiber length
  - Mold design
  - High performance parts
- Emerging short fiber processes
- Properties of parts made by short and long fiber processes

EXTRUSION OF REINFORCED THERMOPLASTICS

This chapter examines the traditional thermoplastic molding processes—extrusion and injection molding. These processes are the most important processes in nonreinforced thermoplastic processing and, therefore, merit extensive examination as potentially important processes for thermoplastic composite processing as well. Extrusion is the more basic of the two processes simply because injection molding depends upon extrusion for the initial melting of the material. Therefore, extrusion will be considered first.

Process Overview

Traditional extrusion is a process of melting the thermoplastic material by conveying pellets or granules of the plastic into a hopper which uniformly meters (usually by gravity) the plastic particles into a barrel which contains a rotating screw with spiral flights. The screw has deep flights in the area under the hopper (which is called the feed zone) to facilitate material movement. The material is conveyed along the screw to a section in which the screw flights get progressively more shallow (the melt zone), thus increasing the friction on the polymer. The polymer is heated by this mechanical action of the screw and by the heat supplied to the outside of the barrel. The action of the screw also imparts mixing to the melt so that, hopefully, the plastic becomes uniformly melted and blended, perhaps with other additives that have been included in the hopper. The material continues along the screw into a section in which the flights of the screw are shallow (the metering zone). Here the screw imparts considerable pressure to the melt as it is conveyed forward in the barrel to eventually reach an opening in the end of the extruder. A die, which is attached at the opening, shapes the viscous plastic melt by forcing the material through a cut in the end of the die which reflects the final shape of the part. The die can contain a rod (called a mandrel or a pin) around which the plastic flows so as to create a hollow part. The material is cooled, usually in a water bath, as it exits the end of the die. The part is actually pulled from the extruder by a mechanical puller which is located downstream from the cooling bath. The relative speed of the puller must match the material output of the extruder which is controlled by the turning speed and size of the screw.

Although the extrusion process is quite flexible and has widespread application in the plastics industry, an inherent limitation of the extrusion process should be remembered—the parts made by extrusion must have a constant cross section. That is, if a pipe were being made, the outside and inside diameters of the pipe would be set by the dimensions of the die and they could not be varied during the extrusion (except for minor adjustments made by pulling the extruded material slightly faster relative to the extrusion speed). Extruded end products include custom profiles (auto trim, house siding, various moldings and edge trim), pipe, tubing, fibers, film, coating (wire insulation and pipe coatings), blow-molded products, and pellets [1].

Compounding

One of the important applications for extrusion besides the formation of rods, pipes or shaped parts, is as an intermediate processing step. The plastic material as it comes out of the polymerization unit will often be contaminated with solvents, may be of nonuniform particle size, may need to have some color or other additives added, or for some other reason needs to be melted and shaped uniformly. This remelting is usually done in an extruder because of the highly efficient melting and excellent blending that can be achieved by this process. One of the additives that is especially important is the addition of short reinforcement fibers. These are normally added into the hopper and then simply compounded into the pellets. This process dictates, to a large extent, the maximum length of the fibers. Because of the small clearances between the screw and the inside of the barrel and the high shear forces generated by the screw, the maximum fiber length is typically 0.75 – 1.25 mm. The shearing action of the screw highly disperses the fibers in the fiber bundle so that each fiber is isolated from all others. In most extruders used for compounding of reinforcement into thermoplastics, this shearing action is minimized, within the constraint of good mixing, so that the fibers are not damaged.

This process of incorporating fibers into thermoplastics has been studied extensively. One study of the fiber compounding process indicated that most of the fiber damage occurred during the melting, with relatively little additional damage during pumping [2]. This study used glass fibers (30%) with nylon pellets. The researchers noted that the average length of well-dispersed fibers increased with decreasing fiber concentration, decreasing melt viscosity, and decreasing screw speed. The processing conditions which preserved a long fiber length also resulted in an increase in undispersed fiber bundles, an unwanted result. In another study [3] using polyethylene and 3.2 mm glass fibers, the data confirmed that damage principally occurred during melting but indicated that fiber length was only slightly affected by melt temperature, screw speed, or fiber content. These results, which conflict with the previously mentioned study, were explained on the basis that fiber/matrix interactions, not fiber/fiber interactions, are responsible for fiber breakage. In yet another study [4] the negative effect of nylon when compared to a polyolefin resin (in this case polypropylene) was confirmed, but so was the strong fiber length dependence on processing conditions which contribute to shear. A study in which a model of this process was proposed [5] which, along with other models seems to explain the diversity of results by pointing out that fiber breakage occurred by the fiber interaction with an unmelted pellet but that other factors, such as shear rate and fiber content, also contributed to the total shear experienced by the fiber.

The use of twin-screw extruders for compounding fibers into resin has the advantage that the fibers can be added directly into the melt section, thus bypassing the most damaging part of the compounding process. Combined with the use of mild mixing conditions in the downstream sections from the fiber input port, the use of twin-screw extruders results in fibers that have substantially less damage than in the more traditional single-screw technology.

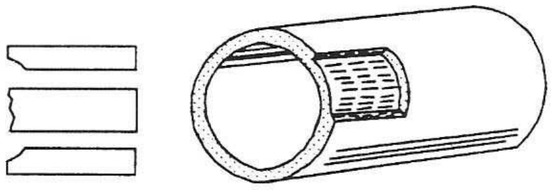
The problems associated with fiber incorporation can largely be avoided by forming the reinforcing fibers during the extrusion process. This *in situ* fiber formation can be achieved by combining a conventional matrix material with a liquid crystal polymer [6]. The liquid crystal materials, typically high performance thermoplastics such as Xydar or Vectra (refer to Chapter 2), maintain their separate integrity and therefore act as a second phase reinforcement. Matrix materials for these composites have included thermoplastic polyester (such as PET), polycarbonate, and polyetherimide.

Finished Part Formation

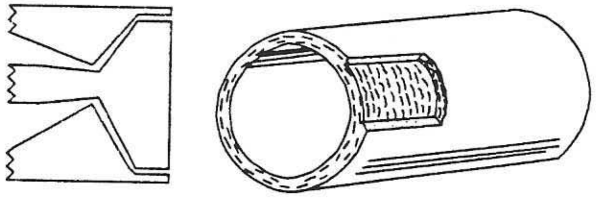
The use of extrusion to form finished composite parts is not common; the primary reasons appear to be the inherent difficulty in processing reinforcements without breakage and the relatively few composite products with uniform cross sections. However, fiber reinforced grades of thermoplastics are available in over 35 different base resins [7]. Most of the resins have fiberglass contents of from 10 to 40% with some as high as 60%. For higher flexural modulus, flexural strength, and retention of properties in humid environments, some also have carbon fibers from 10 to 40%. Aramid reinforced resins are also available which feature improved wear resistance, low warpage, and low coefficient of thermal expansion. These products include grades that have been stabilized for high temperature applications, flame-retardant grades, grades with additives to promote flow, and special formulations to resist hydrolysis at high temperature.

Some composite products are made using an extruder in a process that mimics the manufacture of coated products, such as insulated wire. In this process the material to be coated is introduced into the back of a special die (crosshead die) into which the resin enters from the side. The resin flows to surround and coat the material as the material is drawn through the die. This process has been used successfully to coat fibers to create a continuous belt which has been used in vehicle tires [8].

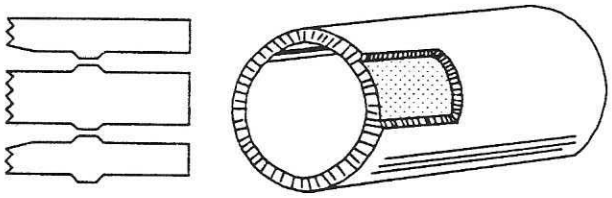
Another innovation involving extrusion of reinforced plastics takes advantage of the tendency of the short fibers to become oriented as they pass through narrow shear regions, such as in the extrusion die. Goettler et al. [9] have studied experimentally and modeled practical die geometries to control fiber orientations in the part. As is seen in Figure 6.1, a conventional die will result in fibers that are axially oriented (along the long direction of the part). By abruptly increasing the mandrel diameter near the outlet of the die, the fiber orientation will change to radial. By placing an obstruction (narrowing of the flow path) in the die, the fiber orientation can be changed



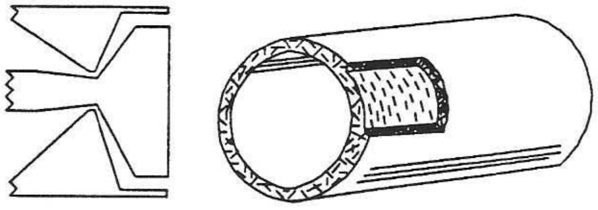
(a) **Conventional Die**



(b) **Expanding Mandrel Die**



(c) **Obstructed Die**



(d) **Combination Die**

FIGURE 6.1. *Fiber orientation by die design (reprinted by permission [11]).*

to be across the thickness of the part. Finally, by combining all of the flow modification techniques, the fibers can be given all orientations. These techniques have been used to manufacture reinforced rubber tubes [10].

INJECTION MOLDING OF REINFORCED THERMOPLASTICS

Process Overview

Injection molding is a cyclical process rather than a continuous process like extrusion. In injection molding an extruder is used to melt the polymer but instead of pumping the polymer out through a die in a continuous manner, the polymer is allowed to accumulate in a cavity inside the barrel just beyond the end of the screw. At a certain time in the cycle, the screw stops rotating and advances forward. This motion pushes (injects) the resin through a nozzle into a closed mold that is attached to the end of the extruder/accumulator. The sprue and runner system connects the nozzle to the gates (openings) of the mold cavities. This injection continues until the cavities in the mold are completely filled. The polymer in the mold cools and solidifies in the shape of the cavities. The injection pressure is continued for part of the cooling time to push (called packing) additional material into the mold and compensate for the shrinkage of the plastic that occurs with cooling. The mold then opens and the part is ejected. While the polymer was cooling in the mold, the screw was retracted and additional molten polymer was pumped into the accumulator cavity at the end of the barrel, ready for the next cycle.

This process is highly efficient and economical because it is easily automated and the cycle times can be very short (on the order of 20 seconds to 2 minutes). The process is capable of making very accurate and extremely complex parts because the cavity is filled with a liquid polymer which is usually formulated to flow easily and the resulting part is usually "net shape," requiring minimal trimming or other postforming operations.

Reinforced Fiber Molding

Injection molding is the dominant process for the processing of thermoplastic composite materials as it is for all nonreinforced thermoplastics. Short fiber reinforced injection-moldable thermoplastics have been available for many years in many base resins and specialty grades (similar to those cited for extrusion). These short fiber compounds represent an advance over nonreinforced and particle-filled polymers by increasing tensile strength, increasing tensile modulus, increasing impact resistance (in brittle polymers), improving dimensional stability, reducing shrinkage, and improving the capability to meet close dimensional tolerances. The high packing pressures employed in injection molding machines usually result in higher mechanical properties than are obtainable from compression (matched die) molded parts when the fibers have been predispersed in the polymer during compounding, as is usually the case. While the compression molding process does considerably less damage to the fibers than injection molding, mixing and dispersion of the fibers during the compression molding process is limited, so that the resulting parts do not take complete advantage of the reinforcement potential of the fibers. However, compression molding normally uses chopped fibers which are many times longer than the short fibers used in injection molding and these longer fibers compensate for the disadvantages in molding [12].

As already indicated, injection molding can damage the fibers, greatly diminishing their positive effect. Studies have shown that in most cases the mixing and shear encountered in the injection molding machine reduce the average fiber length to approximately the same level regardless of the average length in the precompounded material [13]. The opening to the cavity (the gate) is an effective limit to the size of the fibers that can be injection molded. Therefore, the gates and other connecting channels between the barrel and the cavity (runners and sprue) should be as large as possible to admit the longest possible fiber and to minimize separation of the fibers from the polymer.

When injection molding composites, the barrel and nozzle temperatures are usually slightly higher than those recommended for unfilled polymers. The barrel zone temperature is usually maintained high enough to promote melting as quickly as possible without degrading the polymer. To minimize fiber breakage, the heating should come mainly from the heated barrel rather than from friction heat generated by the screw. This was shown in a study of molding conditions in which the parts made with a hotter barrel, especially in the rear section, were stronger [14]. Lower screw speeds and lower injection back pressures also resulted in stronger parts, presumably because the shear forces were lower. The mold temperature should be slightly elevated over nonreinforced materials to provide a resin-rich surface.

A design of experiment study [15] investigated the dependency of mechanical properties of injection-molded parts and key processing variables. The following results were obtained:

- *Fiber length*—Increased tensile strength, flexural strength and modulus of elasticity. Somewhat surprisingly, it also increased elongation.
- *Fiber load*—Increased tensile and flexural strength at a fiber length of 3 mm but decreased tensile strength at a fiber length of 1.5 mm. Increased modulus at both fiber lengths, but the effect was greater

at 3 mm. Decreased elongation at 2.5 mm but had no effect at 3 mm.

- *Temperature*—No effect on tensile strength. Decreased modulus of elasticity, decreased flexural strength and decreased elongation.
- *Mold thickness*—Decreased tensile strength and modulus. Increased elongation and had no significant effect on flexural strength.

Process Modeling

Mathematical models of the injection-molding process have given additional insights into the operation of the process to obtain optimal properties. One major advance in the area of modeling is the use of computer simulations using such programs as MOLDFLOW [16], the Cornell Injection Molding Program [17], Mold Cool, Plastics (SDRC), and Plastics Design. The information available from these programs includes melt-viscosity characterization, simulation of three-dimensional cavity filling, numerical simulation of compression molding, flow simulation of thermoset materials, flow visualization and analyses of fiber-filled polymers, a unified model for filling/packing/cooling stages, process control related to part thickness, cooling-line design, adaptive mesh generation, five-axis NC tool-path verification, and computational techniques for determining surface-surface intersection. In addition to the analyses listed above, the programs can give specific assistance for mold design in the following areas: determining the appropriate number and location of gates, sizing the length and cross-sectional area of the runner system, locating and sizing vents in the cavity to prevent scorching, and determining appropriate processing conditions for the material and mold. The next step in modeling is the prediction of the actual part characteristics such as shrinkage, warpage, and mechanical properties which all imply some understanding of internal stresses. These calculations have been attempted for nonreinforced plastics, but have yet to be reported for fiber-filled materials.

Fiber Orientation

Just as in extrusion, shear forces in either the barrel, during injection, or in the mold can cause fiber orientation. Orientation should be carefully controlled because whatever strength is gained in one direction is lost in another. In some situations, of course, this gain in directional strength can be utilized to strengthen the part in the direction of load, but the process must be well understood to obtain repeatable results.

Models of fiber orientation have been developed that relate the fiber orientation to the flow of the material [18–20]. In general, shearing flows align fibers in the shear direction and stretching flows align fibers in the stretching direction. If composites consisted of rigid fibers in a dilute solution, their orientation and flows could be accurately predicted. However, most composites are concentrated solutions where the behavior is qualitatively similar but quantitatively different. A further complication is that most of the polymers are non-Newtonian fluids and so the flow is strain rate dependent. This situation has also been studied and modeled [21]. Numerical methods, rather than vigorous theories, seem to present the best pathway for obtaining quantitative predictions of orientations.

As indicated in the models, fiber orientation is strongly dependent on the way the material is processed. The key processing variables such as melt temperature, filling time, holding pressure, and holding time have varying effects on the microstructural properties, with melt temperature showing the most profound influence because of its effect on the crystalline structure. The crystalline structure of injection-molded composite parts and the fiber concentration and orientation were found to vary from the skin to the core. Crystalline content is maximized at the skin and becomes almost randomized at the core [22]. Thin sections and high injection speeds have also been shown to cause increases in orientation.

A summary of the parameters is as follows [23]: The fiber orientation in injection-molded parts depends principally on the mold and gate geometry and on the matrix flow behavior. Three distinct regions with different fiber orientations can be identified:

- a skin originating from the expanding melt front
- an intermediate layer where the shear flow oriented the fibers in the direction of flow
- a core that keeps the fiber orientation it acquired in the gate area

Some investigators have utilized the magnetic properties of some metal reinforcements or fillers to obtain the desired orientation in a repeatable manner and to develop a unique class of materials, thermoplastic magnets [24–26]. These materials are magnetic but generally are not conductive and are less than one-third the density of traditional metal magnetic materials. In comparison to ceramic magnets, the thermoplastic composites offer ease and economy of fabrication with complex shapes, are less brittle, and can be molded in thin sections. The greatest shortcoming of magnetic thermoplastic composites is their inability to achieve the same level of magnetic properties as the traditional ceramic or metallic magnets.

Electrical fields can also be used to align fibers. The process developed to accomplish this task [27] produced uniaxially aligned mats of discontinuous graphite fibers by dispersing the fiber bundles in a liquid alignment fluid. The dispersed fibers then moved downward through a uniaxially aligned electric field, where they aligned with the field before settling on the bottom of the apparatus to form the aligned mat. This mat was then heated and consolidated to form aligned composite plates. Further developments have extended the process to more complex alignment patterns, such as radially aligned fibers.

Fiber Length

The reinforcements for thermoplastic composites can be separated according to length into three main groups: continuous fibers, short fibers, and long fibers. The continuous fibers are those that are, in essence, continuous across the part. The processes for building parts using these materials such as layup, filament winding, pultrusion or one of the other traditional thermoset processes were discussed in Chapter 5. The processes considered in this chapter have been extrusion and injection molding for which the short fiber is the most common fiber length. An intermediate fiber length, called long fibers, has been developed that is intended to be used as an alternate in some applications to short fibers but to give better mechanical properties, but not as good as continuous fibers. Thermoplastic resins containing long fibers are intended to be processed in high production methods such as injection molding, as are short fiber materials.

The long fiber composite resin pellets (brand names Verton and Fiberstran®) are produced by pultrusion and their production was discussed at some length in Chapter 5. These long fibers have been incorporated into several resins including nylon 6/6, nylon 6, nylon 6/10, polypropylene, polybutylene terephthalate (PBT), polyethylene terephthalate (PET), PPS, polycarbonate, and thermoplastic urethane [28]. The processing of these materials into finished parts, generally by injection molding, and the comparisons with short fiber processing is the current subject. The processing of any fiber reinforced material should employ the lowest possible mechanical work. This is imperative with long fibers. The barrel and mold temperatures should, therefore, be slightly higher than for neat resins, and the screw rotating speeds should be slightly slower. Injection rates should be lower and hold pressures should also be lower. Use of a free-flow screw tip results in significantly higher tensile strengths. Other suggestions for processing conditions have been recommended and may make some minor improvements in part properties [29].

Fiber distributions for long fibers (originally 10 mm in length) seem to differ from the Gaussian curves of short fibers (all lengths <0.5 mm) in the following ways:

(1) A peak in the distribution at very short lengths (<0.6 mm) which seems to result from any thermoplastic processing method

(2) A peak at >6 mm in most cases, except where the mechanical shearing has been excessive

(3) A large peak in the intermediate range

As might be expected, the use of regrind reinforced materials decreases the mechanical properties, presumably because of the increased fiber degradation from the additional processing.

Mold Design

Improper mold design can be a problem with reinforced composite materials. Sprues and runners should have gentle bends rather than sharp turns. Runner systems should be as simple in geometry as possible thereby promoting a smooth, uninterrupted flow. The gates should be as ample as possible, especially for long fiber reinforced resins, to allow smooth flow into the cavity without sharp angular bends. The large gates will also allow a thorough holding pressure cycle, allowing the solidification to be accommodated without premature freezing at the gate. Dead zones in any area of the mold or runner system should be avoided.

If there are multiple gates into a cavity, if there are converging or diverging flows, or if the material must flow around an insert or core, two or more flows of material are created. These flows must knit together well or the part will be weak at the knit line (also called the weld line or meld line). The presence of reinforcements in the plastic makes the knitting problem more difficult since the reinforcements can protrude forward of the advancing plastic front and interfere with its smooth meeting and joining with the approaching front of the other flow. The strength of knit lines has been studied as a function of processing parameters [30]. In general, the knit lines are weakest for the highest aspect ratio (length/diameter) fibers and at higher fiber contents. When the flows converge at oblique angles, the fibers tend to be oriented parallel to the knit line, while in other areas of the part, the fibers are randomly oriented [31]. The static and fatigue behavior of injection-molded short glass fiber reinforced polycarbonate and nonreinforced polycarbonate were determined for specimens containing knit lines generated by double-gating [32]. The presence of a knit line was seen to decrease the mechanical property performance from 60% retention to 40% retention at 104 cycles and from 40% to 20% retention at 10^6 cycles. Loss of impact strength in the knit line was greater than loss of tensile strength [33]. Increasing packing pressures can improve knit line strength, especially in nonsymmetrical flow patterns [34].

Mold design is, of course, related to part design. Good design principles suggest that uniform wall thickness should be used whenever possible and the height of ribs should be no more than 10 times the thickness. These allow for uniform fiber distribution and avoid fiber bridging. Inserts and other flow-disturbing features should be avoided.

High Performance Parts

The use of injection molding for high performance thermoplastic parts has not been widely accepted. This is probably due to the high performance requirements generally associated with high performance thermoplastics which can only be met with continuous fibers and the inherent processing problems of a very high melting polymer. However, some nonstructural parts (such as an antenna mast nozzle) have been made using high performance resins with injection molding and short carbon fibers [35]. Some of the early reinforced resin pellets suffered from poor fiber-matrix bonding, but that problem seems to have been solved [36]. Some problems remain, however. For instance, the fiber ends serve as stress-riser locations which lower the elongation of the part. The postcuring problem has still not been resolved, that is, should the parts be postcured to improve crystallinity and mechanical properties? If ultimate properties (by this method) are desired, then postcuring should probably be done, but efforts are underway in resin research to give the same crystallinity without the need to postcure.

An interesting study has looked at the entire process of design to production for the injection molding of a reinforced thermoplastic plastic for the aerospace industry [37]. (The part was a launch canister end closure.) Fifteen candidate resins were considered, both high performance and engineering. The material needed to be resistant to SO_2, moisture, and UV light and to have good impact strength and to be processable at 67°C. After a series of tests and evaluations, thermoplastic polyester (PET) was chosen. Development was begun based on the premise that two similar materials could be bonded together during the molding process to form the part. However, the final design used plastic rivets and a two-step molding process. The injection-molded thermoplastic part is currently in production.

EMERGING MANUFACTURING PROCESSES

Several other thermoplastic processes which use short fibers or are otherwise related to extrusion and injection molding are being developed. Most of these are using reinforced plastics only on an experimental basis. Blow molding is one of the traditional thermoplastic processes that is closely related to extrusion and injection molding. It is used to form hollow, thin-walled containers such as bottles. In this process an extruder is used to melt the material but instead of continuously pushing the material out the extruder, the material is formed into a hollow cylinder and extruded into an open mold on a cyclical basis. After the hollow cylinder (called a parison) is in the mold, the mold is closed and air is forced into the parison causing it to expand outward against the walls of the mold. The part is cooled and ejected. The problem with using reinforced resin in blow molding is that the fibers serve as points for the initiation of tears in the resin as it is blown outward. The use of tougher resins and the reduction of cycle times alleviate these problems somewhat and fiberglass-filled nylon parts have been successfully made [38].

Another process, hollow gas molding, is similar to injection molding except that a gas is injected into the mold cavity after the cavity has been partially filled with resin. The injection of the gas pushes the resin out against the walls of the cavity, much like in blow molding. The advantage of this process is that cycles are faster than injection molding, hollow parts with curvatures can be made, and the fibers can be oriented in unusual ways by the combination of shear from cavity filling and then blowing [39].

The fabrication of precision, hollow parts is difficult by injection molding if the hollow part has a narrower neck than body. Blow molding is usually not precise. However, a process that is able to create precise, hollow parts is fusible core (lost metal) molding. This method uses tin-bismuth, a low-melting alloy, as a die case core which is then overmolded with the plastic. After the plastic hardens, the core is then melted out. This process has the advantage of being able to make blind parts where the core cannot be pulled.

The SCORIM (shear controlled orientation of reinforcement in moldings) process is based upon the controlled shearing of the polymer melt in the mold cavity before and during solidification. To achieve the effect, the feed from an injection molding machine is split into a plurality of feeds to the cavity. Packing pressures applied at each feed, independently of the others and of the injection pressure, keep the material in the gates molten when the mold is filled and packed. This process is a contradiction to the normal practice of avoiding multiple injection sites in a mold. The advantages of the method are that complex components can be made that are free from voids, cracks, sink-marks and, most important, weld-line defects [40].

Structural foam products have a foamed core surrounded by a solid skin. The core and the skin are from the same material and are molded simultaneously on a modified injection molding machine. The foaming can be generated either from an internal foaming agent or from gas that is dissolved in the polymer melt. In either case, the injection of the polymer into the mold causes the foaming to occur. These foamed materials have the advantages of high flexural stiffness-to-weight ratios, good dimensional stability compared to other foams and low-cost molds. Problems with the process include poor surface quality and long mold cycles. The surface roughness problem can be solved by using a technique called coinjection molding. In this process two injection molding machines are utilized to mold one material around another or one material on one side and the second material on the other. This second material can be a smooth skin to cover the already formed rigid foam. When mating two parts, one or both of those parts could be reinforced. This process has the advantage of being able to use two different resins in the same injection-molded part.

The recycling of plastics is an important problem that should be addressed by the composites industry. As already discussed, recycling of fiber reinforced materials generally results in shorter fibers because of the increased mechanical work on the fibers. However, the use of fibers to improve the mechanical behavior of recycled neat resins has tremendous potential for reducing the amount of material that is sent to landfills. A recent study has taken this concept even one step further. In this study [41] waste polyethylene was combined with wood fibers, thereby combining two materials that are potential problems in landfills. These materials were combined in a twin-screw extruder. Dispersion of the fibers was a dominating factor achieving good mechanical properties.

PROPERTIES OF PARTS MADE BY SHORT AND LONG FIBER PROCESSES

Because of the differences in processing conditions, the properties of continuous fiber reinforced composites have not been considered in this section but were reported in Chapter 4. This section will focus on comparisons of properties for neat, short and long fiber reinforced parts which were fabricated by extrusion or injection molding. Other considerations such as changes in resin with processing conditions will also be considered.

A key consideration in the determination of mechanical properties is the critical length. As discussed in Chapter 3, this is the minimum fiber length that will accept loads from the matrix. Previously the discussion focused on the bond between the fiber and the matrix, which is a controlling factor in determining critical length. However, because of the mechanical work done on the fibers in extrusion and injection molding, the distribution of fiber lengths is important in determining the strength of the part because fibers which are shorter than the critical length will not contribute to mechanical properties. Some properties are not as affected by critical length as others. Impact strength, which is the ability of the part to absorb energy without breaking, is less affected than tensile strength. The rationale for this is simply that the fibers that are shorter than the critical length can still absorb energy by processes such as fiber pullout, but they cannot carry load, which

is the principal factor in tensile strength. A comparison of the fiber length distributions of conventionally compounded short fiber compounds and pultrusion compounded long fiber compounds showed a much higher number of fibers retaining lengths in excess of the critical length in the long fiber compounds [42]. In another study, however, the average fiber length of the long fibers was reduced from 12 mm to 2 mm, although it was shown to be increased with lower fiber content and lower melt viscosity [43]. These results are similar in virtually all resins. Properties of short and long fiber specimens are reported in Table 6.1.

As seen in Table 6.1, improvements in properties can be profound, in some cases over 100%. The properties seem to improve with higher temperature, indicating that the long fibers have more of an effect as the temperature increases. Other properties may also be affected by the longer fibers. The coefficient of thermal expansion (CTE) has been shown to be lower for long fibers than for short fibers. Creep resistance of long fiber compounds can be 25% higher than short fiber compounds. Some of these property improvements may be due to the potentially superior fiber wetting from the pultrusion process as compared to the extrusion compounding process for the short fibers.

The effect of core thickness on part properties was explored and found to have a strong influence [45]. As the core thickness increased, relative to the thickness of the skin layers, both the flexural and tension moduli decreased strongly. This same study also showed that both flexure and tension moduli increased strongly with fiber length until a length of 1 mm was reached, at which time the increase flattened. Furthermore, the study found no sig-

TABLE 6.1 Properties of Long and Short Fiber Composites [44].

Properties of 50% Glass Reinforced Nylon 66	Long Fibers	Short Fibers
Tensile strength (MPa)		
@ 23°C	241	220
@149°C	132	95
@204°C	57	50
Flexural strength (MPa)		
@ 23°C	400	320
@149°C	163	95
@204°C	69	51
Flexural modulus (GPa)		
@ 23°C	17.2	15.2
@149°C	6.1	3.6
@204°C	5.2	3.3
Compressive strength (MPa)	273	218
Notched Izod Impact (J/m)	266	139

nificant effect on falling weight impact results with processing conditions, presumably indicating that microcrystalline structure does not affect rapid impact toughness. Slow crack propagation impact toughness was, however, found to be dependent on processing with high values reported when the core was thicker.

Studies on fiber orientation in extrusion melt processing of short fiber thermoplastic composites indicated relatively high levels of voids in the extrudates [46]. Evidently some of the voids were present in the neat resin (polycarbonate) but the void content was increased significantly with the compounding of the fibers. The void content was seen to increase with increasing fiber content. In injection molding, the melt cooling in a closed mold under pressure evidently suppresses void formation as fewer voids were found in this process. With these results in mind, low void content parts can best be produced when special efforts are made to eliminate entrapped air (such as venting the extruder) or by adjusting the processing conditions to reduce air entrapment (such as less shear in compounding).

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CHAPTER 7

Forming of Thermoplastic Sheets

This chapter will review the following concepts:

- Processing nonreinforced thermoplastic sheets (thermoforming)
- Processing reinforced thermoplastic sheets
  - Thermoforming
  - Stamp molding or matched-die forming
  - Flexible
  - Diaphragm
  - Incremental
- Sheet formation and composition
- Process auxiliary equipment
- Properties and characterization

The processes discussed thus far in this book have either been for continuous fibers (Chapter 5 – layup, filament winding, pultrusion) or for short fibers (Chapter 6 – injection molding and extrusion). The process wherein sheets are formed into composite parts is one that can be applied to both continuous and short fiber parts, within some restrictions. This process is uniquely suited to thermoplastic matrix materials and has a strong tradition in nonreinforced thermoplastic technology. Various metal processes are also related. The forming of reinforced thermoplastic sheets into parts is a process that holds great promise for inexpensive composite parts manufacture. To better understand this process, the associated process of forming nonreinforced plastic sheets will be examined. This process, called thermoforming, is one of the simplest and least expensive methods for shaping thermoplastic materials.

NONREINFORCED THERMOPLASTIC SHEET PROCESSING (THERMOFORMING)

In this process a thermoplastic sheet is heated to its softening or sag temperature, usually while it is held horizontally. Thermoforming is quite different than most plastic processing methods in that the material is not converted to a liquid, but is only converted to a pliable, semirigid form. The heated, pliable sheet is then placed over a mold (either male or female) and then drawn by vacuum or forced by air or mechanical pressure into or over the mold. The plastic is then held in the mold until it cools and takes the shape of the mold. The molded part is then trimmed from the sheet and given whatever finishing processes are required. The excess sheet is usually reground and reprocessed into more sheet [1].

Some forming can be done without heating the plastic, provided the plastic material has high ductility. These processes are similar to metal forming processes such as forging, drawing, stamping, and coining. The major advantage is, of course, that the part need not be heated, thus saving time and heating expense. However, most plastics lack the ductility to be cold formed to any great degree and have the additional problem of memory which dictates that the parts must be used at low service temperatures to prevent springback or recovery.

Virtually every thermoplastic material can be formed into a sheet and thermoformed. Although each of the materials has its own unique material properties, some characteristics are common to all thermoformed materials and warrant examination. Memory is one such property that has already been mentioned with respect to cold forming. If raised above the forming temperature, the plastic will tend to revert to its nonformed shape (a sheet). This places a limitation on the maximum use temperature, but also has the advantage that mistakes in forming can often be corrected by heating to a temperature above the original forming temperature and reforming. Usually, the heating will not restore the part completely, but some reshaping is often possible.

All the plastic sheets which are to be thermoformed must have hot elongation, that is, the ability to be stretched when hot. This ability is dependent upon many variables such as correct temperature, methods of heating, methods of stretching or forming, choice of mold materials, and speed of forming. A closely related property is melt strength. This means that the material will have sufficient viscosity to be formed but yet retain some shape, even when molten or semimolten.

During the forming step, the material is redistributed. Because most plastic parts are formed from a plastic sheet that is restrained around the edges, when additional area is created by forming, the thickness in the stretched area is reduced.

Several forming methods (Figure 7.1) have been used successfully with nonreinforced thermoplastic sheets. Perhaps the most common of these is forming with a vacuum. In this process the heated sheet, which is held in a frame, is placed over a mold that has had small holes drilled through it. As the sheet is lowered onto the rim of the mold, vacuum is applied through the mold. This causes the sheet to be pulled into a female mold or over a male mold. If the holes have been properly positioned, the plastic material will be stretched into all corners and recesses, thus giving a good duplication of the mold shape. The diameter of the holes should be small so that the plastic material will bridge the holes and no impression of the holes will be seen on the surface of the part. This process produces a part with only one well-defined side (the side touching the mold face). If the sheet is very thick or the draw is deep, especially when the part has steep sides, a mechanical plunger (called a plug) can be used to assist the vacuum in forming the part. The plug pushes against the material before it has completely cooled and stretches some of the material in the center and forces it to the sides. The plug, therefore, forces the material into an area that would otherwise be too thin. Some care must be taken in this method to prevent the plug from pushing through the softened part.

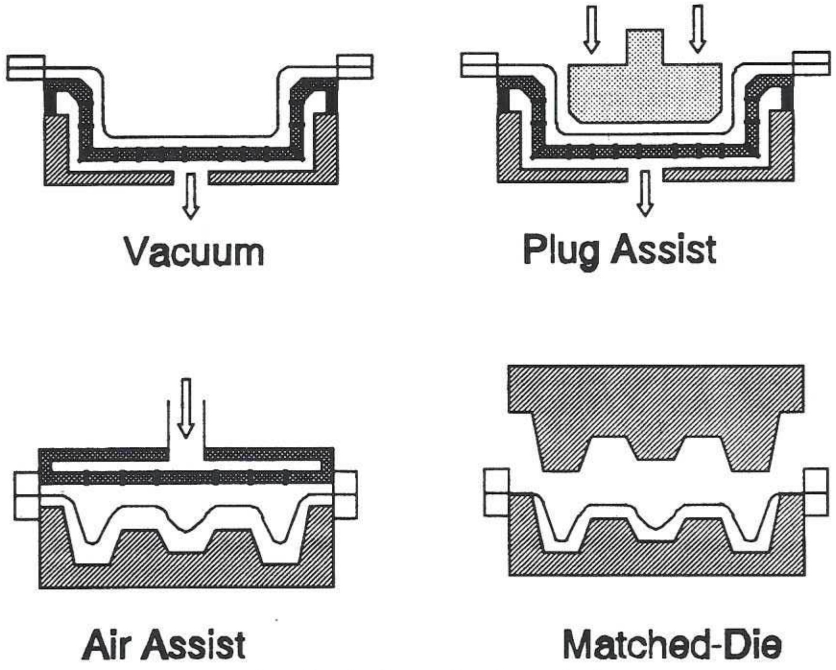


FIGURE 7.1. Thermoforming methods.

Instead of using a mechanical pressure device like the plug, air pressure can be used to press the sheet into the mold. Normally when air pressure is used, a vacuum is not. The advantage of air pressure is that cycles are often faster and part definition can be better because of the high pressures that can be used. Even higher pressures can be obtained when matched dies are used to form the part. This process, also called hot stamping, allows both sides of the part to be well defined because both are against mold surfaces. The problem with hot stamping is that two dies must be made and a press must be used, although the pressure required is not great, but the resulting tolerances and allowable part complexity make the method desirable in some cases. A modification of matched-die molding is hydroforming. This method uses only one matched die. Instead of the other die, a compliant rubber pad is used. When the press is closed, the pad conforms to the shape of the die and thus presses the sheet into the die. This method cannot be used for highly complex shapes.

Thermoforming machines range in complexity from simple manually operated equipment to computer controlled rotary and in-line machines designed for high production efficiency. All of the machines have certain characteristics in common. These include a method to heat the sheet, usually while securing it; a method to move the sheet to meet the mold; and a mold. Very high production units might extrude the sheet and move it in-line to the mold for forming. These would also have automatic, in-line cutting and trimming of the molded parts.

PROCESSING REINFORCED THERMOPLASTIC SHEETS

The forming process for reinforced thermoplastic sheets was developed to meet a need for large parts having higher strength and higher modulus than could be obtained from nonreinforced thermoplastics, but with a faster cycle time than could be achieved with reinforced thermoset materials. The basic process for forming reinforced thermoplastic sheets has some similarities to the thermoforming process for nonreinforced sheets discussed above and has other similarities to SMC matched-die (compression) molding and some similarities to metal forming processes. As with nonreinforced plastic thermoforming, the sheet is heated to a forming (sag) temperature in an external oven, transferred to a mold in a process that can be highly automated, and then forced into or onto the mold and held against the mold surface until cool (or cooled over an external form which increases mold utilization but still prevents springback of the part).

The advantage of the process over nonreinforced thermoforming is, as already mentioned, superior mechanical properties. The advantages over thermoset molding are the indefinite shelf life of the thermoplastic sheets, the shorter mold cycles (often 200 to 500% less), the ability to use an external oven to increase mold utilization, and the ability to make either high performance aerospace or general purpose engineering parts with the same process. Another consideration versus thermosets is that because the temperature only controls viscosity in thermoplastic molding rather than the chemistry of crosslinking as in thermosets, molding conditions are much more flexible. For instance, it would be possible to raise the temperature of the blank to increase fluidity and shorten cycle and then lower the temperature to solidify and thereby minimize internal stresses. The ability to remold thermoplastics to repair or eliminate defects is another advantage over thermosets, especially for the relatively simple parts made by thermoforming. This principle has been demonstrated for high void content parts [2] and for intentionally damaged parts (open-hole compression) [3]. In fact, in the latter study, when the parts were remolded at a higher temperature than the original molding temperature, the mechanical properties improved.

The advantage over injection molding or extrusion would be the ability to make large parts. Although the thermoforming of reinforced plastics is also similar to metal stamping and pressing operations, including the ability to cold form the thermoplastic sheet (although heated is the more common method), some advantages over metal forming are the ability to have varying cross sections and specifically reinforced areas molded into the part, the lower pressures required, greater complexities of parts, and the obvious advantages of the material for certain applications.

One possible question regarding the use of reinforced thermoplastic parts, especially for high volume production, is the ability to recycle or reprocess the trim that is naturally created by the thermoforming process. Scrap or excess material from thermoplastic moldings can be ground up, diluted with additional resin and reused for injection molding [4]. Due to the long fibers present in the usual sheet material, better mechanical properties can be obtained with these moldings compared to moldings from commercial compounds designed for injection molding.

The basic reinforced plastic thermoforming process has been divided into several processes which differ principally by the method of applying pressure to the blanks. Although the nomenclature has not been universally agreed upon, the divisions can be referred to as thermoforming, stamping, flexible forming, diaphragm forming, and incremental forming. Stamping has been further subdivided into stretch forming, flow forming and cold forming. Flexible forming has been subdivided into rubber mold forming, captive rubber forming, and hydroforming. Even though these processes differ principally by the method of applying pressure, they can also be represented in graphical form based upon the complexity of the part and the size of the part made by each process. Such a graphical representation is given in Figure 7.2 [5].

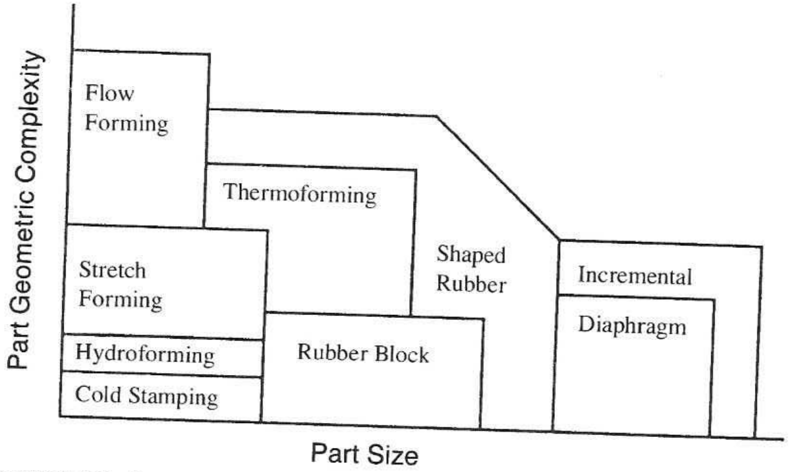


FIGURE 7.2. Diagram representing the applicability of each process based upon part complexity and size.

Thermoforming

This is the reinforced thermoplastic method that is most like the thermoforming processes for nonreinforced materials that have already been discussed. It is characterized by employing only one mold, either male or female, and by pressing the heated part against the mold. The pressure can be exerted by a vacuum, a plug, or by air pressure (see Figure 7.1). The traditional equipment used for nonreinforced has been used successfully, without modification, for both reinforced materials [6].

This method is used to make parts of intermediate size (typically 60 to 90 cm) and of moderate complexity. Some parts that have successfully been made by this method include nose fairing, main-rotor pylon fairing, engine cowling air intake, engine cowling aft, tail-pylon tip cap, tail-cone fairing, tail-rotor gear box fairing, and landing gear strut fairings [7].

Thermoforming is most often used when the fiber orientation must be maintained. Therefore, as noted above, the majority of parts employing this method are from aerospace where performance is at a premium. If deep draws are needed, experience has found that male molds give better performance. For parts with moderate female molds, typically with a 2 to 3° taper draft angle, are better, especially if release is a problem. (Because of high shrinkage, plastic parts tend to shrink onto the outside of male molds.) Female molds are also used when the outside of the part must have a well-defined surface and when the edges need to be strong or thick. Because of the low pressures involved in this method, molds can be made from cast/filled epoxy, urethane, phenolic or polyester, or from cast aluminum.

Stamp Molding or Matched-Die Forming

Although the single mold thermoforming method discussed above closely resembles the high volume conventional thermoforming method, the most common method for forming reinforced thermoplastics uses matched dies in a press to shape the part. This process, which is called stamp molding or matched-die forming (or less often, fast cycle compression molding), is used in preference to the thermoforming method for high volume, reinforced thermoplastic applications where exact fiber control is not necessary but a premium is placed on part definition and short molding cycle. This process usually starts with precut sheets (blanks) which are heated in an oven and then conveyed to a press that contains matched male and female molds. The heated, pliable blanks are clamped and then formed by the closing of the press. The clamping, which is done by pressing the part with a plate or some other retaining mechanism such as clips attached to springs, keeps the fibers under some minimal tension during the deformation to help prevent fiber buckling. The part can be cooled in the press (as is normally done) or removed while warm and cooled on an external form. This process is illustrated in Figure 7.3.

The blanks are heated to a temperature, called the forming temperature, that will soften the resin sufficiently to allow it to be easily shaped and that will allow the fibers to slide. This temperature is typically just below the glass transition temperature, T_g, for amorphous resins and between T_g and

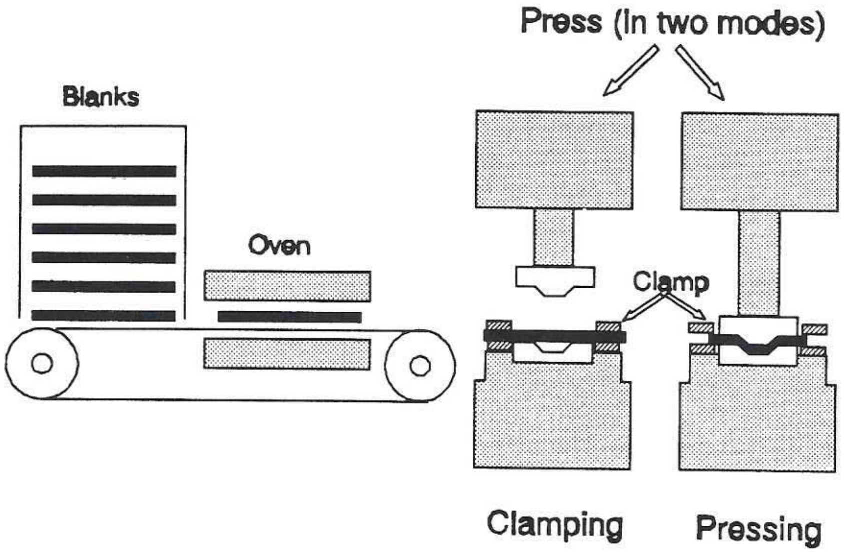


FIGURE 7.3. Press thermoforming of reinforced sheets.

the melting point, T_m, for semicrystalline resins. Although normally cold, the molds are occasionally heated to provide better flow control and to control the crystallinity of the resulting part, thus getting improved properties.

This basic process can be subdivided into two variations: stretch (or stamp) forming and flow forming. In *stretch forming* the part is quickly formed and cooled in the mold. This process is very much like sheet metal stamping and often uses the same equipment. The equipment would be able to exert closing pressures of typically 13,000 kPa and as high as 39,000 kPa with parts as large as 1.8 × 6 meters. The pressing equipment would typically have a single closing speed in the range of 500 to 1300 cm/minute and be able to execute at least 25 strokes per minute over a stroke distance of 5 to 10 cm. (A truck fender liner being made commercially is typically formed in 1.8 seconds/part [8].) Sometimes a floating platen system is used to allow for platen misalignment and to lower the cost of the press [9]. The complexity of the part that can be formed by this process is limited, but the cycle time is very short, usually just the few seconds required to cool the part to the solid state [10]. The process is, therefore, well suited to the high production requirements of the automotive industry and is used there extensively.

Because the resin and fiber movement is quite limited in stretch forming, the blank thickness must be carefully controlled and coordinated with the matched die gap. If this is not properly done, nonuniform pressure can be exerted on the part with a loss of fiber control and poor consolidation and void formation. To compensate for this problem, a slight overcharge is normally used which also allows for part shrinkage and a slight amount of resin flash (leakage). The small amount of resin movement in this process also limits the areal growth of the blank when it is pressed. Therefore, the blanks are normally cut to 95 to 98% of the finished part size.

In some instances the blank need not be heated before it is stamped. Obviously this cold forming variation is even more like sheet metal molding than is heated stamp forming. The advantage of cold forming is the elimination of the heating step and the resultant very short molding cycle. Also, because there is little fiber migration, the surface of the part is usually superior to those methods that heat the resin and therefore allow it to flow. The disadvantage of cold forming is the severe limitation on part complexity and the elimination of the capability to mold bosses, deep draws, or deep ribs. Normally the part cannot be stretched more than 5 to 10%. Memory is also a concern.

The second major variation of the stamp molding or matched-die molding method is *flow forming*. This method differs from stamp molding in that substantial flow of the resin occurs during the molding. In this respect the process is similar to matched-die compression molding of thermoset sheet

molding compound (SMC). In fact, flow forming of thermoplastics and SMC molding would be competitive processes. The advantages of flow forming are the substantially reduced cycle time compared with SMC (there is no need to maintain heat for a curing cycle with thermoplastics) and the obvious advantage of infinite shelf life for the blanks. The disadvantage of flow forming is that the blanks must be heated before they can be molded.

Flow forming has some distinct advantages over stretch forming. In flow forming variable part cross section thicknesses can be obtained. This is done by placing additional material in the mold in selected locations. Because the resin flows, this additional material knits well with the blank and forms a good bond. The flow of the resin also permits parts of much greater complexity than could be made by stamp forming including deep ribs, bosses, and inserts. Furthermore, the melted resin allows more fiber movement and, therefore, less fiber buckling. However, the fiber directional control is not as precise with flow forming as it is with stamp forming, although it is better in flow forming than in SMC molding [11]. Flow molding also requires more precise mold design than stretch molding since the mold edges must mate to control the flow of the resin. A further disadvantage of flow forming versus stretch forming is the thermal stresses and resulting warpage that can occur from the differences in coefficient of thermal expansion between the part and the mold. This is more severe in flow molding because the part is heated more.

Flow forming is also competitive with injection molding. The advantages over injection molding are the ability to use much longer fibers and higher fiber concentrations, to control the placement and orientation of the fibers, less fiber attrition, and the ability to make much larger parts because the compression molding presses can be larger than injection molding machines. The advantage of injection molding is that parts of almost any complexity can be molded whereas with flow forming part dimensional changes of over 50 to 70% are difficult [12]. (One commercial example used a blank of 645 cm^2 to make a finished part of 1160 cm^2 [13].)

Presses that are used for flow molding are the same types as would be used for SMC molding. These are similar to the presses used for stamping but have one significant difference. Whereas the closing speed for stamping is usually constant, the closing speed for flow forming is in two stages. The first stage is fast and moves the mold almost to closed but automatically changes to a much slower speed (25 to 200 mm/minute) for the final closing. This slower speed is needed to allow the resin and fibers to flow properly.

To further ensure that good flow occurs, the resin is normally heated 20 to 30°C higher in flow molding than in stamp molding. Also, much more care must be taken to ensure that the transfer time from the heating zone to the press is very short so as to minimize the heat loss. The molds may also be heated in flow forming, especially for very viscous resins, to ensure proper flow. This mold heating requires mold cooling before part removal which substantially increases the mold cycle and is therefore avoided whenever possible.

A statistical designed experiment was run to identify the key variables in flow forming and to investigate their interactions [14]. The critical measured variable was the flow in the mold which was measured by a special flow tool which measured the flow area. The process variables investigated were pressing speed, pressing force, mold temperature, preheat conditions, and transfer time. The property variables investigated were blank size, fiber content, and fiber type. The pressing speed was identified as the most important variable. The pressing speed was found to be nonlinear with respect to the flow and to reach a maximum at 25.4 mm/second. This maximum condition existed for 40% fiberglass in polypropylene. Should the fiber content, fiber type or resin type be changed, these conditions would vary. Increasing the mold temperature was found to permit lower pressing forces but longer cycle times. Blank size was found to be relatively unimportant. Other variables and a description of the details of the process are given.

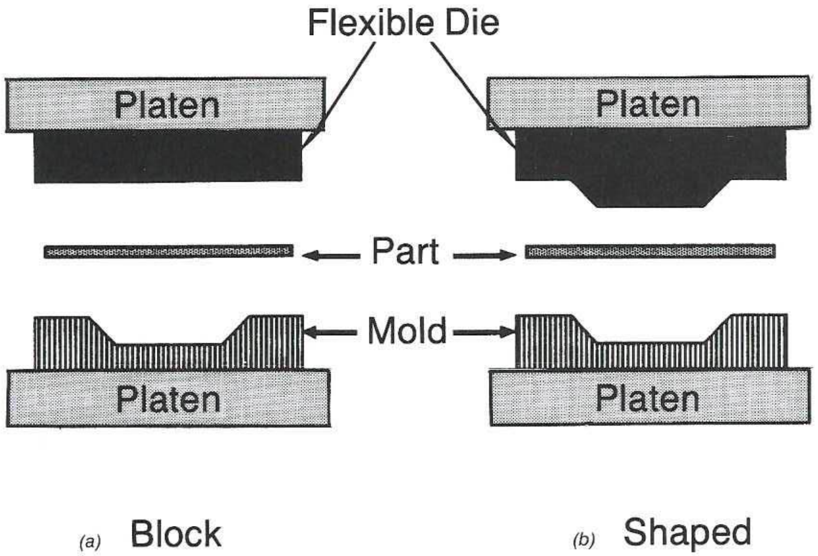
In another statistical designed experiment the factors which contribute to shrinkage in molding a thermoplastic sheet were investigated [15]. Four factors (resin lot, sheet thickness, sheet orientation and mold profile) were studied and found to have statistically significant effects on the shrinkage of the parts. The overall shrinkage of the material tested (PEKK) was found to be less than the allowed and the material was, therefore, qualified for use in the particular aerospace application.

Flexible Die Molding

Some of the problems of matched-die molding can be solved by making one or both of the molds flexible (compliant). Three variations on flexible die molding have been identified. These are rubber molding (either block or shaped), hydroforming and trapped rubber molding.

Rubber molding is illustrated in Figure 7.4. Both blocked and shaped dies have some advantages. Blocked is simpler, but shaped gives better part definition and more even pressure.

The major advantages of flexible die molding versus matched die or thermoforming are the improved movement of the part into crevices and other areas where the resin and fiber do not flow easily. This method, therefore, has fiber and resin movement much like SMC molding and cannot be used if precise fiber control is required. The flexible die also allows for nonmating of the molds or misalignment of the platens. It is, therefore, a forgiving process in terms of processing difficulty. However, if the mold is highly contoured, especially with parts of different depths, the block mold may bridge over the cutaway and cannot be used. The shaped die should alleviate this problem.



(a) Block (b) Shaped

FIGURE 7.4. *Rubber molding illustrating blocked and shaped rubber dies.*

To avoid excessive pressure on the part and possible deformation, the press is usually equipped with a mechanical stop to limit the movement of the platens. This stop is placed so that the mold engages completely with the flexible die but not to the extent that the die would be excessively compressed to distortion. This mechanical stop also improves repeatability of the process.

The flexible dies are often made of a polyurethane foam covered with a firmer silicone layer or simply all silicone rubber material of about a 60 to 70 Shore A hardness. This gives sufficient firmness to get good compression but is soft enough to give good conformation with the metal mold on most molds. The silicone should be chosen to be capable of reaching 230 to 290°C for most thermoplastic applications. The maximum temperature allowable is 340°C [16]. Because of the high processing temperatures of advanced thermoplastics, the use of the mold would be limited. However, because the part can be heated in a separate step, the contact time with the silicone would be short and temperatures up to 370°C might be acceptable.

The properties that affect the life of the rubber (silicone) tool have been related to tear strength. Tear strength decreases with surface nicks, high stresses, and chemical attack. Control of these factors has been shown to increase rubber mold life by 100% [17].

The molding cycle is longer with flexible dies because of their lower heat transfer capability compared with metals. However, silicone rubbers with improved heat transfer are currently being investigated in an attempt to shorten the cure cycle [18].

The second type of flexible die molding, hydroforming, is illustrated in Figure 7.5.

Hydroforming utilizes a flexible membrane which retains a fluid behind it and thus uses hydraulic pressure to form the part against a metal mold. This method is much like the rubber mold method but has the additional capability of adjusting the pressure to match the complexity and other requirements to obtain good consolidation in each mold. The hydroforming method is capable of reaching much higher pressures (up to 7000 MPa). Because of the high pressures, two or three layers of rubber are used to form the membrane and to prevent rupture from sharp edges on the mold. The negative to the many layers of rubber is that the membrane may not compress all areas in complex parts.

The process equipment is much more expensive than either block or shaped rubber molding thus limiting the practical size of the equipment. The advantage in using the hydroform process is that the high pressure allows high production rates for small parts and even permits undercuts if not too severe. Temperature capability of this process is limited by the rubber membrane, usually about the same as with the rubber molding since the membrane is often also made of silicone.

A third flexible molding process is trapped rubber molding. This process utilizes the thermal expansion properties of elastomers to exert pressure on the part and force it against the mold. This method is especially useful if bridging of vacuum bags would be a problem. The part preform is placed inside the mold cavity and silicone rubber powder is placed inside the part.

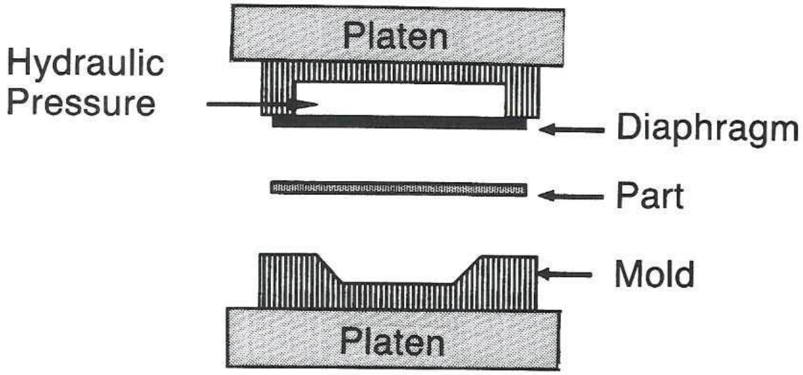


FIGURE 7.5. *Flexible molding–hydroforming.*

Then, as the part is heated, the silicone powder expands and presses the part against the mold. Part definition is reasonably good with this method.

One of the problems with trapped rubber molding has been associated with controlling the pressure. A new method has been developed that allows the pressure to be controlled independent of the composite processing temperature. This new technique using external cooling of the elastomer media to control the pressure, independent of the processing temperature [19]. In the experiment reported upon, a sine wave configuration part was made that was 34.5 cm long with each "period" measuring 6.5 cm in length and 2.5 cm in height. The tool was aluminum and was heated by a platen on the bottom. As with other methods employing rubber, the process temperature is limited by the elastomeric media.

A variation of the trapped rubber molding process uses a flexible elastomeric silicone powder but is on only one side of the part rather than trapped inside. This process, called the Therm-X process, uses a special autoclave for processing. It is especially well suited for complex parts because the powder will not bridge over mold depressions but will give excellent part definition everywhere [20].

Diaphragm Molding

In this process the blank is held between two disposable, plastically deformable diaphragms. The diaphragms are clamped, heated with the blank to processing temperature, deformed slightly (billowed) to consolidate the layers and get good heat uniformity and then deformed over a tool using air pressure, mechanical pressure or hydraulic pressure. In many ways the process is similar to vacuum bag molding. In fact, the pressurization can be done in a press [21], an autoclave [22] or in a conventional oven [23]. The process is illustrated in Figure 7.6.

The purpose of the diaphragms is to hold the blank so that the fibers will be under tension during the forming and avoid the fiber buckling that can often occur if the fibers are placed into compression. Control of fiber orientation is very good. The complexity allowable is limited by the ability of the diaphragm to be deformed.

Two diaphragm materials have been demonstrated. The more common is a superplastic aluminum sheet. The other is a polyimide film. In both cases the molding temperatures are 300 to 400°C. The pressures required for deformation are 1030 kPa for the aluminum or 340 to 689 kPa for the film. The deformation rate is slow when compared to the other sheet forming processes (20 to 100 minute cycles) but that is a laboratory rate and commercial rates may be shorter [24].

For parts with continuous fibers the diaphragms are clamped but not the blank. This allows the fibers to slide while the diaphragm is being deformed.

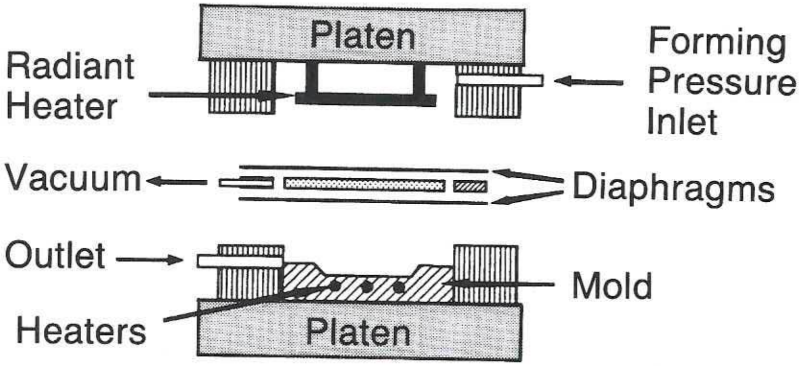


FIGURE 7.6. Diaphragm forming.

The diaphragms must, therefore, be larger than the blank.

Several demonstration parts and some commercial-size parts have been fabricated using this technique. Perhaps the largest is a truck cargo liner box. Another large part was a nose landing gear door for the V-22 Osprey aircraft.

Incremental Forming

This method is designed to create large thermoplastic parts by forming sheets in small to medium sized equipment in an incremental (step-by-step) process. The process requires four basic pieces of equipment. These are the oven, the press, the modular matching molds and the transfer system (which includes the clamping subsystem). The oven can be a conventional IR or hot gas system as would be used with other thermoforming processes. The press would also be of the traditional type used for matched-die stamping. The molds can be either matched metal dies or one may be elastomeric, either mating or block. The transfer system consists of transfer rails, a clamping subsystem and roller bars. These three components work together to hold the laminate in the proper position, transfer the section of the laminate to be formed from the oven to the forming area (between the platens of the press), and transfer the formed section out of the forming area. The transfer rails are the sides of the laminate holding system. The clamping system contains clamps supported by springs mounted in vertical slots in the transfer rails, allow the laminate to move both horizontally and vertically [25]. This process is open-ended, meaning that parts of any length can be made, but the width of the parts is limited by the width of the ovens or the press.

In this process a blank is used that is the size of the finished part. As previously stated, the finished part is envisioned to be very large so only the initial part of the blank is heated. That heated portion is then moved into the mold which is located adjacent to the heating chamber. The initial section of the part is then formed using the thermoforming or stamp molding processes already described. As the first part was moved into the forming area, the second portion was drawn into the adjacent heating zone. Upon completion of the shaping of the first portion, the second could then be moved into the mold and shaped. This process could continue until the entire part is shaped.

Since fibers in the forming area move during forming and the fibers in the cold, solid material do not, some fiber strain occurs. The strain moves through the laminate as various sections are formed, and will be eventually released out the end of the fibers. This molding strain is affected by the size and degree of contouring of the section being molded. The amount of strain needs to be calculated and kept below ultimate failure strain. The amount of material to be heated in each forming section depends upon this factor.

The step-by-step processing method involved in incremental forming permits a significant variation on the standard forming process. Whereas the other forming processes envision parts that are all the same, this method allows parts to be formed in sections where the sections can be different shapes. In other words, section one can be different from section two because the mold can be changed in between the time that the first section is molded and the time the second section is molded. This process is repeated until the entire part is formed, section by section.

This process assumes that a smooth transition exists between each of the sections. This requirement allows some minor overlap between the molding of the sections, that is, the end of section one is molded again as the beginning of section two. The overlap area is thus double-formed, but with proper mold alignment, the second forming operation will not change the shape of the overlap.

Demonstration parts have been made by this technique and have been tested for strength against parts made by thermoforming. No significant decrease in mechanical properties was detected in either the overlap areas or other areas in the part [26].

SHEET FORMATION AND COMPOSITION

The major difference between all of the processes for nonreinforced plastics and all the processes for reinforced thermoplastic sheet is, of course, the reinforcement. In all of the reinforced thermoplastic sheet forming processes, either hot or cold, the part complexity that can be formed is always limited by the movement capability of the fiber reinforcement, although other factors such as mold compliance, may also have a bearing. Three fiber movements are important. The first is movement of one layer of fibers relative to another. The second is movement of fibers within a layer. The third is movement of an individual fiber.

Interlaminar movement is largely controlled by the matrix. If the matrix is not melted and therefore binds the one layer to the next, the maximum movement allowed is the stretching limit (strain to failure) of the fibers or the stretching limit of the resin, whichever is lowest. (The strain to failure for the fibers is almost always less than the resin.) This stretching limit is very small and would severely limit the usefulness of the forming processes were that the limit of deformability. However, in most of the methods discussed, the resin is molten, at least to a sufficient extent that the fibers can slide and accept the deformation without breaking. Therefore, interlaminar sliding is not a major problem if the methods described herein are used.

The displacement of fibers within a layer is essentially the changing of a two-dimensional sheet into a three-dimensional form. This movement of fibers is also affected by the resin. However, even if the matrix is molten, the ability of the fibers to vertically displace may be limited. Fiber orientation has a major effect in this property. Some orientations, such as random swirled fiber mat, are far more compliant than unidirectional tape. Therefore, sheets that are intended for parts that have large vertical displacements are usually made of compliant orientations such as mat.

The third fiber movement, individual fiber displacement, is also limited by the stiffness and ductility of the fibers. This property is the limiting factor in such instances as deforming the fibers into a small radius or in a narrow rib. In these cases, the sliding of one fiber over another is not the issue, but the fiber itself must be able to deform and elongate. Many complex parts have sections that would easily exceed the stretching limit of the fiber.

One method to overcome this limitation is to use shorter fibers. By reducing the fiber length, the size of the allowable deformation is reduced, thus allowing more part complexity. This use of short fibers has already been discussed with respect to injection molding. The difficulty with this approach is that mechanical properties decrease rapidly with decreasing fiber length. Therefore, the longest possible fiber length is used that will still deform into the part shape and can be fabricated using the desired method. The use of chopped fibers is an attempt to maximize fiber length and processing in many composite manufacturing methods.

Another method for increasing the effective length of fibers is the use of long, discontinuous fibers. In this case the fibers are discontinuous but aligned in a unidirectional tape. The discontinuities of the fibers are randomly oriented throughout the tape. This means that the average length of the fibers is quite long with the resulting good mechanical properties. Sheets made from these fibers can be drawn up to 50% with over 90% retention of mechanical properties [27,28].

Commercial sheets of reinforced materials are available with over 15 different resins (such as polypropylene, nylon, urethane, PPS, PEEK, and PEI) although the best resins to use are those with good melt flow even with high fiber content such as PET, PC, ABS, nylon and polysulfone. The reinforcements available include fiberglass, carbon fibers, and aramid, and reinforcement types such as unidirectional tape laminates, fabric laminates, chopped mat laminates, felt, and long, discontinuous fibers. The choice depends on part geometry and mechanical properties desired. (Woven fabric has lower properties than unidirectional tape and is not as deformable but is easier to handle.) Mat is available up to 76 cm wide and .18 cm thick at 40% fiber content. Fabric is also available up to 76 cm wide and .02 cm thick at up to 60% fiber content. Laminates of .1 to .2 cm thick are available with a maximum thickness variation of 4 to 8%.

The sheets can be obtained as fully consolidated laminates with no significant void content, partially consolidated laminates with higher voids, and stacked plies (tacked) with no appreciable consolidation. This is not an exhaustive list but merely represents the range of products available. These laminates, also called preforms, can be formed by any of the methods described in this chapter and the layup sequence will be generally preserved. Details such as additional reinforcement in selected areas or inserts can be added to the preforms and tacked to weld them in place.

Several methods have been introduced to make the sheets. The simplest method is to layup several plies of thermoplastic prepreg material and tack in place. All of the prepreg types discussed in Chapter 3 have been used including melt, powdered, and commingled. These sheets can then be laminated by pressing (10 to 100 kPa) for 10 to 20 minutes. (Longer times allow lower pressures to be used.) If the sheets are to be used for a particular part, the sheets can be precut before laminating.

The use of the long fiber, principally thermoset methods for making thermoplastic parts, was discussed in Chapter 5. Several of those methods are well suited to the fabrication of thermoplastic sheets. Perhaps the most obvious is the use of the automated tape laying machine. One of the major drawbacks of this machine was the limitation on part complexity because of the difficulty of moving the head over steep angles and into small crevices. In the case of sheets, this problem is eliminated. Because the layup head consolidates as it lays down the material, a separate consolidation step may not be necessary. Therefore, production rates would be high and the process ideally suited for sheet preparation.

Filament winding and pultrusion can also be used effectively for the fabrication of sheet materials. These high productivity processes could be used to make and consolidate the sheets in one continuous or semicontinuous process. Pultrusion would depend on the ability of the process to wet the fibers, but the fibers could be drawn through a sheet die to obtain the proper consolidation and shape. In the case of filament winding, the material could be wound onto a large diameter mandrel so that the curvature of the part is large, and then removed by cutting the part longitudinally to make a flat sheet. Some pressing may be necessary, but if the curvature is large enough, the sheets could likely be used directly in the thermoforming process. Layers with almost any orientation could be made by this process, thus giving the same flexibility as hand layup with the advantage of automated layup. This process has already been demonstrated for the production of thermoset sheet materials and has been called Computer Integrated Broadgoods Robotic Center (CIBROC) [29].

Another method is the direct formation of a sheet with extruded thermoplastic resin [30,31]. In this process continuous double-belt lamination equipment is used. The resin is delivered between continuous fibrous mat or fabric using a conventional sheet die. The impregnation takes place in the laminator. Temperature, pressure, and residence time are the key factors that must be controlled to obtain good wetting. The material is cooled in a cooling zone and emerges as a continuous sheet. Variations of the same process have also been used for lamination. A series of sheet extruders can be used on-line, enabling the introduction of more than two layers of mat and, if desired, different polymers between the reinforcement layers.

Sheets can also be made by a wet slurry process that is similar to paper making. Chopped fibers are combined with powdered resin and surfactants in a water bath. The fiber bundles disperse into individual fibers as the slurry is stirred. The slurry (which may be in the form of a foam) is then pumped onto a conveyor where most of the water is removed. The mat of fibers is then dried, heated to the resin melting temperature, and pressed to form the sheet. The advantage of this process is the good adhesion that is possible between resin and reinforcement [32].

The largest product is polypropylene resin on a chopped fiberglass mat with about 40% glass content and 74 to 96 MPa tensile strength. This product, called GMT (Glass Mat Thermoplastic sheet), is being used for automotive and industrial applications [33]. A nylon sheet that is also widely used has 34% glass content and tensile strength of 135 MPa and a HDT of 222°C. In the case of GMT, precut blanks of the material are heated to about 315°C in 2 to 3 minutes. The pliable blank is then indexed to a preheated mold at 135°C in a fast-closing press. This can be the mechanical type used for metal stamping or a hydraulic compression molding press, as long as it has a closing speed of 500 to 1300 centimeters/minute. Molding pressures are typically 13 to 21 MPa unless the part calls for materials flow of 15 centimeters or more, when the requisite pressure may be as much as 25 MPa [34]. The GMT sheet has been used commercially as bumper beams and instrument panel knee bolsters [35].

Another product is a 1.2 × 3.6 meter preform made from three layers of woven glass oriented in (45/90/45) directions that have been consolidated with PEI matrix in a compression press at about 471°C for 15 minutes. The preform is then molded by thermoforming. A variation of this method lays up several of the PEI/glass preforms separated by a PEI sheet to which foaming agent has been added. The core is then placed in a mold and covered with PEI film. As the preform heats, the foam expands and presses against the mold (much like trapped rubber molding). The resulting part is being tried as an automotive panel [36].

PROCESS AUXILIARY EQUIPMENT

Much of the equipment needed for thermoforming of reinforced sheets is standard for either the nonreinforced plastics or for metal stamping. Three parts of the process are not standard. These are the heating, slip frames, and molds. Molds for thermoforming will be discussed in Chapter 9 along with all other thermoplastic molds.

Heating of the thermoplastic sheets is a major part of the process. Three types of heating systems are used – infrared (IR), hot air, and contact heating. IR heating has the advantage of very short heatup times (1 to 2 minutes) which facilitates short cycles and small ovens. However, IR heating can be absorbed at the surface of the part resulting in a thermal gradient through the part thickness. This problem can result in a surface that is degraded before the interior of the sheet reaches the molding temperature. IR would, therefore, be good for thin parts and for well-consolidated laminates. Parts with gentle contours where highly uniform temperatures are not required would also be acceptably heated by IR.

Hot air has the advantage of being the most uniform heating method, especially for nonconsolidated sheets. An advantage of this method is that any heating will cause the fibers to move which results in a lofting of the sheets which gives more accessibility to the hot air. Therefore, it gets better as the laminate gets hotter. However, the heating time is the longest of the three most common methods because of the poor heat capacity of air.

Contact heating is accomplished when the laminate is placed in a heated press. The advantage is fast heatup. The problem is that sheets often stick to the surface and the process is not well suited to a continuous line.

Other heating methods which have been attempted are radio frequency (rf) heating, ultrasonic heating and lasers. The rf heating has the problem that it is geometry dependent and requires shielding from the operator. Ultrasonic heating requires rather expensive equipment and is difficult to perform over large areas. Lasers also have high equipment costs and are difficult for large areas.

The slip frames are another piece of equipment used in thermoforming reinforced thermoplastics that is not used in other processes. The purpose of the sheets is to provide tension during the forming process and thus prevent fiber buckling or sheet wrinkling. The tensioning devices cannot hold too tightly or the fibers could fracture. Thus they provide controlled slippage. These devices also assist in maintaining fiber orientation.

Two types of slip frames are currently being used. In the first, called perimeter tensioning, the part is pinched between a frame and the mold. When the mold closes, the part is gradually pulled out of the frame and into the mold. The second method is point tensioning. This method employs many clamps around the part. Each clamp is attached to a spring which provides the controlled tension desired. One advantage of the springs is that they allow the part to rotate out of the plane. This feature gives better force direction to the fibers and allows for greater variations in draw depth. When the point tensioning system is used, an edge binding is often placed on the blank. This edge binding gives a place for a firm grip and also shields the springs and clamps from the heat.

PROPERTIES AND MODELING

The properties of several molded thermoplastic sheets compare favorably with the properties of similar epoxy resin sheets. A reinforcement efficiency, e, can be defined which corrects the rule of mixtures for the orientation and the length of the fibers and makes this comparison easier. This efficiency factor is defined by the following equation.

$$e = e_o\, e_i \tag{7.1}$$

The rule of mixtures for short, nonparallel fibers would be expressed as

$$E_c = E_m V_m + E_f V_f e_o e_i \tag{7.2}$$

The higher the efficiency factor, the more structurally efficient is the fiber and, by implication, the process. The data are given in Table 7.1 [37].

Other composite properties are excellent for molded thermoplastic sheets. Some mechanical properties for several types of sheets are given in Table 7.2 [38].

Several mathematical models have been developed to calculate several of the key mechanical properties of parts formed from thermoplastic sheets [39–46]. Smiley and Pipes specifically assume that the fibers are inelastic, that the fiber ends are unconstrained and that there is no axial loading on the fibers. It further assumes that the transverse spreading of the fibers during the molding process is caused by the forming pressure to give local thickening or thinning. However, no change in local volume fraction occurs in the molding. The results of this model confirm that fiber distribution can be predicted for three-dimensional shapes formed from flat thermoplastic sheets. The shapes included hemispheres, hat sections, and pyramids. Convergence of the numerical analysis was within 0.1%. The model can also be used to predict geometrical limits for shaped parts from flat sheets.

TABLE 7.1 Reinforcement Efficiencies of Thermoplastic and Thermoset Composites.

Matrix	Reinforcement	Volume Fraction	Tensile Strength (MPa)	Reinforcement Efficiency (e)
PP	Long chopped	0.19	120.0	0.20
PP	Noncrimp fabric	0.24	275.1	0.44
PP	Twill weave	0.33	236.5	0.27
PP	Twill weave	0.45	270.0	0.23
PP	Short chopped	0.19	103.4	0.17
PP	Swirl mat	0.19	120.0	0.20
PET	Twill weave	0.37	237.1	0.21
PBT	Twill weave	0.28	208.4	0.24
PBT	Long chopped	0.16	120.6	0.20
Nylon 12	Atochem weave	0.33	209.9	0.24
PEEK	Random mat	0.31	227.5	0.21
Epoxy	Twill weave	0.39	251.3	0.26
Epoxy	Noncrimp fabric	0.42	427.2	0.41
Epoxy	Random mat	0.43	250.4	0.22
SMC	Long chopped	0.35	158.6	0.13

Several types of fiber/resin movement have been identified and used to assist in the formulation of the models. These various movements can be divided into the following types: axial extension, transverse fiber flow, interlaminar slip, and intralaminar shear. These types are represented in Figure 7.7.

TABLE 7.2 Physical Properties of Thermoplastic Composites Made from Molded Sheets.

Matrix	Reinforcement	Volume Fraction	Tensile Strength (MPa)	Modulus (GPa)	Impact Strength (J/cm)
PET	Twill weave	0.37	237.1	13.4	9.7
PP	Twill weave	0.45	270.0	16.2	11.1
PP	Noncrimp fabric	0.24	275.1	7.6	–
PP	Long chopped	0.19	120.0	6.3	3.0
PP	Swirl mat	0.19	120.0	5.0	7.8

Gutowski et al. studied the flow due to applied compressive forces and noted that wrinkling is due to induced compressive forces on the fibers. When the stresses become high enough to overcome resistance to transverse shear before axial shear, the fiber buckles and creates a wrinkle. These stresses could, however, be relieved if bending took place over a sufficiently long time to allow shear relaxation. The equation developed by Gutowski et al., which governs shear relaxation in a viscoelastic composite, shows this time dependence and indicates that the maximum fiber length permitted before buckling also depends on the relaxation time. This equation is given in Equation (7.3)

$$T_s = \frac{4}{V_f(1 - V_f)} \left(\frac{l}{h}\right)^2 \frac{\mu}{E} \tag{7.3}$$

where:

T_s is the time constant to allow the shear stresses to relax.
V_f is the fiber volume fraction.
E is the transverse fiber modulus.
l is the fiber length.
h is the height (thickness) of the fiber.
μ is the resin flow constant.

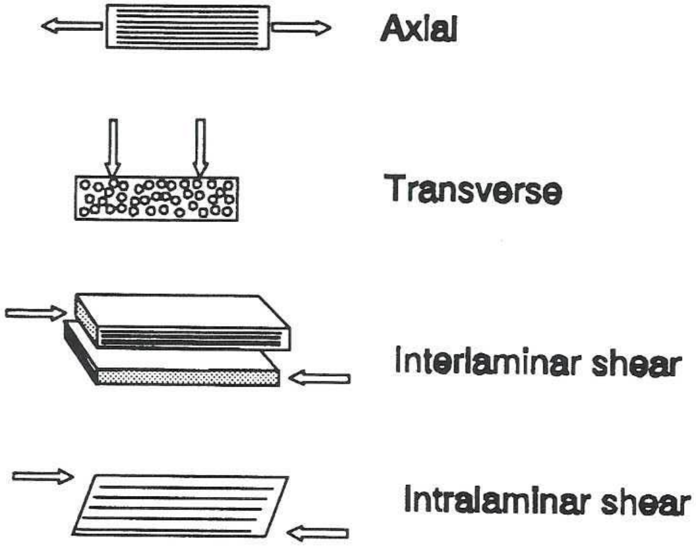


FIGURE 7.7. Deformation mechanisms.

This equation indicates that some of the most important variables when forming thermoplastics are forming speed, length of the part, or more specifically, the length of the fibers, and the resin viscosity, i.e., resin selected and temperature. Soll and Gutowski confirmed this equation experimentally and showed that tensile forces as small as 200 kPa can prevent fiber buckling. They also showed the effectiveness of reforming to remove wrinkling.

Okine points out that the shape to be formed by dictates both the blank characteristics and the molding method. With this in mind, he then develops several rules of thumb that are derived from his model. The rules of thumb which can serve well as a summary of the thermoforming method are given by Okine as follows:

- *Sheet selection*—For applications with parts of gentle curvature and not requiring high mechanical properties use a woven fabric, preferably a fine weave. When a multi-ply, unidirectional tape is used, an unconsolidated laminate with individual impregnated layers (uniplies) reduces interply interaction and hence is better in most forming situations. However, handling problems may make its use difficult. For parts requiring draw, especially in multicavity (repeated sections) as in beaded panels, the ordered staple sheet structure is most suited.
- *Forming method*—Press forming is the simplest and usually the most readily available and so tends to be the first choice. In using matched-die tooling, it is preferable to make one-half of the tooling flexible to aid uniform part consolidation. Matched-die press forming seems to be most suitable for woven fabrics. Excellent results have also been achieved using a matched-metal/silicone rubber die arrangement for ordered staple sheets in press forming. Work on the other forming methods is limited. However, diaphragm forming (this may equally apply to autoclave forming) has been shown to provide excellent control of fiber placement in certain classes of geometries, such as a hemisphere, when used for multi-ply continuous fiber sheets.
- *Forming conditions*—The resin in the sheet should generally be at melt temperature during forming or shaping, especially for ordered staple material. After shaping, a consolidation pressure is required over the whole part surface until it is cooled to below the resin T_g. Sheet clamping or a means of providing tensile stresses in the sheet during forming is necessary to minimize wrinkling.
- *Tool design*—Considerations for tooling are generally the same as for sheet metal forming dies or compression molding. However,

tool contact with the deforming material should be in such a way as to maximize uniform pressurization of the sheet surface at all times. This reduces lateral fiber displacements due to squeeze flow.

Some design rules of thumb can also be formulated as follows:

- The minimum part radii should be two times the laminate thickness.
- The part should have no undercuts without actuated tooling.
- The draft angles should be 15°.
- The draw ratio (smallest part length/height) should be 1:3.
- Parts of various geometries can be molded with geometries increasing in difficulty as:
  - relatively flat
  - deep, single curvature, constant cross section, ribs
  - deep, single, nonconstant cross section
  - pans and troughs (closed end shapes)
  - double curvatures
  - convoluted surfaces
  - deep cross-sectional intersections

FORMABLE SANDWICH MATERIALS

The use of a sandwich material made from knitted fabric of glass or carbon fibers impregnated with a thermoplastic binder gives a unique capability to the use of sandwich structures [47]. This core material has a three-dimensional network structure that is coated with thermoplastic composite and, in its most common form, is compressed and cooled. The material is then placed between composite face sheets and heated to the point of softening of the thermoplastic binder in the core. Because of the internal stresses in the coiled fibers in the core, the core material will expand to fill the space between the face sheets or will push the face sheets to fill the mold. If the face sheets are also thermoplastic composites, the entire structure can be heated and pressed, using the methods described previously, to give a formed sandwich material. This structure would be much simpler to fabricate than would a traditional, shaped sandwich which requires cutting and bonding of the core material.

SUMMARY

Several methods have been discussed for forming thermoplastic sheets. The use of these methods can be overlapping, but some have particular use for small parts and others for large parts. Some are best applied to complex parts and others to simple parts. As already discussed, Figure 7.2 indicates the current areas of application for each of these methods on the basis of part size and part complexity. This chart is an obvious simplification and, furthermore, ignores advances in the methods and ignores the creation of new methods. However, the figure does indicate the diversity of methods that are available for converting flat thermoplastic reinforced sheets into finished parts and suggests the efficiencies available with this general processing concept.

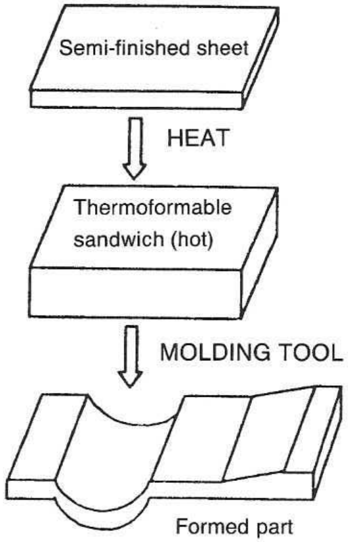


FIGURE 7.8. *Processing of thermoplastic composite sandwich.*

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CHAPTER 8

Molding/Forming Preshaped Thermoplastics

This chapter will review the following concepts:

- Roll forming
- Die forming
- Unconstrained forming
- Continuous sheet forming

The major difference between the processes discussed in this chapter and those discussed in Chapter 7 is the shape of the material before forming. In Chapter 7 this shape was limited to a sheet or blank. In this chapter, other shapes will be considered. These other shapes can be nonformed (such as flat strips) or formed (such as I-beams). They can be continuous (strips or rods) or discrete (I-beams). Some of the processes envision that standard shapes would be kept in inventory and then, as required, be shaped to fit the specific application. All of these processes take advantage of the ability of thermoplastics to be heated to a softened state and then formed and quickly cooled to a rigid, newly shaped part.

The preformed shapes can be made by any process that gives consolidation of the several layers and produces the shape needed for the ensuing forming process. Examples of these preforming/consolidation processes would be pultrusion, extrusion, and layup.

ROLL FORMING

As normally practiced, this process is a continuous, automated method for shaping simple parts which have a constant cross section. The feedstock material is normally continuous fiber strip (laminate) that is made by pultrusion or layup (often automated). The strip could be unidirectional or multidirectional, as the application may dictate. The strip would be fully consolidated to avoid any movement of one layer relative to the others. Any sliding of the layers relative to the others could result in improper alignment in the final part. This is especially important in thermoplastics where tack is absent and the retention of the layers in position is difficult in the nonconsolidated form.

The roll forming method was originally developed for metal working. In the metal process a flat strip of metal (such as aluminum) is passed through a series of paired rolls (each pair matching top and bottom) and is progressively formed to a desired uniform shape in cross section. Among the many products made by this method are window and screen frame members, bicycle wheel rims, garage door trolley rails, and metal siding [1].

When adapted for thermoplastics, the major difference between metal and plastic roll forming is that the strip material is heated prior to the forming. This has often been accomplished with an infrared heating oven. The process for thermoplastics is shown in Figure 8.1.

Several shapes have been produced using this technique. Some of the most common are T, Z, L, C, and hat sections [2]. More complicated shapes such as a wing spar have been made by roll forming, in this case with the additional use of an autoclave for the cross-members.

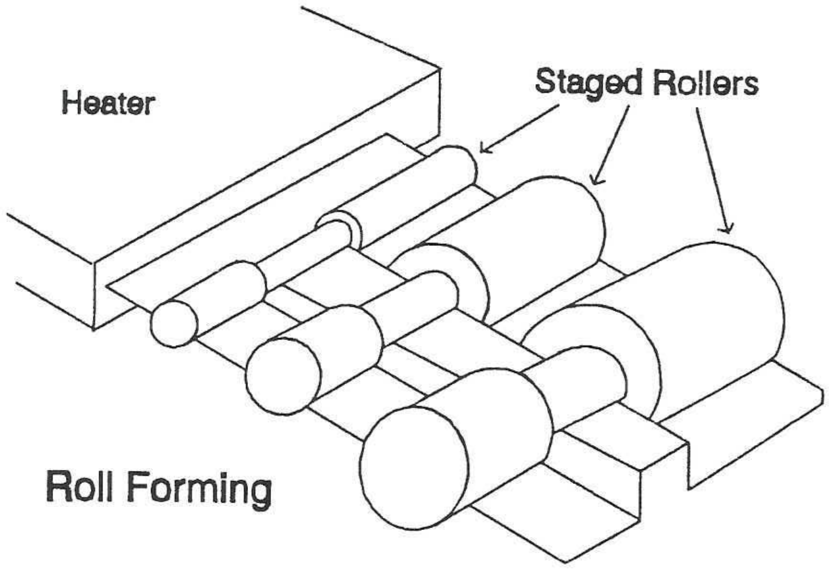

FIGURE 8.1. Roll forming of thermoplastic composites.

Simple parts were formed at speeds up to 9 m/minute. Other authors have reported even higher speeds of fabrication [3].

A method that is closely related to roll forming has been developed and extensively studied at Stanford University [4,5]. In this method a workpiece, which is usually flat, is passed through a compact heated active forming region, bending the workpiece locally only where it is hot within the active forming zone. The criteria for forming are that the workpiece which has left the active forming region must be rigid (because it is largely unsupported but must still retain its formed shape); the material just leaving the active forming region must always be bent to its correct final radius of curvature; and, of greatest importance, no length changes may be induced in the plane of the plies by these bending operations (because the continuous reinforcing fibers are essentially inextensible in tension and will buckle if placed in substantial compression). The goal is to form the desired final shape at each location in a flat stack of prepreg plies and simultaneously consolidate the plies together while that location is within the active forming region.

In general any forming that is done in the center of a composite requires that the entire composite be softened to the forming stage so that the fibers will slide to allow for the out-of-plane deformation. In die-less forming, however, a method for introducing a bend in the center of the part without the requirement to heat the entire part has been developed. This method utilizes a concept called kinematically admissible bending. In this concept the types of bends to be introduced are divided into two groups—those in which net bending is nonzero and those in which net bending is zero. When net bending is nonzero, the fibers must move or slide to accommodate the out-of-plane deformation, whereas in zero bending, the shape of the desired bend does not require any fiber sliding because all the movement required is local in the vicinity of the deformation. These two types of bends are illustrated in Figure 8.2.

To form a bend with a single central bend (nonzero net bending), the bend can be introduced at the edge of the workpiece where the layers are free to slide over each other. The bend can then be propagated along the workpiece while the workpiece moves through the active forming region. If a part happens to have two equal and opposite bends, which results in zero net bending, these can be introduced directly into the middle of the workpiece. Each of the two bends can then be propagated to its desired location as with the nonzero bend.

The concept is not limited to bends in a given direction. In general, any bend can be formed by introducing the nonzero component of the net bending at the edge and then propagating the bend to the desired location and initiating any zero bends wherever desired. In some cases multiple passes were necessary to form long, complex curved parts.

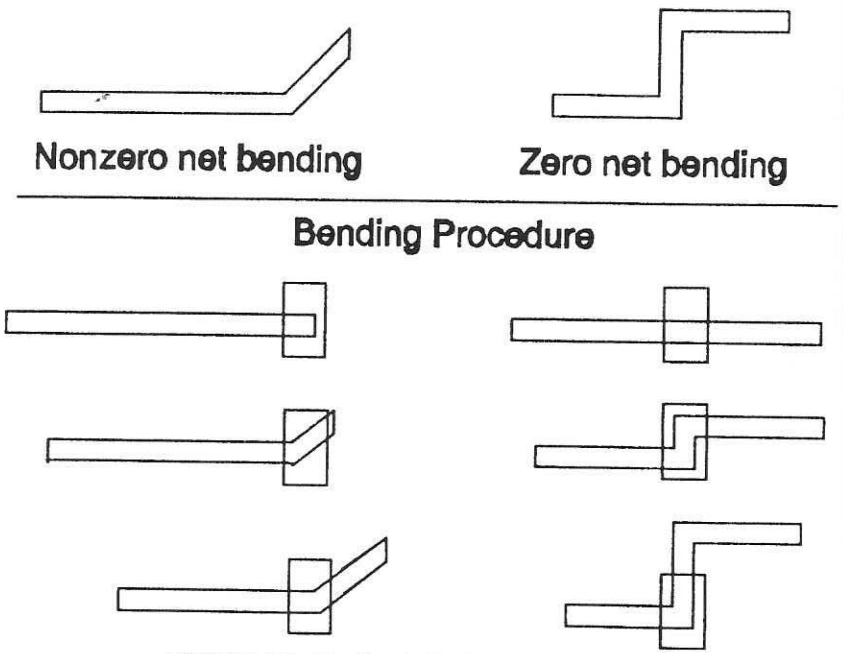

FIGURE 8.2. Bending in die-less forming method.

The method chosen for introducing and propagating these bends is with rollers, much as discussed previously in roll forming. Such a roll forming device has been fabricated and used to make several parts by the die-less forming method. The machine has been used to produce acceptable parts and confirm the model which has also been developed. However, the orientation of the plies within the workpiece has some effect on the final shape and shape retention of the part and must be accounted for to avoid overcurvature in the part.

DIE FORMING

In roll forming and its related processes, no die is used. The part is simply shaped by the action of rollers which are configured to give the desired bend to the part. Another approach to the shaping of preformed composite parts is the use of dies. The parts can be preheated and then introduced into the dies for forming or they can be heated in the dies directly (by contact heating).

Die forming is especially useful when parts which already have a complex shape are to be further formed. For instance, die forming might be used to shape I-beams which have been preformed in some previous operation (such as pultrusion). These "stock" I-beams, which would be inventoried as straight pieces, could then be formed to shape in a die, perhaps to fit the curvature of a fuselage. The advantage is that the forming could be done quickly and with inexpensive tooling. When simple curves are to be done, roll forming would also work, but die forming gives the additional capability of complex shapes.

The simplest form of die forming for thermoplastics is the shaping of flat strips of thermoplastic material into a shape by passing the strips through a heated die. This process, which is illustrated in Figure 8.3, has many features that are similar to pultrusion.

The strips of thermoplastic material are drawn into a heated die and are then formed into the desired shape. As with other pultrusion-like processes, the cross-sectional shape of the part must be constant. Several strips could be drawn simultaneously into the dies to produce a part that has multidirectional fibers and layers. The difficulty with this process that must be overcome is to achieve adequate consolidation of the layers. The pressures in the dies are, therefore, quite high and the line speeds are relatively slow.

The products formed by this conversion of strip to I-beams or other shapes can be subsequently formed. The subsequent forming can be done continuously or batch-wise. A process to do continuous postforming that fits conceptually between roll forming and die forming is illustrated in Figure 8.4. This process uses a forming section that may be either a die or rollers or a combination of the two. This process differs from conventional roll forming in that it starts with a shape (such as an I-beam) rather than with

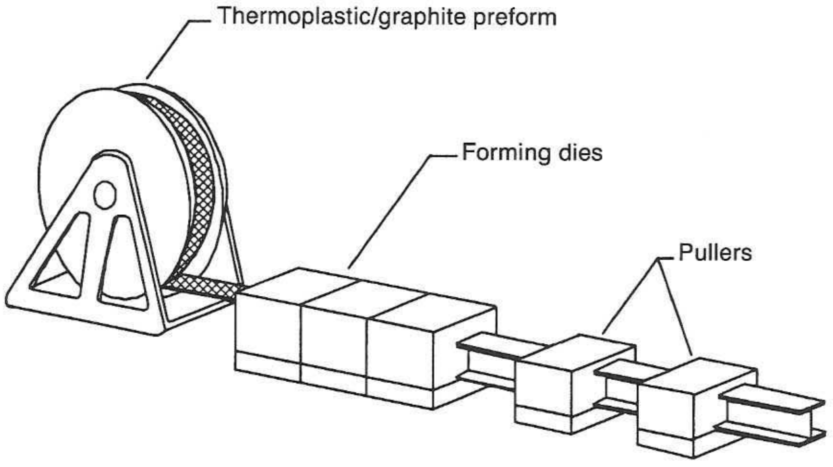

FIGURE 8.3. Forming a strip into an I-beam shape.

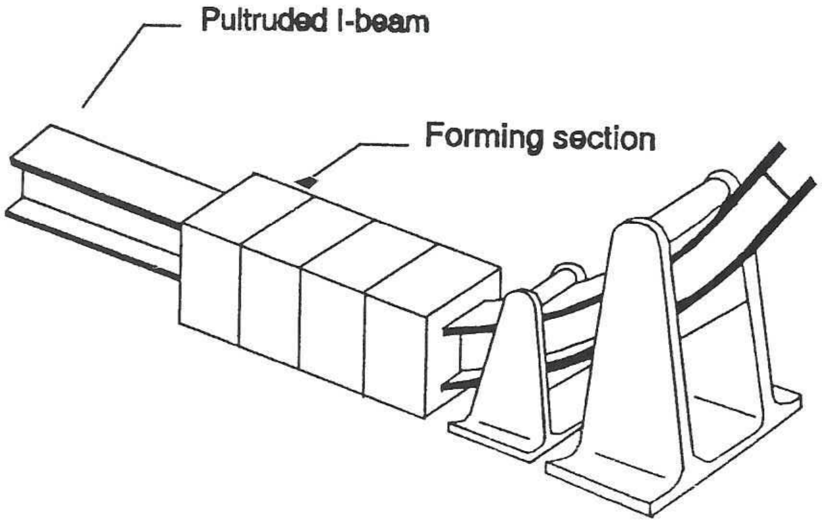

FIGURE 8.4. Forming a shape by a die/roller combination.

flat strips. A limitation of this process is that the bends or shaping of the incoming part must not be severe. This bending is limited by the ability to locally deform the fibers and the resin. If the deformation is greater than the strain to fail of the fibers, they will break. The alternate is that the entire beam be heated to allow fiber slippage over the whole part.

The use of batch-wise die-forming to shape I-beams (and conceptually other shapes) was demonstrated by Snyder, Strong and Lawson [6,7]. In these studies the I-beams were made by hand layup of PPS/continuous carbon fiber prepreg and consolidated using a vacuum bag. After consolidation into the I-beam shape, the parts were separated into two groups—controls and parts to be shaped. To preserve the I-beam shape during forming, silicone pads were placed along the web of the I-beam. These supported the web and the flanges during the forming operation, but were sufficiently compliant to allow the part to be deformed into the desired curvature. Top and bottom aluminum slip sheets were also placed on the parts (see Figure 8.5). The parts to be shaped were then introduced into the mold. In this case the mold consisted of top and bottom base plates, side plates to hold the silicone sheets in place, and male and female mold parts (see Figure 8.6).

As might be expected, complete heating of the I-beams for their entire length was required to allow the fibers to slide and not create fiber buckling or wrinkling. However, if this sliding was allowed, tests of the stiffness of the formed beams relative to the unformed beams indicated only a slight reduction in stiffness after bending. This bending has been modeled by Bank

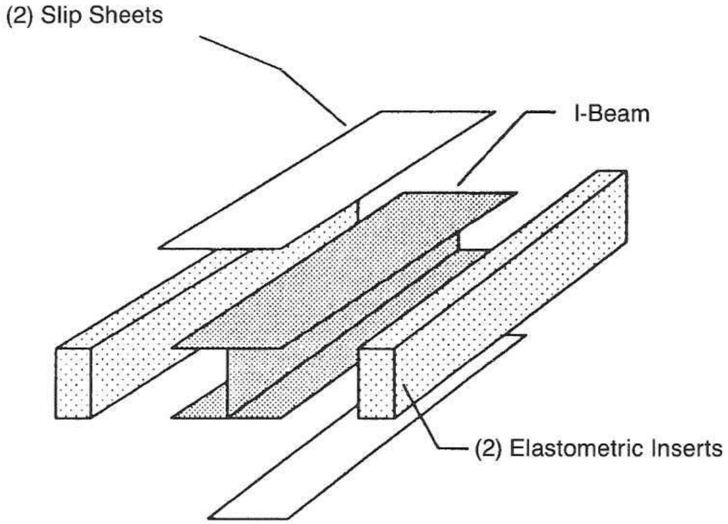

FIGURE 8.5. Support materials for I-beam postforming.

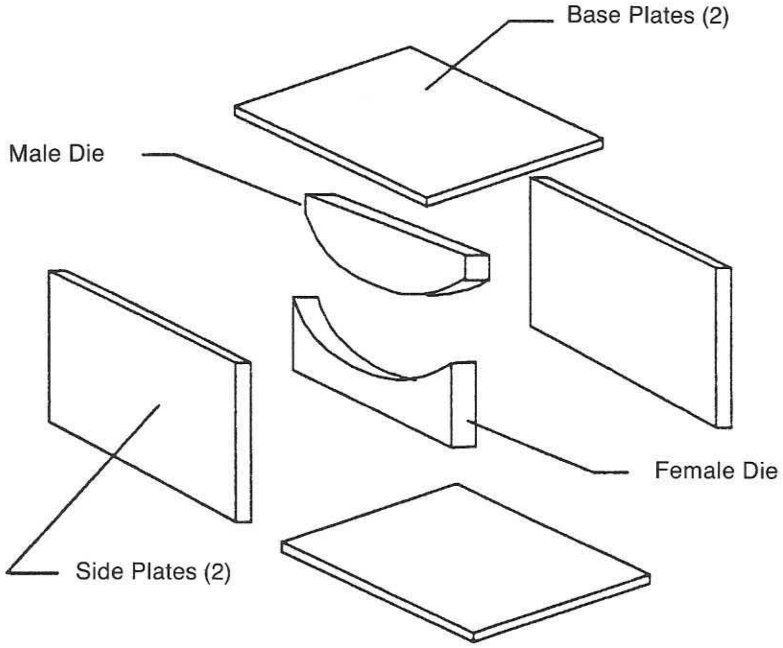

FIGURE 8.6. Postforming of a thermoplastic I-beam.

and Bednarczyk [8]. The die-forming method appears to be suitable for the forming of stock parts into customized shapes.

UNCONSTRAINED FORMING

Although not as useful as roll or die forming, unconstrained forming has some advantages and applications in specific instances. In this method forming is done without rolls, dies, or any other constraint on the part.

Initial studies of unconstrained forming illustrated many of the problems that must be properly addressed if this method is to be used [9,10]. Pultruded rods were formed by placing one end into a forming jig and then simply heating and then deflecting the rods. The deflection was done using a tensile/compression machine so that a constant deformation rate would be maintained. As might be expected, the fibers on the inside of the bend were compressed and buckled. The bent rods were then rebent into the straight shape. Inspection revealed that the fibers did not return to their original straightness but were wavy. In some cases the resin failed when the rods were rebent. Somewhat better results were obtained when the bend section of the rods was enclosed in a spring. The spring seemed to give some additional tension to the fibers and prevented some of the buckling. These studies illustrate the difficulties in unconstrained forming.

In another study the fibers were successfully bent without being constrained. In this case, however, the fibers were kept under tension during the forming step. This unique application involved the fabrication of a mooring cable for marine applications [11]. The basic building-block of the mooring cable was a small diameter, fiber reinforced thermoplastic wire, which was manufactured by pultruding several towpregs together in a heated die. The wires were then thermoformed into a seven-wire strand by twisting the wires together at a temperature above the softening point of the thermoplastic. Several high performance matrices were used with continuous carbon and aramid fibers. The preferred material was a thermoplastic polyimide with carbon fiber. The strengths of the flexible twisted strands approached the theoretical strength of unidirectional composite laminates. The most difficulty in using the thermoplastic strands was reported to be with the termination system (end fittings) so that the load could be shared over all the fibers.

CONTINUOUS SHEET FORMING

Two capabilities of thermoplastics provide the opportunity to form continuous sheets into continuous shaped parts. These two capabilities are the infinite shelf life of thermoplastics which allows them to be rolled and stored

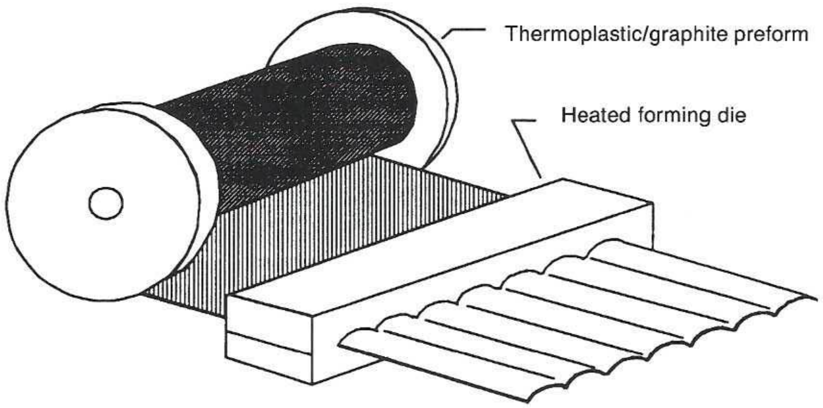

FIGURE 8.7. *Forming a continuous thermoplastic sheet.*

as a standard shape to be formed later, and the ease of forming the material with heat and very little pressure. The combination of these properties suggests a process wherein continuous thermoplastic sheets are fed into or pulled through a hot forming die which imparts a shape on the thermoplastic material. This process is illustrated in Figure 8.7.

The product of this process is very much like a product that might be made by pultrusion or extrusion. The advantage of continuous sheet forming is that the process is likely to be quite rapid and the die can be simple.

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CHAPTER 9

Molds and Tooling

This chapter will review the following concepts concerning molds and tooling:

- Selection
- Design
- Materials
- Fabrication
- Mold/tool use

SELECTION

Molds or tooling are used to define the shape of the composite part and one or more of the surfaces, depending on the type of tooling. The requirements for the tooling are conceptually quite simple in that the tooling must simply provide a mechanism for giving a part the desired shape at the end of the mold cycle. The molds used for thermoplastic composites manufacture are similar to those that would be used for thermoset composites. Some differences obviously exist, and these will generally be discussed in the sections that are applicable.

The choice of tooling is a complicated decision that must look at many factors. Several of these factors are interrelated, but will be discussed individually for simplicity. The first factor to be considered, which is related to the use and design of the part, is whether only one or more than one surface needs to be carefully defined. Normally, only the surface against the mold will have a smooth finish and be dimensionally accurate. If one surface is to be defined, the molds can often be made of materials that need not withstand high forming pressures and can, therefore, be very large. If more than one surface must be carefully controlled, the molds are usually metal and are much smaller. Typical examples of the single surface molds are those used in layup. The mold defines one surface of the part and the other surface is defined by the vacuum bagging system (usually by the release cloth and bleeder). Another single surface mold would be a filament wound type. In this case the filament winding mandrel usually defines the part. However, an alternate method of consolidation in filament winding is to use a clam shell mold on the outside of the part, which has been wound onto a mandrel covered with a flexible membrane (usually a urethane sheet). The clam shell is placed over the part and then a vacuum and heat are applied in the clam shell. This vacuum pulls the flexible membrane outward which presses the composite layers against the clam shell which consolidates because of the fluidity of the resin at the high temperature. The temperature is then reduced, while the part is still under pressure, and the resin solidifies while in contact with the inside of the clam shell. This method has been used for parts as large as a private airplane fuselage (Beech Starship) [1]. A minor consideration regarding the number of surfaces to be defined is related to whether the surface that is not defined by the mold could be machined or otherwise smoothed to the required tolerances.

The shape of the part is another important factor that has a major impact on the mold. As already alluded to above, the size of the part may determine whether the mold defines one side (large and small parts) or more than one side (small parts only). This latter requirement is simply because of the high pressures normally involved in matched die processes which normally dictate a large press. In the case of thermoplastics, however, some processes allow two or more surfaces to be defined with low pressures. These processes would include incremental forming, postforming and roll forming. Long parts can also be made with pultrusion and extrusion, although the cross-sectional areas of parts made by these processes must be small. To the extent that liquid composite molding (RTM and RIM) can be done with thermoplastics, these processes are also of moderately low pressure and therefore have the potential for making large parts with more than one surface defined.

Another shape consideration is the presence of undercuts. Should these be present, the mold must be moveable. This consideration usually limits the complexity of the mold and often also the mold size and material. Small parts made by injection molding are typical of the types that would contain undercuts. These are usually steel molds and are relatively small. Complexity can be high, but only at the expense of fiber length. Another mold type that permits undercuts is flexible tooling, provided it is pressurized or is forced into the undercut by some mechanical means. Still another tooling system that permits undercuts is disposable tooling, such as plaster or eutectic salt mandrels for filament winding. In these cases, the mandrel is simply dissolved after the part is formed. Another example of disposable tooling is the use of castable and removable wash-out tooling material (CARE-MOLD) for engine exhaust flaps and a forward fuselage section. The flaps were made of a thermoset and the fuselage section of a thermoplastic [2]. The CARE-MOLD process allows the fabricator to co-cure and co-consolidate integral stiffeners into composite parts because of its ability to be removed after molding.

Part strength, stiffness, or other mechanical property requirements, especially as a function of weight, are other considerations that influence mold selection. The mechanical properties of the part are often highly dependent on the fiber placement and length. The strength of the mold is a function of the magnitude and the duration of the forces placed upon the mold during part consolidation. Normally large safety factors are used for the mold so failure in any one instance would be rare, except that over an extended time, the wear on the mold may cause a significant loss in strength and could result in failure. These factors are important in determining the part manufacturing process and, therefore, the mold type. Closely related to these decisions are the number of parts and the production rate required. When the quantity of parts to be produced and the production rate are small, the tooling costs would normally be small, unless very high accuracy is required and paid for. Therefore, low volume parts would tend to have only one side defined as these molds usually cost less than molds defining multiple surfaces. The machinery for making the parts would also be lower in cost with relatively more human craftsmanship involved. The expected longevity of the mold is also an important factor in mold selection that is related to part quantity.

A factor determining mold selection that is intertwined with all of the other factors already discussed is the manufacturing process selection. This affects the number of part surfaces to be defined, the mold design, the mold materials, the mold longevity, and countless other mold-related factors. In spite of the complex relationship between process and mold design, the processes can be divided into two groups – those which define one surface and those which define more than one surface. Such a list is given in Table 9.1.

The disparity of the number of processes defining one surface versus the number defining two surfaces is less a reflection of the amount of parts made by the processes than of the interest and research that has gone into the development of processes that produce net shapes, that is, parts that are fully defined as they exit the mold. Long-term economics, especially in markets outside of aerospace, strongly favor the processes which define all surfaces of the part. Rubber tool forming was placed on the single surface side because the side of the part touching the rubber is usually less well defined than the other and so can best be considered a single-side process.

TABLE 9.1 Thermoplastic Composite Processes Divided by the Number of Part Surfaces Defined.

Single Surface Defined	Multiple Surfaces Defined
Layup	Compression molding
Filament winding	Pultrusion
Vacuum forming	Injection molding
Rubber tool forming	Extrusion
	Diaphragm molding
	Stamping
	Incremental forming
	Roll forming
	Postforming
	Liquid composite molding (RTM/RIM)

MOLD DESIGN

After the general type of mold has been selected, the specific mold design must be made. Becker gives a list of 21 issues that should be considered in mold design [3]. These issues are:

- having a mold that produces the required geometric shape and dimensions
- temperature – Is the upper temperature achievable? Are the heating and cooling rates sufficient?
- structural stability during heat cycling
- facilitation of use of lower cost composite materials when feasible
- transportability and handling ease
- facilitation of composite part release
- generation of desired composite surface texture
- which part surfaces the mold should establish
- whether or not the mold will properly cure the composite
- durability sufficient for the required production run
- construction completion within the allotted lead time
- alterability to accommodate design changes and repairability should damage occur
- low operating energy costs
- ease of obtaining duplicate tools if required
- suitability for the part size; this is especially important for very large parts
- processing capability sufficient to produce the desired type and size of tool

- ability to provide the required pressure on the composite at all locations
- confidence of suitability for the task – limiting risk taking to experimental molding situations
- the coefficient of thermal expansion (CTE) of the tooling material which must match that of the composite when both heating and cooling are being supplied by the mold
- if the CTEs do not match, making dimensional compensations in the mold to provide the correct part tolerance, and generally oversizing the mold to account for compact part shrinkage
- acquisition affordability for the production quantities required

Some comments relating specifically to the design of injection molding tools are appropriate because of the complexity of these tools. Because injection molding is such a volume-sensitive process, the mold is critically important in profitability. The number and arrangement of cavities should be given careful consideration. Multicavity molds increase production efficiency, but are more costly to build. Multicavity molds can be used to produce the same part in all the cavities or different parts (in which case it is called a family mold). Whenever the cost of building the mold and the volume of parts justify it, multicavity molds producing the same part in all cavities are to be encouraged. Family molds, however, have some drawbacks that must be considered along with the advantages. One drawback is that if one of the cavities is damaged, the entire assembly (family molds usually make parts that all go into one assembly) may be compromised. Furthermore, the balancing of the flows between the various-sized cavities can be difficult, thus leading to imperfectly molded parts. The advantage is, of course, that all of the parts for an assembly can be molded simultaneously and only one mold need be made and run. Family molds are, therefore, best for limited production runs and for parts where the closest tolerances need not be met. Injection molding tools often have cores which define the hollow spaces in parts. These cores can be either solid or collapsible (for undercuts, and blind threaded holes). The placement and design of the cores should be carefully considered. The runner system for injection molds is also an area that merits careful consideration. Not only is the processing cycle dependent upon the runner system, but so is the orientation of the polymer and fibers in the part which may affect part quality and mechanical properties. Hot runner systems permit the molding of parts without the need to remove the runners from the finished part, but the molds are heated and therefore are more expensive and often lead to longer cycle times, difficulties in clogging and temperature control [4]. Gate size and shape as well as vents are also considerations which should be made to avoid undesired fiber orientation in the mold filling process. Mold cooling is also a consideration for part uniformity and cycle time. Several software products are available to assist in the design and optimization of injection molds.

An interesting development in the design of tooling is the use of integrally heated molds with nonautoclave consolidation of thermoplastics. Significant time and labor savings were demonstrated by abandoning some of the traditional thermoset curing concepts and using, instead, concepts specifically suited to thermoplastics [5].

MATERIALS

The major difference between molds for thermoset parts and for thermoplastic parts is likely in the materials that are required. The high performance thermoplastics, in particular, have very high processing temperatures compared with thermosets. These high temperatures require mold materials that have much higher temperature capabilities than the normal epoxy/carbon fiber materials used for most thermosets. Even when the mold epoxy is a special mold-making formulation, the highest use temperature is usually only about 232°C, far less than the melting points of many of the thermoplastics which are in the 370°C range. These temperature difficulties become even more important with molds that are to receive repeated and frequent cycling. Thermoplastic mold materials therefore are more likely to be metallic than are thermoset molds, although other materials such as polyimides and monolithic graphite are also acceptable. Unlike thermosets, however, thermoplastic materials are rarely used for molds. The principal reason is that the thermoplastics have softening temperatures that are significantly below their melting points. Therefore, if a material must be melted or nearly so to be formed properly, it could not be formed in a mold made of the same material because the mold would soften before the molding temperature was reached.

Another advantage of metal molds for thermoplastics is the high heat conductivity of metals in comparison with composites. In most cases, the thermoplastic materials are heated prior to their entering the mold. The purpose of the mold is, therefore, to shape the part while it is hot and then to cool the part. The higher heat transfer allows this cooling to be accomplished rapidly, thereby shortening the mold cycle. As indicated in Table 9.2, monolithic graphite also has very high heat conductivity and would be an excellent mold material from this viewpoint. The disadvantages of the metallic mold materials are the high coefficient of thermal expansion compared with composites (see Table 9.2).

TABLE 9.2 Thermal Conductivity and Expansion Properties [6].

	Thermal Conductivity ($w/cm^2 {}^\circ C$)	Thermal Expansion ($mm/mm \cdot K$)
Fiberglass/epoxy	.00168 – .00448	$11-35 \times 10^{-6}$
Graphite	1.7588	7.9×10^{-6}
Soft steel	0.4732	11.9×10^{-6}
Aluminum	1.2144 – 2.1776	25.5×10^{-6}
Nickel	0.5863	13.7×10^{-6}
Alumina (ceramic)	0.3518	6.4×10^{-6}

A material option that may have some advantages for thermoplastics is a metal-faced composite. The metal facing, usually nickel, is applied by spraying onto the composite mold (like a gel coat) or by electrodeposition. This type of mold gives longer life because of its abrasion resistance, and also gives a somewhat higher heat conductivity. These advantages are limited, however, because the mass of the metal is not large, but can be largely overcome if the mold is made of monolithic graphite.

FABRICATION

Several options are available for the fabrication sequence of the mold. However, in all of the standard sequences the first step involves the fabrication of a prototype part. This prototype or pattern can be made of almost any material because the purpose of the prototype is to define the design of the part and to ensure that the dimensions called out in the drawings are correct. Because of the wide selection in permissible materials, the easiest materials to work are usually chosen. High quality wood pattern lumber, though sometimes difficult to obtain and expensive to purchase, is nevertheless an important material for the patternmaker. Wood is an ideal material because it carves readily and little labor is required to eliminate defects that could adversely affect a model. In processes much like wood, plastic blocks can also be machined to the desired shape. Syntactic foams which are made by incorporating small glass, plastic or ceramic spheres into a thermosetting resin can also be used for prototypes. These are also machined to the prototype dimensions. The machining can often be done with a multiaxis head mounted on a gantry system (much like the system that would be used in automated layup of prepreg). This machine would be computer numerical controlled (CNC) and would, therefore, cut the part based upon a tool path that had been developed on a computer. Several computer aided design

(CAD) systems have the capability to develop the part dimensions on the computer and then download these directly to a machining center where the CNC code is used to machine the part.

After verification of the dimensions and acceptability of the prototype, two general methods can be followed to make the mold. In one method, a composite or plaster mold is made by laying strips of the mold material (which might be prepreg in the composites case) directly onto the surface of the prototype. (Alternately a box could be built around the prototype and the mold could be cast over the prototype surface.) This provides an easy way to ensure duplication of the surface. The mold surface is generally reinforced and supported with a rigid substructure and is then removed from the prototype and finished by repairing any damage and applying mold release agents to the mold surface [7]. The second method of making the mold is to machine it directly, much as the prototype was machined. This is the method that is followed with "hard" tooling, that is, metal tooling. CNC programs derived from CAD drawings are often used in this process.

Several considerations for mold making have been suggested and are as follows [8]:

- choice of a metal or nonmetal material for the mold or tool
- temperature at which the mold is to be used
- part and mold tolerances
- size of the mold or tool
- undercuts, hardware, and inserts (if any)
- mold wall thickness
- tapering and draft angles
- inside and outside radii of the tool or mold
- special reinforcements, such as ribs or fillers
- warpage due to substructure support
- parting and trim lines
- holes, rails, and attachments
- surface finish
- post-mold making handling and storage

MOLD/TOOL USE

Typically molds are subjected to four steps in the part fabrication cycle—mold preparation, charging of the mold with the unformed part material (such as prepreg layup or injection into a mold), consolidation and solidification, and demolding. Each of the four steps has a unique environment. Mold preparation for soft (nonmetal) tooling, which is often large, is usually done in a separate area from the layup and molding areas. For hard (metal) tooling, the molds are usually prepared in the molding area. During mold preparation the mold is carefully cleaned of residual resin, it is repaired where necessary, and is then treated with mold release (parting agents) to facilitate part removal after the next molding cycle. Hard tools require little mold preparation.

The charging of soft tools is usually done by laying up prepreg materials onto the surface of the tool. For hard tools the charging is done by injection or by placing the heated blank into the mold.

The consolidation step (which is the curing step for thermosets) is accomplished by closing the mold and allowing the thermoplastic material to harden in the shape of the mold cavity. For molds that define only one side of the part, the closing is done by applying a vacuum bag and the other related bagging materials and then placing the assembly under pressure. Consolidation is accomplished with pressure and heat. This can be done by a press or a vacuum.

Demolding is accomplished in hard tools by using knock-out pins. These slide against the hardened part and push it from the mold. With soft tooling, the demolding is much more delicate and is usually accomplished by carefully working the part off of the mold.

Extending mold life is dependent upon the mold design, use and handling. The design should be robust, that is, able to withstand normal and even occasional rough handling. One of the most important methods for imparting robustness to a mold is by the use of rolled tool edges. A mold with such an edge is illustrated in Figure 9.1.

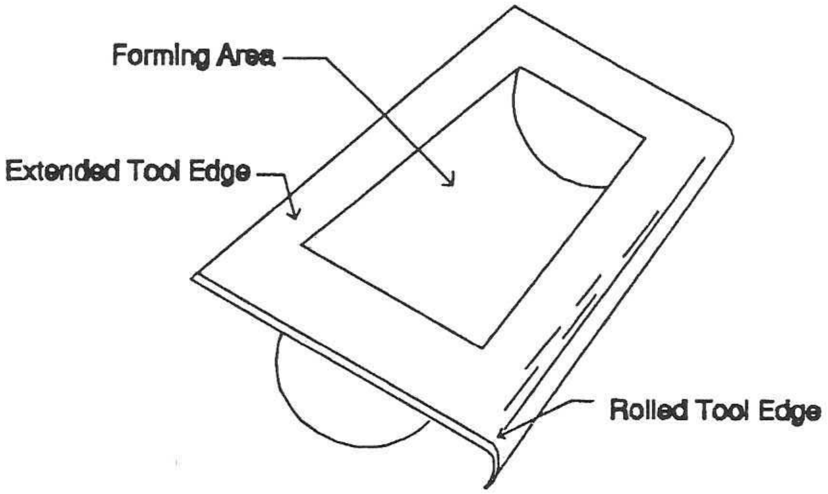

FIGURE 9.1. Rolled edge mold design.

Another design criterion is the allowance for wide trim areas so that metal trimming shims can be used. These shims are placed under the layup at the edge of the trim area when the layup strips are cut. In this manner the cutting is done against the shim rather than against the tool surface. The use of abrasive-resistant surfaces (such as metal coating for soft tooling and tool steel or chrome for hard tools) will also add significantly to mold life.

The storage and handling of molds is as important to extending mold life as any other factor. Before tools are stored they should be coated with release agents and then covered to protect the surfaces. The storage and handling areas should be carefully planned so as to be convenient and accessible from the mold preparation and molding areas. Standardization of transport equipment will assist in protecting the molds as the substructure can be designed specifically to accommodate the likely contact points from the transport equipment. This same concept is applicable in the design of the storage facilities.

The mold should be backed with a substantial substructure to prevent warpage and to give robustness during handling, although not so heavy that moving the mold becomes, itself, a potentially damaging process. The most common substructure is an eggcrate system in which the mold surface is backed by a network of interconnected boxes. This system gives rigidity but is lightweight. Other systems include integrally stiffened molds in which stiffeners are attached (usually bonded) directly to the reverse side of the mold. The support structure can be less substantial in these cases.

Generally, mold surfaces are not treated to withstand the effects of ultraviolet light or other harsh environments. Therefore, storage and handling should generally be kept indoors with care that the molds are not exposed to direct sunlight (even through windows). To avoid inadvertent abrasion of the surface, the molds should be kept in a clean, relatively dust-free room.

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CHAPTER 10

Finishing and Repair

This chapter will review the following concepts:

- Joining and assembly
- Machining and cutting
- Repair
- Annealing
- Crosslinking of thermoplastics

Finishing of composites embodies several key concepts. The first concerns the joining of composite parts to other components to form an assembly. Another concept in finishing is machining and cutting which must be done to almost all composite parts. These concepts are then applied to the special case of composite repair. Finally, the special aspects of thermoplastic finishing are discussed.

JOINING AND ASSEMBLY

Thermoset and thermoplastic composites have traditionally been joined by either mechanical joints, adhesive bonds, or less commonly, solvent bonding (except for the methods of joining that are unique to thermoplastics which will be discussed later) [1]. These joints can either be planned at predetermined locations in the structure (such as joining two sections of a structure together), or unplanned repairs that could be needed anywhere in the structure. The methods involved in mechanical joining of composites are similar to those used with metals, that is, drilling and countersinking holes through the composite structures to be joined and then inserting fasteners through the holes and parts to complete the joint, but with the caution that composite materials are often much stiffer and more brittle than metals.

Because of the brittle nature of composites, the joints are far more important and difficult to design than with the more ductile metal materials. The yielding of ductile metals usually reduces the stress concentrations around bolt holes, whereas with composites these stresses are not relieved except for the debonding of fiber laminates which is generally to be avoided and prevented whenever possible. A further reason for emphasizing the importance of joints in the design of composite structures is that the highly complex and seemingly complete laminate design programs create the illusion that optimized composite structures will be tailored precisely to match the load conditions and stiffness requirements. However, the real capability of bolted joints compared with the capability predicted in such highly idealized materials is often unacceptably low. Hence, the laminate can never be loaded to the levels suggested by lamination theory. Fortunately, the strength of composite structures with both loaded and unloaded holes actually depends only slightly on the fiber pattern (for nearly quasi-isotropic laminates) and the laminate theories can be used to give reasonable results if appropriate safety design factors are used. The design and analysis of bolted or riveted joints in fibrous composites remain very much an art because of the need to rely on empirical correction factors. Mechanically fastened joints differ from bonded composite joints in one further aspect: the presence of holes ensures that the joint strength can never exceed the local laminate strength. Indeed, after years of research and development, it appears that only the most carefully designed bolted composite joints will be even half as strong as the basic laminate. The simpler bolted joint configurations will attain no more than a third of the laminate strength [2].

Most of the typical types of fasteners used with metals such as rivets, bolts, pins, and blind fasteners, are also used with composites. Just as is the case with metals, the choice of fastener material is important to avoid galvanic corrosion between the fastener and the metals to be joined. Because carbon fibers are electrically conductive, galvanic corrosion can occur with many fasteners—aluminum and cadmium-plated being two of the worst. This problem is reduced using nickel, titanium, or nonmetal (often composite) fasteners or by separating the fastener from the carbon with a glass-reinforced outer layer or with a sealant. The fastener shape most compatible with composites is generally the head with the largest contact area. This reduces the localized stresses which arise when the joint is placed in tension. Very small fasteners are rarely used as pullout may occur.

Adhesive bonding, which consists of interposing a layer of an adhesive composition that is chemically different from the composites to be bonded (the adherends), is the most common alternate to mechanical joints. The choice of whether the joining should be by mechanical or adhesive means is complicated and depends on the specific situation. For instance, the advantages of adhesive joints over mechanical joints include the following:

- Adhesive bonds have lower stress concentrations than mechanical joints.
- Adhesive bonds eliminate potential delamination caused by the drilling required for mechanical joining.
- When the loading is first applied, adhesive bonds have less permanent set.
- Adhesive bonded joints weigh less than mechanically bonded joints.
- Adhesive bonds permit smooth external surfaces at the joint.
- Adhesive bonds are usually less expensive.
- Adhesive bonds allow the assembly of dissimilar materials without regard to galvanic corrosion.
- Mechanical joining may not be practical for thin sections.
- Adhesive bonding has less sensitivity to cyclic loading.
- Mechanical joints often have problems in bolt bearing strength of the composite.

The advantages of the mechanical joining method include:

- Adhesive bonds can be sensitive to creep.
- Mechanical joints are much stronger in peel loading than adhesive bonds.
- Adhesive bonds are more difficult to inspect.
- Mechanical joints can be designed for access, whereas adhesive bonds are permanently fixed.
- The surface preparation for adhesive bonds is much more extensive than for mechanical joints.
- The mating of the surfaces (shape, configuration, etc.) is more critical for adhesive bonding than for mechanical joining.
- Mechanical joints are generally less sensitive to thermal, water, and other environmental degradation (except for corrosion).
- Adhesively bonded joints are sensitive to different thermal expansion coefficients of the adherends [3].

The strength of the adhesive bond is primarily dependent on the ability of the adhesive material to become attached to the surfaces of the adherends, and on the strength of the adhesive itself. The nature of the adhesive and its compatibility with the surface of the adherends is of primary importance. For this reason, the adhesive must be chosen carefully for each set of adherend materials. Furthermore, the surfaces of the adherends must be carefully prepared to properly accept the adhesive. In addition, four key design factors strongly influence the strength of the bond: amount of overlap of the adherends, coverage (that is, the amount of the adherend surface actually covered by the adhesive), thickness of the adhesive bond material, and interlaminar shear strength [4].

An analysis of the effect of flaws and defects in the adhesive indicated that there is no reason for the high peel stresses to occur in well-designed structural bonded joints, even though the standard lap-shear test coupon is strongly influenced by the induced peel stresses. Further, the greater thickness of porous bonds than of adjacent structurally sound bond areas makes the porous bonds less stiff so that they usually transfer load to the sound areas rather than become overloaded and fail themselves. Structural bonded joints in most lightly loaded structures have very considerable tolerance for all bond flaws and do not need structural repairs. Usually, all that is needed is to seal the edges with a rubber-based material to prevent ingress of moisture. The key to understanding the tolerance or sensitivity of adhesive bonds to flaws or porosity is that there is almost complete insensitivity to even quite large defects provided that the defect is located somewhere other than at the critical location (usually at the ends of the overlap). Bond defects become really significant only when they are large enough to alter the distribution of the load transfer through the bond so that they cause a shift in the critical location (usually to an edge of that defect) [5].

Both thermoplastics and thermosets can be bonded by solvent welding. In this method the surfaces to be bonded are wiped with a solvent and then clamped together while still tacky. The solvent softens (plasticizes) the resins and allows some migration of the polymer chains across the interface (or into the interphase) to achieve the bonding. This method is most effective, of course, when the resin can be readily solvated. The high performance thermoplastics have very few solvents as is also true of crosslinked thermosets. Therefore, this method has limited application for advanced composite materials. On the other hand, engineering thermoplastics are readily bonded by solvents. When solvent bonding, it is important to soften enough of the resin to provide complete contact and eliminate air bubbles but not so much that the material is squeezed out when clamped or takes excessive time to bond [6].

Thermoplastic materials can be bonded by yet another method. This method is called fusion bonding or welding and involves the melting of the surfaces to be bonded. The thermoset equivalent to fusion bonding is called co-curing. The difference between co-curing and fusion bonding is that in co-curing the parts are not fully cured and are simply cured simultaneously, relying on the heat associated with curing to lower the viscosity of the resins. With fusion bonding the parts can be fully cured and shaped but could then be melted and joined. Both co-curing and fusion bonding require the migration of molecules across the interface (or into the interphase) to achieve a good bond.

Several techniques are available to introduce the energy required to melt the surfaces – the types of fusion bonding are generally classified by these energy input methods. The most common of these heating methods are: infrared, dielectric/microwave, laser, resistance, induction, ultrasonic welding, friction, hot plate, and hot gas. In all of these methods, five basic steps are involved in establishing a good bond between the thermoplastic composite parts [7]:

(1) Surface preparation
(2) Heating or energy input
(3) Pressing
(4) Molecular diffusion
(5) Cooling

The most important consideration in surface preparation is the removal of surface contaminant. Residual grease, oils, and mold release from the laminating or molding process are the most common contaminants. These are most easily removed by using a solvent wipe. Careful analysis has shown that mold release, in particular, diffuses into the composite material during the molding operation and is not totally removed using a solvent wipe. However, in all but the most severe cases and most exacting bonding requirements, this small residue after the solvent wipe was unimportant in affecting the bond. In cases where extreme cleanliness is required, acid etches and ablution by cold (rf) plasma have proven to be successful. The plasma may also increase the number of active bonding sites on the surface and give increased adhesion by chemical bonding.

The pressing of the heated materials will suppress deconsolidation and will squeeze air out of the bonded area. This process is dominated by the squeezing flow mechanism and has been shown to follow a power viscosity law, although a complete description is quite complicated because of the varied geometries that can be encountered [8].

The diffusion of molecules need not involve large scale molecular movement in order to achieve a good bond. Instead, polymer segmental motion is sufficient. For semicrystalline resins diffusion and randomization take place almost instantaneously as compared to the time required for flow and wetting. On the other hand, for amorphous resins heated only slightly above the T_g, the diffusion process may be the rate limiting step in the bonding of thermoplastic composites [9].

During cooling, it is important that the pressure remain until the resin has sufficient strength and stiffness to suppress deconsolidation and warping. The cooling period is the time when semicrystalline polymers reform their crystal structure which is important for mechanical and chemical properties. As this may be a slow process, controlled cooling may be required to achieve optimum properties.

Each of the heating or energy input methods will be discussed in detail below but a general model of the heat-flow process has been developed which demonstrates the importance of boundary conditions and the mold heat transfer capability [10].

Infrared heating is the most basic of the heating methods and is also used to heat thermoplastic materials prior to being formed in thermoforming operations as discussed in Chapter 7. This method depends on the ability of the material to absorb radiation from the infrared source. While infrared is especially well suited to fusion bonding because it principally heats only the surface, the thin layer of heating depth and the large heated area lead to rapid heat loss and may make this method impractical for production operations.

Dielectric/microwave heating uses higher energy to heat the molecules than infrared. These higher energies are absorbed more deeply in the composite part, thus causing the entire structure to become heated. The heat retention is, therefore, superior to infrared. At some frequencies, carbon fiber-filled composites will become reflective rather than absorptive and the composite will not be heated by these methods.

Laser heating has the advantage that the heated area can be limited only to the bond zone. As with infrared, the laser penetration may be quite shallow and attempts to heat to a higher temperature or for a longer time may cause decomposition and warpage.

Resistance heating uses an electric current passing though a resistive element to generate the heat. As most composites are nonconductive (except for carbon fibers), a conductor that is compatible with the composite must be inserted in order to use resistance heating. Because of this limitation, resistance heating is typically limited to only carbon fiber reinforced composites. The carbon fibers will permit the material to be heated, but because the fibers are uniformly distributed in most composites, the heating will also be distributed and will extend beyond the bond zone. Of course, the carbon or other conductive fibers can be limited to only the desired bond zone (with other fibers used elsewhere), but this is generally not a practical solution.

Induction heating uses a magnetic field to generate eddy currents within a conductor which dissipates energy as heat due to internal electrical resistance of the material. As with resistance heating, this method requires that the composite material be conductive, or that a conductor be present to generate the eddy currents. Since most composites are not conductive (except for those filled with carbon fibers), the conductor must be placed into or along the composite. Induction heating has the disadvantage that large areas are heated, often extending beyond the desired bond zone. It has, however, given good bonding, even in production-like environments [11] and a model of the process has explained well the heating patterns noted [12].

Ultrasonic welding uses molecular vibrations induced by ultrasonic radiation to heat the sample. While these vibrations are generated widely, the radiation can be focused by two methods to limit the heated area. One method is to expose only the area near the bond zone. While this method can also be employed with some of the other heating systems, the instant-on/instant-off nature of the ultrasonic radiation and the ease of delivery of the ultrasonic signal through a small sending unit, makes ultrasonic especially suited to limiting the heated area. The second method that is used (usually in conjunction with the first) is to direct the energy to a specific portion of the part by a geometrical modification of the part, such as small points or ridges on the part in the bonding zone. Because of the small volume of these areas, the energy per unit volume is higher and hence these areas will melt sooner than surrounding areas. These small points or ridges are commonly called energy directors. This ability to focus the energy is advantageous when a small bond zone is needed but has proven to be difficult for large parts.

Because of its frequent use in nonreinforced thermoplastics and apparent applicability to joining thermoplastic composites, ultrasonic welding has been studied more extensively than the other heating methods. One study confirmed that neat resin energy directors allowed much larger joints to be formed and improved the quality of the bonds in PEEK/carbon fiber composite joints [13]. A designed experiment study of the welding variables indicated that bond strength increased with increasing time, pressure, and amplitude of the ultrasonic signal. Some of the parameters, especially amplitude and pressure, work together to improve bond strength.

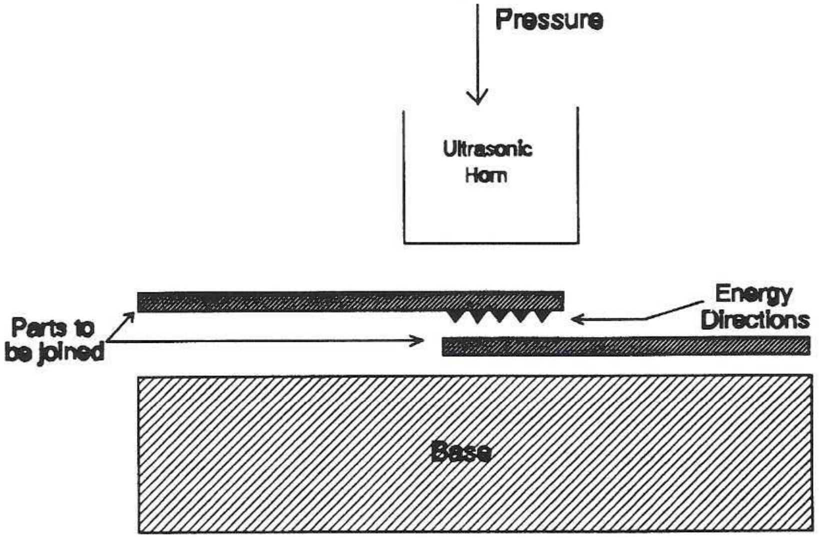

FIGURE 10.1. Ultrasonic welding system.

Another study reported that the strength of the ultrasonically welded bond is strongly dependent on total energy and peak power applied during processing. A technique to control the melt front propagation, especially with an effort to minimize sample thickness variations, involved initiating welding at the center of the bond zone rather than at an edge. This gives more evenly distributed pressure and may assist in pushing air out of the bond zone [14].

A third study created a model of the ultrasonic welding process and demonstrated that the melting of the neat resin energy director was a key to the bond strength. This model indicated that the energy director melted first and then formed a puddle of resin which solidified because of heat transfer to the surrounding area. Upon further heating, this puddle re-liquified and flowed, under pressure, to cover the surface of the adherend over the bond zone [15].

Friction or spin welding involves placing the two materials to be heated in contact and then rubbing them together until the friction from this operation heats the surfaces to melting. The parts are then aligned and clamped in place. The heating can be increased if the rubbing is done simultaneously with vibrational heating, such as with ultrasonics (but without energy directors). One major objection to the use of this method for composites is that the fibers can become misaligned during the rubbing motion. An advantage of this method is that the heating is very rapid and is localized to the bond zone.

Hot plate is simply placing a heated plate or tool in contact with the thermoplastic. This is the method most commonly used to tack thermoplastic sheets in place during hand layup operations. The size of part to be welded by this process is dependent upon the size of the plate. Some large automotive plates have been joined by this method [16]. Plates of corrosion-resistant metals (such as nickel) are commonly used in this method.

Hot gas involves the use of a jet of super-heated air or gas (such as nitrogen) that is directed onto the surface to be melted. Depending upon the equipment used, very high gas temperatures can be used which result in rapid heating of the composite part, but may also lead to polymer degradation.

With so many methods available for heating of thermoplastics and, therefore, potentially useful in fusion bonding, some comparative studies are useful. Studies have compared resistance welding, vibration welding, induction welding co-consolidation, and microwave welding with adhesive bonding and mechanical fastening for APC-2 (PEEK/graphite fiber) materials. Lap shear strengths were determined for the materials and are presented in Table 10.1 [17,18]. In another study of thermoplastic bonding, several of the methods in the other studies were used and some additional methods [19]. Several bonding methods have also been reported as successful with PPS composites [20]. While the comparisons are probably valid in general terms, exact comparisons between studies should not be made as the similarity of sample preparation and other testing conditions may not have been identical. A comparison of the studies seems to reinforce the conclusion drawn by Todd that there is not a "best" joining method and that each method will be useful.

TABLE 10.1 Lap Shear Strengths of Various Bonding Methods.

	Average Lap Strength (MPa)		
Material	Maguire Study	Todd Study	Silverman Study
Adhesive	15.75	30	17.4–41.6
Resistance	23.88	36	25.5
Vibration	39.29	7.7	–
Induction	welder failure	32	–
Mechanical (rivets)	failed prematurely	–	–
Co-consolidation	–	40	35.6*
Ultrasonic	–	38	15.1
Focused IR	–	–	32.0

*Used a thermoplastic film which was co-consolidated to the adherends.

MACHINING AND CUTTING

Although composites are often molded to a near-net shape (that is, an almost finished shape), trimming, finishing, and assembly into larger structures may be required, such as cargo doors on an aircraft. Therefore, the trimming, finishing, and assembly of composite materials is an important consideration. In some of these processes, the potential for damaging or otherwise weakening the composite (delamination, fiber fraying, drill break-through, etc.) is quite great and care must be taken to maintain the composites' properties.

The diversity of the components of a composite material causes some significant problems in machining and cutting. The fiber reinforcements are brittle, strong, abrasive materials with high melting points whereas the resin matrices are softer, more pliable and have much lower melting or softening temperatures. Ideally these would be cut with different cutting tools and cutting methods, but the materials are intermingled which dictates a constant shifting from one type of material to another in the course of cutting and machining which means that the cutting conditions and tools must be a compromise between the optimum for each of the materials.

The differences between cutting and machining thermoset and thermoplastic composites are almost indistinguishable in some materials but are pronounced in others. For instance, the high performance thermoplastics, with their high melting points, are similar in cutting and machining to high performance thermosets. On the other hand, machining of engineering thermoplastic composites is much different from thermosets because of their lower melting points. The cutting of the engineering thermoplastic composites is more closely related to cutting of filled engineering thermoplastics than to thermoset composites.

The most common methods used to cut and machine composites are mechanical, probably because of the widespread availability of metal cutting equipment. Conventional metalworking mills, lathes, circular saws, router cutters, and grinding machines have been used to cut composites with varying levels of success. In most cases the cutting conditions and cutting tools have been significantly altered from metal-cutting conditions. Some guidelines for cutting composites seem to apply across all the composites, while other conditions are specific for the resin, for the fiber, or for both.

In general, only sharp tools should be used, and the procedures should produce small chips rather than the large chips common to metal cutting. Therefore, compared to metal cutting, turning speeds should be high and feed rates, rake angle, and depth of cut should be low. A limitation on all of these parameters would be the softening of the matrix. Cutting fluids have been used successfully in some cases. In fact, some cutting fluids designed specifically for composites have been developed, although not yet extensively used. The cutting fluid should not, of course, have a solvent or crazing effect on the matrix. Because of the potential for delamination, the composite structure should be backed in any cut-off or drilling operation. In milling operations, both edges should be cut and then the center can be cut, rather than starting at one edge and working towards the opposite edge. By cutting the center last, the possibility of breaking off the last portion cut is reduced.

Drilling of composites is an important cutting operation, in part because of the continued widespread use of mechanical fasteners and because of the electronic circuit board industry where wires are placed through the composite circuit board. Conventional metal-drilling machines can be used, but the drills should be specifically tailored for composites. Drill bits should have a large positive rake angle without becoming so large that the cutting edge gets very thin and dulls quickly. (The rake angle is the angle between the tool face and vertical.) This large positive rake angle (which means that the tool face is slicing into the part) will allow the drill to penetrate into the material with less force and, therefore, avoid the heat which arises from shear forces and friction. The positive angle would tend to push the fibers aside, whereas a cutter with a smaller or neutral angle would tend to pack the fibers in front of the tool which would increase the cutting forces (and heat) required to cut. The resulting chips are small and granular (sawdust-like) and should not fuse together, which would be an indication of too high a feed rate or pressure. Therefore, drills with high helix angles and wide, polished flutes are recommended to facilitate chip lifting and removal. An air blast may also help chip removal and cooling. Peck drilling, where the tool is repeatedly advanced into the hole a preset amount and then retracted to remove chips and dissipate heat, has been very successful, especially when drilling sandwich materials.

When cutting composites, a pointed drill bit geometry can prevent delamination and fiber breakout because of the lower thrust forces on the exit of the hole. A drill bit design that has proven to be very successful for cutting carbon fiber and glass fiber reinforced composites is called a spade drill/countersink bit. The problem of cutting aramid fibers is more difficult than with carbon or glass. The aramid fibers are much tougher, thus having more elongation and resistance to cutting. With aramid, the fibers tend to shred rather than be cut. Research has found that, if the aramid fibers are preloaded (stretched) and then cut, cleanly cut fibers will result. For a rotating tool (such as a drill) this requirement dictates a C-shaped cutting edge that cuts from the outside toward the center. In this way the fibers are engaged by the tool at the edge of the hole, stretched, and then cut by the following part of the cutting edge. The tools must be kept sharp for adequate performance with these materials.

Carbide and, especially, polycrystalline diamond (PCD) inserts significantly increased drill cutter life compared to high-quality steel bits. PCD cutters often last many times as long as conventional cutters.

A study of milling of composites further emphasizes the advantage of PCD cutting tools over other types [21]. PCD cutters had approximately one-tenth as much wear as carbide cutters and almost one-half the surface roughness, with a helical flute design being far stronger than straight flutes. Wear was also less when cutting perpendicular to the fiber direction rather than parallel to the fibers. As expected, lower feed rate and lower width of cut also resulted in less tool wear, but surprisingly tool wear was not strongly sensitive to cutting speed.

The use of diamond cutters for band saws and grinding wheels has also proven to be successful in cutting composites. The diamond materials are embedded onto the cutting surfaces as would carbide cutting pieces. The greater abrasion resistance of the diamond, however, seems to be the key to its longer life.

Composites have also been successfully cut and machined by methods other than traditional metal-cutting methods. The most widely used of these nontraditional methods are water-jet cutting, laser cutting and electrical discharge machining (EDM). Water-jet cutting, in particular, is gaining support as a method to cut composite materials. This method utilizes a fine, high-pressure jet of water to impact and, therefore, cut or erode the material.

In this process, intensifier pumps increase the pressure of the filtered water to high levels (typically 400 MPa) which is then pumped at low volumes (4 to 8 l/min) through an orifice (0.25 mm diameter) and then onto the part to be cut. Abrasives can be added (usually after the primary jet is formed) to give additional cutting capability.

Water-jet cutting can be initiated at any point on the part, but because delamination is more likely at the initiation of the cutting, the normal procedure is to begin cutting at an edge or in an area away from the finished part and then move into the desired area. Delamination can be reduced by decreasing the cutting speed and increasing the water pressure. Water-jet machines can be numerically controlled and are capable of cutting complex patterns with a small kerf and with good repeatability.

Disadvantages to water-jet cutting are the high noise, danger of accidental hand damage from the jet, disposal or filtering requirements and high cost of the equipment. Otherwise, however, water-jet cutting has proven to be exceptional in its applicability to most composite materials, giving good quality cuts at speeds up to 20 m/min.

Lasers are another method of cutting composites that has been well accepted, especially for drilling printed circuit boards. The action of the laser is to melt or vaporize the material and thereby to cut through it. This can most readily be done with thin sections, especially when the thicker sections tend to puddle in the cutting area and need additional energy to vaporize them. This added energy can cause the surrounding area to be adversely affected by the heat, thus giving a sometimes undesirable edge effect. In a comparative study of water-jet cutting and laser cutting, the extent of the heat-affected zone was investigated by making cuts in very thin samples and tracking the loss of strength [22]. The critical width, within which the edge effects dominate, appeared to be in the region of 6 mm. No equivalent limit was noted for the water-jet cutting.

An advantage of laser cutting is a kerf that is even narrower and more accurate than that of water-jet cutting. Lasers are also good near part edges, especially because there is no pressure on the part and, therefore, no delamination. Aramid fibers are readily cut with lasers.

Electrical discharge machining (EDM) is a method of cutting conductive materials that has had good acceptance when metals must be cut very precisely or when the geometries are especially difficult. The requirement for conductivity has limited the use of EDM in composites, but where the composite material is sufficiently conductive (as in carbon fiber reinforced materials), EDM is an acceptable cutting method. Both plunge and wire EDM methods have been shown to be acceptable cutting methods, even when the conductive part is small. EDM cutting rates are 33 mm/hr for plunge cutting and up to 190 mm/hr for wire cutting which are somewhat slower than the other cutting methods. However, precision is very good and the heat-affected zone is small (approximately .02 – .07 mm) [23].

REPAIR

Damage represents a major problem for many composite applications because of the inherent randomness of the damage. Fatigue degradation can be anticipated by cyclic testing and then compensated for in design, but damage is so variable in both extent and timing that design compensation is impractical. Therefore, damage is handled on a case-by-case basis, usually according to the following steps: (1) find the damage, (2) define the extent of the damage, (3) calculate damage effect, (4) specify the repair method, (5) accomplish the repair, and (6) evaluate the repair [24]. Finding damage is usually either done visually or by nondestructive testing. The detection of manufacturing or hidden defects has proven to be largely unnecessary because of the excellent design and manufacturing quality that has been demonstrated. Therefore, visual inspection is not limited to inspection of the surfaces of the part to determine whether some in-use damage has occurred. Nondestructive inspection is used to detect fatigue and nonvisual defects and is done on a regular maintenance basis.

The extent of the damage can be determined with several nondestructive testing methods although ultrasonic testing, radiographic inspection, and tap hammers are the most common. The effect of the damage is calculated depending on the extent and the application. Rules for establishing the effect would be established for each application. These rules depend upon a consistent characterization of the damage. To assist in that characterization a pictorial classification system has been developed.

Three types of repair methods are commonly used: bolt on a patch, bond on a patch, or cut away damaged material and laminate new materials. The choice of repair method is also dependent on the application and suggested repair methods are often outlined by the manufacturer. Repair kits are often available to assist in making the repair. In this way patch size is limited by limiting the size of the patch included in the kit. Integrity of the repair is, therefore, controlled to some extent by the kitting concept. If the repair is to be a cured adhesive or a laminated section, portable curing systems are available which give computer controlled heatup and appropriate documentation for the repair cure. These systems use heating blankets or tape to cure the part.

The bolted patch was originated for aluminum aircraft and worked well because of its similarity to the overall construction method used in these aircraft. The problem with the use of a bolted patch with composite materials, even when the patch is made of composites, is that composites

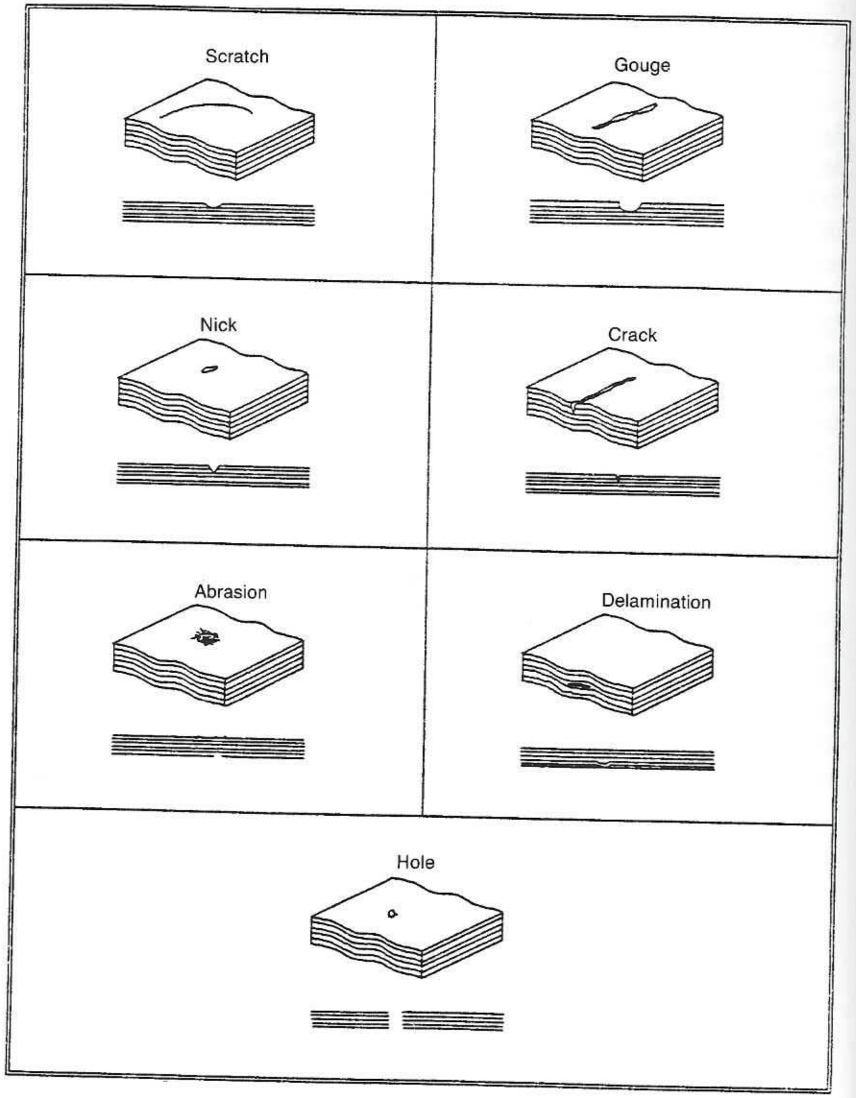

FIGURE 10.2. Damage types.

have poor mechanical properties as a result of the holes that must be drilled to put on the patch. Additional problems are the increased weight of the mechanical patch, the possibility of corrosion of the metal fasteners in the carbon-fiber composite, and the disruption of radar cross section in stealth aircraft.

Bonded patches eliminate some of the problems of bolted-on patches. No corrosion occurs and the radar cross section can be approximately maintained, but the weight is still increased. The mechanical properties are not improved by the addition of the bond because nothing is done about the area that has been damaged, it has simply been covered up, although reinforced with the patch. The repair method in which the damage is cut out and new layers of material added is the most time-consuming and difficult repair method but comes the closest to restoring the original properties.

Repair technology for composites has been principally developed in the aircraft industry for thermoset materials. However, the bolted patch and bonded patches work as well for thermoplastics as for thermosets. The cut-out repair method poses some problems for thermoplastics, but also presents some opportunities for improvement over the thermoset method. Because thermoplastics can be melted and reformed, the patch can be bonded in place, after the damage section has been removed, by melting both the patch and the surrounding material. This technique would utilize the fusion methods described previously. This thermoplastic method would have some advantages over the thermoset method. For instance, the repair may fuse with the surrounding material so well that matrix discontinuities would be negligible. Furthermore, surface preparation is generally less troublesome with the fusion repair. The repair may also be simpler to effect by simply pressing the repair section while heating to achieve consolidation rather than requiring the elaborate and sometimes difficult vacuum bagging needed for thermoset repairs.

Several studies have investigated the use of the thermoplastic joining methods for repair applications. In one study PPS, PAI, and PC reinforced with glass (30–40%) and PEEK and PPS reinforced with carbon (30%) were repaired by induction, adhesive bonding (using an epoxy adhesive), adhesive with heating by induction, adhesive bonding (using an epoxy adhesive), adhesive with heating by induction, ultrasonic welding, and inert gas welding [25]. Properties were reported to be acceptable and repair procedures fully compatible with the requirements for field repair. Another study which examined thermal fusion and ultrasonic welding of PPS and PC reported that thermal fusion is superior to ultrasonic because of the large surface area to be repaired in the test cases [26]. Breaking strengths of repaired samples were compared with the breaking strengths of non-damaged samples and shown to range from 0% (no bond) to 127% of the original strength. Tensile, shear and compression strengths were examined.

The best case was PC bonded to PC, with PPS to PPS next best and PC to PPS the worst. All bonds were single lap types. A third study noted that ultrasonic did not produce an acceptable patch using PEEK/graphite as the patch and the substructure, but that induction and resistance methods gave good repairs. The hot gas and infrared methods gave good patches but also caused distortion in the surrounding areas [27].

In a further study PEEK/carbon fiber laminates were impact damaged and then repaired using a thermal plate heating method. Tensile and flexural strength tests as well as ultrasonic and visual inspection revealed good property recovery and apparent internal crack healing. This healing is a property that is unique to thermoplastics and should be used effectively in making repairs [28].

ANNEALING

Because many thermoplastic resins are semicrystalline, especially those used for high performance applications, the control of the crystallinity of the resin is important for the optimization of mechanical and physical properties. This crystallinity can be affected by thermal treatments after the part has been shaped to its final form. These thermal treatments, usually called annealing, utilize the presence of the fibers to assist in nucleating the crystals and, therefore, can achieve even higher crystallinities than in the neat resins. This crystallinity can also be enhanced by slow cooling which allows time for the migration and orientation of the polymers into a crystalline form. Although many mechanical properties are improved by this crystallinity, the toughness of the composite is reduced. This reduction is because the amorphous matrix is tougher and it forces the crack to propagate closer to the fiber surface, thus reducing the bonding and subsequent strength of the composite [29].

CROSSLINKING

The overriding difference between thermosets and thermoplastics is that thermosets are crosslinked and thermoplastics are not. However, the crosslinking of thermoplastics after they have been finally formed is a well-known technique to improve some key physical and mechanical properties. For instance, insulation (plastic) wire and irrigation tubing are crosslinked to improve their resistance to environmental stress cracking. Crosslinking has also been shown to improve stability to ultraviolet radiation and therefore prolong useful life of thermoplastic tubing [30]. Similarly, large rotationally molded tanks and trash containers are crosslinked to prolong their useful life. Crosslinking is also the basis of the behavior of shrink tubing.

This crosslinking has been achieved by chemical methods (especially in rotationally molded parts) and by irradiation methods (for tubing and wire insulation). The most effective type of radiation has been shown to be accelerated electrons. The thermoplastic material is passed through a beam of electrons which have been accelerated by electrical or magnetic fields. The cost of these machines is quite high, but they have high throughput and accomplish a task not easily done by other methods.

In light of this extensive use of crosslinking for thermoplastics, electron beam crosslinking has been investigated for use in composites. Two applications have received study. One application is the use of electron beams to achieve crosslinking in thermosets. This is seen as an alternative to thermal activation of the crosslinking reactions, and has been shown to be more efficient than thermal cures in some cases [31,32]. The other application is the improvement of mechanical properties in traditional high performance thermoplastic composites (such as PPS or PEEK). Although the studies are preliminary and radiation conditions have not been optimized, statistically significant improvements in tensile strength and modulus have been demonstrated [33,34]. Another related study has examined the compressive strength and modulus, shear strength, and the flexural strength of electron irradiated thermoplastic composites and found similar improvements [35].

The basic properties of thermoplastics present some opportunities to form the parts and then develop additional property improvements or usefulness by postforming treatments. Some of these treatments are required for use, such as repair and joining, but can result in improved methods because of the thermoplastic capabilities. Other operations, such as annealing or crosslinking hold potential for improved properties and, therefore, increased use.

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CHAPTER 11

Design, Applications, and Costs

This chapter will review the following concepts:

- Design considerations
- Testing and quality assurance
- Applications for thermoplastic composites
- Costs

DESIGN CONCEPTS

The initial step in design of any product is to understand the requirements. Several systems have been developed to assist designers in this task. Some of these systems and concepts are Quality Function Deployment and the Expanded House of Quality, Total Quality Management, Value Engineering, Simultaneous Engineering, Design for Manufacturing, and Design for Assembly [1 – 9]. These systems are not independent but are different ways of attempting to meet the goal of achieving the best design possible within the parameters of manufacturing and customer needs.

For composites, the general requirements can be summarized as follows: cost, loads (static, fatigue, thermal, and structural resonance), environmental effects (service temperatures, moisture, fluid resistance, corrosion, lightning strike, and electromagnetic interference), service life, reliability, repairability/maintainability, and others which may exist for a particular application. Cost is usually such an important consideration that it will be discussed separately.

The design for loads is often the most critical of the design tasks. The first requirement to be able to design for loads is, of course, to define what the loads are likely to be. After the loads are defined, the design of the composite part can often be made using a laminate design program or, in the case of short fiber reinforced parts, a plastics design program. These programs may combine finite element analysis into the design process or may be based on more fundamental theory or may be empirical. Appropriate safety factors have been developed for several composite materials and for several applications to allow for the uncertainties in load environments. These analyses should also consider the "drivers," that is, the criteria that are the most important. In composites, the driver is often stiffness which must be satisfied within a permissible volume envelope. These constraints add complexity to the load analysis.

While composites are much more difficult than metals to design for loading, composites are also much more efficient because composites can be tailored to meet the specific loads that are expected. An approach that both simplifies the laminate calculations and adds insight to the process is to consider metal analogues of the composite parts. For instance, a composite laminate with a layup such as $(0/+45/-45/90)_s$ is structurally analogous to an I-beam in 0° loading and to other somewhat conventional metal shapes (like beams) when loaded in other directions [10]. This same article gives three rules of laminate design that improve the performance of composite structures. The rules are:

(1) Avoid a 0° or a 90° ply on the surface.
(2) Limit the change in angle between adjacent plies to no more than 60°.
(3) Limit the number of adjacent plies of the same orientation to 5 or 6.

Rule 1 results from Poisson's effect, which causes microcracking between the fibers. This is a particular problem when there is compression load in the fiber direction, transverse tension load, or bending. After repeated loading the surface ply will delaminate. Rule 2 is based on evidence that properties are reduced when adjacent plies are 90° apart in orientation. This is due to the high interlaminar stresses which are induced. Rule 3 is based on the interlaminar edge stresses which can induce cracking. It requires that we look at stresses induced in a laminate due to the strain compatibility between plies. Plies of different orientation will tend to cancel the edge effects in others. For instance, if a 0° ply is strained in the 0° direction, it will also have contraction in the 90° direction by Poisson's rule. However, if that ply is coupled to a 90°-oriented ply adjacent to it, the 90° strain would be constrained by the fibers in the 90°-oriented ply. Hence, the magnitudes of interlaminar normal stresses are dependent on the stacking sequence of the laminate and are lowest when plies of the same orientation are separated.

The design of joints remains a particular problem with composites but studies of composite joint design are now establishing rules that will vastly simplify the process in the future [11]. The many options available for joining thermoplastic composites (see Chapter 10), in particular, have given the designer more options in joint design than with thermoset composite materials.

The consideration of manufacturing process must also be made in designing for load. The many processes discussed in this book point out the ways that a composite can be made, but they also point out the diversity. The control of the fiber placement, however, remains one of the major criteria for choosing the manufacturing process. Other considerations associated with manufacturing are the tolerances, physical property constraints, costs, and uniquenesses because of the resin.

The resistance of the composite structure to environmental effects, the anticipated service life, and the reliability will probably be determined experimentally because of the complicated nature of these interactions on a particular part. However, past information on similar parts and current research may be very valuable in this area. Appropriate safety factors will often be added to allow for deterioration from use. The ability to repair and maintain the part is often neglected in the design, but is becoming more important for composites because of the critical applications that composites are now being put into. Part of the design process may include a maintenance program to ensure acceptable long-term performance of the part.

The designer may also be benefitted by getting the answers to the following questions:

- *What is the history of the product?* This will give insight into the rationale behind some of the design decisions that were made. The history can be gleaned from company sources (people and records), library references, trade magazines, and customers.
- *How would it be built if it were metal?* The object of this question is not to be able to duplicate the shape or design of metal, but to understand what competitive materials might be used and how they would compare. It may also be useful to understand which of the unique properties of a composite are being fully utilized, or if the part is simply a metal design that has been changed to a composite.
- *What are some related applications?* The answer to this question may give some ideas in borrowing design concepts that would work.
- *What research is being done in the application?* Composites are an active area of research and new concepts in design and materials are constantly being reported. In many cases the design problems are familiar to many groups and may have already been solved.
- *What are the biases of the customer?* These biases might be individual or corporate. Marketing people within the designer's company should be helpful in discovering the answer to this question.

The load design process must also include a selection of materials. The choice of fibers is the most important component in load design, but the resin is also important and is of primary importance in other properties such as environmental resistance, toughness, temperature resistance, and others as has been discussed in previous chapters. The materials chosen will also affect the processing method, often dictating the method to be used. It is not surprising, therefore, that thermoplastic composites have some design rules and considerations that are unique. A "scorecard" system of design can assist in selecting the optimal materials for a particular application. This type of system is common in plastics [12] and has also been applied to thermoplastic composites [13].

A composite design system that has been developed specifically for thermoplastic composites is called FOMMA (Fiber Orientation, Module, Monolith and Assembly) [14]. The fiber orientation concept is based on the efficient use of directional fibers, especially the noninterruption of the fiber path. The system also suggests that either the fibers converge into one or several fittings, lugs, etc., which carry a very highly concentrated load or that the fiber load be spread over the entire structure. The normal design method would be intermediate between those with fittings being placed in reinforced areas but not fully converged or diverged. The fibers should also be kept in straight lines, even in curved sections. This implies the use of geodesic angles in curved areas. The final fiber orientation concept is that fibers should be wrapped around rather than chopped off when they are terminated at the edge of a structure.

The modular concept suggests that the number of parts be reduced by molding parts together rather than by joining them into an assembly. The modular concept may require complicated or special tooling to be accomplished successfully. The monolithic concept is similar to the modular but approaches the concept from the manufacturing viewpoint, that is, every effort should be made to reduce the number of parts manufactured, even if the process needs to be radically changed. For thermoplastics, where postforming is possible, complex shapes can often be made more easily in this monolithic environment than with metal or thermoset parts. Whenever possible, assembly should be done by co-consolidation of the parts, that is heat and join them when they are consolidated. This gives higher strength and integrity than adhesive or mechanical joints.

The design of short fiber reinforced thermoplastic composites is difficult to generalize because the properties are so dependent upon the matrix properties (as opposed to the continuous fiber case where the properties are much more fiber dependent). Therefore, as a rule, short fiber reinforced material designs start with the design of the nonreinforced analog [15]. Some of the specific changes in part design that should be considered when using reinforcements include:

- *Part shrinkage*—This is inversely proportional to the amount of reinforcement and is also dependent on the anisotropy of the fibers, part thickness, mold design and location, mold temperature, melt temperature and various processing variables.
- *Dimensional tolerances*—Tolerances depend on the anisotropy of the material as it is a function of shrinkage. Stiffening by edge turning is preferable to stiffening by thickening as edge trimming preserves the uniform thickness of the part and, therefore, uniform cooling.
- *Warpage*—The restricted flow of fibers, especially around corners can cause warpage as shown in Figure 11.1. The problem is best solved by rounding corners, using "T" configurations, bracing with a box structure or injecting with a gate at the corner.
- *Draft/undercuts*—The low shrinkage of reinforced parts and their higher stiffness suggests that more draft should be designed into the part to facilitate ejection from the mold. Deep undercuts should be avoided since the stiffness makes part removal unfeasible.
- *Ribs/flanges/beads*—These are usually added to a part to increase stiffness without increasing wall thickness. They improve material flow and control warpage. For reinforced parts, provision should be made for stiffeners in the original design, but they should not be added until the part is actually made and their need confirmed.
- *Bosses/studs*—These are usually used to reinforce holes and to

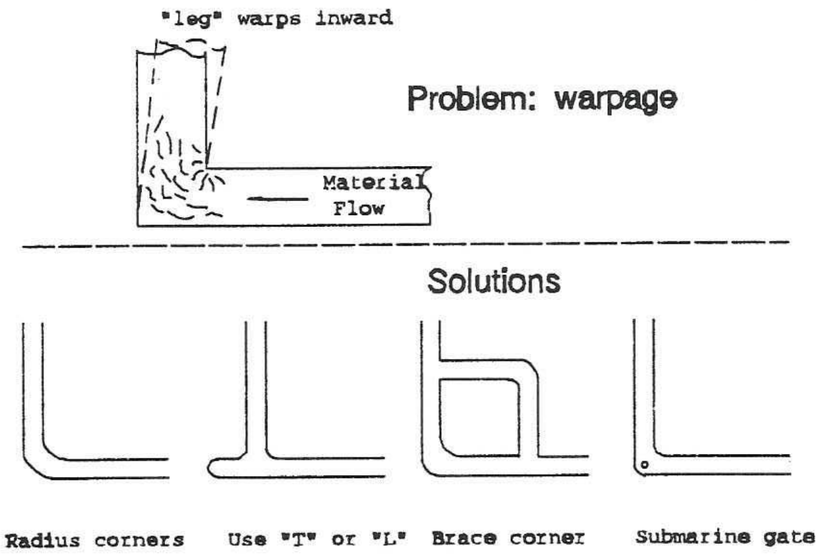

FIGURE 11.1. *Warpage in fiber reinforced parts.*

provide mounting locations. They should have rounded corners and large fillet radii to ensure good movement of the material.

- *Holes*—Generally, holes are closer to final tolerance because of the greater stiffness of the reinforced material. A chamfered opening to lead the screw into the hole is recommended.
- *Fillets/radii*—The higher rigidity of reinforced materials leads to notch-type impact susceptibility. Therefore, fillets should have large radii to eliminate stress concentrations.
- *Wall thickness*—This should be kept as uniform as possible with any variations gradually blended. Thin walls are permissible provided that the walls exceed the fiber length. Normal wall thicknesses would be 0.10 to 0.18 inches with minimums of 0.05 inches and maximums of 0.5 inches.
- *Weld/parting lines*—These are the result of the mating of the mold sections and should be placed to improve appearance and minimize finishing operations, within the restraints of mold opening and material flow restrictions. Weld lines should also be placed to avoid areas of high stress concentration.
- *Inserts*—These should be located perpendicularly to parting lines and secured so they will not be displaced during material flow under pressure. Knurled ends will increase the ability of the insert to be retained. All sharp corners should have a radius, including those on the knurl. Various minimum wall thickness requirements and pin thickness requirements should be observed, and these depend upon the type of resin to be molded.
- *Joint design*—The bonding area should carry the load equally, placing the major stresses in shear or tension to minimize cleavage and peel stresses.

TESTING AND QUALITY CONTROL

The importance of composites demands that unique, comprehensive quality methods be developed for their design, fabrication, testing, and evaluation. Their inherent anisotropy and nonhomogeneity create problems for many conventional design, production, and testing procedures; however, through the use of new and emerging techniques, these difficulties can be overcome. The most important tests for thermoplastic composites are generally the same tests used for thermosets. These tests would include tests associated with basic part properties to give information about design and use, and also tests concerned with quality control and process verification. The design/use tests could be either destructive (such as tensile, compression, and flexural) or nondestructive (such as ultrasonic, X-ray, or acoustic emission inspection). As much as possible, the preferred tests would be those defined and regulated by testing and standards societies such as the American Society for Testing and Materials (ASTM). When the standard test procedures are not appropriate, companies have developed their own tests (such as Boeing's compression after impact test). Descriptions of the most important tests are available in many texts and handbooks [16–18]. The uniformity of these test methods is one of their values because data from several sources can, at least in theory, be compared directly.

The properties which have been presented throughout this text and the many papers and books cited herein have chiefly been of the design/use variety. These tests focus on the characterization of the material for some intended application or design data.

Modern manufacturing is generally based on the statistical control of a process or, less ideally, the statistical evaluation of the products and must be anticipated in the design of the product, material selection, and the process. The statistics required for this control are generated by careful testing, inspection, and monitoring. The testing of composites for quality and process control is complicated by the application-specific nature of composite materials (which are tailored to meet specific needs) and the dependency of the properties on the microlevel nature of the ingredients and the processes by which they are formed. This high degree of dependency, a notable advantage, is also responsible for the unintentional wide variations that occur in material properties when input and process parameters are not optimally controlled. Suboptimal control in these areas can present many problems in controlling quality. For example, it is said that the material characteristics of components made from sheet molding compound (SMC) depend on nearly 150 material and process variables [19].

The control of a manufacturing process depends on the recognition of the variables which determine product quality and then the control of those variables within acceptable limits. The process suggested by Ishikawa which produces a chart of the likely variables, known as the cause and effect diagram or the fish-bone diagram, has proven to be an excellent tool [20]. The importance of these causes (variables) can be determined by using a factorial designed experiment or Taguchi method which examines the effects of the variables singly and in combination [21,22]. After the most sensitive variables in controlling the process are defined, which includes an examination of the process itself to insure that it is operating in control (that is, the only variations in the process are random), a scheme to control the important variables within certain acceptable ranges can be devised and implemented. The control of the process is done by monitoring the key variables and changing the points at which they are controlled so as to keep them within the acceptable limits. When this is done, the process remains in control and good quality parts are made. This entire process is called statistical process control (SPC). The process just described has been applied to filament winding, one of the most important composite manufacturing processes, and the key process variables and their interactions identified [23].

The role of product testing under SPC is to verify that the variable ranges and other conditions are behaving as expected. The product testing is also to establish a baseline against which improvements in quality can be measured and to ensure that some variable which was overlooked or whose relationship to the process was inadequately known, does not cause the process to deviate from acceptable product conditions.

When SPC has not been implemented, the role of testing is to intercept and eliminate poor quality products by actual testing of the product against standards. Therefore, whether SPC is operational or not, the product must still be inspected. It is desirable that the product not be destroyed in the inspection process. Therefore, nondestructive testing (NDT) is used whenever possible. Some of the important NDT methods for composite parts are described in Table 11.1 [24].

Although most performance and quality testing of thermoplastic composites is the same as for thermosets, some unique considerations should be given to these tests because of the differences in the two materials. For instance, the wet-out of fibers is especially difficult with thermoplastics and should, therefore, be examined closely to insure good quality parts. The processing parameters are dependent, to some extent, upon the wet-out and so the early determination of the wet-out is needed to set proper processing conditions. Several high performance thermoplastic composites have been studied to determine the quality of the products based upon postimpregnated fiber wet-out, fiber orientation, and fiber type. Fiber wet-out was seen to be the most critical parameter for achieving good parts [25].

TABLE 11.1 Nondestructive Testing Methods.

Anomalies Detected	Test Method
Adhesive bonding Fiber orientation	Acousto-ultrasonics Low frequency ultrasonics
Voids Porosity Fiber wet-out Fiber flow lines Fiber knit lines Fiber orientation Delamination Resin richness	Ultrasonic pulse echo Ultrasonic through-transmission X-radiography X-ray, real time
Metal/conductive coating thickness	Eddy current (high frequency) Beta backscatter
Surface pits, cracks	Dye penetrant
Waviness Surface discontinuities	Profilometer/light reflection
Resin cure	Infrared/thermography
Component damage development Delamination due to fatigue Fatigue damage	Infrared/thermography Vibrothermography Acoustic emission

Used by permission. P. K. Mallick and S. Newman, eds. 1990. "Quality Systems for Automotive Plastics," in *Composite Materials Technology.* Munich: Carl Hanser Verlag.

APPLICATIONS FOR THERMOPLASTIC COMPOSITES

Certainly the number of applications for short fiber reinforced thermoplastic composites dwarfs not only all other types of thermoplastic composite parts but all composite parts. These products, which are usually injection molded or extruded, have been readily accepted as a tough, strong, or high temperature grade of conventional plastics. In many cases the reinforcement can be used to increase the properties of a low-cost resin such that a high-cost resin is not needed. In other cases, the reinforcement in a high-cost resin allows the plastic to compete against an even higher priced metal, or to meet the requirements of a metal at a much lower weight.

The applications of short fiber thermoplastics are too numerous to list, but some typical examples from several different markets illustrate the diversity of current applications and are given in Table 11.2.

The growth of long fiber thermoplastic composites in some of these same markets reflects the growing interest in composites, especially thermoplastics, in nonaerospace applications. Perhaps the application with the greatest potential is automotive body panels. These panels, chiefly made of glass reinforced polypropylene have demonstrated excellent properties with some important advantages over metal. The panels are made by thermoforming techniques and so processing costs are low. Bumpers and bumper fascia are another application that has the promise of large volumes and improved mechanical properties over metals. Drive shafts and leaf springs are also important automotive applications that are well suited to composites, both thermoset and thermoplastics, although thermoplastics have some important advantages. Other long fiber thermoplastic applications in automobiles include seat frames, bumper beams, battery trays, load floors, front-end structures, head lamp retainers, rocker panels, valve covers, spare tire covers, and under-engine covers [26].

The high performance required of most aerospace parts generally dictates the use of continuous fibers in composite parts. The relative newness of thermoplastics and the need to certify all materials for each application have

TABLE 11.2 Short Fiber Thermoplastic Applications [27].

Market	Application
Automotive	Rear end panel Valve stem oil seats Carburetor spacer plates Ignition coil bobbins Breaker plate control arm Transmission thrust washers Camper tops Camper holding tank Battery cases Battery clamp Trailer brake housing Instrument panels Window louvers Lamp housings Finder liners Windshield washer tank Gas caps Fuel pumps Fuel vapor separators Distributor cap Gear shift consoles Torque-converter cover Quarter window latch Alternator rectifier assembly Air cleaner tray Radiator fan shroud Air vent control housing Lamp housing Steering gear selector Windshield washer motor Handle turn signal
Construction/industrial	Block and tackle Septic tanks Tie rods for concrete form Pallets Luggage Bus and aircraft luggage racks Pruning shears handle Wristwatch back plate Mop head Water softener valve Gears Bearings Safety razor

TABLE 11.2 (continued).

Market	Application
Appliances	Electric drill handle Water meter housing Centrifugal pump Electric knife handle Humidifiers, air conditioner housings Office copier housing Valve automatic washer
Electrical-electronic	Fluorescent light fixture Electric connectors Coil bobbins Motor brush holders Timer parts Coaxial switch mounting panel Speed sensing switches Gears for timer Electrical fuel pump housing
Recreational	Little league baseball bat Canoe Paddle tennis racquet Motion picture projector housing Microphone stand Tape recorder housing Fishing rod

delayed the use of thermoplastics. The principal applications have been where thermosets could perform just as well. However, as more thermoplastic parts are certified and the aircraft designers gain knowledge of their performance, the number of applications employing thermoplastics will undoubtedly increase, especially for applications where thermoplastic properties are superior, such as toughness [28].

Selected aerospace parts, usually nonstructural, are being investigated as potential uses for short fiber thermoplastic composites. The major driving force in these applications is cost versus traditional metals or thermosets. An example of this replacement is aerosurface components on subsonic missiles. The thermoplastic design would eliminate costly labor-intensive assembly and processing operations such as machining for finished metal components and compression molding or hand layup and autoclave cure for thermoset components [29].

Other applications for fiber reinforced thermoplastics include the leisure and sporting goods industry. Some of the products include camera housings, tennis and racquetball racquets, fishing reel frames and brackets, baseball bats, trigger housings, practice bullets, gun stocks, rifle scope bodies, magazine clips, and magazine clip followers. The musical instrument industry has replaced wooden drumsticks with glass and carbon fiber reinforced nylon composites. Fiber reinforced nylon is also used in bicycle toe clips, pedals, and water bottle cages. Arrows, golf club shafts, golf club heads, ski pole handles, ski locks, ski boat and model airplane propellers, toy train parts, attaché cases, and skateboard decks illustrate the diversity of applications now being implemented or considered [30]. Several medical applications, including hip joint replacements are also being investigated.

COSTS

For short fiber thermoplastic composites, the cost factors are well known. These materials have been used extensively for many years and have demonstrated their cost effectiveness, generally as substitute materials for metals or more expensive, nonreinforced resins. Part designs for short fiber reinforced thermoplastics are similar to those for nonreinforced parts, as are processing costs. Some economic advantages are available when reinforced materials are used because of the possibility of shorter cycle times because the parts can be thinner and the reinforcement makes the part stiffer, thus allowing the part to be ejected from the mold at a higher temperature (earlier time). But these processing and material cost advantages are small except when compared with metals, nonreinforced thermoset and more expensive thermoplastic resins.

The economic factors associated with the manufacture of continuous fiber thermoplastic composites parts are much more complex and reach far beyond a simple analysis of materials costs. This is especially true because the high performance thermoplastics are priced at development levels and do not reflect the long-term expected values. Industrial experience indicates that in a mature manufacturing process, the manufacturing costs are 1.5 to 2.5 times the raw material costs. Thus, factors can be allocated, admittedly in a fairly arbitrary way, to demonstrate process costs. Based on these simple approximations, there is no intrinsic reason why high performance thermoplastic resins should be more expensive than thermosets in the long run, once economies of scale have been achieved [31]. In another study, however, the costs of prepregging thermoplastic materials are estimated to be 1.8 to 3 times more expensive than thermoset prepreg materials [32]. In spite of these higher material costs, however, the part costs are estimated to be 40% below the thermoset part cost for the melt and solvent prepreg processes and 20% below or equal to the thermoset part cost, respectively, for the powder or commingling process. Furthermore, the use of a formable sheet is seen to give only minimal advantage for a very simple part but a significant cost advantage for more complex shapes.

A more detailed economic model has been developed for the manufacturing costs of thermoplastic composites [33]. Several raw materials were considered in the model ranging in cost from woven thermoset fabric (the baseline comparison material) to thermoplastic preconsolidated flat sheet, which is over seven times more expensive on a weight basis. For simplicity the model assumes that a single-curvature composite skin part is to be made. A large number of manufacturing processes were evaluated ranging in complexity from the simple press forming of the preconsolidated sheet to the multistep hand layup, vacuum bagging and autoclave-curing process. Because the allocation of overhead costs can have a great impact on the validity of the model analyses, the individual factors making up the overhead costs were separately identified and costed as far as possible.

One analysis quantifies the cost of using an autoclave to consolidate the part. The use of an autoclave was found to increase the cost of the part significantly (about 30%). Over 68% of these increased costs originate from the high tool costs, with another 21% of autoclave costs from the costs associated with bagging. However, even with lower tooling costs (as would be obtained with metal or nickel-plated molds), the autoclave process was the most expensive.

The model was also used to investigate the tradeoff between the cost of raw materials and the labor costs associated with the use of a particular material form. In general, the lower cost material forms, such as unidirectional tape, require more labor to make the final part than would a preconsolidated flat sheet. This analysis showed that the lower labor cost processes resulted in the lowest overall cost. However, if automation is added to the analysis, the lower cost materials could easily become the most cost effective.

The overall conclusions of the model study indicate that the most expensive process is the use of unidirectional tape, hand cut, autoclave consolidated with bagging. The lowest cost process was automated layup of unidirectional tape with press consolidation. The baseline thermoset process was about midway in cost between the thermoplastic processes.

Other studies have looked at separate portions of the costs picture. Design and assembly are important but savings in these areas are difficult to quantify. It is believed that the higher fracture toughness of thermoplastics should allow material and weight savings (demonstrated to be 6%) if they are applied to structures that have previously been designed and meet a damage tolerance standard. The design allowable improvements in areas such as open-hole compression/tension and fatigue could have similar results. Unique thermoplastic bonding capabilities could also bring significant savings [34].

An analysis of the economics of continuous fiber thermoplastics in the automotive industry illustrates that several composite manufacturing methods such as layup, filament winding, pultrusion, RTM, RIM, and SMC compression molding can compete with proper automation and product integration (unitization) [35].

SUMMARY

The potential for continuous fiber thermoplastic composites to expand into aerospace, automotive, and other large markets appears to be clearly defined. The manufacturing methods to accomplish these product introductions have been demonstrated, although not optimized. The raw materials are in reasonably convenient forms, but expensive as yet because of low volumes. Other thermoplastic composite materials (short fibers) have been well accepted in the marketplace. It seems the only factor left to complete the picture is time.

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