1

Introduction

1.1 Basic Definitions

Just what is a "composite material?" A casual definition might be: "a composite material is one in which two (or more) materials are bonded together to form a third material." Although not incorrect, upon further reflection it becomes clear that this definition is far too broad, since it implies that essentially *all* materials can be considered to be a "composite." For example, the (nominal) composition of the 2024 aluminum alloy is 93.5% Al, 4.4% Cu, 0.6% Mn, and 1.5% Mg [1]. Hence, according to the broad definition stated above, this common aluminum alloy could be considered to be a "composite," since it consists of four materials (aluminum, copper, manganese, and magnesium) bonded together at the atomic level to form the 2024 alloy. In a similar sense, virtually all metal alloys, polymers, and ceramics satisfy this broad definition of a composite, since all of these materials contain more than one type of elemental atom.

An important characteristic that is missing in the initial broad definition is a consideration of physical scale. Another definition of a "composite material," which includes a reference to a physical scale and is appropriate for present purposes, is as follows.

A composite material is a material *system* consisting of two (or more) materials which are distinct at a physical scale greater than about 1×10^{-6} m (1 µm), and which are bonded together at the atomic and/or molecular levels.

As a point of reference, the diameter of a human hair ranges from about 30 to $60 \,\mu\text{m}$. Objects of this size are easily seen with the aid of an optical microscope. Hence, when composite materials are viewed under an optical microscope the distinct constituent materials (or distinct material phases) that form the composite are easily distinguished.

Structural composites typically consist of a high strength, high stiffness *reinforcing material*, embedded within a relatively low strength, low stiffness *matrix material*. Ideally, the reinforcing and matrix materials interact to produce a composite whose properties are superior to either of the two constituent materials alone. Many naturally occurring materials can be viewed as composites. A good example is wood and laminated wood products.

Wood is a natural composite, with a readily apparent grain structure. Grains are formed by long parallel strands of reinforcing cellulose fibers, bonded together by a glue-like matrix material called lignin. Since cellulose fibers have a substantially higher stiffness and strength than lignin, wood exhibits higher stiffness and strength parallel to the grain than transverse to the grains. In *laminated* wood products (which range from the large laminated beams used in a church cathedral to a common sheet of plywood) relatively thin layers of wood are adhesively bonded together. The individual layers are called "plies," and are arranged such that the grain direction varies from one layer to the next. Thus, *laminated* wood products have high stiffness/ strength in more than one direction.

Although composites have been used in a variety of structural applications for centuries, modern (or advanced) composites are a relatively recent development, having been in existence for about 70 years. Modern composites may be classified according to the size or shape of the reinforcing material used. Four common classifications of reinforcements are

- *Particulates,* which are roughly spherical particles with diameters typically ranging from about 1 to 100 μm
- Whiskers, with lengths less than about 10 mm
- Short (or chopped) fibers, with a length ranging from about 10 to 200 mm
- Continuous fibers, whose length are, in effect, infinite

Whiskers, short fibers, and continuous fibers all have very small diameters relative to their length; the diameter of these products range from about 5 to $200 \,\mu$ m.

Distinctly different types of advanced composites can be produced using any of the above reinforcements. For example, three types of composites based on continuous fibers are shown in Figure 1.1: *unidirectional* composites, *woven* composites, and *braided* composites. In a unidirectional composite all fibers are aligned in the same direction and embedded within a matrix material. In contrast, woven composites are formed by first weaving continuous fibers into a fabric and then embedding the fabric in a matrix. Hence, a single layer of a woven composite contains fibers in two orthogonal directions. In contrast, a single layer in a braided composite typically contains two or three nonorthogonal fiber directions. Braided composites are then formed by embedding the fabric in a matrix. Additional discussion of these types of composites is provided in Section 1.4.

As implied in Figure 1.1, composite products based on continuous fibers are usually produced in the form of thin layers. A single layer of these products is called a *lamina* or *ply*, following the nomenclature used with laminated wood products. The thickness of a single ply formed using unidirectional fibers ranges from about 0.12 to 0.20 mm (0.005–0.008 in.), whereas the thickness of a single ply of a woven or braided fabric ranges from about 0.25 to 0.40 mm



FIGURE 1.1

Different types of composites based on continuous fibers. (a) A single layer (or "ply") of a unidirectional composite; (b) a single layer (or "ply") of a woven fabric composite; (c) a single layer (or "ply") of a braided fabric composite.

(0.010–0.16 in.). Obviously, a single composite ply is quite thin. To produce a composite structure with a significant thickness many plies are stacked together to form a composite *laminate*. Conceptually any number of plies may be used in the laminate, but in practice the number of plies usually ranges from about 10 plies to (in unusual cases) perhaps as many as 200 plies. The fiber represents the reinforcing material in these composites. Hence, the orientation of the fibers is (in general) varied from one ply to the next, so as to provide high stiffness and strength in more than one direction (as is the case in plywood). It is also possible to use a combination of unidirectional, woven, and/or braided plies within the same laminate. For example, it is common to use a woven or braided fabric as the two outermost *facesheets* of a laminate, and to use unidirectional plies at interior positions.

In all composites the reinforcement is embedded within a matrix material. The matrix may be polymeric, metallic, or ceramic. In fact, composite materials are often classified on the basis of the matrix material used, rather than the reinforcing material. That is, modern composites can be categorized into three main types: polymer–matrix, metal–matrix, or ceramic–matrix composite materials. Usually, the reinforcing material governs the stiffness and strength of a composite. In contrast, the matrix material usually governs the thermal stability. Polymeric–matrix composites are used in applications involving relatively modest temperatures (service temperatures of 200°C or less, say). Metal–matrix composites are used at temperatures up to about 700°C, while ceramic–matrix composites are used at ultra-high temperatures (up to about 1200°C or greater). The matrix also defines several additional characteristics of the composite material system. Some additional roles of the matrix are

- To provide the physical form of the composite
- To bind the fibers together
- To protect the fibers from aggressive (chemical) environments, or mechanical damage (e.g., due to abrasion)
- To transfer and redistribute stresses between fibers, between plies, and in areas of discontinuities in load or geometry

To summarize the preceding discussion, there are many types of composite materials, both natural and man-made. Composites can be classified according to the physical form of the reinforcing material (particulate, whisker, short fiber, or continuous fiber reinforcement), by the type of matrix material used (metal, ceramic, or polymeric matrix), by the orientation of the reinforcement (unidirectional, woven, or braided), or by some combination thereof. The temperature the composite material/structure will experience in service often dictates the type of composite used in a given application.

The primary focus of this textbook is the structural analysis of *polymeric* composite materials and structures. Metal- and ceramic-matrix composites will not be further discussed, although many of the analysis methods developed herein may be applied to these types of composites as well. Since our focus is the structural analysis of polymeric composites, we will not be greatly considered with the behavior of the individual *constituent* materials. That is, we will not be greatly concerned with the behavior of an unreinforced polymer, nor with the behavior of an individual reinforcing fiber. Instead, we will be concerned with the behavior of the composite formed by combining these two constituents. Nevertheless, a structural engineer who wishes to use polymeric composites effectively in practice must understand at least the rudiments of polymer and fiber science, in much the same way as an engineer working with metal alloys must understand at least the rudiments of metallurgy. Towards that end a brief introduction to polymeric and fibrous materials is provided in the following two sections, respectively. At minimum, the reader should become acquainted with the terminology used to describe polymeric and fibrous materials, since such terms have naturally been carried over to the polymeric composites technical community.

1.2 Polymeric Materials

A brief introduction to polymeric materials is provided in this section. This introduction is necessarily incomplete. The reader interested in a more detailed discussion is referred to the many available texts and/or web-based resources devoted to modern polymers (see, e.g., [2–5]).

1.2.1 Basic Concepts

The term "polymer" comes from the Greek words *poly* (meaning many) and *mers* (meaning units). Quite literally, a polymer consists of "many units." Polymer molecules are made up of thousands of repeating chemical units, and have molecular weights ranging from about 10³ to 10⁷.

As an illustrative example, consider the single chemical mer shown in Figure 1.2. This mer is called *ethylene* (or *ethene*), and consists of two carbon atoms and four hydrogen atoms. The two lines between the carbon (C) atoms indicate a double covalent bond,* whereas the single line between the hydrogen (H) and carbon atoms represents a single covalent bond. The chemical composition of the ethylene mer is sometimes written C_2H_4 or $CH_2=CH_2$.

Under the proper conditions the double covalent bond between the two carbon atoms can be converted to a single covalent bond, which allows each of the two carbon atoms to form a new covalent bond with a suitable neighboring atom. A suitable neighboring atom would be a carbon atom in a neighboring ethylene mer, for example. If "*n*" ethylene mers join together in this way, the chemical composition of the resulting molecule can be represented as $C_{2n}H_{4n}$, where *n* is any positive integer. Hence, a "chain" of ethylene mers join together to form the well-known polymer *polyethylene* (literally, many ethylenes), as shown in Figure 1.3. The process of causing a monomer to chemically react and form a long molecule in this fashion is called *polymerization*.

The single ethylene unit is an example of a *monomer* (one mer). At room temperature a bulk sample of the ethylene monomer is a low-viscosity fluid.

FIGURE 1.2 The monomer "ethylene."

^{*} As fully described in any introductory chemistry text, a "covalent bond" is formed when two atoms share an electron pair, so as to fill an incompletely filled valence level.



FIGURE 1.3 The polymer "polyethylene."

If two ethylene monomers bond together the resulting chemical entity has two repeating units and is called a *dimer*. Similarly, the chemical entity formed by three repeating units is called a *trimer*. The molecular weight of a dimer is twice that of the monomer, the molecular weight of a trimer is three times that of the monomer, etc. Prior to polymerization, most polymeric materials exist as relatively low-viscosity fluids known as *oligomers* (a few mers). The individual molecules within an oligomer possess a range of molecular weights, typically containing perhaps 2–20 mers.

It should be clear from the above discussion that a specific molecular weight cannot be assigned to a polymer. Rather, the molecules within a bulk sample of a polymer are of differing lengths and hence exhibit a range in molecular weight. The *average molecular weight* of a bulk sample of a polymer is increased as the polymerization process is initiated and progresses. Another measure of the "size" of the polymeric molecule is the *degree of polymerization*, defined as the ratio of the average molecular weight of the polymer molecule divided by the molecular weight of the repeating chemical unit within the molecular chain.

The average molecular weight of a polymeric sample (or, equivalently, the degree of polymerization) depends on the conditions under which it was polymerized. Now, virtually *all* physical properties exhibited by a polymer (e.g., strength, stiffness, density, thermal expansion coefficient, etc.) are dictated by the average molecular weight. Therefore, a fundamental point that must be appreciated by the structural engineer is that the properties exhibited by any polymer (or any polymeric composite) *depend on the circumstances under which it was polymerized*.

As a general rule, the volume of a bulk sample of a monomer decreases during polymerization. That is, the bulk sample shrinks as the polymerization process proceeds. This may have serious ramifications if the polymer is to be used in structural applications. For example, if a fiber(s) is embedded within the sample during the polymerization process (as is the case for most fiber-reinforced polymeric composite systems), then shrinkage of the matrix causes residual stresses to develop during polymerization. This effect contributes to the so-called *cure stresses*, which are present in most polymeric composites. As will be seen in later chapters, cure stresses arise from two primary sources. The first is shrinkage of the matrix during

Introduction

polymerization, as just described. The second is stresses that arise due to temperature effects. In many cases the composite is polymerized at an elevated temperature (175°C, say), and then cooled to room temperature (20°C). The thermal expansion coefficient of the matrix is typically much higher than the fibers, so during cooldown the matrix is placed in tension while the fiber is placed in compression. Cure stresses due to shrinkage during cure and/or temperature effects can be quite high relative to the strength of the polymer itself, and ultimately contribute towards failure of the composite.

1.2.2 Addition versus Condensation Polymers

Although in the case of polyethylene the repeat unit is equivalent to the original ethylene monomer, this is not always the case. In fact, in many instances the repeat unit is derived from two (or more) monomers. A typical example is Nylon 6,6. The polymerization process for this polymer is shown schematically in Figure 1.4. Two monomers are used to produce Nylon 6,6: hexamethylene diamine (chemical composition: $C_6H_{16}N_2$) and adipic acid (chemical composition: $CO_2H(CH_2)_4CO_2H$). Note that the repeat unit of Nylon 6,6 (hexamethylene adipamide) is not equivalent to either of the two original monomers.

A low-molecular weight byproduct (i.e., H_2O) is produced during the polymerization of Nylon 6,6. This is characteristic of *condensation polymers*.



FIGURE 1.4 Polymerization of Nylon 6,6.

That is, if both a high-molecular weight polymer as well as a low-molecular weight byproduct is formed during the polymerization process, the polymer is classified as a condensation polymer. Conversely, *addition polymers* are those for which no byproduct is formed, which implies that all atoms present in the original monomer(s) occur somewhere within the repeat unit. Generally speaking, condensation polymers shrink to a greater extent during the polymerization process than do addition polymers. Residual stresses caused by shrinkage during polymerization are often a concern in structural composites, and hence difficulties with residual stresses can often be minimized if an addition polymer is used in these applications.

1.2.3 Molecular Structure

The molecular structure of a fully polymerized polymer can be roughly grouped into one of three major types: *linear, branched,* or *crosslinked* polymers. The three types of molecular structure are shown schematically in Figure 1.5.

A single molecule of a *linear polymer* can be visualized as beads on a string, where each bead represents a repeat unit. It should be emphasized that the length of these "strings" is enormous; if a typical linear molecule were scaled up so as to be 10 mm in diameter, it would be roughly 4 km long. In a bulk sample these long *macromolecules* become entangled and twisted together, much like a bowl of cooked spaghetti. Obviously, as the average molecular weight (i.e., the average length) of the polymer molecule is increased, the number of entanglements is increased.

As already discussed, the atoms in repeat units are bonded together by strong covalent bonds. In a similar way, neighboring molecules are bonded together by so-called secondary bond forces (also called van der Waals forces). The magnitude of secondary bond forces increase as the average molecular weight is increased. Therefore, at the macroscopic scale the stiffness and strength exhibited by a bulk polymer is directly related to its molecular weight and number of entanglements.

If all of the repeat units within a linear polymer are identical, the polymer is called as a *homopolymer*. Polyethylene is a good example of a linear homopolymer. However, it is possible to produce linear polymers that consist of two separate and distinct repeat units. Such materials are called *copolymers*. In *linear random copolymers* the two distinct repeat units appear randomly along the backbone of the molecule. In contrast, for *linear block copolymers*, the two distinct repeat units form long continuous segments within the polymer chain. A good example of a common copolymer is acrylonitrile-butadiene-styrene, commonly known as "ABS."

The second major type of polymeric molecular structure is the *branched polymer* (see Figure 1.5). In branched polymers relatively short side chains are covalently bonded to the primary backbone of the macromolecule. As before, the stiffness of a bulk sample of a branched polymer is related to



FIGURE 1.5

Types of polymer molecular structure. (a) Linear; (b) branched; (c) crosslinked.

secondary bond forces and the number of entanglements between molecules. Since the branches greatly increase the number of entanglements, the macroscopic stiffness of a branched polymer will, in general, be greater than the macroscopic stiffness of a linear polymer of similar average molecular weight. In many branched polymers the branches consist of the same chemical repeat unit as the backbone of the molecular chain. However, in some cases the branch may have a distinctly different chemical repeat unit than the main backbone of the molecule. Such materials are called *graft copolymers*.

Finally, the third major type of molecular structure is the *crosslinked or network polymer* (see Figure 1.5). During polymerization of such polymers a *crosslink* (i.e., a covalent bond) is formed between individual molecular chains. Hence, once polymerization (i.e., crosslinking) is complete a vast

9

molecular network is formed. In the limit, a single molecule can no longer be identified. A bulk sample of a highly crosslinked polymer may be thought of as a single molecule.

Returning to the analogy of cooked spaghetti, one can imagine that a single spaghetti noodle could be extracted without damage from the bowl if the noodle were pulled slowly and carefully, allowing the noodle to "slide" past its' neighbors. In much the same way, an individual molecule could also be extracted (at least conceptually) from a bulk sample of a linear or branched polymer. This is not the case for a fully polymerized crosslinked polymer, however. Since the "individual" molecular chains within a crosslinked polymer are themselves linked together by covalent bonds, the entire molecular network can be considered to be a single molecule. Although regions of the chain in a crosslinked polymer may slide past each other, eventually relative motion between segments is limited by the crosslinks between segments.

1.2.4 Thermoplastic versus Thermoset Polymers

Suppose a bulk sample of a linear or branched polymer exists as a solid material at room temperature, and is subsequently heated. Owing to the increase in thermal energy, the average distance between individual molecular chains is increased as temperature is increased. This results in an increase in molecular mobility and a decrease in macroscopic stiffness. That is, as molecules move apart both secondary bond forces as well as the degree of entanglement decrease, resulting in a decrease in stiffness at the macroscopic level. Eventually a temperature is reached at which secondary bond forces are negligible. This allows the polymer molecules to slide freely past each other and the polymer "melts." Typically, melting does not occur at a single temperature, but rather over a temperature range of about 15–20°C.

A polymer that can be melted (i.e., a linear or branched polymer) is called a *thermoplastic polymer*. In contrast, a crosslinked polymer cannot be melted and is called a *thermoset polymer*. If a crosslinked polymer is heated it will exhibit a decrease in stiffness at the macroscopic structural level, since the average distance between individual segments of the molecular network is increased as temperature is increased. The crosslinks do not allow indefinite relative motion between segments, however, and eventually limit molecular motion. Therefore, a crosslinked polymer will not melt.

Of course, if the temperature increase is excessive then the covalent bonds which form both the backbone of the molecule as well as any crosslinks are broken and chemical degradation occurs. That is, both thermoplastic and thermoset polymers are destroyed at excessively high temperatures.

A point of confusion, especially for the nonspecialist, is that polymers are often classified according to some characteristic chemical linkage within the molecular chain, and in many cases polymers within a given classification may be produced as either a thermoplastic or thermoset. Thus, for example, polyester can be produced as either a thermoplastic polymer or a thermoset polymer. A thermoplastic polyester can be melted, whereas a thermoset polyester cannot.

1.2.5 Amorphous versus Semicrystalline Thermoplastics

The molecular structure of a thermoplastic polymer may be *amorphous* or semicrystalline.* The molecular structure of an amorphous thermoplastic is completely random; that is, the molecular chains are randomly oriented and entangled, with no discernible pattern. In contrast, in a semicrystalline thermoplastic there exist regions of highly ordered molecular arrays. An idealized representation of a crystalline region is shown in Figure 1.6. As indicated, in the crystalline region the main backbone of the molecular chain undulates back and forth such that the thickness of the crystalline region is usually (about) 10 nm. The crystalline region may extend over an area with a length dimension ranging from (about) 100 to 1000 nm. Hence, the crystalline regions are typically plate-like. The high degree of order within the crystalline array allows for close molecular spacing, and hence exceptionally high bonding forces between molecules in the crystalline region. Therefore, at the macroscale a semicrystalline thermoplastic typically has a higher strength, stiffness, and density than an otherwise comparable amorphous thermoplastic. No thermoplastic is completely crystalline, however. Instead, regions of crystallinity are surrounded by amorphous regions, as shown schematically in Figure 1.7. Most semicrystalline thermoplastic are 10-50% amorphous (by volume).

Since secondary bond forces are higher in crystalline regions, amorphous regions melt at a lower temperature than crystalline regions. Therefore, semicrystalline thermoplastics may exhibit crystalline regions in both solid and liquid forms, and are known as *liquid-crystal polymers*.





^{*} In practice, a semicrystalline thermoplastic is often called a *crystalline* polymer.



FIGURE 1.7

Molecular structure of a semicrystalline thermoplastic, showing crystalline and amorphous regions.

1.2.6 A-, B-, and C-Staged Thermosets

Three more-or-less distinct conditions are recognized during polymerization of a thermoset polymer. The original resin or oligomer is typically a lowviscosity, low-molecular weight fluid, consisting of molecules with perhaps 2–10 repeat units. A thermoset resin is said to be *A-Staged* when in this form. As the polymerization process is initiated (usually by the introduction of a catalyst, by an increase in temperature, or by some combination thereof), the molecular weight and viscosity of the oligomer increase rapidly. If the temperature of the partially polymerized thermoset is suddenly reduced the polymerization process will stop, or at least be dramatically slowed, and the polymer will exist in an intermediate stage. The thermoset resin is said to be *B-Staged* when in this form. If the B-staged thermoset is subsequently reheated the polymerization process resumes and continues until the maximum possible molecular weight has been reached. The thermoset is then said to be *C-Staged*, that is, the polymer is *fully polymerized*.

Suppliers of composites based on thermoset polymers often B-stage their product and sell it to their customers in this form. This requires that the B-staged composite be stored by the customer at low temperatures prior to use (typically at temperatures below about -15° C or 0°F). Refrigeration is required so that the thermosetting resin does not polymerize beyond the B-stage during storage. The polymerization process is reinitiated and completed (i.e., the composite is C-staged) during final fabrication of a composite part, typically through the application of heat and pressure. Most commercially available thermoset composites are C-staged (or cured) at a temperature of either 120°C or 175°C (250°F or 350°F).

1.2.7 The Glass Transition Temperature

Stiffness and strength are physical properties of obvious importance to the structural engineer. Both of these properties are temperature dependent. The effect of temperature on the stiffness of a polymer is summarized in Figure 1.8. Thermoset and thermoplastic polymers exhibit the same general



FIGURE 1.8 Effects of temperature on polymer stiffness.

temperature dependence, except that at high temperatures thermoplastics melt whereas thermosets do not. All polymers exhibit a sudden decrease in stiffness as temperature is increased to a value called the *glass-transition temperature*, T_{g} . At temperatures well below the T_{g} polymer stiffness decreases gradually with an increase in temperature. At these low (relative to the T_{e}) temperatures polymers are said to be in a "glassy" state and are relatively brittle. In contrast, at temperatures well above the T_g all polymers are "rubbery" and ductile. Thus, the $T_{\rm g}$ denotes the transition between glassy and rubbery regimes. This transition is associated with a sudden increase in mobility of segments within the molecular chain, and typically occurs over a range of 10–15°C. At temperatures well below the T_{g} the polymer molecules are firmly bonded together and cannot easily slide past each other. Consequently the polymer is "glassy," and exhibits a high stiffness and strength but relatively low ductility. Conversely, at temperatures well above the T_{g} the molecular spacing is increased such that the molecular chains (or segments of those chains) are mobile and can readily slide past each other if force is applied. Consequently the polymer is "rubbery" and exhibits a relatively lower stiffness and strength but higher ductility. As implied in Figure 1.8, for amorphous thermoplastics the change in stiffness (and other physical properties) that occurs as the T_g is approached may be 1–2 orders of *magnitude*. This astonishing decrease in stiffness occurs over a temperature range of only 10-20°. A marked decrease in stiffness also occurs for semicrystalline thermoplastics and crosslinked thermosets, although in general the magnitude of the decrease is less than for amorphous thermoplastics. If temperature is raised high enough then a thermoplastic polymer will melt and stiffness tends towards zero. The temperature region at which melting occurs is denoted by $T_{\rm m}$ in Figure 1.8, although as previously discussed

	Typical Glass Transition Temperature, $T_{\rm g}$		Typical Melting Temperature, T _m	
Polymer	°C	°F	°C	°F
Polyester (thermoplastic)	80	175	250	480
Polyphenylene-sulfide (thermoplastic)	85	185	280	540
Polyester (thermoset)	150	300	Not applicable	Not applicable
Epoxy (thermoset)	175	350	Not applicable	Not applicable
Polyetheretherketone (thermoplastic)	200	390	340	650
Polyetherimide (thermoplastic)	215	420	370	700
Bismaleimide (thermoset)	230	450	Not applicable	Not applicable
Polyimide (thermoset)	260	500	Not applicable	Not applicable
Liquid-crystal polyester (thermoplastic)	360	650	370	700

TABLE 1.1

Approximate Glass Transition Temperatures for Some Polymers Used in PMCs

Note: All temperatures approximate and depend on specific polymerization conditions.

a thermoplastic does not exhibit a unique melting temperature but rather melts over a temperature range that depends on average molecular weight. Thermoset polymers cannot be melted.

The T_g has been illustrated in Figure 1.8 by demonstrating the change in stiffness as temperature is increased. Most other macroscopic physical characteristics (density, strength, thermal expansion coefficient, heat capacity, etc.) also change sharply at this transition. Hence, the T_g can be measured by monitoring any of these physical properties as a function of temperature. The T_g exhibited by a few polymers used in PMCs is listed in Table 1.1.

1.3 Fibrous Materials

The fiber types most commonly used in PMCs are

- Glass
- Aramid
- Graphite or carbon
- Ultra high-density polyethylene

Introduction

In all cases the fiber diameters are quite small, ranging from about 5 to 12 μ m for glass, aramid, or graphite fibers, and from about 25 to 40 μ m for polyethylene fibers.

Some of the terminology used to describe fibers will be defined here. The terms *fiber* and *filament* are used interchangeably. An *end* (also called a *strand*) is a collection of a given number of fibers gathered together. If the fibers are twisted, the collection of fibers is called a *yarn*. The ends are themselves gathered together to form a *tow* (also called *roving*). The fibers are usually coated with a *size* (also called a *finish*). The size is applied for several reasons, including

- To bind the fibers in the strand
- To lubricate the fibers during fabrication
- To serve as a coupling and wetting agent to insure a satisfactory adhesive bond between the fiber and matrix materials

Tow sizes are specified in terms of thousands of fibers/filaments per tow. For example, a "6 k tow" implies that the tow consists of about 6000 individual fibers.

1.3.1 Glass Fibers

Eight different types of glass fibers are defined in an ASTM standard [6]. These are: A-glass, AR-glass, C-glass, D-glass, E-glass, E-CR-glass, R-glass, and S-glass fibers. In all cases the glass fibers consist primarily of silica (SiO₂), and additional oxides are added to enhance properties particularly suited for the intended application. For example, AR-glass fibers exhibit an increased resistance to corrosion by akali, whereas C-glass fibers have increased resistance to corrosion by acids.

The fibers are produced by blending all constituents in a large vat, followed by melting in a furnace at a temperature of about 1260°C (2300°F). The molten glass is then drawn through platinum bushings with hundreds of small diameter holes, followed by rapid cooldown. A sizing is applied to the fibers, which are then combined into a strand and wound onto a spool.

The glass fibers most commonly used in PMCs are either E-glass or S-glass. E-glass ("e"lectrical glass) is so named because of its high electrical resistivity, whereas S-glass ("s"tructural glass) is so named because it exhibits higher high stiffness and strength than other types of glass fibers. E-glass fibers have very good properties and are relatively inexpensive, however, so E-glass fibers are widely used in structural composite applications despite the improved mechanical properties provided by S-glass fibers. The compositions of E- and S-glass fibers are listed in Table 1.2, and typical mechanical properties are listed in Table 1.3.

TABLE [·]

Constituents Used to Produce E- and S-Glass Fibers

Constituent	E-Glass Weight%	S-Glass Weight%
	E Gluss Weight //	o Giuss Weight /
SiO ₂ (Silica)	52–56	64–66
Al ₂ O ₃ (aluminum oxide or alumina)	12–16	24–25
B ₂ O ₃ (boron trioxide)	5-10	_
CaO (calcium oxide or quicklime)	16–25	0-0.2
MgO (magnesium oxide)	0–5	9–10
Na ₂ O (sodium oxide)	0–2	0-0.2
K ₂ O (potassium oxide)	0–2	0-0.2
Fe_2O_3 (ferric oxide)	0-0.8	0-0.1
CaF ₂ (fluorite)	0–1	—

TABLE 1.3

Property	E-Glass	S-Glass
Density, g/cm ³	2.60	2.50
(lb/in. ³)	(0.094)	(0.090)
Young's modulus, GPa	72	87
(Msi)	(10.5)	(12.6)
Tensile strength, MPa	3450	4310
(ksi)	(500)	(625)
Tensile elongation, %	4.8	5.0
Coefficient of thermal expansion, $\mu m/m/^{\circ}C$	5.0	5.6
(µin./in./°F)	(2.8)	(3.1)

1.3.2 Aramid Fibers

Aramid is a generic name for a class of synthetic organic *polymeric* fibers (also called aromatic polyamide fibers). The aramid fiber produced by the DuPont Corp and marketed under the trade name KevlarTM is probably the best-known aramid fiber. This fiber is based on poly [*p*-phenylene terephthalamide], which is a member of the aramid family of polymers. The basic repeat unit is shown in Figure 1.9. Kevlar fibers are produced using a mechanical drawing process that aligns the backbone of the polymeric molecular chain with the fiber axis. Although covalent bonding (i.e., cross-linking) does not occur between the elongated polymer chains, a strong secondary bond forms between adjacent hydrogen (H) and oxygen (O) atoms. The resulting fibers are, therefore, highly anisotropic since strong covalent bonds are formed in the fiber axial direction, whereas relatively weaker hydrogen bonds are formed in directions transverse to the fiber axis. That

16

Introduction



FIGURE 1.9

Repeat unit of poly[*p*-phenylene terephthalamide], or Kevlar[™].

TABLE 1.4

Typical Properties of Kevlar 29 and Kevlar 49 Fibers

Property	Kevlar 29	Kevlar 49	
Density, g/cm ³	1.44	1.44	
(lb/in. ³)	(0.052)	(0.052)	
Young's modulus, GPa	70	112	
(Msi)	(10)	(16)	
Tensile strength, MPa	2920	3000	
(ksi)	(424)	(435)	
Tensile elongation, %	3.6	2.4	
Coefficient of thermal expansion, µm/m/°C	-3.9	-4.9	
(µin./in./°F)	(-2.2)	(-2.7)	

Note: All properties measured in axial direction of fiber.

is, Kevlar fibers have very high tensile strength and stiffness in the axial direction of the fiber, but relatively low tensile strength and stiffness in the transverse direction.

New forms of Kevlar and other aramid fibers are introduced almost continuously to the marketplace. At present there are at least eight different grads of Kevlar fiber, each with a different combination of properties and cost. Kevlar 49 is most commonly used in PMCs, although occasionally the less-expensive Kevlar 29 fiber is used as well. Nominal mechanical and physical properties for Kevlar 29 and 49 fibers are listed in Table 1.4. Of particular interest is the *negative* coefficient of thermal expansion these fibers exhibit in the axial direction.

1.3.3 Graphite and Carbon Fibers

The terms "graphite" and "carbon" are often used interchangeably within the composites community. The elemental carbon content of either type of fiber is above 90%, and the stiffest and strongest fibers have elemental carbon contents approaching 100%. Some effort has been made to standardize these terms by defining *graphite fibers* as those that have

- A carbon content above 95%
- Been heat treated at temperatures in excess of 1700°C (3100°F)
- Been stretched during heat treatment to produce a high degree of preferred crystalline orientation
- A Young's modulus on the order of 345 GPa (50 Msi)

Fibers that do not satisfy all of the above conditions are called *carbon fibers* under this standard. However, as stated above in practice this definition is not widely followed, and the terms "graphite" and "carbon" are often used interchangeably.

Both graphite and carbon fibers are produced by thermal decomposition of an organic (i.e., polymeric) fiber or "precursor" at high pressures and temperatures. The three most common precursors are

- Polyacrylonitrile (PAN), a synthetic polymer with a repeat unit of $[C_3H_3N]_n$
- Rayon, a semisynthetic fiber produced using the natural polymer cellulose with a repeat unit of [C₆H₁₀O₅]_n
- Pitch, a generic name for a range of highly viscous solid polymers

Pitch can be derived either from petroleum products, in which case it is sometimes called "petroleum pitch," or from plants.

Details of the specific steps followed during fabrication of a specific carbon or graphite fiber are proprietary and can only be described in a general manner. During the fabrication process the precursor is drawn into a thread and then oxidized at temperatures ranging from about 230°C to 260°C (450– 500°F) to form an extended carbon network. The precursor is then subjected to a carbonization treatment, during which noncarbon atoms are driven off. This step typically involves temperatures ranging from 700°C to 1000°C (1290–1800°F), and is conducted in an inert atmosphere. Finally, during the graphitization process the fibers are subjected to a combination of high temperature and tensile elongation. Maximum temperatures reached during this step range from 1500°C to 2000°C (2700–3600°F), and determine in large part the strength and/or stiffness exhibited by the fiber.

These processing steps results in a carbon-based crystalline structure called "graphite." The graphite crystalline structure is shown in Figure 1.10. Carbon atoms are arranged in parallel planes or sheets called graphene, as shown in Figure 1.10a. Each carbon atom within a graphene plane is covalently bonded to three neighboring carbon atoms, resulting in a pattern of hexagonal rings of carbon atoms within the graphene plane, as seen most clearly in Figure 1.10b,c. High fiber strength and stiffness is achieved



FIGURE 1.10

Graphite crystalline structures present in carbon or graphite fibers. (a) Graphite crystalline structure (side view); (b) graphitic graphite crystalline structure (orthogonal view); (c) turbostratic graphite crystalline structure (orthogonal view).

by causing the graphene planes to be aligned with the fiber axial direction. Although the carbon atoms within graphene planes are covalently bonded, adjacent graphene sheets are bonded by relatively weaker van der Waals forces. Consequently graphite/carbon fibers are highly anisotropic (as are Kevlar fibers), since the weaker secondary forces act transverse to the fiber axis.

As implied in Figure 1.10b,c, the graphene sheets may be tightly packed with a high degree of regularity (called *graphitic* graphite), or may be relatively loosely packed with less regularity (called *turbostratic* graphite). Fiber produced using the PAN precursor tends to exhibit a high-volume percentage of turbostratic graphite, leading to high tensile strength. In contrast, fiber produced using the pitch precursor tends to exhibit a high-volume percentage of graphitic graphite, leading to high tensile stiffness. Fibers are available with varying levels of both type of crystalline graphite, and

Property	Low Modulus	Intermediate Modulus	Ultra-High Modulus
Density, g/cm ³	1.8	1.9	2.2
(lb/in. ³)	(0.065)	(0.069)	(0.079)
Young's modulus, GPa	230	370	900
(Msi)	(34)	(53)	(130)
Tensile strength, MPa	3450	2480	3800
(ksi)	(500)	(360)	(550)
Elongation, %	1.1	0.5	0.4
Coefficient of thermal expansion, µm/m/°C	-0.4	-0.5	-0.5
(µin./in./°F)	(-0.2)	(-0.3)	(-0.3)

TABLE 1.5

Typical Properties of Commercially Available Graphite (or Carbon) Fibers

hence commercial fibers exhibit a range of stiffness and strength. Mechanical and physical properties typical of low-modulus, intermediate modulus, and ultra-high modulus fibers are listed in Table 1.5.

1.3.4 Polyethylene Fibers

A high strength, high modulus polyethylene fiber called Spectra was developed at Allied Signal Technologies during the 1980s. Spectra is based on ultra high molecular weight polyethylene (UHMWPE). It has a specific gravity of 0.97, meaning that it is the only reinforcing fiber available which is lighter than water. Spectra is available in three classifications, Spectra 900, 1000, and 2000, and several grades are available in each class. Nominal properties are listed in Table 1.6. The high specific strength of the fiber makes it particularly attractive for tensile applications. The glass transition temperature of UHMWPE is in the range from -20° C to 0° C, and hence the fiber is in the rubbery state at room temperatures, and exhibits time-dependent (viscoelastic) behavior. This feature imparts outstanding impact resistance and

TABLE 1.6

Property	Spectra 900	Spectra 1000	Spectra 2000
Specific gravity	0.97	0.97	0.97
Young's modulus, GPa	70	105	115
(Msi)	(10)	(15)	(17)
Tensile strength, MPa	2600	3200	3400
(ksi)	(380)	(465)	(490)
Elongation, %	3.8	3.0	3.0
Coefficient of thermal expansion, $\mu m/m/^{\circ}C$	>70	>70	>70
(μin./in./°F)	(>38)	(>38)	(>38)

Approximate Properties of Spectra Fibers

20

toughness, but may lead to undesirable creep effects under long-term sustained loading. The melting temperature of the fiber is about 150°C (300°F), and hence the use of polyethylene fibers is limited to relatively modest temperatures. The thermal expansion coefficients of Spectra fibers have apparently not been measured; values listed in Table 1.6 are estimates based on the properties of bulk high-molecular-weight polyethylene.

1.4 Commercially Available Forms

1.4.1 Discontinuous Fibers

Virtually all of the continuous fibers described in Section 1.3 are also available in the form of discontinuous fibers. Discontinuous fibers are embedded within a matrix, and may be randomly oriented (in which case the composite is isotropic at the macroscale), or may be oriented to some extent (in which case the composite is anisotropic at the macroscale). Orientation of discontinuous fibers, if it occurs, is usually induced during the fabrication process used to create the composite material/structure; fiber alignment often mirrors the flow direction during injection molding, for example. Discontinuous fibers are roughly classified according to length, as follows:

- *Milled fibers* are produced by grinding the continuous fiber into very short lengths. For example, milled graphite fibers are available with lengths ranging from about 0.3 to 3 mm (0.0012–0.12 in.), and milled glass fibers are available with lengths ranging from about 0.4 to 6 mm (0.0016–0.24 in).
- *Chopped fibers (or strands)* have a longer length than milled fibers, and composites produced using chopped fibers usually have higher strengths and stiffnesses than those produced using milled fibers. Chopped graphite fibers are available with lengths ranging from about 3 to 50 mm (0.12–2.0 in.), while chopped glass fibers are available with lengths ranging from about 6 to 50 mm (0.24–2.0 in.).

In general, the mechanical properties of the composite produced using discontinuous fibers (the strength or stiffness, say) are not as good as those which can be obtained using continuous fibers. However, discontinuous fibers allow the use of relatively inexpensive, high-speed manufacturing processes such as injection molding or compression molding, and have, therefore, been widely used in applications in which extremely high strength or stiffness is not required.

One of the most widely used composites systems based on the use of discontinuous fibers is known generically as "sheet-molding compound" (SMC). In its most common form SMC consists of chopped glass fibers

embedded within a thermosetting polyester resin. However, other resins (e.g., vinyl esters or epoxies), and/or other fibers (e.g., chopped graphite or aramid fibers) are also used in SMC material systems. Components produced using SMC are normally manufactured using compression molding.

1.4.2 Roving Spools

Most continuous fiber types are available in the form of spools of roving, that is, roving wound onto a cylindrical tube, and ultimately resembling a large spool of thread. As mentioned in Section 1.3, roving is also known as tow. The size of tow (or roving) is usually expressed in terms of the number of fibers contained in a single tow. For example, a specific glass fiber might be available in the form of 2k, 3k, 6k, or 12k tow. In this case the product is available in tows containing from 2000 to 12,000 fibers. Fibers purchased in this form are usually "dry," and are combined with a polymer, metal, or ceramic matrices during a subsequent manufacturing operation such as filament winding or pultrusion.

1.4.3 Woven Fabrics

Most types of high-performance continuous fibers can be woven to form a fabric. Weaving is accomplished using looms specially modified for use with high-performance fibers, which are stiffer than those customarily used in the textile industry. The weaving process is illustrated in Figure 1.11.



FIGURE 1.11

A loom producing a glass fiber fabric using the plain weave pattern. (Adapted from www. nauticexpo.com/prod/nida-core-corporation/glass-fiber-fabric-multiaxial-27841-192139.html.)

Introduction

Woven fabrics are produced in various widths up to about 120 cm (48 in.), and are available in (essentially) infinite lengths. Two terms associated with woven fabrics are

- The tow or yarn running along the length of the fabric is called the *warp*. The warp direction is parallel to the long axis of the woven fabric.
- The tow or yarn running perpendicular to the warp is called the *fill* tow (also called the *weft* or the *woof* tow). The fill direction is perpendicular to the warp direction.

Some common fabric weaves are shown schematically in Figure 1.12. The *plain weave* (also called a *simple weave*) is shown in Figure 1.12a and is being



FIGURE 1.12

Some common woven fabrics used with high-performance fibers. (a) Plain weave pattern; (b) basket weave pattern; (c) four-harness (crowfoot) weave pattern; (d) 2×2 twill weave pattern. (From Donnet, J.-B. et al. *Carbon Fibers*, 3rd edition, Marcel Dekker, Inc., New York, 1998, ISBN 0-8247-0172-0.)

produced using the loom shown in Figure 1.11. The plain weave is the simplest fabric pattern available and is most commonly used. It is produced by repetitively weaving a given warp tow over one fill tow and under the next. The point at which a tow passes over/under another tow is called a *crossover point*. The plain weave pattern results in a very stable and firm fabric that exhibits minimum distortion (e.g., fiber slippage) during handling. A *basket weave*, shown in Figure 1.12b, is a variation of the simple weave pattern in which two (or more) warp tows pass over an equal number of fill tows, forming a rectangular pattern similar to a plain weave.

A family of woven fabric patterns known as *satin weaves* provides better *drape characteristics* than a plain weave. That is, a satin weave is more pliable and will more readily conform to complex-curved surfaces than plain weaves. The *four-harness satin weave* (also known as a *crowfoot* weave) is shown in Figure 1.12c. In this case, one warp tow passes over three adjacent fill tows and then under one fill tow. Similar satin weave patterns include the *five-harness satin weave*, wherein one warp tow passes over four fill tows and then under one fill tow, and the *eight-harness satin weave*, wherein one warp tow passes over seven fill tows and then under one fill tows.

A *twill weave* pattern in shown in Figure 1.12d. Two adjacent warp tow pass over two adjacent fill tow, forming a diagonal 2-over/2-under pattern known as a 2×2 twill. Similarly, a 4×4 twill would be based on a 4-over/4-under weave pattern.

The stiffness and strength of woven fabrics is typically less than that achieved with unidirectional fibers. This decrease is due to fiber waviness. That is, in any woven fabric the tow is required to pass over/under one (or more) neighboring tow(s) at each crossover point, resulting in pre-existing fiber waviness. Upon application of a tensile load the fibers within a ply tend to straighten, resulting in a lower stiffness than would be achieved if the ply contained initially straight unidirectional fibers. Further, due to the weave pattern the fibers are not allowed to straighten fully and are subjected to bending stresses, resulting in fiber failures at lower tensile loads than would otherwise be achieved if the ply contained unidirectional fibers. This effect is most pronounced in the case of plain weaves, since each tow passes over/ under each neighboring tow. For plain weaves the through-thickness distribution of tow in the warp and fill directions is identical. Consequently, the strength and stiffness of plain weaves is usually identical in the warp and fill directions.

In contrast, for satin weaves the through-thickness distribution of tow is inherently asymmetric. Referring to Figure 1.12c, for example, for the fourharness satin weave pattern the warp tow are primarily within the "top" half of the fabric (as sketched), whereas the fill tow are primarily within the lower half. The asymmetric through-thickness distribution of tow causes a coupling between in-plane loading and bending deflections. That is, if a uniform tensile load is applied to the midplane of a single layer of a satin weave fabric, the fabric will not only stretch but will also deflect out-of-plane (i.e., bend). Similarly, the crossover points not symmetric with respect to either the warp or fill directions. This causes a coupling between in-plane loading and in-plane shear strain. That is, an in-plane shear strain is induced if a uniform tensile load is applied to a single layer of a satin weave fabric [8].

A woven fabric is in essence a 2D structure consisting of orthogonal warp and fill tows interlaced within a plane. Weaving or stitching several layers of a woven fabric together can produce a woven structure with a significant thickness. Structures produced in this fashion are called "3D weaves."

1.4.4 Braided Fabrics

Note from the preceding section that woven fabrics contain reinforcing tow in two orthogonal directions—namely, the warp and fill directions. In contrast, braided fabrics typically contain tow oriented in two (or more) nonorthogonal directions. Three common braiding patterns are shown in Figure 1.13. It is apparent from this figure that a braided fabric contains *bias* tows that intersect at a total included angle 2α . The angle α is called either the *braid angle* or the *bias angle*. Although the braid angle can be varied over a wide range, there is always some minimum and maximum possible value that depends on width of the tow and details of the braiding equipment used. Note that if $\alpha = 45^{\circ}$ then the bias tow are in fact orthogonal and the braided fabric shown in Figure 1.13a,b are equivalent to a woven fabric. A braided fabric is described using the designation " $n \times n$," where *n* is the number of tows between crossover points. A 1 × 1 and 2 × 2 bias braided fabric is



FIGURE 1.13

Some common braided fabrics used with high-performance fibers. (a) 1×1 bias braid pattern; (b) 2×2 bias braid pattern; (c) 1×1 triaxial braid pattern. (After Donnet, J.-B. et al. *Carbon Fibers*, 3rd edition, Marcel Dekker, Inc., New York, 1998, ISBN 0-8247-0172-0.)

shown in Figure 1.13a,b, respectively. A 1×1 triaxial-braided fabric is shown in Figure 1.13c. In this case, a third *axial* tow is present.

Braided fabrics are produced in tubular form as shown in Figure 1.14. Tows are dispensed from two sets of roving spools, traveling in opposite directions on two outer circular races. The roving spools pass sequentially from one race to the other, producing the interwoven pattern that is readily apparent in Figure 1.14a. The tows are drawn toward the center of the braider and pass through a forming plate with circular opening. If a triaxial braid is to be produced then a third set of tows (not shown in Figure 1.14) is fed vertically through the center region of braider and interwoven with the bias tows. The surface texture of the braided tubes is dictated by the number and



FIGURE 1.14

Braided fiber tubes. (a) Carriers passing through the central forming plate in a braider; (b) braided carbon fiber tubes of identical diameters, produced using a different number of tows and tow sizes. (Photo courtesy of A & P Technology: www.braider.com.) size of the tows used. For example, two braided carbon tubes with the same diameter are shown in Figure 1.14b. The one on the left was produced using a 96-carrier braider and 12k carbon tow. In contrast, the tube on the right was produced using a 400-carrier braider and 1k carbon tow, resulting in a tube with substantially smoother surface texture. If desired, braided tubes may subsequently be slit lengthwise to form a flat braided fabric.

1.4.5 Pre-Impregnated Products or "Prepreg"

As is obvious from the preceding discussion, at some point during fabrication of a polymer composite the reinforcing fiber must be embedded within a polymeric matrix. One approach is to combine the fiber and resin during the manufacturing operation in which the final form of the composite structure is defined. Three manufacturing processes in which this approach is taken are filament winding (briefly described in Section 1.5.3), pultrusion (Section 1.5.4), and resin-transfer molding (Section 1.5.5).

An alternative approach is to combine the fiber and matrix in an intermediate step, resulting in an intermediate product. In this case either individual tow or a thin fabric of tow (which may be a unidirectional, woven, or braided fabric) are embedded within a polymeric matrix and delivered to the user in this form. Because the fibers have already been embedded within a polymeric matrix when delivered, the fibers are said to have been "preimpregnated" with resin, and products delivered in this condition are commonly known as "prepreg."

One method used to impregnate a large number of unidirectional tows with resin is sketched in Figure 1.15 [9]. As indicated, tows delivered from a





large number of roving spools are arranged in a relatively narrow band. The tows are passed through a resin bath and then wound onto a roll. An inert backing sheet (also called a *scrim cloth*) is placed between layers on the roll to maintain a physical separation between layers and to aid during subsequent handling and processing. The tow/fibers are subjected to various surface pretreatments just prior to entering the resin bath. The pretreatments are proprietary but are intended to cause good wetting of the fiber by the resin, which ultimately helps ensure good adhesion between the fibers and polymer matrix in the cured composite. Products produced in this fashion are commonly known as "prepreg tape" (Figure 1.15b). Prepreg tape is available in width ranging from about 75 to 1220 mm (3–48 in.). Prepreg fabrics, produced using either woven or braided fabrics instead of unidirectional tows, are produced using similar techniques and are available in widths ranging from about 75 to 1220 mm.

A variety of fabrication methods have been developed based on the use of prepreg materials. A few such techniques will be described in Section 1.5.

The first commercially successful prepreg materials were based on Bstaged epoxy resins. As discussed in Section 1.2, in the B-staged condition a thermoset resin has been partially polymerized, resulting in a relatively high viscosity, which aids in handling B-staged prepreg materials. However, prepreg must be kept at low temperatures until used, otherwise the resin continues to polymerize and slowly harden. This requires that the prepreg be shipped to the user in a refrigerated condition (for small amounts this is often accomplished using insulated shipping containers and dry ice). Further, the user must keep the stock of prepreg refrigerated until used. Typically storage temperatures are required to be -15° C (0°F) or below. In practice the prepreg material stock is removed from freezer, the amount of prepreg necessary is removed from the roll of stock, and the remaining stock is returned to the freezer. Hence, the cumulative "out-time" that a given roll of prepreg stock has experienced (i.e., total amount of time a roll has been out of a freezer) must be monitored and recorded. The need to store thermoset prepreg in a refrigerated condition and to maintain accurate records of cumulative outtime is a significant disadvantage, since these factors add significantly to the final cost of the composite structure.

Prepreg materials based on thermoplastic resins are also commercially available. In this case the polymeric matrix is a fully cured thermoplastic polymer, and hence the prepreg does not require refrigeration during shipping or storage, which is a distinct advantage.

Heat and/or pressure are applied during final fabrication of a composite based on prepreg materials. In the case of thermoset prepregs, the heat and pressure serve to complete polymerization of the polymeric resin, that is, the composite is "C-staged." For thermoplastic prepreg the objective is not necessarily to complete polymerization but rather to decrease the viscosity of the thermoplastic matrix so as to consolidate individual plies within the laminate.

1.5 Manufacturing Processes

A complete review of the many different manufacturing processes used to produce polymeric composite materials and structures is beyond the scope of this presentation. The most common manufacturing techniques will be briefly described here.

1.5.1 Layup Techniques

Many composites are produced using the tapes or fabrics discussed in the preceding section. These may be unidirectional tape, woven fabrics, or braided fabrics. These products are typically relatively thin. "Layup" simply refers to the process of stacking several layers together, much like a deck of cards. Stacking several layers together produces a laminate of significant thickness. The most direct method of producing a multi-ply composite laminate is to simply stack the desired number of layers of fabric by hand, referred to as "hand-layup" (see Figure 1.16). The layers may consist of either "dry" fabrics (i.e., fabrics which have not yet been impregnated with a resin) or prepreg materials. As will be discussed in later chapters, fiber angles are typically varied from one ply to the next, so as to insure adequate stiffness and strength in more than one direction.

Although hand-layup is simple and straightforward, it is labor intensive and, therefore, costly. It can also be very cumbersome if a large structure is being produced, such as a fuselage panel intended for use in a modern commercial aircraft. Therefore, various computer-controlled machines have been developed that automate the process of assembling the ply stack using prepreg materials. These include tow-placement and tape-placement machines (Figure 1.17). In either case, a roll (or rolls) of prepreg material is mounted on the head of a computer-controlled robot-arm or gantry.



FIGURE 1.16 Hand-layup of composite prepreg on a curved tool.



FIGURE 1.17

A computer-controlled tape-laying machine. (a) Producing a curved composite panel using the tool shown near the center of the image; (b) close-up via of the dispensing head.

The appropriate number of layers of prepreg is placed on a tool surface automatically and in the desired orientation. Although the capital costs of modern tow- or tape-placement machines may be very high, overall this approach is often less costly than hand-layup if production quantities are sufficiently high.

In the case of dry fabrics (which are usually either woven or braided fabrics), the stack must be impregnated with a low-viscosity polymeric resin following assembly of the fiber stack. Conceptually, this may be accomplished by pouring liquidous resin over the dry fiber stack, and using a squeegee or similar device to assist the resin to wet the fibers within the stack. This technique is commonly used in the recreational boat-building industry, for example. However, it is very difficult to insure uniform penetration of the resin and wetting of the fibers through the thickness of the stack, to insure that no air pockets remain trapped in the stack, and to avoid distortion of the fiber patterns while forcing resin into the fibrous assembly. There are also potential health issues associated with continually exposing workers to nonpolymerized resins. Hence, the technique of impregnating a dry fiber stack using hand-held tools such as squeegees is rarely employed in industries requiring low variability in stiffness and strength and/or high volumes, such as the aerospace or automotive industries, for example. Alternate methods of impregnating a dry fiber stack with resin have been developed, such as resin transfer molding (discussed in Section 1.5.5). These alternate techniques result in a composite with a much more uniform matrix volume fraction and almost no void content.

A major advantage of using prepreg materials, of course, is that the fibers have been impregnated with resin a priori. It is, therefore, much easier to maintain the desired matrix volume fraction and to avoid entrapped airpockets. Further, prepreg material based on a B-staged thermoset are typically "tacky" (i.e., prepreg materials adhere to neighboring plies much like common masking tape), and hence once a given ply has been placed in the desired orientation it is less likely to move or be distorted relative to neighboring plies than is the case with dry fabrics.

1.5.2 Autoclave Process Cycles

Following layup (which may be accomplished using hand-layup, automatic tow- or tape-placement machines, or other techniques) the individual plies must be consolidated to form a solid laminate. Usually consolidation occurs through the application of pressure and heat. Whereas a simple hot press can be used for this purpose, applying pressure and heat using an *autoclave* produces highest-quality composites. An autoclave is simply a closed pressure vessel that can be used to apply a precisely controlled and simultaneous cycle of vacuum, pressure, and elevated temperature to the laminate during the consolidation process.

Although many variations exist, a typical assembly used to consolidate a laminate using an autoclave is shown in Figure 1.18. Some of the details of the assembly are as follows:

- The final shape of the composite is defined by a rigid *tool*. A simple flat tool is shown in Figure 1.18, but in practice the tool is rarely flat but instead mirrors the contour(s) desired in the final product (curved tools are shown in Figures 1.16 and 1.17, for example). Various materials may be used to produce the tool, including steel alloys, aluminum alloys, nickel alloys, ceramics, or composite materials.
- The tool surface is coated with a *release agent*. Various liquid or wax release agents are available which are either sprayed or wiped onto the surface. The purpose of the release agent is to prevent adherence between the tool and the polymeric matrix.
- A *peel ply* is placed next to both upper and lower surfaces of the composite laminate. The release ply does not develop a strong bond



FIGURE 1.18

Typical assembly used to consolidate a polymeric composite laminate using an autoclave (expanded edge view).

to the composite, and hence can be easily removed following consolidation. The peel ply may be porous or nonporous. Porous peel plies allow resin to pass through the ply and be adsorbed by an adjacent bleeder/breather cloth (see below). Note that the surface texture of the consolidated laminate will be a mirror image of the peel ply used. For example, Teflon-coated porous glass fabrics are often used as peel plies, and these fabrics have a cloth-like surface texture. Hence, a composite laminate consolidated against such fabrics will exhibit a cloth-like surface texture as well.

- One or more layers of a *breather/bleeder cloth* is placed adjacent to the porous peel ply. The bleeder cloth has the texture of rather stiff cotton. Its' purpose is to allow any gases released to be vented (hence the adjective *breather*).
- And also to adsorb any resin that passed through the porous peel ply (hence the adjective *bleeder*). The breather/bleeder is usually a glass, polyester, or jute cloth.
- An *edge dam* is placed around the periphery of the laminate. The edge dam is intended to maintain the position and resin content of the laminate edges.
- A *pressure plate* (also called a *caul plate*) is placed over the breather/ bleeder cloth. The pressure plate insures a uniform distribution of pressures over the surface of the laminate.
- The entire assembly is sealed within a *vacuum film or bag*. Often this is a relatively thick (5 mm, say) layer of silicone rubber. Sealant tape is used to adhere the vacuum film to the tool surface, providing a pressure-tight seal around the periphery of the vacuum film.
- The volume within the vacuum bag is evacuated by means of a *vac-uum port*, which is often permanently attached to the silicone rubber vacuum film. The vacuum port often features a quick-disconnect fitting, which allows for easy connection to a vacuum pump or line.

Following vacuum bagging of the laminate, the assembly is placed within an autoclave, the autoclave is sealed, and the thermo-mechanical process cycle that will consolidate the composite is initiated. A bagged composite laminate being loaded into an autoclave is shown in Figure 1.19.

The thermo-mechanical process cycle imposed using an autoclave varies from one composite prepreg system to the next, and also depends on part configuration (e.g., part thickness). Recall that if the prepreg is based on a B-stage thermoset resin, then the autoclave is used to complete polymerization of the resin, that is, the composite is C-staged. Alternatively, if the prepreg is based on a thermoplastic, the pressure and heat applied during the autoclave cycle softens the matrix and insures polymer flow across the ply interfaces. The laminate is then solidified upon cooling.

Introduction



FIGURE 1.19

A vacuum bagged composite laminate being loaded into an autoclave.

A typical cure cycle, suitable for use with standard thermosetting resin systems such as epoxies, is as follows.

- Draw and hold a vacuum within the vacuum bag, resulting in a pressure of roughly 100 kPa (14.7 psi) applied to the laminate. The vacuum is typically maintained for about 30 min, and is intended to remove any entrapped air or volatiles, and to hold the laminate in place.
- While maintaining a vacuum, increase the temperature from room temperature to about 120°C (250°F), at a rate of about 2.8°C/min (5°F/min). Maintain this temperature for 30 min. During this 30-min dwell time any remaining air or other volatiles are removed.
- Increase the internal autoclave pressure from atmospheric to about 585 kPa (85 psi), at a rate of 21 kPa/min (3 psi/min). Release vacuum when autoclave pressure reaches 138 kPa (20 psi).
- Increase temperature from 120°C to 175°C (350°F), at a rate of about 2.8°C/min (5°F/min). Maintain at 175°C for 2 h. Polymerization of the thermosetting resin matrix is completed during this 2-h dwell.
- Cool to room temperature at a rate of about 2.8°C/min (5°F/min), release autoclave pressure, and remove cured laminate from the autoclave.

The polymerization process for many thermosetting resins, including epoxies, is an exothermic reaction. Consequently an inert gas (usually nitrogen) is used as the pressuring medium in most autoclave cure cycles, to avoid initiation of a fire within the autoclave chamber.

Process cycles used with thermoplastic prepregs are similar, except that higher temperatures (500°C or higher) are usually involved.

1.5.3 Filament Winding

Filament winding is an automated process in which tow is wound onto a mandrel at controlled position and orientation. A filament winder being used to produce a small pressure vessel is shown in Figure 1.20. During operation, the mandrel rotates about its axis, and a fiber carriage simultaneously moves in a controlled manner along the length of the mandrel. The angle at which fibers are placed on the mandrel surface is a function of the mandrel diameter, rate of mandrel rotation, and translational speed of the fiber carriage.

If dry tows are used, then the tow must pass through a liquid resin bath before being wound onto the mandrel. In this case the process is often referred to as "wet" filament winding. Often fiber tension provides sufficient compaction of the laminate, and so no additional external pressure is required. If a thermosetting resin that cures at room temperature is used, following completion of the winding operation the structure is simply left in the winder until polymerization is complete.

Of course, if prepreg tow is used then the tow is already impregnated with a resin and is not passed through a resin bath. This process is called "dry" filament winding. In this case heat and pressure are normally required to complete polymerization of the resin (in the case of a thermosetting polymer matrix) or to cause resin flow and consolidation (in the case of a thermoplastic polymer matrix). The appropriate heat and pressure are usually applied using an autoclave.

For simple wound shapes with open ends (such as cylindrical tubes) the mandrel is usually a simple solid cylinder whose surface has been coated with a release agent. In this case, the mandrel is forced out of the internal cavity after consolidation of the composite. Mandrel design and configuration become more complex when a shape with restricted openings at the



FIGURE 1.20 A filament winder being used to produce a pressure vessel.

ends is produced (such as the pressure tank shown in Figure 1.20). In these cases, the mandrel must somehow be removed after the part is consolidated. Several different types of mandrel designs are used in these cases, including

- *Soluble mandrels,* which are made from a material which can be dissolved in some fashion after the cure process is complete. In this approach the mandrel is cast and machined to the desired shape, the composite part is filament wound over the mandrel, the part is cured, and the mandrel is then simply dissolved. The wall of the composite structure must obviously have at least one opening, such that the dissolved (and now liquidous) mandrel material can be drained from the internal cavity. Soluble mandrels can be made from metallic alloys with suitably low-melting temperatures, eutectic salts, sand with water soluble binders, or various plasters.
- *Removable (or collapsible) mandrels,* which resemble giant 3D puzzles. That is, the entire mandrel can be taken apart piece-by-piece. The composite structure being wound must have at least one wall opening, which allows the mandrel pieces to be removed from the internal cavity after cure. Obviously, the mandrel is designed such that no single piece is larger than the available opening(s).
- *Inflatable mandrels,* which take on the desired shape when pressurized and then are simply deflated and removed after winding and consolidation.
- *Metal or polymer liners*, which are actually a modification of the inflatable mandrel concept. Liners can be described as metal or polymer "balloons," and remain in the filament wound vessel after cure. The liner does not contribute significantly to the strength or stiffness of the structure. In fact, the wall thickness of the liner is often so small that an internal pressure must be applied to the liner during the winding process to avoid buckling of the liner wall. Metal liners are almost always used in composite pressure vessels, where allowable leakage rates are very low, or in filament wound chemical storage tanks where corrosive liquids are stored.

1.5.4 Pultrusion

Pultrusion is a fabrication process in which continuous tows or fabrics impregnated with resin are pulled through a forming die, as shown schematically in Figure 1.21 [10]. If dry tow or fabric is used then the tow/fabric must pass through a resin bath prior to entering the forming die. In this case, the process is called "wet" pultrusion. If prepreg material is used then there is no need for a resin bath and the process is called "dry" pultrusion. The



FIGURE 1.21 Sketch of a typical pultruder.

cross-sectional shape is defined by the die and is, therefore, constant along the length of the part. The principal attraction of pultrusion is that very high production rates are possible, as compared with other composite manufacturing techniques. Finished pultruded parts with various cross-sections are shown in Figure 1.22.



FIGURE 1.22 Finished pultruded parts.



FIGURE 1.23 Summary of the resin-transfer molding process.

1.5.5 Resin Transfer Molding

In the resin transfer molding (RTM) process a dry fiber *preform* is placed within a cavity formed between two matched metal molds, as shown in schematically in Figure 1.23. The dry preform is often produced by stitching together woven or braided fabrics. Liquidous resin is forced into the cavity under pressure via a port located in the upper or lower mold halves. Air originally within the internal cavity (or other gases that evolve during cure of the resin) is allowed to escape via one or more air vents. Alternatively, a vacuum pump may be used to evacuate the internal cavity, which also assists in drawing the resin into the cavity. When a vacuum is used the process is one form of "vacuum-assisted resin transfer molding" (VARTM). Both the upper and the lower molds must be sufficiently rigid so as to resist the internal pressures applied and to maintain the desired shape of the internal cavity. Usually the closed molds are placed within a press, which provides a clamping pressure to assist in keeping the molds closed.

1.6 Scope of This Book

A broad overview of modern composite materials and manufacturing processes has been provided in preceding sections. It should be clear from this discussion that composite material systems is a multidisciplinary subject, involving topics drawn from polymer chemistry, fiber science, surface chemistry and adhesion, materials testing, structural analysis, and manufacturing techniques, to name a few. It is simply not possible to cover all of these topics in any depth in a single textbook. Accordingly, the material presented in this book represents a small fraction of the scientific and technological developments that have ultimately led to the successful use of modern composite material systems. Specifically, the focus of this text is the *structural* analysis of *laminated*, *continuous-fiber polymeric composite materials*, *and structures*.

Having identified the structural analysis of laminated continuous-fiber polymeric composites as our focus, we must make still another decision: at what *physical scale* should we frame our analysis? The importance of physical scale has already been discussed in Section 1.1 in conjunction with the very definition of a "composite material." Specifically, we have defined a composite as a material system consisting of two (or more) materials that are distinct at a physical scale greater than about 1 μ m, and which are bonded together at the atomic and/or molecular levels. Fibers commonly used in polymeric composites possess diameters ranging from about 5 to 40 μ m (Section 1.3). Therefore, we could perform a structural analysis at a physical scale comparable to the fiber diameter. Alternatively, laminated polymeric composites consist of well-defined layers (called plies) of fibers embedded in a polymeric matrix. The thickness of these layers range from about 0.125 to 0.250 mm (Section 1.4). We could, therefore, elect to begin a structural analysis at a physical scale comparable to the thickness of a single ply.

A distinction is drawn between structural analyses that begin at these two different physical scales. Analyses that are framed at a physical scale corresponding to the fiber diameter (or below) are classified as micromechanics analyses, whereas those framed at a physical scale corresponding to a single ply thickness (or above) are classified as macromechanics analyses. This distinction is comparable to the traditional distinction between *metallurgy* and continuum mechanics. That is, metallurgy typically involves the study of the crystalline nature of metals and metal alloys, and is, therefore, framed at a physical scale roughly corresponding to atomic dimensions. A metallurgist might attempt to predict Young's modulus* of a given metal alloy, based on knowledge of the constituent atoms and crystalline structure present in the alloy, for example. In contrast, continuum mechanics is formulated at a much larger physical scale, such that the existence of individual atoms is not perceptible. In continuum mechanics a metal or metal alloy is said to be "homogeneous," even though it actually consists of several different atomic species. A structural engineer wishing to apply a solution based on continuum mechanics would simply measure Young's modulus exhibited by the metal alloy of interest, rather than trying to predict it based on knowledge of the atomic crystalline structure.

In much the same way, composite micromechanics analyses are concerned with the predicting properties of composites based on the particular fiber and matrix materials involved, the spacing and orientation of the fibers, the adhesion (or lack thereof) between fiber and matrix, etc. For example,

^{*} The definition of various material properties of interest to the structural engineer, such as Young's modulus, will be reviewed and discussed in greater detail in Chapter 3.

suppose that a unidirectional graphite-epoxy composite is to be produced by combining graphite fibers with a known Young's modulus (E_f) and an epoxy matrix with a known Young's modulus (E_m). An analysis framed at a physical scale corresponding to the fiber diameter, that is, a micromechanics analysis, is required to predict the Young's modulus that will be exhibited by the composite (E_c) formed using these two constituents.

In contrast, composite macromechanics analyses are framed at a physical scale corresponding to the ply thickness (or above). The existence or properties of individual fibers or the matrix material is not recognized (in a mathematical sense) in a macromechanics analysis. Instead, the ply is treated as a homogeneous layer whose properties are identical at all points, although they differ in different directions. Details of fiber or matrix type, fiber spacing, fiber orientation, etc., are represented in a macromechanics analysis only indirectly, via properties defined for the composite ply as a whole, rather than as properties of the individual constituents.

Finally then, the scope of this book is: macromechanics-based structural analysis of laminated, continuous-fiber, polymeric composites.

Micromechanics-based structural analyses will not be discussed in any detail. A simple micromechanics model that may be used to predict ply stiffness based on knowledge of fiber and matrix properties, called the *rule-of-mixtures*, will be developed in Section 3.6. However, the material devoted to micromechanics in this text is abbreviated and does not do justice to the many advances made in this area. The lack of emphasis on micromechanical topics is not meant to imply that such analyses are unimportant. Quite the contrary, micromechanics analyses are crucial during development of new composite material systems, since it is only through a detailed understanding of the behavior of composites at this physical scale that new and improved materials can be created. Micromechanics has been minimized herein simply due to space restrictions. The reader interested in learning more about micromechanics is referred to several excellent texts that cover this topic in greater detail, a few of which are [11–14].

References

- 1. *ASM Metals Reference Book*, 2nd edition, American Society of Metals, Metals Park, OH, 1983, ISBN 0-87170-156-1.
- Rodriguez, F., Principles of Polymer Systems, 3rd edition, Hemisphere Pub. Co., New York, 1989, ISBN 0-89116-176-7.
- 3. Young, R.J., and Lovell, P.A., *Introduction to Polymers*, 2nd edition, Chapman & Hall Pub. Co., New York, 1989, ISBN 0-412-30630-1.
- 4. Strong, A.B., *Plastics: Materials and Processing*, 3rd edition, Prentice-Hall, Upper Saddle River, NJ, 2006, ISBN 0-13-021626-7.

- 5. *The Macrogalleria*, a website maintained by personnel at the University of Southern Mississippi and devoted to polymeric materials: http://pslc.ws/macrog/index.htm.
- ASTM Standard C162-05 2010, Standard Terminology of Glass and Glass Products, ASTM International, West Conshohocken, PA, 2003, 10.1520/C0162-05R10, www.astm.org.
- Donnet, J.-B., Wang, T.K., Peng, J.C.M., and Reboillat, M., *Carbon Fibers*, 3rd edition, Marcel Dekker, Inc., New York, 1998, ISBN 0-8247-0172-0.
- Cox, B., and Flanagan, G., Handbook of Analytical Methods for Textile Composites, NASA Contractor Report 4750, NASA-Langley Res. Ctr., 1997.
- 9. Kalpakjian, S., *Manufacturing Processes for Engineering Materials*, 3rd edition, Addison-Wesley Longman, Inc., Menlo Park, CA, 1997, ISBN 0-201-82370-5.
- Schwartz, M.M., Composite Materials Handbook, McGraw-Hill Book Co., New York, 1983, ISBN 0-07-055743-8.
- 11. Hyer, M.W., *Stress Analysis of Fiber-Reinforced Composite Materials*, McGraw-Hill Book Co., New York, 1998, ISBN 0-07-016700-1.
- Herakovich, C.T., Mechanics of Fibrous Composites, John Wiley & Sons, New York, 1998, ISBN 0-471-10636-4.
- Jones, R.M., Mechanics of Composite Materials, McGraw-Hill Book Co., New York, 1975, ISBN 0-07-032790-4.
- Hull, D., An Introduction to Composite Materials, Cambridge University Press, Cambridge, UK, 1981. ISBN 0-521-23991-5.