COMPOSITE MATERIALS

1. Introduction

Composite materials are multiphase materials obtained by artificial combination of different materials, so as to attain properties that the individual components by themselves cannot attain. The concept of improved performance is broad and includes increased strength or reinforcement of one material by the addition of another material, as well as increased toughness, decreased coefficient of thermal expansion, and increased thermal or electrical conductivity.

An example of a composite material is a lightweight structural material (as used for aircraft) that is obtained by embedding continuous carbon fibers in one or more orientations in a polymer matrix. The fibers provide the strength and stiffness, while the polymer serves as the binder.

Another example is concrete, which is a structural composite (as used for highways) obtained by combining (through mixing) cement (the matrix, ie, the binder, obtained by a reaction, known as hydration, between cement and water), sand (fine aggregate), gravel (coarse aggregate), and optionally other ingredients that are known as admixtures. Short fibers and silica fume (a fine SiO_2 particulate) are examples of admixtures.

2. History

Performance improvement is the well-known purpose in the alloying of metals and in the incorporation of chopped straw into clay for bricks by the ancient Egyptians and of plant fibers into pottery by the Incas and Mayans. These ancient productions of composite materials consisted of reinforcing brittle materials with fibrous substances. In both cases, the mechanics of the reinforcement was such as to reduce and control the production of cracks in the brittle material during fabrication or drying (1).

The modern interest in composite materials can be traced to the development of Bakelite, or phenolic resin, in 1906. Bakelite was a hard, brittle material that had few if any mechanical applications on its own. However, the addition of a filler—the earliest applications used short cellulose fibers (1)—yielded Bakelite molding compounds that were strong and tough and found early applications in mass-produced automobile components. The wood flour additive improved Bakelite's processibility and physical, chemical, and electrical properties, as well as reducing its cost (2,3).

In 1920, experiments showed that bulk glass, which has a tensile strength of $\sim$200 MPa (29,000 psi), could be produced in fiber form with strengths of $\sim$4 GPa (580,000 psi). The strengths of the glass fibers increased rapidly as the glass was drawn to smaller diameters. It was also observed that the strength of the glass fibers decreased with length, implying that the glass fibers were very sensitive to surface defects. The incorporation of strong glass fibers in plastic matrices produced practical bulk materials in which the plastic matrix functioned as a binder, transferring load to the fibers and separating the fibers. The fibers were thus protected and prevented from coming in contact with one another and possibly reducing their strength by abrasion. The term reinforced plastics, commonly used for these materials, is, therefore, misapplied (1,4), inasmuch as it is the plastic that maintains the strength of the fiber, rather than the fiber that reinforces the plastic. Early applications of glass-reinforced plastics date back to the end of World War II, when radomes were fabricated by wet lay-up of yarns of glass woven into cloth and impregnated with polyester resin. Glass-reinforced plastics are still used for radomes in aerospace and submarine applications. Large volumes of chopped strand mat (CSM) consisting of short lengths of glass fibers (25–75 mm) randomly arranged have been used in marine and automotive applications.

In the early 1960s there was a significant increase in interest in the science of composite materials when very strong and stiff, but brittle, ceramic, boron, and carbon fibers became available. These new fibers were at least as strong as the glass fibers of the same diameter but $\sim$5–10 times stiffer (ie, higher in the elastic modulus). The term advanced composites has been coined to cover those reinforced plastics containing continuous, strong and stiff fibers such as carbon (graphite), boron, aramid, or glass. Advanced composites have been developed primarily for the aerospace industry, in which the demand for strong and stiff lightweight structures overcame the prohibitive costs of early composite materials systems. Currently, advanced composite materials, mainly carbon fiber reinforced epoxy composites, are used widely in military aircraft and increasingly in civil aircraft. The largest volume usage of these materials has, however, been in the recreational area in applications such as tennis rackets and golf club shafts (5).

3. Composite Classification According to the Matrix Material

Composites can be classified according to their matrix material. The main classes of composites are thus polymer–matrix, cement–matrix, metal–matrix, carbon–matrix, and ceramic–matrix composites (6).

Polymer–matrix and cement–matrix composites are the most common, due to the low cost of fabrication. Polymer–matrix composites are used for lightweight structures (aircraft, sporting goods, wheel chairs, etc), in addition to vibration damping, electronic enclosures, asphalt (composite with pitch, a polymer, as the matrix), solder replacement, etc.

Cement-matrix composites in the form of concrete (with fine and coarse aggregates), steel reinforced concrete, mortar (with fine aggregate, but no coarse aggregate) or cement paste (without any aggregate) are used for civil structures, prefabricated housing, architectural precasts, masonry, landfill cover, thermal insulation, sound absorption, etc.

Carbon–matrix composites are important for lightweight structures (eg, Space Shuttle) and components (eg, aircraft brakes) that need to withstand high temperatures, but they are relatively expensive due to the high cost of fabrication. Carbon–matrix composites suffer from their tendency to be oxidized ($C + O_2 \rightarrow CO_2$), thereby becoming vapor.

Ceramic–matrix composites are superior to carbon–matrix composites in the oxidation resistance, but they are not as well developed as carbon–matrix composites.

Metal-matrix composites with aluminum as the matrix are used for lightweight structures and low thermal-expansion electronic enclosures, but their applications are limited by the high cost of fabrication and by galvanic corrosion.

4. Composite Classification According to Geometry

Composites can also be classified according to the geometry as fibrous, laminated, and particulate (7).

4.1. Fibrous Composites. These composites consist of fibers in a matrix. The fibers may be (*1*) short or discontinuous and randomly arranged, (*2*) continuous filaments arranged parallel to each other, (*3*) woven rovings (collections of bundles of continuous filaments), or (*4*) braided sheaths (8). In the case of chopped strand mats, the random fiber arrangement is planar (ie, two-dimensionally random). In whisker (needle-shaped crystals or filaments of carbon or ceramics) reinforced materials, the arrangement is usually three-dimensional and the resulting composites are macroscopically homogeneous.

4.2. Laminates. Two or more layers of material bonded together form a laminated composite. Common examples of laminates are in automobile windshields (laminated glass) and bimetal thermostats (9). In both cases homogeneous, isotropic layers of materials are bonded together to form nonhomogeneous composite laminates (see LAMINATED MATERIALS, GLASS).

Plastic laminated sheets produced in 1913 led to the formation of the Formica Products Company and the commercial introduction, in 1931, of decorative laminates consisting of a urea–formaldehyde surface on an unrefined (kraft) paper core impregnated with phenolic resin and compressed and heated between polished steel platens (8,10). The decorative surface laminates are usually $\sim$1.6 mm thick and bonded to wood (a natural composite), plywood (another laminate), or particle board (a particulate composite). Since 1937, the surface layer of most decorative laminates has been fabricated with melamine–formaldehyde, which can be prepared with mineral fillers, thus offering improved heat and moisture resistance and allowing a wide range of decorative effects (10,11).

Plywood is a laminate consisting of thin sheets of wood arranged with the grain in alternate sheets at right angles (12) (see BUILDING MATERIALS, SURVEY; WOOD-BASED COMPOSITES AND LAMINATES). Invented in the mid-nineteenth century using natural based adhesives, the manufacture of plywood was greatly improved by the introduction of phenolic resins (10,11). Indeed, plywood accounts for $> 60\%$ of the total phenolic resin production (13).

Fiber composite laminates often consist of unidirectional (parallel) continuous fibers in a polymer matrix, with the individual layers, plies or laminae stacked with selected fiber angles so as to produce specific laminate stiffness and strength values. Laminates are also made by stacking layers of mats or woven fabric, which have many possible weave configurations (14,15). The arrangement of the layers of a laminate is known as the stacking sequence. Laminates can be classified as unidirectional, in which case all, or nearly all (8), of the fibers lie in the same direction (5). A schematic of a unidirectional laminate is shown in Figure 1. Unidirectional laminates are orthogonal with respect to their principal axes which are parallel to the fibers (7) and perpendicular to the fibers (1), as indicated in Figure 1. Unidirectional laminae can be stacked so as to tailor the laminate to produce a wide range of mechanical responses. A commonly used code for specifying the stacking sequence of a laminate uses the subscript T for the total stacking sequence, starting from the top surface, and the subscript S for a laminate that is symmetric about the midplane (5). The laminate shown in Figure 2 could be referred to as $[0/\theta/0]_T$ or $[0/\theta]_s$, where the bar above θ denotes a ply that is symmetrically placed about the middle surface of the laminate. A common stacking sequence is cross-ply, in which the fibers in each ply are at 0° or 90°; eg, the laminate $[0/90]_S$ is a four-ply symmetric cross-ply laminate with the top and bottom surface fiber directions at 0°. Another common laminate uses the angle-ply stacking sequence, in which the fiber orientations are $\pm\theta$. Often the plies are balanced so that there are equal numbers of $+\theta$ and $-\theta$ plies. The laminate $[45/-45]_S$ has a balanced symmetric angle-ply stacking sequence. If the reference direction were rotated by 45°, then this angle-ply laminate would be represented as the cross-ply laminate with the stacking sequence $[0/90]_S$. The four-ply laminate $[45/-45/0/90]_T$ is not symmetric (5). Both the cross-ply and angle-ply laminates are examples of bidirectional laminates (5). Quasi-isotropic laminates are multidirectional laminates that have two equivalent (isotropic) elastic constants in the plane of the laminate (4,5,7). Examples of quasi-isotropic laminates are $[0/60/-60]_T$, $[0/60/-60]_S$, and $[0/45/-45/90]_S$. Even though the first example is not a symmetric laminate, it is defined as quasi-isotropic because the definition refers only to the in-plane stiffness properties (7). In all the laminates mentioned so far the thickness of each ply is the same. Such laminates are sometimes referred to as regular laminates. Special laminate properties can be obtained by using asymmetric (16) or unbalanced laminates, as in the case of the Grumman X-29A aircraft, which has a forward-swept wing configuration in which the laminate is tailored to counteract (through coupling between flexure and torsion) the aeroelastically unstable effects of the upward twisting tendency of the wing (17).

4.3. Particulate Composites. These composites encompass a wide range of materials. As the word *particulate* suggests, the reinforcing phase is often spherical or at least has dimensions of similar order in all directions. Examples are concrete, filled polymers (18), solid rocket propellants, and metal and ceramic particles in metal matrices (7).

Concrete consists of an aggregate of coarse (>5 mm) or fine particles (gravel, crushed rock, sand, slag, etc) bound in a cement matrix, with the aggregate content constituting typically 66–78% by weight (19). In concrete, the role of the aggregate has often been regarded as that of an inert filler, introduced to reduce cost (20). However, significant technical improvements in volume stability, durability (20), and strength and stiffness (18,20) are obtained with concrete in comparison with cement (qv).

In polymeric materials, particles are used as fillers to improve strength, toughness, processibility, dimensional stability, frictional wear and lubrication properties, and, in some cases, resistance to ultraviolet radiation (21,22). The particle characteristics can be classified as sphere, cube, block, flake, and fiber (21). Common fillers (qv) are glass (spheres), calcite (cube and block), kaolin, mica and talc (flakes), and wood flour (flake) (21). The scale of the particles used depends on the role and ranges from submicrometer to several hundred micrometers. In some cases, the filler can improve some properties while degrading others, as in nylon-6,6, which has improved strength and stiffness but reduced impact strength when filled with 30% glass (23).

Solid rocket propellants represent a very special case of a particulate composite in which inorganic propellant particles, ~75% by volume, are bound in an organic matrix such as polyurethane. An essential requirement is that the composite be uniform to promote a steady burning reaction (1). Further examples of particulate composites are those with metal matrices and include cermets (ie, ceramic–metal combinations), which consist of ceramic particles in a metal matrix, and dispersion hardened alloys, in which the particles may be metal oxides or intermetallic compounds with smaller diameters and lower volume fractions than those in cermets (7). The general nature of particulate reinforcement is such that the resulting composite material is macroscopically isotropic.

5. Applications

5.1. Structural Applications. Structural materials are predominantly metal and polymer-based materials, although they also include carbon- and ceramic-based materials, which are valuable for high temperature structures. Among the metal-based structural materials, steel and aluminum alloys are dominant. Steel is advantageous in the high strength, whereas aluminum is advantageous in the low density. For high temperature applications, intermetallic compounds (such as NiAl) have emerged, though they suffer from their brittleness. Metal–matrix composites are superior to the corresponding metal matrix in the high modulus, high creep resistance, and low thermal expansion coefficient, but they are expensive due to the processing cost.

Among the cement-based structural materials, concrete is dominant. Although concrete is an old material, improvement in the long-term durability is needed, as suggested by the degradation of bridges and highways in developed countries. The improvement pertains to decrease in the drying shrinkage (shrinkage of the concrete during curing or hydration), as the shrinkage can cause cracks. It also pertains to decrease in the fluid permeability, as water permeating into steel reinforced concrete can cause corrosion of the reinforcing steel. Moreover, it pertains to improvement in the freeze–thaw durability, which is the ability of the concrete to withstand temperature variations between temperatures <0 (freezing of water in concrete) and those $>0°C$ (thawing of water in concrete).

Among the polymer-based structural materials, fiber reinforced polymers are dominant, due to their combination of high strength and low density. All polymer-based materials suffer from their inability to withstand high temperatures. This inability can be due to the thermal stress resulting from the thermal expansion mismatch between the polymer matrix and the fibers. (The coefficient of thermal expansion is typically much lower for the fibers than for the matrix.) The inability can also be due to the softening of the polymer matrix at the glass transition temperature T_g, in addition to the low melting temperature of the polymer matrix.

5.2. Electronic Applications.

The dominant material for electrical connections is solder (eg, Sn–Pb alloy). However, the difference in the coefficient of thermal expansion (CTE) between the two members that are joined by the solder causes the solder to experience thermal fatigue upon thermal cycling, which is encountered during operation. The thermal fatigue can lead to failure of the solder joint. Polymer–matrix composites in paste form and containing electrically conducting fillers are being developed to replace solder. Another problem lies in the lead (poisonous) used in solder to improve the rheology of the liquid solder. Lead-free solders are being developed.

Heat sinks are materials with a high thermal conductivity. They are used to dissipate heat from electronics. Because they are joined to materials of a low CTE (eg, a printed circuit board in the form of a continuous fiber polymer–matrix composite), they need to have a low CTE also. Hence, materials exhibiting both a high thermal conductivity and a low CTE are needed for heat sinks. Copper is a metal with a high thermal conductivity, but its CTE is too high. Therefore, copper is reinforced with continuous carbon fibers, molybdenum particles, or other fillers of low CTE.

6. Reinforcements

The choice of reinforcement for a particular engineering application is likely to depend on a large number of parameters, including strength, stiffness, environmental stability, long-term characteristics, and cost. At present, carbon, glass, and aramid fibers account for $> 95\%$ of the industrial market, with increasing use in areas such as the aerospace, automotive, construction, biomedical, and sport sectors. No single fiber type can be said to be truly superior to another; each has its own merits as well as shortcomings. The stress–strain responses obtained by bending typical carbon, glass, and aramid fibers are summarized in Figure 3. The test gage length should be specified when the tensile strength is reported. The tensile strength of a brittle fiber depends on the gage length. Carbon fibers generally offer the highest strengths and stiffnesses but can be brittle, failing at relatively low applied strains. Glass fibers offer intermediate strengths and higher failure strains but exhibit lower moduli. Aramid fibers such as Kevlar, a proprietary material developed by Du Pont, have lower strengths but are capable of absorbing considerable energy without fracture. Rather than using strength and stiffness as the performance parameters for material selection, specific properties obtained by normalizing the property with respect to the density (ρ) of the fiber are often quoted. For tensile or compressive members, the specific strength (σ/ρ) yields the largest load-carrying capacity for a given mass and the specific stiffness (E/ρ) produces the smallest deflection for a given mass (18). A convenient way of comparing fibers is to plot specific strength against specific modulus, as shown in Figure 4. The data presented in Figure 4 consist of the properties of the fiber types discussed in the following sections, with the values for steel wire also shown for comparison. Because some of the fibers are extremely sensitive to flaws, the values of the specific strengths may be subject to wide variations.

The following sections also include brief presentations of manufacturing procedures because the final properties of the fibers depend on the processing conditions. For more about the structure or mechanical characteristics of the fibers, the reader is directed to more comprehensive discussions presented elsewhere in the *Encyclopedia* or in the literature (8,24–30).

6.1. Glass Fibers. Glass fibers represent the most frequently used reinforcement in modern polymer composites. This popularity results from their relatively low cost and high tensile strength. In bulk form, glass is brittle, having a relatively low strength. However, when extruded and drawn into fine fibers, the strength of glass increases enormously, by as much as two orders of magnitude. Glass-fiber-reinforced composites are currently used in a wide variety of applications, including boat construction and the automotive and aerospace industries. Many types of glass fiber are available, each having specific properties and characteristics. The most commonly used fibers, E-glass, contain ~14% Al_2O_3, 18% CaO, 5% MgO, 8% B_2O_3, and 1% $Na_2O + K_2O$ as well as SiO_2 (silica) (see GLASS).

Glass fibers are produced by dry mixing the individual components and then heating them to form a melt. The temperature of the melt depends on the glass composition, but is typically ~1250°C. The molten glass then passes into the fiber-drawing furnace and subsequently flows through a large number of tiny orifices forming fine filaments. By pulling these filaments swiftly and continuously, the glass can be drawn into fine circular fibers with a diameter typically between 10 and 13 μm. In this form, glass fibers can be damaged very easily; a slight touch can cause a significant reduction in strength. It is common practice, therefore, to apply a size, a surface coating, to protect the fibers during handling and prevent damage during any subsequent processing stages, such as weaving. The size needs to be carefully formulated so as to hold the individual fibers together and afford sufficient lubrication when they come in contact with the processing equipment. Once the fibers have been woven into their final form, a coupling agent is applied. The coupling agent reacts with the fiber and matrix phases of the composite material to promote a strong bond at the interface.

Standard E-glass fibers are inexpensive to manufacture and offer satisfactory mechanical properties, such as a modulus of 72 GPa (1.04×10^7 psi) and a tensile strength of ~3.45 GPa (500,000 psi) (27). E-glass fibers are used extensively in automotive and marine applications, in the sports industry, and in chemical plants. Certain applications, however, require higher modulus fibers, which can be achieved by incorporating greater quantities of Al_2O_3 and MgO into the basic silica compound. Higher modulus, 87 GPa (1.26×10^7 psi), and strength, 4.6 GPa (667,000 psi), are achieved with S-glass fibers (27), which are used in the aerospace sector, where the increased production cost is offset by the significant reduction in weight of parts manufactured using such fibers. Other types of glass fibers that offer superior resistance in acidic and alkaline environments, radiation protection, and also dielectric characteristics are also available, albeit at a higher cost than the basic E-glass fiber.

Other advantages of glass fibers include their good energy-absorbing characteristics when used in composite form and their ability to resist very high temperatures; also, they do not burn, do not absorb water, have a low coefficient of thermal expansion, and offer excellent electrical insulation. Their greatest limitation is, however, their relatively low modulus. One means of overcoming this limitation is to combine glass fibers with a higher modulus fiber, eg, carbon fibers, so that the merits of both fibers combine to produce a strong, stiff, hybrid composite material.

6.2. Carbon Fibers. Although fine carbon filaments were first manufactured from a cellulose base material (8) as long ago as 1880, modern production and manufacturing of carbon fibers began in significant quantities in the early 1960s. The mechanical properties offered by carbon fiber composites, such as high strength and stiffness, are directly attributable to the highly anisotropic nature of the carbon crystal (see CARBON AND GRAPHITE FIBERS). The current technology for manufacturing carbon fibers is based on the thermal decomposition of organic precursor materials such as polyacrylonitrile (PAN) and pitch. Early efforts aimed at developing processes using rayon precursors were found to produce a low yield of carbon fibers with relatively low strength and modulus (28). Generally, the stages in the production of carbon fibers from the various organic precursors can be identified as spinning, stabilization, carbonization, and graphitization. Most carbon fibers are based on the PAN precursor, which is first pumped through a spinneret into a coagulating bath. The spinneret contains between 1000 and 320,000 holes producing tows of continuous fibers (24). Stretching the tow after spinning has the effect of increasing the strength and modulus of the carbon fibers (30). These intermediate modulus (IM) fibers have finer diameters than the unstretched high strength (HS) fibers, as a result of the postdrawing process, and moduli and strengths of up to 300 GPa (4.35×10^7 psi) and 5.2 GPa (754,000 psi), respectively. In the stabilization process, which is needed to convert the precursor into a thermally stable form capable of withstanding the high temperatures and processing rates with a good yield (28), the PAN fibers are oxidized in air at 200–300°C, under strain. The carbonization stage involves rapid pyrolysis in an inert atmosphere, typically nitrogen, at temperatures between 1000 and 1500°C. This procedure yields the previously mentioned high strength fibers, which have a modulus of ~230 GPa (3.3×10^7 psi) and a strength of ~3.3 GPa (478,500 psi). The strength of the PAN-based carbon fibers reaches a maximum at a carbonization temperature of ~1500°C (24,29,31). In this stage of processing almost all elements other than carbon are eliminated as volatiles, with some residual amounts of nitrogen, perhaps, and stretched ring carbon structures are produced (28). High modulus (HM) fibers can be produced by subsequently heating in an argon atmosphere to a temperature between 2000 and 3200°C in the graphitization stage. For carbon fibers produced using rayon precursors, the graphitization is usually performed with the fibers under strain, making the process expensive and, as a result of the relatively low yield, inefficient.

Although the terms *graphite* and *carbon* are often used interchangeably, they are also used to distinguish graphite fibers, which have been subjected to heat treatment at temperatures >1700°C, have some degree of preferred orientation, and have tensile moduli of the order of 345 GPa, from carbon fibers, which have lower degrees of preferred orientation, heat-treatment temperatures, and tensile moduli (8). The term *graphite fibers* can also refer to carbon fibers that are heated at temperatures >2000°C (30).

Carbon fibers produced from pitch precursors can be manufactured by spinning, carbonization and graphitization at temperatures similar to those used in the manufacture of PAN-based fibers. The isotropic pitch precursor has not proved attractive to industry, although discontinuous carbon fibers made from isotropic pitch are low cost and thus useful as an admixture in concrete. However, a process based on anisotropic mesophase pitch (30), in which commercial pitch is spun and polymerized to form the mesophase, which is then melt spun, stabilized in air at ~300°C, carbonized at 1300°C, and graphitized at 3000°C, produces ultrahigh modulus (UHM) carbon fibers. In this process, tension is not required in the stabilization and graphitization stages.

Surface treatment of fibers is an important stage in the manufacturing process. The primary aim of such treatment is to improve the adhesion between the fiber and the matrix and to improve handleability (29,32). The types of treatment are oxidative gas or dry oxidation, wet oxidation, and aqueous electrolytic or anodic oxidation. Anodic oxidation, which uses electrolytes such as sulfuric acid, potassium sulfate, or sodium hydroxide and oxidation times of 1–10 min, is the main industrial process (32). Oxidation treatments involving temperatures of ~2800°C (8) have led to significant increases in fiber strength by removing volume and surface flaws, thus resulting in the production of very high strength fibers. Finally, an organic coating, or size, is applied to the fibers. Often this coating is the same as the matrix used in the composite (29).

Pitch-based fibers generally have higher moduli, but lower strengths than their PAN-based counterparts. The specific properties of the various types of carbon fibers are compared in Figure 4. Pitch-based fibers also have higher electrical conductivity, which can be an important consideration in certain circumstances, for example, for use in electromagnetic interference (EMI) shielding.

Carbon-fiber-reinforced plastic composites are currently used in primary and secondary aircraft structures, helicopter rotor blades, sporting goods such as fishing rods and tennis rackets, and certain biomedical applications. As well as offering superior stiffness and strength, carbon fibers offer good thermal stability, a low and negative (-0.5 to -1.2×10^{-6}/°C) axial coefficient of thermal expansion (6), and excellent fatigue resistance when used in a composite form. Laminated composites based on carbon fibers suffer certain limitations, perhaps the most significant being their relatively low energy-absorbing capacity, their poor resistance to transverse impact loading and their tendency to delaminate (ie, local separation of the plies in the laminate). They also suffer from poor abrasion resistance, are attacked by certain acids, and undergo galvanic corrosion when brought into contact with certain metals and allows.

6.3. Aramid Fibers. Aromatic polyamide fibers exhibiting a range of mechanical properties are available from several manufacturers, perhaps the best known being Du Pont's proprietary fiber Kevlar. These fibers possess many unique properties, such as high specific tensile strength and modulus (see Fig. 4). Aramid fibers have good chemical resistance to water, hydrocarbons, and solvents. They also show excellent flame retardant characteristics (see HIGH PERFORMANCE; POLYAMIDES, GENERAL).

Aramid fibers are formed by mixing a polymer, poly(*p*-phenyleneterephthalamide), with a strong acidic solution and extruding the mixture through spinnerets at a temperature between 50 and 100°C. The fibers are cooled and then washed thoroughly before being dried on bobbins. The properties of the aramid fibers can be modified by using solvent additives or by using a postspinning heat treatment. Aramid fibers with relatively low moduli, such as Kevlar 29 (K-29 in Fig. 4), find use in energy-absorbing applications such as bullet-resistant and other protective clothing, helmets, and ropes. The higher modulus counterpart, Kevlar 49 (K-49 in Fig. 4), is used in high performance engineering applications such as the manufacture of load-bearing components for the aerospace industry where it is used in filament-wound rocket motor cases (33).

Kevlar fibers are highly crystalline in structure, with rigid molecular chains oriented in their longitudinal direction (27). The weak hydrogen bonds in the transverse direction result in a highly anisotropic fiber with low transverse tensile strengths. Consequently, when heavily loaded, such fibers tend to split extensively or to fibrillate, which is clearly a limitation in certain applications. Other limitations of these fibers include their low compressive strength, sometimes poor adhesion to polymer matrices, and tendency to absorb water. Special tooling is needed for cutting or machining.

6.4. Other Fibers. Boron fibers attracted considerable attention in the 1960s and 1970s as a result of their high modulus and strength (~400 and 3.5 GPa, respectively). Each filament of boron fibers consists of a core of either tungsten wire or carbon fiber on which a layer of boron is applied (34). The boron is vapor deposited onto the central filament from a boron trichloride-hydrogen solution. The resulting fibers have a large cross-section, typically between 100 and 200 μm, and, therefore, offer very high stability in compressive stress fields. Boron fiber-epoxy composites were used in the stabilizers of the Grumman F-14 and McDonnel Douglas F-15 aircraft (7,24). Currently, boron fibers are more commonly used in metal matrices such as aluminum and magnesium. Boron-reinforced plastics, however, still find use as repair patches for damaged aircraft structures as well as in certain sporting goods, such as fishing rods and golf club shafts (24).

Polyethylene fibers are attracting considerable interest owing to their high specific strength and stiffness as well as their excellent energy-absorbing capability. Two methods are used to manufacture polyethylene fibers (see FIBERS, OLEFIN). The first involves the extrusion and drawing of a medium molecular weight polyethylene. The second method involves dissolving the polymer in a solvent and spinning at a temperature of ~140°C. The fibers so produced offer tensile strengths up to 3.2 GPa (464,000 psi) and moduli as high as 170 GPa (2.5×10^7 psi) (24). The specific strength and modulus of high performance polyethylene fibers compare very favorably with those of aramid and carbon fibers (see Fig. 4). However, their wider application is limited by relatively poor compressive properties and a low melting point, 150°C.

Silicon carbide fibers exhibit high temperature stability and, therefore, find use as reinforcements in certain metal matrix composites (24). Silicon carbide fibers have also been considered for use with high temperature polymeric matrices, such as phenolic resins, capable of operating at temperatures up to 300°C. Silicon carbide fibers can be made in a number of ways, eg, by vapor deposition on carbon fibers. The fibers manufactured in this way have large diameters (up to 150 μm), and relatively high Young's modulus and tensile strength, typically as much as 430 GPa (6.2×10^7 psi) and 3.5 GPa (507,500 psi), respectively (24,34) (see REFRACTOEY FIBERS).

7. Matrix Materials

The mechanical properties of composites based on the fibers discussed depend not only on the characteristics of the fibers but also on those of the matrix itself as well as on the fiber-matrix interface.

7.1. Polymer Matrices. The matrix in a polymer composite serves both to maintain the position and orientation of the fibers and to protect them from potentially degrading environments. Polymer matrices may be thermosets or thermoplastics. Thermosetting polymers are rigid, cross-linked materials that degrade rather than melt at high temperatures; thermoplastics are linear or branched molecules that soften upon heating. A comparison of the mechanical properties and relative cost of various thermosetting and thermoplastic materials is given in Table 1 (35), and the critical composite property, interlaminar fracture toughness G_{Ic}, is shown in Figure 5 (36,37). Thermoset-based composites are somewhat less expensive than thermoplastic-based composites, but have lower heat distortion temperatures and poorer toughness when tested in an interlaminar mode (36). The majority of present day composite components are still based largely on thermosetting matrices, such as unsaturated polyesters, epoxies, and phenolic resins (see COMPOSITE MATERIALS, THERMOSET POLYMER-MATRIX).

Thermosetting Matrices. Unsaturated polyester resins represent one of the most commonly used matrix systems employed in the manufacture of composite components. The marine industry in particular has profitted greatly from the moderate cost and ease of use of polyester resins. Several types of polyester resins are presently available, offering a wide range of properties such as superior strength or resistance to acidic environments. The curing reaction of polyester resins is exothermic, providing heat to further accelerate the curing process. Composites based on polyester resins are generally manufactured using hand lay-up or spray-up techniques. Large, single-piece components, such as boat hulls and radomes, can be manufactured using polyesters, although care has to be taken when manufacturing thick laminates to ensure that the exothermic heat generation does not damage or degrade the composite. Standard polyester resins offer lower tensile strengths than many of the other thermosets and are limited in terms of their upper operating temperature (see POLYESTERS, UNSATURATED).

Vinyl ester resins generally offer mechanical properties superior to those of polyester matrices but at an increased cost. Vinyl esters are chemically similar to epoxy resins but are manufactured via a cold-curing process similar to that used in the manufacture of polyester resins. Vinyl esters offer superior resistance to water and chemical attack and are used in such applications as underground pipes, tank liners, and storage tanks (see VINYL ACETAL POLYMERS).

Phenolic resins, once a popular matrix material for composite materials, have in recent years been superseded by polyesters and epoxies. Nevertheless, phenolic resins still find considerable use in applications where high temperature stability and fire resistance are of paramount importance. Typical examples of the use of phenolic resins in the marine industry include internal bulkheads, decks, and certain finishings. The curing process involves significant production of water, often resulting in the formation of voids within the volume of the material. Further, the fact that phenolics are prone to absorb water in humid or aqueous conditions somewhat limits their widespread application. Phenolic resins are also used as the adhesive in plywood, and phenolic molding compounds have wide use in household appliances and in the automotive, aerospace, and electrical industries (12).

As a result of their increased cost, epoxy resins tend to be used as matrices for high performance continuous fiber composites. Epoxies offer mechanical properties and water resistance superior to those of polyesters, as well as lower shrinkage during cure. The cure process involves the addition of a hardener and possibly an accelerator as well as a temperature cycle between 60 and 180°C. The resulting mechanical characteristics of the resin depend on the cross-link density of the polymer. High temperature matrices, such as those used in the aerospace sector, tend to have higher cross-link densities and are therefore more brittle. The toughness of epoxy resins can be increased by reducing the cross-link density or by adding a lower modulus phase, such as carboxyl terminated butadiene acrylonitrile (CTBN) rubber or thermoplastic additives. Epoxy-based composites have been used widely in aircraft structures such as rudders, torsion boxes, spoilers, engine pylon fairings, and in racing car bodies. Although very stiff composites result when epoxy resins are combined with carbon fibers, their resistance to localized impact loading is often poor. Indeed, relatively low energy impacts, such as those associated with a dropped tool, can introduce large areas of delamination and thereby significantly reduce residual strength. Repair technology for thermoset-based composites is not very advanced, and a greater understanding of the significance of various defects on load-bearing ability is required.

For higher temperature applications, thermosetting addition polyimides are becoming increasingly important. Polyimide matrix materials were developed in an attempt to produce composites capable of withstanding temperatures of 316°C (600°F) (38,39). One such system is the PMR-15 (*in situ p*olymerization of *m*onomer *r*eactants) polyimide developed at NASA Lewis Research Center. Cure temperatures tend to be higher and cure cycles tend to be longer so that the cost of polyimide systems is greater than that of epoxies. Composites made from polyimide prepreg are generally brittle at room temperature, although significant improvements in toughness are being achieved in new material formulations. For aerospace applications, polyimides have attractive hot-wet properties, but special attention has to be paid to the fiber-matrix interface and the fiber sizing employed (24). Applications of PMR-15-carbon fiber composites include jet-engine cowlings, ducts, compressor blades, and flaps and fairings (24,38).

Thermoplastic Matrices. Many of the thermoplastic-based composites such as carbon-fiber-reinforced PEEK offer excellent resistance to impact loading (40) and are thereby suitable for use in high performance engineering applications. Other interesting aspects of these composites include the possibility of thermoforming and shaping at elevated temperature and the potential for thermal joining and repair, as well as recycling. Long fiber thermoplastic composites can be manufactured directly from preimpregnated sheets of fibers by a film-stacking sequence in which layers of fibers and film are stacked alternately, using plies of commingled polymer filaments and reinforcing fibers, or they can be manufactured from thermoplastic rovinge such as thermoplastic impregnated fibers (FIT).

Carbon fiber-PEEK is a semicrystalline thermoplastic matrix composite. The base polymer is extremely expensive compared with many of the thermosetting matrices, so the PEEK composites are being considered for use in high performance engineering parts such as aerospace components (see POLYETHERS). PEEK is a very ductile aromatic polymer (40) with a strain to failure in excess of 100%. Composites based on this polymer are capable, therefore, of absorbing considerable energy before incurring damage. This quality is most evident under impact conditions where delaminated areas for a given incident energy may be three times smaller than in comparable epoxy-based composites (41,42). Carbon fiber-PEEK also offers high interlaminar fracture toughness (see Fig. 5), as well as superior fatigue properties. Large areas of delamination such as those induced by impact loading can be repaired successfully within short periods of time (43). One of the disadvantages of PEEK-based composites, however, is that they require high processing temperatures, typically 380–400°C. Also, it is suggested that a rapid cooling rate be employed in order to ensure that the resulting degree of crystallinity is not too high (44).

Poly(phenylene sulfide) (PPS) is another semicrystalline polymer used in the composites industry. PPS-based composites are generally processed at 330°C and subsequently cooled rapidly in order to avoid excessive crystallization and reduced toughness. The superior fire-retardant characteristics of PPS-based composites result in applications where fire resistance is an important design consideration. Laminated composites based on this material have shown poor resistance to transverse impact as a result of the poor adhesion of the fibers to the semicrystalline matrix. A PPS material more recently developed by Phillips Petroleum, AVTEL, has improved fiber–matrix interfacial properties, and promises, therefore, an enhanced resistance to transverse impact (see POLYMERS CONTAINING SULFUR, POLY(PHENYLENE SULFIDE)).

A number of amorphous thermoplastics are presently employed as matrices in long fiber composites, including PES, polysulfone (PSU), and PEI. All offer superior resistance to impact loading and higher interlaminar fracture toughnesses than do most epoxies. However, the amorphous nature of such polymers results in a lower solvent resistance, clearly a limitation of composites based on such polymers are to be used in aggressive environments.

7.2. Other Matrix Materials. Advanced materials, eg, structural components, in aerospace vehicles also employ ceramics and metals as composite matrices (see COMPOSITE MATERIALS, CERAMIC-MATRIX; METAL-MATRIX COMPOSITES).

8. Fabrication

A large number of methods are presently available for manufacturing long fiber composites. The cost of finished components depends not only on the price of the raw materials but also on labor costs and energy requirements. Many composite components are manufactured by hand, involving relatively long manufacturing cycles. Large engineering components, such as boat hulls, are frequently manufactured using hand lay-up or spray-up techniques. The whole cycle may last several months, involving a large work force. Considerable effort is being made to find cheaper, more efficient ways to manufacture composite parts and structures. Some of the more commonly employed techniques used to manufacture such parts are outlined in the following. For more information, the reader is directed to Refs. 24 and 25.

8.1. Overview of Fabrication Methods. Fiber composites are most commonly fabricated by the impregnation (or infiltration) of the matrix or matrix precursor in the liquid state into the fiber preform, which is most commonly in the form of a woven fabric. In the case of composites in the shape of tubes, the fibers may be impregnated in the form of a continuous bundle (called a tow) from a spool and subsequently the bundles may be wound on a mandrel. Instead of impregnation, the fibers and matrix material may be intermixed in the solid state by commingling reinforcing fibers and matrix fibers, by coating the reinforcing fibers with the matrix material, by sandwiching reinforcing fibers with foils of the matrix material, and in other ways. After impregnation or intermixing, consolidation is carried out, often under heat and pressure.

Polymer-matrix composites are much easier to fabricate than metal-matrix, carbon-matrix, and ceramic-matrix composites, whether the polymer is a thermoset or a thermoplastic. This is because of the relatively low processing temperatures required for fabricating polymer-matrix composites. For thermosets, such as epoxy, phenolic, and furfuryl resin, the processing temperature typically ranges from room temperature to $\sim 200^\circ$C; for thermoplastics, such as polyimide (PI), PES, PEEK, PEI, and PPS, the processing temperature typically ranges from 300 to 400°C.

Thermosets (especially epoxy) have long been used as polymer matrices for carbon fiber composites. During curing, usually performed in the presence of heat and pressure, a thermoset resin hardens gradually due to the completion of polymerization and the associated cross-linking of the polymer molecules. Thermoplastics have recently become important because of their greater ductility and processing speed compared to thermosets, and the recent availability of thermoplastics that can withstand high temperatures. The higher processing speed of thermoplastics is due to the fact that amorphous thermoplastics soften immediately upon heating above the glass T_g and the softened material can be shaped easily. Subsequent cooling completes the processing. In contrast, the curing of a thermoset resin is a reaction that occurs gradually.

Epoxy is by far the most widely used polymer matrix for carbon fibers. Trade names of epoxy include Epon, Epi-rez, D.E.R., Epotuf and Araldite. Epoxy has an excellent combination of mechanical properties and corrosion resistance, is dimensionally stable, exhibits good adhesion, and is relatively inexpensive. Moreover, the low molecular weight of uncured epoxide resins in the liquid state results in exceptionally high molecular mobility during processing. This mobility helps the resin to quickly spread on the surface of carbon fiber, eg.

Surface treatment of a reinforcement is valuable for improving the bonding between the reinforcement and the polymer matrix. In the case of the reinforcement being carbon fibers, surface treatments involve oxidation treatments and the use of coupling agents, wetting agents, and/or sizes (sizings or coatings).

Carbon fibers need treatment both for thermosets and thermoplastics. As the processing temperature is usually higher for thermoplastics than thermosets, the treatment must be stable to a higher temperature (300–400°C) when a thermoplastic is used.

Short-fiber or particulate composites are usually fabricated by mixing the fibers or particles with a liquid resin to form a slurry, and then molding to form a composite. The liquid resin is the unpolymerized or partially polymerized matrix material in the case of a thermoset; it is the molten polymer or the polymer dissolved in a solvent in the case of a thermoplastic. The molding methods are those conventionally used for polymers by themselves. For thermoplastics, the methods include injection molding (heating above the melting temperature of the thermoplastic and forcing the slurry into a closed die opening by using a screw mechanism), extrusion (forcing the slurry through a die opening by using a screw mechanism), calendering (pouring the slurry into a set of rollers with a small opening between adjacent rollers to form a thin sheet), and thermoforming (heating above the softening temperature of the thermoplastic and forming over a die (using matching dies, a vacuum, or air pressure), or without a die (using movable rollers)). For thermosets, compression molding or matched die molding (applying a high pressure and temperature to the slurry in a die to harden the thermoset) is commonly used. The casting of the slurry into a mold is not usually suitable because the difference in density between the resin and the fibers causes the fibers to float or sink, unless the viscosity of the resin is carefully adjusted. For forming a composite coating, the fiber-resin or particle-resin slurry can be sprayed instead of molded.

Continuous fiber composites are commonly fabricated by hand lay-up of unidirectional fiber tapes or woven fabrics and impregnation with a resin. The molding, called bag molding, is done by placing the tapes or fabrics in a die and introducing high-pressure gases or a vacuum via a bag to force the individual plies together. Bag molding is widely used to fabricate large composite components for the skins of aircraft.

A method for forming unidirectional fiber composite parts with a constant cross-section (eg, round, rectangular, pipe, plate, I-shaped) is pultrusion, in which fibers are drawn from spools, passed through a polymer resin bath for impregnation, and gathered together to produce a particular shape before entering a heated die.

A method for forming continuous fiber composites of intricate shapes is resin transfer molding (RTM), in which a fiber pre-form (usually prepared by braiding and held under compression in a mold) is impregnated with a resin. The resin is admitted at one end of the mold and is forced by pressure through the mold and pre-form. Subsequently the resin is cured. This method is limited to resins of low viscosity, such as epoxy.

A method for forming continuous fiber composites in the shape of cylinders or related objects is filament winding, which involves wrapping continuous fibers from a spool around a form of mandrel. The fibers can be impregnated with a resin before or after winding. Filament winding is used to make pressure tanks. The winding pattern is a part of the composite design. The temperature of the mandrel, the impregnation temperature of the resin, the impregnation time, the tension of the fibers, and the pressure of the fiber winding are processing parameters that need to be controlled.

The schedule for variation of the temperature and pressure during curing and consolidation of prepregs to form a thermoset-matrix composite must be carefully controlled. Curing refers to the polymerization and cross-linking relations that occur upon heating and lead to the polymer, whereas consolidation refers to the application of pressure to obtain proper fiber-matrix bonding, low void content, and the final shape of the part. Curing and consolidation are usually performed together as one process.

The fabrication of carbon–carbon composites is carried out by using four main methods, namely, (*1*) liquid-phase impregnation (LPI), (*2*) hot isostatic pressure impregnation carbonization (HIPIC), (*3*) hot pressing, and (*4*) chemical vapor infiltration (CVI).

All of the methods (except, in some cases, CVI) involve firstly the preparation of a prepreg by either wet winding continuous carbon fibers with pitch or resin (eg, phenolic), or wetting woven carbon fiber fabrics with pitch or resin. Unidirectional carbon fiber tapes are not as commonly used as woven fabrics, because fabric lay-ups tend to result in more interlocking between the plies. For highly directional carbon–carbon composites, fabrics that have a greater number of fibers in the warp direction than the fill direction may be used. After prepreg preparation and, in the case of fabrics, fabric lay-up, the pitch or resin needs to be pyrolyzed or carbonized by heating at 350–850°C. Due to the shrinkage of the pitch or resin during carbonization (which is accompanied by the evolution of volatiles), additional pitch or resin is impregnated in the case of LPI and HIPIC, and carbonization is carried out under pressure in the case of hot pressing. In LPI carbonization and impregnation are carried out as distinct steps, whereas in HIPIC carbonization and impregnation are performed together as a single step.

The most popular method for the fabrication of metal–matrix composites is the infiltration of a pre-form by a liquid metal under pressure. The low viscosity of liquid metals compared to resins or glasses makes infiltration very appropriate for metal-matrix composites. Nevertheless, pressure is required because of the difficulty for the liquid metal to wet the reinforcement.

8.2. Hand and Spray Lay-Up.

Hand lay-up techniques are used quite extensively in the marine industry for constructing relatively small numbers of large components. Typically, parts are manufactured using a female mold onto which a gel coat is applied. The structure can then be built up using sheets of fiber plies or mats and applying a polymer resin (typically a catalyzed polyester) with a brush. Fiber placement is increasingly performed automatically. For large structures, the fibers and resin are dispensed from a gantry that spans the width of the structure. Composites with fiber weight fractions between 25 and 45% can be manufactured using the procedure.

A similar technique, spray-up molding, involves spraying short fibers (25–50 mm in length) mixed with a catalyzed resin onto the mold. The glass–resin mixture is then consolidated by manually rolling the surface. Typically, spray lay-up results in laminates with fiber weight fractions of between 25 and 30%. Advantages of the hand and spray lay-up techniques include low equipment and tooling costs, the ability to include inserts, and the ability to manufacture sandwich constructions. Both procedures have drawbacks, including high labor costs, low production rates, and poor reproducibility, as well as the fact that only one surface has a high quality finish.

8.3. Filament Winding. Bodies of revolution such as cylinders and spherical shells can be manufactured economically by filament winding (24). Continuous fiber bundles (tows) are wound onto a rotating mandrel. The fibers may be impregnated with resin (most frequently a thermoset) just before being wound onto the mandrel (wet winding) or may be preimpregnated with a partially cured matrix (dry winding). The positioning of the fibers is achieved by a feeder arm located in front of the rotating mandrel. The wrap angle, that is, the angle between the fiber and the axis of the mandrel, can usually be varied between 0 and almost 90°, thereby enabling multidirectional components to be realized relatively easily. Once the winding process is finished the whole fixture is cured in an oven in order to yield the desired mechanical properties and structural integrity. The mandrel is then removed by dissolving (for salt- and sand-based mandrels), melting (for low melting point alloys), or collapsing and dismantling (for steel mandrels). In the case of making thermoplastic-based composites by filament winding, the preimpregnated tow or tape is heated by a hot-air blower just before being wound onto the mandrel. This procedure is attractive because the need for a subsequent curing process is removed. Filament winding requires a considerably greater financial investment than do conventional had lay-up techniques. However, increased expense is in part offset by the greater reproducibility of the resulting parts as well as by the higher production rate.

Parts with fiber volume fractions up to 60% can be fabricated by filament winding. The procedure is often used to manufacture composite rocket motors, corrosion-resistant tanks and storage containers, and piping for below-ground applications.

8.4. Autoclave Molding. Bag molding methods include vacuum bag, pressure bag, and autoclave molding (45). Autoclave molding is well suited to the manufacture of large, high quality components. The autoclave itself is a cylindrical pressure vessel capable of generating pressures up to several atmospheres. Heating of the autoclave and, thereby, the composite is achieved by a series of electrical heaters. The composite part is placed against the mold surface and backed with porous PTFE film and a bleeder layer made of glass-fiber cloth, as shown in Figure 6. This layer serves to absorb any excess resin that escapes from the composite during curing. The whole construction is then covered by a vacuum membrane enabling a vacuum to be created within the stack. The cure cycle for a typical epoxy-based composite (Fiberdux 913) is (*1*) the autoclave is heated to 90°C at between 2 and 5°C/min, and a vacuum of 75 kPa (560 mm Hg) is applied; (*2*) the temperature is maintained at 90°C for 30 min in order to allow resin flow; (*3*) 700 kPa (6.9 atm) pressure is applied to the autoclave; (*4*) the vacuum is vented when the pressure reaches 140 kPa (1.4 atm); (*5*) the temperature is increased to 120°C and maintained for 1 h. In this stage, gelation and curing take place. (*6*) The part is cooled and is removed when the temperature falls $>90^\circ$C.

The processing cycle is long and relatively expensive. Autoclave molding is used most commonly, therefore, for manufacturing limited high quality components, such as parts for the aerospace industry. The cross-section of an autoclave-molded carbon fiber composite is shown in the micrograph in Figure 7 in which the interface between plies of different fiber orientation are clearly visible and are associated with resin-rich regions.

8.5. Compression Molding. This molding method is used to manufacture small- and intermediate-sized high quality parts at relatively high rates. A typical flash mold is shown schematically in Figure 8. Flash is the term used to refer to the extruded material that is typically found along the parting lines of a mold (8). The desired number of layers of preimpregnated composite are placed in the lower mold, and the upper mold is lowered until the required pressure is achieved. The composite is then heated according to the required cycle. Certain polymers, such as epoxy resins, flow during processing. For this reason, flash grooves are often machined into the perimeter of the lower mold to catch any excess resin. In order to achieve a high quality surface, great care has to be taken in the manufacture of the mold surfaces. After continued use, the surfaces need to be replaced in order to maintain the desired tolerances. In spite of the costs involved in the production and maintenance of the mold, compression molding represents a relatively inexpensive and practical means of producing high quality composite parts.

8.6. Pultrusion. This technique is commonly used for producing continuous sections of unidirectionally reinforced polymers (46) (Fig. 9). Typically, continuous fibers are pulled through a resin bath and then through a series of wiper rings that serve to remove any excess resin. The fiber–resin mixture is then pulled through a spider, which separates and evenly distributes the fibers before passing into the die. Once in the die, the material is heated, resulting in gelation and curing of the resin. On leaving the die, the composite is sufficiently hard and strong to be pulled mechanically to a large-diameter collecting drum or to a cutter wheel. All the commonly used continuous fibers, such as carbon, glass, and Kevlar, can be pultruded. Pultrusion of hybrid composites is also possible. Thermosetting resins such as polyester and epoxy are commonly used; thermoplastic matrix composites can also be pultruded (47).

8.7. Resin Transfer Molding. Resin transfer molding (RTM) allows the economical manufacture of high quality composites. Dry fibers, which may have the form of a continuous strand mat, or a unidirectional, woven or knitted preform, are placed in a closed mold and resin is then introduced into the mold under external pressure or vacuum. The resin cures under the action of its own exotherm, or heat may be applied to the mold to complete the curing process. Early applications of the resin transfer molding technique employed unsaturated polyester resins. Polyester and vinyl ester resins are used in resin-transfer-molded consumer products, pipes, pressure vessels, and automotive applications. Epoxy resins have also been developed for resin transfer molding of high quality, high fiber volume fraction composite components in electronic and aerospace applications (48).

8.8. Composite Interface Engineering. A composite material typically consists of one or more fillers (fibrous or particulate) in a certain matrix. A carbon fiber composite refers to a composite in which at least one of the fillers is carbon fibers, either short or continuous, unidirectional or multidirectional, woven or nonwoven. The matrix is usually a polymer, a metal, a carbon, a ceramic, or a combination of different materials. Except for sandwich composites, the matrix is three-dimensionally continuous, whereas the filler can be three-dimensionally discontinuous or continuous. Carbon fiber fillers are usually three-dimensionally discontinuous, unless the fibers are three-dimensionally interconnected by weaving or by the use of a binder such as carbon.

The high strength and modulus of carbon fibers makes them useful as a reinforcement for polymers, metals, carbons, and ceramics, even though they are brittle. Effective reinforcement requires good bonding between the fibers and the matrix, especially for short fibers. For an ideally unidirectional composite (ie, one containing continuous fibers all in the same direction) containing fibers of modulus much higher than that of the matrix, the longitudinal tensile strength is quite independent of the fiber–matrix bonding, but the transverse tensile strength and the flexural strength (for bending in longitudinal or transverse directions) increase with increasing fiber–matrix bonding. On the other hand, excessive fiber–matrix bonding can cause a composite with a brittle matrix (eg, carbon and ceramics) to become more brittle, as the strong fiber–matrix bonding causes cracks to propagate straightly, in the direction perpendicular to the fiber–matrix interface without being deflected to propagate along this interface. In the case of a composite with a ductile matrix (eg, metals and polymers), a crack initiating in the brittle fiber tends to be blunted when it reaches the ductile matrix, even when the fiber-matrix bonding is strong. Therefore, an optimum degree of fiber–matrix bonding (ie, not too strong and not too weak) is needed for brittle-matrix composites, whereas a high degree of fiber–matrix bonding is preferred for ductile–matrix composites.

The mechanisms of fiber–matrix bonding include chemical bonding, interdiffusion, van der Waals bonding, and mechanical interlocking. Chemical bonding gives a relatively large bonding force, provided that the density of chemical bonds across the fiber–matrix interface is sufficiently high and that a brittle reaction product is absent at the fiber–matrix interface. The density of chemical bonds can be increased by chemical treatments of the fibers or by sizings on the fibers. Interdiffusion at the fiber–matrix interface also results in bonding, though its occurrence requires the interface to be rather clean. Mechanical interlocking between the fibers and the matrix is an important contribution to the bonding if the fibers form a three-dimensional network. Otherwise, the fibers should have a rough surface in order for a small degree of mechanical interlocking to take place.

Chemical bonding, interdiffusion and van der Waals bonding require the fibers to be in intimate contact with the matrix. For intimate contact to take place, the matrix or matrix precursor must be able to wet the surfaces of the carbon fibers during infiltration of the matrix or matrix precursor into the carbon fiber preform. Wetting is governed by the surface energies. Chemical treatments and coatings can be applied to the fibers to enhance wetting through their effects on the surface energies. The choice of treatment or coating depends on the matrix. A related method is to add a wetting agent to the matrix or matrix precursor before infiltration. As the wettability may vary with temperature, the infiltration temperature can be chosen to enhance wetting. Although wetting is governed by thermodynamics, it is strongly affected by kinetics. Thus, yet another way to enhance wetting is the use of a high pressure during infiltration.

The occurrence of a reaction between the fibers and the matrix helps the wetting and bonding between the fibers and the matrix. However, an excessive reaction degrades the fibers, and the reaction product(s) may be undesirable for the mechanical, thermal, or moisture resistance properties of the composite. Therefore, an optimum amount of reaction is preferred.

Carbon fibers are electrically and thermally conductive, in contrast to the nonconducting nature of polymer and ceramic matrices. Therefore, carbon fibers can serve not only as a reinforcement, but also as an additive for enhancing the electrical or thermal conductivity. Furthermore, carbon fibers have nearly zero coefficient of thermal expansion, so they can also serve as an additive for lowering the CTE. The combination of high thermal conductivity and low thermal expansion makes carbon fiber composites useful for heat sinks in electronics and for space structures that require dimensional stability. As the thermal conductivity of carbon fibers increases with the degree of graphitization, applications requiring a high thermal conductivity should use the graphitic fibers, such as the high modulus pitch-based fibers and the vapor grown carbon fibers. Carbon fibers are more cathodic than practically any metal, so in a metal matrix, a galvanic couple is formed with the metal as the anode. This causes corrosion of the metal. The corrosion product tends to be unstable in moisture and causes pitting, which aggravates corrosion. To alleviate this problem, carbon fiber metal-matrix composites are often coated.

The carbon fibers in a carbon–matrix composite (called carbon–carbon composite) serve to strengthen the composite, as the carbon fibers are much stronger than the carbon matrix due to the crystallographic texture (preferred crystallographic orientation) in each fiber. Moreover, the carbon fibers serve to toughen the composite, as the debonding between the fibers and the matrix provides a mechanism for energy absorption during mechanical deformation. In addition to having attractive mechanical properties, carbon–carbon composites are more thermally conductive than carbon fiber polymer–matrix composites. However, at elevated temperatures (>320°C), carbon–carbon composites degrade due to the oxidation of carbon (especially the carbon matrix), which forms CO_2 gas. To alleviate this problem, carbon–carbon composites are coated.

Carbon fiber ceramic-matrix composites are more oxidation resistant than carbon–carbon composites. The most common form of such composites is carbon fiber reinforced concrete. Although the oxidation of carbon is catalyzed by an alkaline environment and concrete is alkaline, the chemical stability of carbon fibers in concrete is superior to that of competitive fibers, such as polypropylene, glass, and steel. Composites containing carbon fibers in more advanced ceramic matrices (such as SiC) are rapidly being developed.

9. Performance

Polymer–matrix composites can be classified according to whether the matrix is a thermoset or a thermoplastic. Thermoset–matrix composites are by tradition far more common, but thermoplastic–matrix composites are under rapid development. The advantages of thermoplastic–matrix composites compared to thermoset–matrix composites include the following:

Lower manufacturing cost

- No cure.
- Unlimited shelf-life.
- Reprocessing possible (for repair and recycling).
- Less health risks due to chemicals during processing.
- Low moisture content.
- Thermal shaping possible.
- Weldability (fusion bonding possible).

Better performance

- High toughness (damage tolerance).
- Good hot/wet properties.
- High environmental tolerance.

The disadvantages of thermoplastic–matrix composites include the following:

- Limitations in processing methods.
- High processing temperatures.
- High viscosities.
- Prepreg (collection of continuous fibers aligned to form a sheet that has been impregnated with the polymer or polymer precursor) being stiff and dry when solvent is not used (ie, not drapeable or tacky).
- Fiber surface treatments less developed.

Carbon fiber polymer–matrix composites have the following attractive properties:

- Low density (40% lower than aluminum).
- High strength (as strong as high strength steels).
- High stiffness (stiffer than titanium, yet much lower in density).
- Good fatigue resistance (a virtually unlimited life under fatigue loading).
- Good creep resistance.
- Low friction coefficient and good wear resistance (a 40 wt.% short carbon fiber nylon–matrix composite has a friction coefficient nearly as low as Teflon and unlubricated wear properties approaching those of lubricated steel).
- Toughness and damage tolerance (can be designed by using laminate orientation to be tougher and much more damage tolerant than metals).
- Chemical resistance (chemical resistance controlled by the polymer matrix).
- Corrosion resistance (impervious to corrosion).
- Dimensional stability (can be designed for zero coefficient of thermal expansion).

- Vibration damping ability (excellent structural damping when compared with metals).
- Low electrical resistivity.
- High EMI shielding effectiveness.
- High thermal conductivity.

The mechanical properties of carbon–carbon composites are much superior to those of conventional graphite. Three-dimensional carbon–carbon composites are particularly attractive. Their preform structure can be tailored in three directions. The three-dimensional integrated preform structure results in superior damage tolerance and minimum delamination crack growth under interlaminar shearing compared with two-dimensional laminate carbon–carbon composites.

Compared to the metal itself, a carbon fiber metal–matrix composite is characterized by a higher strength/density ratio (ie, specific strength), a higher modulus/density ratio (ie, specific modulus), better fatigue resistance, better high temperature mechanical properties (a higher strength and a lower creep rate), a lower CTE, and better wear resistance.

Compared to carbon fiber polymer–matrix composites, a carbon fiber metal–matrix composite is characterized by higher temperature resistance, higher fire resistance, higher transverse strength and modulus, the lack of moisture absorption, a higher thermal conductivity, a lower electrical resistivity, better radiation resistance, and absence of outgassing.

On the other hand, a metal–matrix composite has the following disadvantages compared to the metal itself and the corresponding polymer-matrix composite: higher fabrication cost and limited service experience.

Although cement is a ceramic material, ceramic–matrix composites usually refer to those with silicon carbide, silicon nitride, alumina, mullite, glasses and other ceramic matrices that are not cement.

Ceramic–matrix fiber composites are gaining increasing attention because the good oxidation resistance of the ceramic matrix (compared to a carbon matrix) makes the composites attractive for high temperature applications (eg, aerospace and engine components). The fibers serve mainly to increase toughness and strength (tensile and flexural) of the composite due to their tendency to be partially pulled out during the deformation. This pullout absorbs energy, thereby toughening the composite. Although the fiber pullout has its advantage, the bonding between the fibers and the matrix must still be sufficiently good in order for the fibers to strengthen the composite effectively. Therefore, the control of the bonding between the fibers and the matrix is important for the development of these composites.

10. Theories of Reinforcement

The advantages of composites include improved stiffness and strength of the composite material system compared with the base line or unreinforced material. For example, the introduction of straw into bricks and plant fibers into pottery by early civilizations resulted in improved strength of the bricks and pottery by preventing cracking induced in drying out of the brittle (crack-sensitive) materials. Brittle materials can be strengthened by increasing toughness. In composites, enhanced toughness can be achieved by increasing the energy required to initiate and propagate a crack through the brittle matrix. Increased work of fracture has been obtained in composites through debonding at the fiber–matrix interface; frictional interaction between the fiber and the matrix as fibers bridging a matrix crack are pulled out of the matrix as the crack extends and opens; deformation of the fibers; and fiber fracture. In the case of brittle matrix composites, small quantities of reinforcing material are needed to achieve the desired performance. Fiber volume fraction is a quantitative measure of degree of reinforcement of the matrix material in a fiber-reinforced composite. If the volume of a composite material is V and the volume of the fibers is V_{f} and that of the matrix is V_{m} then

$$V = V_{\mathrm{f}} + V_{\mathrm{m}}$$

Similarly for weights W, W_{f}, and W_{m}

$$W = W_{\mathrm{f}} + W_{\mathrm{m}}$$

The density ρ of the composite material is then related to the density of the fiber ρ_{f} and matrix ρ_{m} by the rule of mixtures:

$$\rho = \upsilon_{\mathrm{f}}\rho_{\mathrm{f}} + \upsilon_{\mathrm{m}}\rho_{\mathrm{m}}$$

where

$$\upsilon_{\mathrm{f}} = \frac{V_{\mathrm{f}}}{V}$$

$$\upsilon_{\mathrm{m}} = \frac{V_{\mathrm{m}}}{V}$$

and υ_{f} and υ_{m} are the fiber and matrix volume fractions, respectively. Thus, for carbon fibers with a density of 1.8 g/cm^3 in an epoxy resin with a density of 1.2 g/cm^3, the density of the composite as a function of the fiber volume fraction is given in Figure 10.

The stiffness of E_1 of a unidirectional lamina in the fiber direction is also given approximately by the rule of mixtures:

$$E_{\mathrm{l}} = \upsilon_{\mathrm{f}}E_{\mathrm{f}} + \upsilon_{\mathrm{m}}E_{\mathrm{m}}$$

For the case of high modulus fibers such as carbon fibers with $E_{\mathrm{f}} = 240$ GPa (3.5×10^7 psi), in a polymer matrix, such as epoxy resin with $E_{\mathrm{m}} = 3.0$ GPa (450,000 psi), the extensional modulus is approximately proportional to the fiber volume fraction and the modulus of the fibers:

$$E_{\mathrm{l}} \approx \upsilon_{\mathrm{f}}E_{\mathrm{f}}$$

Thus the addition of the stiff carbon fibers has a very great effect in stiffening the epoxy matrix. For the commonly used fiber volume fraction of 0.6 the unidirectional carbon-epoxy lamina has a predicted extensional stiffness $E_1 = 145$ GPa (2.1×10^7 psi).

The relationship between fiber and matrix moduli and fiber volume fraction for a unidirectional lamina loaded in the direction transverse to the fibers is not simple. A lower bound (*1*) is given by the expression of the series spring model,

$$\frac{1}{E_2} = \frac{v_f}{E_f} + \frac{v_m}{E_m}$$

and an upper bound is provided by the rule of mixtures, or parallel spring model. Generally, the fibers may be anisotropic, so that only the transverse fiber modulus should be used. Since this property is difficult to measure (6), it is usual to employ the axial fiber properties and assume isotropic behavior of the constituents in the micromechanics models. A simple model has been developed for the extensional modulus of fibrous and particulate composites using a combination of the series and parallel spring models (49):

$$\frac{E_2}{E_m} = \frac{X}{1 - X\left(1 - \frac{E_m}{E_f}\right)} + (1 - X)$$

where X depends on the reinforcement and packing geometry. For example, for fibers of circular cross-section in a square array,

$$\sqrt{\frac{2v_f}{\pi}} < X < \sqrt{\frac{4v_f}{\pi}}$$

An estimate of the shear modulus G_{12} is also given by an expression based on the series spring model

$$\frac{1}{G_{12}} = \frac{v_f}{G_f} + \frac{v_m}{G_m}$$

The variation of the in-plane shear modulus normalized with respect to the matrix modulus as a function of the fiber volume fraction is shown in Figure 11. As noted earlier, it is generally difficult to measure the shear modulus of the fibers, which may themselves be anisotropic. The equation should be used with caution.

Poisson's ratio, ν_{12}, is the negative of the ratio of the strain transverse to the fiber direction, ϵ_2, and the strain in the fiber direction, ϵ_1, when the lamina is loaded in the fiber direction and can also be expressed in terms of the properties of the constituents through the rule of mixtures.

$$\nu_{12} = v_f \nu_f + v_m \nu_m$$

The difference between the bounds defined by the simple models can be large, so that more advanced theories are needed to predict the transverse modulus of unidirectional composites from the constituent properties and fiber volume fractions (1). The Halpin-Tsai equations (50) provide one example of these advanced theories in which the rule of mixtures expressions for the extensional modulus and Poisson's ratio are complemented by the equation

$$\frac{M}{M_{\mathrm{m}}} = \frac{1 + \xi \eta v_{\mathrm{f}}}{1 - \eta v_{\mathrm{f}}}$$

where

$$\eta = \frac{\left(\dfrac{M_{\mathrm{f}}}{M_{\mathrm{m}}}\right) - 1}{\left(\dfrac{M_{\mathrm{f}}}{M_{\mathrm{m}}}\right) + \xi}$$

M is the composite property (E_1, G_{12}, ν_{23}), and M_{f} and M_{m} are the corresponding fiber and matrix properties. The principal problem in the application of the Halpin-Tsai equations lies in determining the value of ξ, which depends on the fiber and packing geometry and loading conditions (1).

Strength predictions of composites are in general quite complex and somewhat limited. This is particularly true of compressive and shear strengths, which are needed, together with the tensile strengths, in composite failure prediction.

The tensile strength of a unidirectional lamina loaded in the fiber direction can be estimated from the properties of the fiber and matrix for a special set of circumstances. If all of the fibers have the same tensile strength σ_{f} and the composite is linear elastic until failure of the fibers, then the strength of the composite is given by

$$\sigma_{\mathrm{c}} = \sigma_{\mathrm{f}} v_{\mathrm{f}} + \epsilon_{\mathrm{mf}} E_{\mathrm{m}} v_{\mathrm{m}}$$

where ϵ_{mf} is the strain in the matrix when the fibers fail. For carbon fibers in epoxy resin the tensile strength of the composite is predicted to be approximately proportional to the fiber volume fraction. The assumption of a constant failure stress of the fibers is unrealistic. This strength prediction relates to a fiber-dominated model. However, at low values of fiber volume fraction the fiber-dominated model is invalid. This is seen clearly in the limiting case of zero fiber volume fraction when the matrix strength σ_{m} is observed. For very low values of fiber volume fraction, the composite tensile strength is given approximately by the matrix-dominated model:

$$\sigma_{\mathrm{c}} = \sigma_{\mathrm{m}}(1 - v_{\mathrm{f}})$$

Both tensile strength equations are illustrated in Figure 12 using data typical of graphite fibers in epoxy resin.

The four quantities E_1, E_2, G_{12}, and ν_{12} are sufficient to define the stress–strain law for a unidirectional or woven fiber ply under plane stress, loaded in the principal material directions.

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} \frac{E_1}{1-v_{12}v_{21}} & \frac{v_{12}E_2}{1-v_{12}v_{21}} & 0 \\ \frac{v_{12}E_2}{1-v_{12}v_{21}} & \frac{E_2}{1-v_{12}v_{21}} & 0 \\ 0 & 0 & G_{12} \end{bmatrix} \quad \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \gamma_{12} \end{Bmatrix}$$

where

$$v_{21} = \frac{v_{12}E_2}{E_1}$$

This stress–strain relationship is often written as (1)

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} Q_{11} & Q_{12} & 0 \\ Q_{12} & Q_{22} & 0 \\ 0 & 0 & Q_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \gamma_{12} \end{Bmatrix} \quad or \quad (\sigma) = [Q](\epsilon)$$

where $[Q]$ is the reduced stiffness matrix.

The stress–strain relationship is used in conjunction with the rules for determining the stress and strain components with respect to some angle θ relative to the fiber direction to obtain the stress–strain relationship for a lamina loaded under plane strain conditions where the fibers are at an angle θ to the loading axis. When the material axes and loading axes are not coincident, then coupling between shear and extension occurs and

$$\begin{Bmatrix} \sigma_x \\ \sigma_x \\ \tau_{xy} \end{Bmatrix} = \begin{bmatrix} \bar{Q}_{11} & \bar{Q}_{12} & \bar{Q}_{16} \\ \bar{Q}_{12} & \bar{Q}_{22} & \bar{Q}_{26} \\ \bar{Q}_{16} & \bar{Q}_{26} & \bar{Q}_{66} \end{bmatrix} \quad \begin{Bmatrix} \epsilon_x \\ \epsilon_y \\ \gamma_{xy} \end{Bmatrix}$$

or

$$(\sigma) = \left[\bar{\mathrm{Q}}\right] (\epsilon)$$

in which the transformed stiffness terms are related to the reduced stiffnesses and angle θ by (1)

$$\begin{aligned}
\bar{Q}_{11} &= Q_{11}\cos^4\theta + 2\,(Q_{12} + 2\,Q_{66})\sin^2\theta\cos^2\theta + Q_{22}\sin^4\theta \\
\bar{Q}_{12} &= (Q_{11} + Q_{22} - 4\,Q_{66})\sin^2\theta\cos^2\theta + Q_{12}\,\left(\sin^4\theta + \cos^4\theta\right) \\
\bar{Q}_{22} &= Q_{11}\sin^4\theta + 2\,(Q_{12} + 2\,Q_{66})\sin^2\theta\cos^2\theta + Q_{22}\cos^4\theta \\
\bar{Q}_{16} &= (Q_{11} - Q_{12} - 2\,Q_{66})\sin\theta\cos^3\theta + (Q_{12} - Q_{22} + 2\,Q_{66})\sin^3\theta\cos\theta \\
\bar{Q}_{26} &= (Q_{11} - Q_{12} - 2\,Q_{66})\sin^3\theta\cos\theta + (Q_{12} - Q_{22} + 2\,Q_{66})\sin\theta\cos^3\theta \\
\bar{Q}_{66} &= (Q_{11} + Q_{22} - 2\,Q_{12} - Q_{66})\sin^2\theta\cos^2\theta + Q_{66}\left(\sin^4\theta + \cos^4\theta\right)
\end{aligned}$$

Classical laminated plate theory is used to determine the stiffness of laminated composites. Details of the Kirchoff-Love hypothesis on which the theory is based can be found in standard texts (1,7,51). Essentially, the strains in each ply of the laminate are represented as middle surface strains ($\epsilon_x{}^o$, $\lambda_y{}^o$, $\gamma_{xy}{}^o$) plus a component that is proportional to the curvatures and twist (κ_x, κ_y, κ_{xy}) and the distance, z, the ply is from the middle surface (Fig. 13).

$$\left\{\begin{array}{c}\epsilon_x\\ \epsilon_y\\ \gamma_{xy}\end{array}\right\} = \left\{\begin{array}{c}\epsilon_x^o\\ \epsilon_y^o\\ \gamma_{xy}^o\end{array}\right\} + z\left\{\begin{array}{c}\kappa_x\\ \kappa_y\\ \kappa_{xy}\end{array}\right\}$$

The resultant forces (N_x, N_y, N_{xy}) and moments (M_x, M_y, M_{xy}) are determined by integrations of the stresses in each ply.

$$\left\{\begin{array}{c}N_x\\ N_y\\ N_{xy}\end{array}\right\} = \int_{-t/2}^{t/2}\left\{\begin{array}{c}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{array}\right\}_k dz$$

and

$$\left\{\begin{array}{c}M_x\\ M_y\\ M_{xy}\end{array}\right\} = \int_{-t/2}^{t/2}\left\{\begin{array}{c}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{array}\right\}_k z\,dz$$

where k denotes the kth ply located at a distance z from the laminate middle surface and t is the thickness of the laminate (Fig. 13). The stiffness of the laminate is then given as

$$\left\{\begin{array}{c}N_x\\ N_y\\ N_{xy}\end{array}\right\} = \begin{bmatrix}A_{11} & A_{12} & A_{16}\\ A_{12} & A_{22} & A_{26}\\ A_{16} & A_{26} & A_{66}\end{bmatrix}\left\{\begin{array}{c}\epsilon_x^o\\ \epsilon_y^o\\ \gamma_{xy}^o\end{array}\right\} + \begin{bmatrix}B_{11} & B_{12} & B_{16}\\ B_{12} & B_{22} & B_{26}\\ B_{16} & B_{26} & B_{66}\end{bmatrix}\left\{\begin{array}{c}\kappa_x\\ \kappa_y\\ \kappa_{xy}\end{array}\right\}$$

and

$$\left\{\begin{array}{c}M_x\\ M_y\\ M_{xy}\end{array}\right\} = \begin{bmatrix}B_{11} & B_{12} & B_{16}\\ B_{12} & B_{22} & B_{26}\\ B_{16} & B_{26} & B_{66}\end{bmatrix}\left\{\begin{array}{c}\epsilon_x^o\\ \epsilon_y^o\\ \gamma_{xy}^o\end{array}\right\} + \begin{bmatrix}D_{11} & D_{12} & D_{16}\\ D_{12} & D_{22} & D_{26}\\ D_{16} & D_{26} & D_{66}\end{bmatrix}\left\{\begin{array}{c}\kappa_x\\ \kappa_y\\ \kappa_{xy}\end{array}\right\}$$

where the coefficients of the laminate stiffness matrices are given in terms of the ply stiffnesses as

$$(A_{ij}, B_{ij}, D_{ij}) = \int \bar{Q}_{ij}\left(1, z, z^2\right) dz$$

or, for a laminate with N plies,

$$A_{ij} = \sum_{k=1}^{N} (\bar{Q}_{ij})_k (z_k - z_{k-1})$$

$$B_{ij} = \frac{1}{2}\sum_{k=1}^{N} (\bar{Q}_{\mathrm{ij}})_k (z_k^2 - z_{k-1}^2)$$

$$D_{ij} = \frac{1}{3}\sum_{k=1}^{N} (\bar{Q}_{ij})_k (z_k^3 - z_{k-1}^3)$$

An important observation is that generally there will be coupling between extension and bending. A laminate that is symmetric about the middle surface does not suffer from this coupling because the terms of the $[B]$ matrix are zero. A further coupling problem, that of shear-extension coupling, can arise in the $[A]$ matrix, as it did in the lamina stiffness matrix $[\bar{\mathrm{Q}}]$, if the terms A_{16} and A_{26} are not zero. This coupling is eliminated in balanced laminates that have equal numbers of plies of orientations θ and $-\theta$. Thus the majority of laminates are fabricated as balanced symmetric laminates. Coupling between bending and twisting can also be problematic. It is not generally possible to achieve zero values of D_{16} and D_{26}, so it is usual to ensure that these terms are small by using laminates with large numbers of alternating layers (6,51).

Quasi-isotropic laminates have the same in-plane stiffness properties in all directions (1), which are defined in terms of the $[A]$ matrix of the laminate. For the laminate to be quasi-isotropic,

$$A_{11} = A_{22} \quad \text{and} \quad A_{11} - A_{12} = 2\,A_{66}$$

and the laminate has two equivalent elastic constants (7). For the case of a quasi-isotropic laminate with highly isotropic plies the equivalent elastic constants can be expressed as

$$E \approx \frac{3}{8}E_1 + \frac{5}{8}E_2 \quad \text{and} \quad G \approx \frac{1}{8}E_1 + \frac{1}{4}E_2$$

These approximations can also be used for laminates in which the fibers are randomly oriented, provided that the modulus of the fibers is much greater than that of the matrix.

The strength of laminates is usually predicted from a combination of laminated plate theory and a failure criterion for the individual lamina. A general treatment of composite failure criteria is beyond the scope of the present discussion. Broadly, however, composite failure criteria are of two types: noninteractive, such as maximum stress or maximum strain, in which the lamina is taken to fail when a critical value of stress or strain is reached parallel or transverse to the fibers in tension, compression, or shear; or interactive, such as the Tsai-Hill or Tsai-Wu (1,7) type, in which failure is taken to be when some combination of stresses occurs. Generally, the ply materials do not have the same strengths in tension and compression, so that five ply strengths must be determined:

X	the tensile strength parallel to the fibers
X′	the compressive strength parallel to the fibers
Y	the tensile strength in the plane of the ply perpendicular to the fibers
Y′	the compressive strength in the plane of the ply perpendicular to the fibers
S	the in-plane shear strength

These values are determined by experiment. It is, however, by no means a trivial task to measure the lamina compressive and shear strengths (52,53). Also the failure of the first ply of a laminate does not necessarily coincide with the maximum load that the laminate can sustain. In many practical composite laminates first-ply failure may be accompanied by a very small reduction in the laminate stiffness. Local ply-level failures can reduce the stress-raising effects of notches and enhance fatigue performance (54).

11. Economic Considerations

In the form of fiber-reinforced unidirectional and multidirectional composites very high values of strength and stiffness can be achieved with fiber volume fractions of ∼60%. Excellent fatigue properties can also be obtained (54). Transverse impact damage tolerance, which was an early limiting factor in carbon fiber composites, has been improved greatly through the development of high strain to failure fibers and tough matrix and interleaf materials. However, these improvements in properties have been associated with significant increases in the material costs. There have been many applications in which cost has been a secondary factor to performance, such as in the military aerospace fields (24). However, cost has become the critical issue in the continued development and application of advanced composite materials. Composite components can be fabricated through various routes depending on the quality of the end product, and economies in the finished cost can be made by reducing the number of parts and attachments and assembly operations. In comparing costs it is important to include the life-cycle costs. In the oil and gas industry significant reductions in the life-cycle costs can be achieved by replacing steel with fiber-reinforced plastics. Another very large market with enormous potential for the applications of medium technology composites is the automotive industry.

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DEBORAH D. L. CHUNG
University at Buffalo,
State University of New York Buffalo, N.Y.

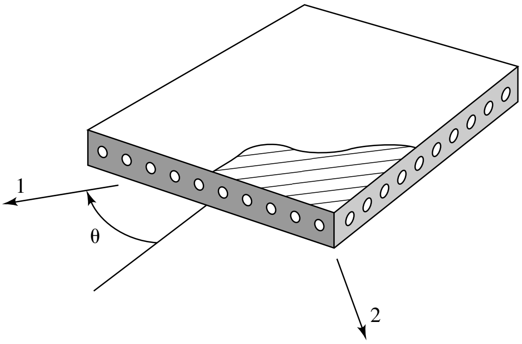


Fig. 1. A unidirectional lamina. The material axes are labeled 1 for the fiber direction and 2 for the direction transverse to the fibers.

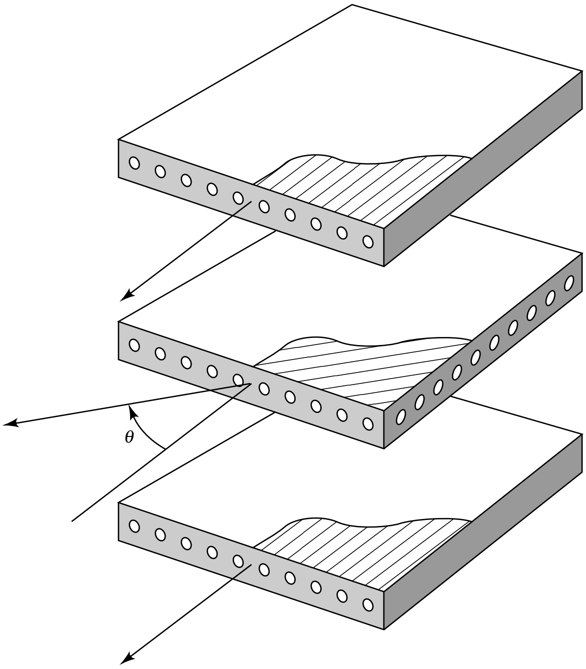


Fig. 2. Three layers of unidirectional material stacked together to form a laminate.

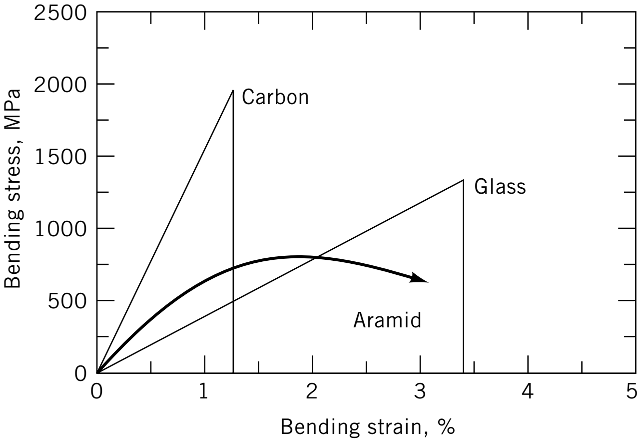


Fig. 3. Bending stress versus bending strain for typical carbon, glass, and aramid fibers. To convert MPa to psi, multiply by 145.

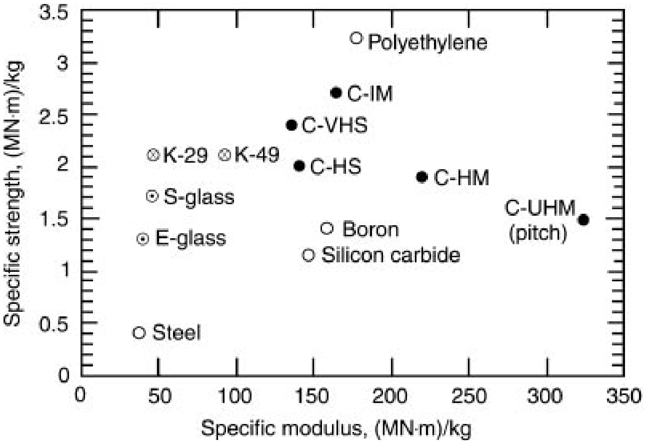


Fig. 4. Specific properties of reinforcing fibers for composite materials. K-29 and K-49 represent Kevlar aramid fibers. Other designations are explained more fully in the text. To convert (MN·m)/kg to (lbf·in.)/lb, multiply by 4.03×10^6.

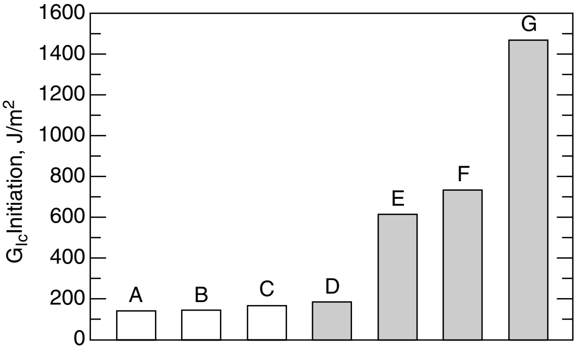


Fig. 5. Interlaminar fracture toughness, G_{Ic}, for a number of thermosetting and thermoplastic composites (36,37). Open white bars represent glass-fiber composites; shaded bars are for carbon fibers. The materials are A, polyester (unidirectional); B, vinyl ester (CSM = chopped strand mat); C, epoxy (R/BR1424); D, epoxy (T300/914); E, PPS; F, PES; and G, PEEK. To convert J/m^2 to ftlbf/in.^{2} multiply by 2100.

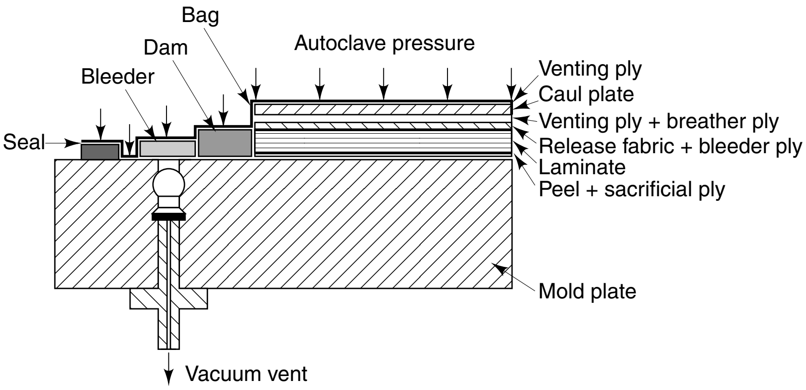


Fig. 6. Autoclave molding of a thermoset-based composite.

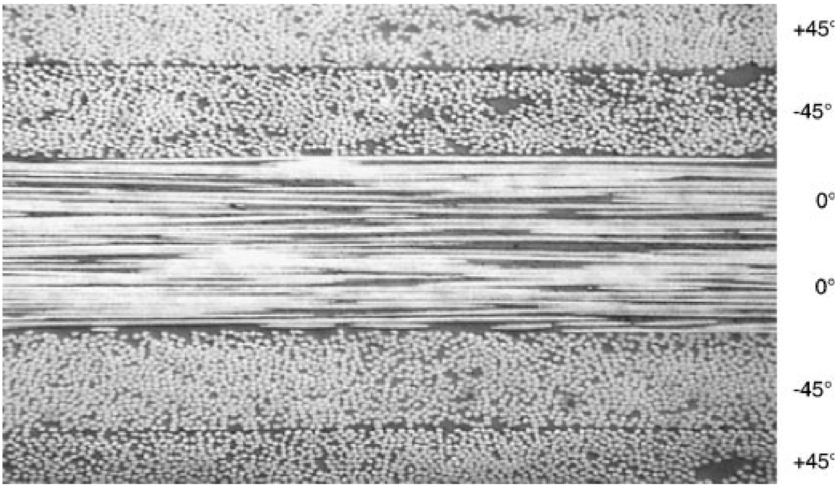


Fig. 7. Micrographic cross-section of an autoclaved carbon fiber composite.

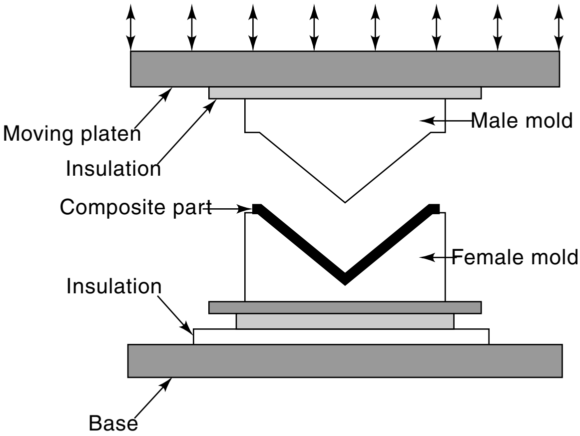


Fig. 8. Compression molding in matched diks.

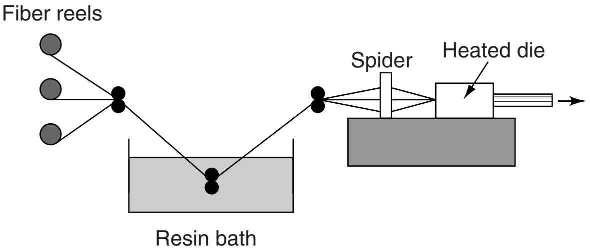


Fig. 9. Schematic representation of pultrusion process for making continuous fiber rods.

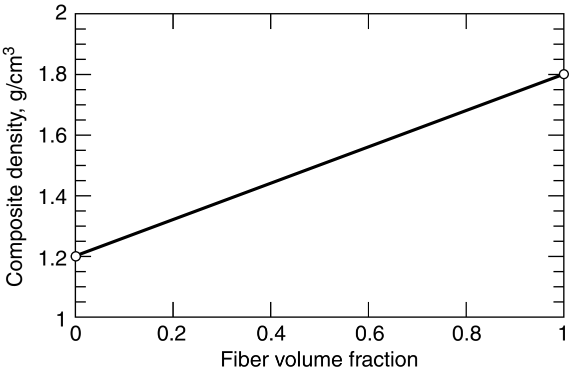


Fig. 10. The variation of the density of carbon-fiber reinforced epoxy resin with the fiber volume fraction, based on the rule of mixtures.

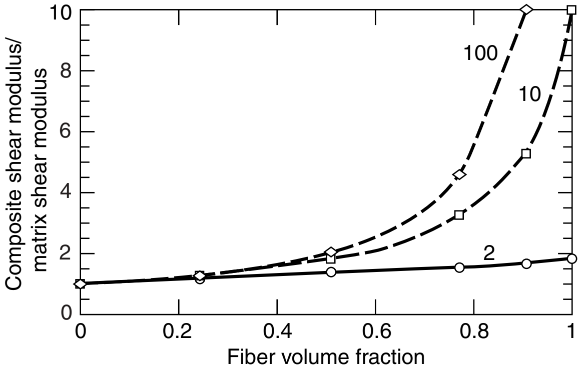
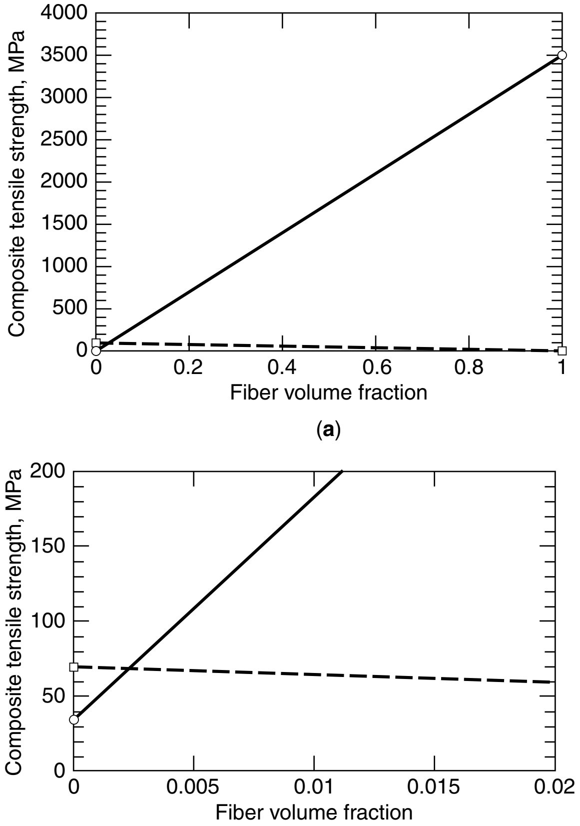


Fig. 11. The variation of the shear modulus G_{12} of carbon-fiber-reinforced epoxy resin as a function of the fiber volume fraction for several values of the ratio of the fiber shear modulus to that of the matrix (G_f/G_m). Ratios are noted on the curves (2).



(**a**)

(**b**)

Fig. 12. (**a**) The variation of the tensile strength of unidirectional carbon-fiber-reinforced epoxy resin as a function of the fiber volume fraction. (**b**) The variation of the tensile strength of unidirectional carbon-fiber-reinforced epoxy resin as a function of the fiber volume fraction for low fiber volume fractions.

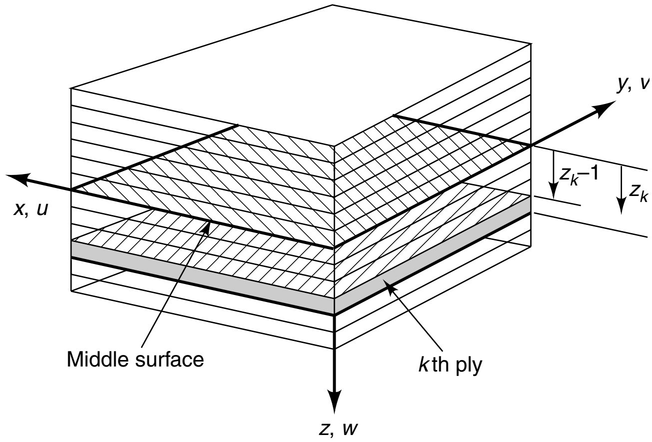


Fig. 13. Schematic of a laminate with the coordinates and ply notation used in laminated plate theory.

Table 1. **Mechanical Properties and Relative Costs of Thermosetting and Thermoplastic Composites**

Matrix material[a]	Young's modulus GPa[b]	Tensile strength, MPa[c]	Heat distortion temp, °C	Relative cost[d]
		Thermosets		
polyester	3.6	60	95	1
vinyl ester	3.4	83	110	1.8
epoxy	3.0	85	110	2.3
phenolic	3.0	50	120	0.8
		Thermoplastics		
PES	2.8	84[e]	203	6
PEI	3.0	105[e]	200	7
PEEK	3.7	92[e]	140	25

[a] PES = polyethersulfone, PEI = polyetherimide, PEEK = polyetheretherketone.

[b] To convert GPa to psi, multiply by 145,000.

[c] To convert MPa to psi, multiply by 145.

[d] Relative to the 1988 cost of isophthalic polyester (35).

[e] Yield stress.