A common debate about the definition of composite materials among composite engineers and materials scientists continues to this day. More recently, biomedical engineers have used the term composite prolifically for newly developed biomaterials, and it might be argued that not every usage of the term composite for a biomaterial would satisfy the traditional composite engineer, who is used to thinking in terms of fibers, matrices, and laminates. That said, defining composites a certain way in this chapter is not meant to preclude its use outside this definition.

The difficulty lies, on the one hand, in the depth of the material to which the definition refers. Practically everything is a composite material in some sense, except for pure elements. For example, a common piece of metal is a composite (polycrystal) of many grains (or single crystals). Thus alloys, ceramics, steels, etc., would be considered composites if the definition refers to the microstructure. However, if it is the macrostructure that concerns us, then we get the traditional treatment of composites as a materials system of different macroconstituents.1

On the other hand, there is also a question in this definition regarding how these macroconstituents are brought together and for what purpose. For instance, thin coatings on a material do not make it a typical composite, and the same could be said about adding resin-extending fillers to plastics, although the constituents exist at the macrostructure. Furthermore, a structure that is assembled with components made of different materials does not qualify it to be a composite. Thus a pacemaker lead that has a metallic core and a polymeric sheath would not be considered a composite in the strict sense, whereas a catheter tube polymer reinforced with embedded braided metal wires would. In addition, foams and porous coatings on materials will not be considered composites in this discussion.

The following is an operational definition for the purpose of this chapter:

A composite material consists of two or more physically and/or chemically distinct, suitably arranged or distributed materials with an interface separating them. It has characteristics that are not depicted by any of the components in isolation, these specific characteristics being the purpose of combining the materials.
Composite materials have a bulk phase, which is continuous, called the *matrix*, and one or more dispersed, noncontinuous phases, called the *reinforcement*, which usually has superior mechanical or thermal properties to the matrix. The region between the two can be simply a surface, called an *interface*, or a third phase, called an *interphase*. An example of the latter is a layer of coupling agent coated on glass fibers that facilitates adhesion of the glass to the matrix polymer.

The essence of the concept of composites is this: the bulk phase accepts the load over a large surface area and transfers it to the reinforcement phase, which, being different, changes the mechanical properties of the composite suitably, whether it is strength, stiffness, toughness, or fatigue resistance. For instance, in structural polymer composites, the reinforcement is much stiffer than the matrix, making the composite several times stiffer than the bulk polymer and resulting in a reduction in bulk strain on deformation, as seen in Fig. 12.1. The significance here lies in the fact that there are numerous matrix materials and as many reinforcement types that can be combined in countless ways to produce just the desired properties.

The concept of composite materials is ancient: to combine different materials to produce a new material with performance and efficiency unattainable by the individual constituents. An example is adding straw to mud for building stronger mud walls. Some more recent examples, but before engineered materials became prominent, are steel rods in concrete, cement and asphalt mixed with sand, fiberglass in resin, etc. In nature, examples abound: a palm leaf, cellulose fibers in a lignin matrix (wood), collagen fibers in an apatite matrix (bone), etc.

Most research in engineered composite materials has been done since the mid-1960s. Today, given the most efficient design of, say, an aerospace structure, a boat, or a motor, we can make a composite material that meets or exceeds the performance requirements. The benefits are mostly in weight and cost, measured in terms of ratios such as stiffness/weight, strength/weight, etc. Advances in biomedical composites have been focused on the design of dental and orthopedic implants, which are mainly structural applications. However, tremendous stiffness and strength improvement is not always the concern in the design of biomedical composites and even less so for large weight savings. Other concerns, such as biocompatibility, precise property matching, mimicking natural structures, etc., can become more important, yet these too are areas where composites offer much promise in device design. Engineers and materials scientists who are used to working with traditional materials such as metal alloys, ceramics, and plastics are increasingly challenged to design with composites that have different physical characteristics, mechanical behaviors, and processing methods.

**FIGURE 12.1** High-modulus fiber opposes strain around it in a low-modulus matrix, *(a)* Before deformation; *(b)* after deformation. Arrows indicate force direction. *(Adapted from Ref. 1.)*
In the design of composite problem solutions, particularly load-bearing implants, it is important to base the design on a firm theoretical understanding of composites to avoid creating new problems while trying to solve an existing one. Three factors need to be considered rationally: material selection for the bulk and reinforcement phases, internal and external structure of the device, and a suitable processing method.  

12.2 CLASSIFICATION

The factors that most contribute to the engineering performance of the composite include:

1. Materials that make up the individual components
2. Quantity, form, and arrangement of the components
3. Interaction between the components

Of these, the reinforcement system in a composite material strongly determines the properties achievable in a composite. It is thus convenient and common to classify composites according to the characteristics of the reinforcement. These can include the shape, size, orientation, composition, distribution, and manner of incorporation of the reinforcement. For the purposes of a discussion of biomedical composites, this results in two broad groups, namely, fiber-reinforced and particle-reinforced composites. Figure 12.2 shows further divisions within these groups.

Composite materials can also be broadly classified based simply on the matrix material used. This is often done more for processing than for performance purposes. Thus there are polymer-matrix composites (PMCs), ceramic-matrix composites (CMCs), or metal-matrix composites (MMCs). The last type is an advanced composite uncommon in biomedical applications and is mostly used for high-temperature applications.

12.3 CONSTITUENTS

12.3.1 Matrices

The matrix in a composite is the continuous bulk phase that envelopes the reinforcement phase either completely or partially. It serves several important functions. It holds the fibers or particles in place, and in oriented composites, it maintains the preferred direction of fibers. The matrix transfers the applied load to the reinforcement and redistributes the stress. When used with brittle fibers, the matrix helps increase fracture toughness because it is typically of a lower stiffness material and can tolerate greater elongation and shear forces than the reinforcement. The matrix also determines the environmental durability of the composite by resisting chemical, hygroscopic, and thermal stresses and protecting the reinforcement from these stresses. The matrix also greatly influences the processing characteristics of a composite.

Common matrices in biomedical composites are listed in Table 12.1. In nonmedical applications, thermosets make up the bulk of the matrix materials, particularly in structural and aerospace applications, where high stiffness and temperature resistance are very important requirements. In most medical applications, however, thermoplastics are the matrix materials of choice due to their non-reactive nature, processing flexibility, and generally greater toughness. Also, thermosets are non-degradable, whereas some thermoplastics can be designed to be biodegradable. Instead of using off-the-shelf materials, new matrices are constantly being developed for medical applications that have designed reactivity, flexibility, and strength. Resorbable matrices are useful when a composite is not permanently needed once implanted, but it is challenging to design a stiff reinforcing material that
has a comparable degradation rate to such matrices. Ceramic matrices are used for their compressive properties and bioactive possibilities but suffer from poor fracture toughness.

12.3.2 Fibers

A great majority of materials is stronger and stiffer in the fibrous form than in any other form. This explains the emphasis on using fibers in composite materials design, particularly in structural applications, where they are the principal load-carrying component. Fibers have a very high aspect ratio of length to diameter compared with particles and whiskers, and the smaller the diameter, the greater is the strength of the fiber due to a reduction in surface flaws. Many properties of a composite are determined by the length, orientation, and volume fraction of fibers of a given type.

Fibers are often manufactured as continuous filaments, with diameters in the range of 5 to 50 µm, and then they are arranged to produce tows, yarns, strands, rovings, mats, etc. These are used to
fabricate continuous-fiber composites, often for large structural applications. Filaments can be chopped to form short fibers ranging in length from 3 to 50 mm that are used to make discontinuous or short-fiber composites, more commonly for low-cost applications or small intricate parts. Whiskers are fibers made of single crystals with very small diameters around 10 \( \mu \)m, but their aspect ratio is high (>100). They have very high strengths but also high manufacturing cost. Compared with continuous-fiber composites, short-fiber composites are less efficient in the use of fibers and in achieving a desired orientation, but they are also less limited in design and processing possibilities and can come very close to achieving their theoretical strength.

Both continuous and short fibers can be oriented in one, two, or three dimensions, resulting in unidirectional, planar, and random reinforcement systems. The volume fraction of fibers oriented in a given direction strongly affects the physical properties of a composite in that direction. Unidirectional and planar reinforced composites exhibit anisotropy; i.e., their properties vary depending on the axis of measurement. The third composite type is isotropic, having equal properties in all directions. As mentioned earlier, it is difficult to orient short fibers, particularly in mold-filling processes, and the resulting composites tend to be isotropic. Laminate composites are a type of fiber-reinforced composite consisting of anisotropic layers or plies bonded together that can differ in

<table>
<thead>
<tr>
<th>Table 12.1 Constituents of Biomedical Composites</th>
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<tbody>
<tr>
<td><strong>Matrix</strong></td>
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<tr>
<td>Thermosets</td>
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<td>Epoxy</td>
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<tr>
<td>Polyacrylates</td>
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<td>Polymethacrylates</td>
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<td>Polymers</td>
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<tr>
<td>Silicones</td>
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<td>Thermoplastics</td>
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<td>Polymers (PP, PE)</td>
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<td>Polyolefins</td>
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<td>UHMWPE</td>
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<td>Polycarbonate</td>
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<td>Polysulfones</td>
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<td>Poly(ether ketones)</td>
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<tr>
<td>Polymers</td>
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<tr>
<td>Inorganic</td>
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<tr>
<td>Hydroxyapatite</td>
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<tr>
<td>Glass ceramics</td>
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<td>Calcium carbonate</td>
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<td>Resorbable polymers</td>
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<td>polyglycolide and their</td>
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<tr>
<td>copolymers</td>
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<tr>
<td>Polydioxanone</td>
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<tr>
<td>Poly(hydroxy butyrate)</td>
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<tr>
<td>Alginate</td>
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<tr>
<td>Chitosan</td>
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<td>Collagen</td>
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relative fiber orientation and volume fraction. This allows high-fiber-volume fractions and three-dimensional orientation not achievable in isotropic short-fiber composites.

Table 12.1 lists some fibers common in biomedical composites. There are many naturally occurring fibers, such as cotton, flax, collagen, jute, wood, hemp, hair, wool, silk, etc., but these have extremely varying properties and present many processing challenges. Among these, collagen fibers have been successfully utilized in tissue engineering of skin and ligament. Borosilicate glass fiber is ubiquitous in the composites industry but not common in biomedical composites, where, instead, adsorbable bioglass fibers made from calcium phosphate have found some applications. Carbon fiber is as strong as glass fiber but is several times stiffer owing to its fine structure of axially aligned graphite crystallites and is also lighter than glass. It is used extensively to make high-strength lightweight composites in prosthetic structural components, where the fatigue resistance of carbon-fiber composites is also an advantage. Carbon fibers tend to be brittle and are anisotropic, particularly in their thermal properties. They also add electrical conductivity to a composite, which can have corrosive effects next to metallic implants. Among polymers, highly oriented aramid fibers such as Kevlar are used in orthopedic applications because of their high resistance to impact fracture. However, Kevlar has very poor compressive properties, making it unsuitable for bending applications, and it is difficult to process due to its strong cut-through resistance. Teflon and polyester (Dacron) fibers are used to make vascular prostheses that are flexible. Polylactide and polyglycolide and their copolymers are used to make fiber composites in which adsorbability is more important than mechanical properties.

12.3.3 Particles

Particles can be added to a matrix to improve mechanical properties such as toughness and hardness. Other properties, such as dimensional stability, electrical insulation, and thermal conductivity, can also be controlled effectively by particles, especially when added to polymer matrices. Particulate reinforcement is randomly distributed in a matrix, resulting in isotropic composites. Particles can either strengthen or weaken a matrix depending on its shape, stiffness, and bonding strength with the matrix. Spherical particles are less effective than platelet- or flakelike particles in adding stiffness. Hard particles in a low-modulus polymer increase stiffness, whereas compliant particles such as silicone rubber, when added to a stiff polymer matrix, result in a softer composite. Fillers are nonreinforcing particles such as carbon black and glass microspheres that are added more for economic and not performance purposes.

Particulate reinforcement in biomedical composites is used widely for ceramic matrices in dental and bone-analogue applications. The most common such particle form is hydroxyapatite, a natural component of bone where it exists in a composite structure with collagen. Hydroxyapatite particles have very poor mechanical properties and may serve more as a bioactive than reinforcement component.

12.3.4 Interface

The transfer and distribution of stresses from the matrix to the fibers or particles occur through the interface separating them. The area at the interface and the strength of the interfacial bond greatly affect the final composite properties and long-term property retention. A low interfacial area denotes poor wetting of the fiber with the matrix material. Wetting can be enhanced by processing methods in which there is greater pressure (metal matrices) or lower-viscosity flow (polymer matrices). When mechanical coupling is not sufficient, coupling agents are often used to coat fibers to improve chemical compatibility with the matrix.

Interfacial shear strength determines the fiber-matrix debonding process and thus the sequence and relative magnitude of the different failure mechanisms in a composite. Strong interfaces common in polymer matrix composites make ductile matrices very stiff but also lower the fracture toughness. Weak interfaces in ceramic matrix composites make brittle matrices tough by promoting matrix crack but also lower strength and stiffness.
12.4 PROCESSING

12.4.1 Polymer-Matrix Composites

Continuous-fiber composites can be made in a variety of ways, such as manual layup of laminates, filament winding, pultrusion, and resin transfer molding. Manual layup involves stacking preimpregnated (or prepreg) tapes and sheets of parallel-fiber filaments held together by thermoplastic resin or partially cured thermoset resin, followed by autoclaving. This is not very expensive and not suitable for small medical implants. Like layup, filament winding allows for high-fiber-volume fraction and control of properties but is limited to tubular shapes, and the fibers cannot be oriented along the axis of the component. Pultrusion is ideal for very stiff composite rods and beams and can be used for making orthodontic arch wires. Resin transfer molding allows very complex shapes and short cycle times but requires expert design of preforms and molds. Compression molding is another method suitable for both thermosets and thermoplastics.

Short-fiber thermoplastic composites are typically injection molded, which allows rapid, high-volume, and economical production but requires expensive tooling. The fiber length and volume fraction are limited by this method, and fiber orientation and distribution are difficult to control.

12.4.2 Ceramic-Matrix Composites

Ceramic-matrix composites are manufactured commonly by either pressing methods or infiltration methods. In the former, the reinforcement is mixed with a powder of the matrix, which is densified by hot pressing or hot isostatic pressing (HIP). Near-zero porosity can be achieved, but the simultaneous high pressure and temperature can degrade fibers or result in a strong interfacial bond that may reduce fracture toughness. In infiltration methods, a sintered fibrous or paniculate preform is filled by the matrix by such methods as chemical vapor deposition, glass melt infiltration, and preceramic polymer or sol infiltration. Alumina-glass dental composites are made by this method. This method has the advantage of complex shape capability, low pressure, and flexible fiber architecture. Disadvantages are high matrix porosity (>10 percent) and long fabrication cycles. Particulate reinforcement can also be used through tape-casting and slip-casting the initial preform.

12.5 PHYSICAL PROPERTIES

Composite materials can be designed to have a wide range of physical and biochemical properties, making it important to develop predictive models to aid in designing with the many complex variables that face the composites engineer. Although these models tend be complicated due to the microstructure of composites, it is important to resist the temptation to treat a composite as a black box with gross properties because this macroscopic approach does not have the predictive power crucial for failure analysis. There have been three general approaches to predicting the basic mechanical properties of a composite:

1. Mechanics of materials models
2. Theory of elasticity models
3. Semiempirical models

12.5.1 Mechanics of Materials Models

The mechanics of materials model uses simple analytical equations to arrive at effective properties of a composite, using simplifying assumptions about the stress and strain distribution in a representative
volume element of the composite. This approach results in the common rule of mixtures equations for composites, where properties are relative to the volume fraction of the fibers and matrix.

Physical properties such as density are easily calculated by the following equations:

\[ V_f + V_m + V_v = 1 \]  \hspace{1cm} (12.1)

\[ \rho_c = \rho_f V_f + \rho_m V_m \]  \hspace{1cm} (12.2)

where \( V_f, V_m, \) and \( V_v \) are the volume fractions of the fiber, matrix, and voids, respectively, and similarly, \( \rho_c, \rho_f, \) and \( \rho_m \) are densities of the composite, fiber, and matrix.

The rule of mixtures is useful in roughly estimating upper and lower bounds of mechanical properties of an oriented fibrous composite, where the matrix is isotropic and the fiber orthotropic, with coordinate 1 the principal fiber direction and coordinate 2 transverse to it. For the upper bound, the Voight model is used (Fig. 12.3), where it is assumed that the strain is the same in the fiber and matrix. For the lower bound, the Reuss model is used, where the stress is assumed to be the same. This gives the following equations for composite moduli:

\[ E_{1c} = E_f V_f + E_m V_m \]  \hspace{1cm} (12.3)

\[ \frac{1}{E_{2c}} = \frac{V_f}{E_f} + \frac{V_m}{E_m} \]  \hspace{1cm} (12.4)

\[ \frac{1}{G_{12c}} = \frac{V_f}{G_{12f}} + \frac{V_m}{G_m} \]  \hspace{1cm} (12.5)

where \( E \) and \( G \) are the Young's modulus and shear modulus, respectively. The equations for transverse modulus and shear modulus are known as the inverse law of mixtures. Some fibers, such as carbon, have different properties along their longitudinal and transverse axes that the preceding equations can take into account.

**FIGURE 12.3** Composite stress models: (a) Voight or isostrain; (b) Reuss or isostress. Arrows indicate tension force direction.
The rule of mixtures equations have several drawbacks. The isostrain assumption in the Voight model implies strain compatibility between the phases, which is very unlikely because of different Poisson’s contractions of the phases. The isostress assumption in the Reuss model is also unrealistic since the fibers cannot be treated as a sheet. Despite this, these equations are often adequate to predict experimental results in unidirectional composites. A basic limitation of the rule of mixtures occurs when the matrix material yields, and the stress becomes constant in the matrix while continuing to increase in the fiber.

The ultimate tensile strength of a fibrous composite \( \sigma_c^* \) depends on whether failure is fiber-dominated or matrix-dominated. The latter is common when \( V_f \) is small. One result of such treatment is

\[
\sigma_c^* = \frac{\sigma_{mf}^* E_f V_f + \sigma_{m}^* V_m}{E_f V_f + E_m V_m} \tag{12.6}
\]

where \( \sigma_{mf}^* \) is the fracture strength of the matrix.

Other results from this simple analytical approach for orthotropic composites are

\[
\alpha_{1c} = \frac{E_f \alpha_f V_f + E_m \alpha_m V_m}{E_f V_f + E_m V_m} \tag{12.7}
\]

\[
C_c = \frac{1}{\rho_c} (\rho_f C_f V_f + \rho_m C_m V_m) \tag{12.8}
\]

\[
K_{1c} = K_f V_f + K_m V_m \tag{12.9}
\]

where \( \alpha \) is the coefficient of thermal expansion, \( C \) is the specific heat, and \( K \) is the thermal conductivity. The coefficient of hygroscopic expansion \( \beta \) can be found by substituting \( \alpha \) with \( \beta \) above. These results are for the longitudinal directions only.

### 12.5.2 Theory of Elasticity Models

In this approach, no assumptions are made about the stress and strain distributions per unit volume. The specific fiber-packing geometry is taken into account, as is the difference in Poisson’s ratio between the fiber and matrix phases. The equations of elasticity are to be satisfied at every point in the composite, and numerical solutions generally are required for the complex geometries of the representative volume elements. Such a treatment provides for tighter upper and lower bounds on the elastic properties than estimated by the rule of mixtures, as is described in the references used in this section.

One illustrative result for the longitudinal Young’s modulus is

\[
E_{1c} = \frac{[2(\nu_f - \nu_m)^2 E_f V_f E_m V_m]}{E_m V_m (1 - \nu_f - 2\nu_f^2) + E_f V_f (1 - \nu_m - 2\nu_m^2) + (1 - \nu_m)]} + E_m + (E_f - E_m) V_f \tag{12.10}
\]

where \( \nu_f \) and \( \nu_m \) are the Poisson’s ratios of the fiber and matrix, respectively. Very small differences in the Poisson’s ratios of the phases cause such equations to be simplified to the rule of mixtures.

### 12.5.3 Semiempirical Models

Curve-fitting parameters are used in semiempirical and generalized equations to predict experimental results. The most common model was developed by Halpin and Tsai, and it has been modified for aligned discontinuous fiber composites to produce such results as the following for the longitudinal modulus:
and the Halpin-Tsai curve-fitting parameter is assumed to be $\xi = 2L/d$, where $L$ is the length and $d$ the diameter of the fiber. The expression can be simply substituted to also obtain $E_2$ and $G_{12}$ using experimental values for $\xi$.

For two-dimensional randomly oriented fibers in a composite, approximating theory of elasticity equations with experimental results yielded this equation for the planar isotropic composite stiffness and shear modulus in terms of the longitudinal and transverse moduli of an identical but aligned composite system with fibers of the same aspect ratio:

$$E_c = \frac{1}{\eta}E_1 + \frac{1}{\frac{E_1}{E_m} - \frac{1}{\eta}}$$

(12.13)

$$G_c = \frac{1}{\eta}E_1 + \frac{1}{\frac{E_1}{E_m} + \eta}$$

(12.14)

For a three-dimensional random orientation of fibers, a slightly different equation is proposed for the isotropic tensile modulus:

$$E_c = \frac{1}{\eta}E_1 + \frac{1}{\frac{E_1}{E_m} + \eta}$$

(12.15)

The stiffness of particulate composites can be predicted depending on the shape of the particles. For a dilute concentration of rigid spherical particles, the composite stiffness is approximated by

$$E_c = \frac{5(E_p - E_m)V_p + E_m}{3 + 2E_p/E_m}$$

(12.16)

where $E_p$ and $V_p$ are the stiffness and volume fraction of particles, respectively.

It is important to note that any model for composite behavior requires experimental validation and may prove to be quite inaccurate for not taking into account many irregularities typical in composite design and processing. In addition, these results are usually valid for static and short-term loading.

### 12.6 Fracture and Fatigue Failure

Failure of fiber-reinforced composites is generally preceded by an accumulation of different types of internal damage that slowly or catastrophically renders a composite structure unsafe. The damage can be process-induced, such as nonuniform curing control of a dental resin, or it can be service-induced, such as undesired water absorption. Fiber breaking, fiber bridging, fiber pullout, matrix cracking, and interface debonding are the failure mechanisms common in all composites, but the sequence and interaction of these mechanisms depend on the type of loading and the properties of the constituents, as well as on the interfacial shear strength (Fig. 12.4). Various fracture mechanics theories are available for failure analysis of composites, among them the maximum stress theory and the maximum strain theory described in more detail in Ref. 5.

Energy absorption and crack deflection during fracture lead to increased toughness of the composite. The two most important energy-absorbing failure mechanisms in a fiber-reinforced composite are debonding at the fiber-matrix interface and fiber pullout. If the interface bonds relatively easily, the crack propagation is interrupted by the debonding process, and instead of moving through the fiber, the crack is deflected along the fiber surface, allowing the fiber to carry higher loads. Fiber pullout occurs because fibers do not all break at the crack plane but at random
locations away from this plane. If the pullout occurs against high frictional forces or shear stresses at the interface, there maybe a significant increase in fracture toughness. The same holds true for particulate reinforcements, although here crack deflection is more common than bridging and pullout due to the smaller aspect ratio. In an alumina-glass composite, as shown in Fig. 12.5, indentation cracks in the glass matrix are deflected around the angular alumina granules in (a) but not as much in (b), where the cracks propagate more through the granules, indicating a stronger interface but more likely lower toughness. In laminate composites, delamination loads between the layers from in-plane shear loads are a common failure mechanism, initiating at the free edge of the plate or a hole, e.g., where screws would go in a carbon-reinforced bone plate.

Long-term durability of composites is a challenging and still developing area of study. Unlike many metallic biomaterials, the static strength of most load-bearing composite materials does not correlate well with their long-term performance, especially under cyclic loading. The reasons for this include fatigue damage, matrix creep, and stress relaxation, as well as environmental effects at the implant site. Fatigue damage and implant life are difficult to predict, unlike for metals, which have a distinct endurance stress limit below which the material can be loaded an infinite number of times without failure. Many composites do not exhibit an endurance limit. In addition, the loads on implants are highly variable both in direction and magnitude and between patients, and the most damaging loads may occur randomly as a result of accidents. Water absorption in polymer matrices can cause swelling and have a plasticizing effect, which is problematic in dental composites and bone

![Failure mechanisms in a unidirectional fiber composite. (Adapted from Ref.3.)](image-url)
cements, although this is a very slow phenomenon. Visoelastic effects such as the strain-rate dependence of stiffness and long-term creep are proportional to the column fraction of matrix such that highly reinforced continuous-fiber composites are less prone than short-fiber composites.

12.7 BIOLOGIC RESPONSE

In designing biomedical composites and predicting their performance, several issues must be considered regarding the biological response. As the number of constituent materials in a composite increases, so can the variations in the host response. Additional tests are necessary to establish that while the individual materials may be by themselves biocompatible, their specific composition, arrangement, and interaction are also biocompatible. This has implications for both the flexibility of design and obtaining regulatory approval. The potential of composite design to obtain the desired set of properties can be restricted by being conservative in the choice and number of materials used. Even if all the materials used may be approved by the Food and Drug Administration (FDA), their particular combination in a composite may require additional approval.

Materials can elicit a different host response in the bulk form than in the fibrous or particulate form. For instance, UHMWPE, as in an acetabular cup of a hip prosthesis, is generally biocompatible, whereas its fibrous form, as in a finely woven fabric, has been shown to produce a different, more adverse reaction. Furthermore, when the discontinuous phase is particles, whiskers, platelets, or microspheres with dimensions on a cellular scale, the inflammatory response can include their ingestion by immune cells and transport to other parts of the body. This can be accompanied by the release of enzymes that can adversely affect the performance of the composite, such as by altering the degradation kinetics of a biodegradable composite. The composite can be designed in such a way that the fibers or particles are not exposed to the host, but this is challenging because it involves elimination of all voids at the fiber-matrix or particle-matrix interface during processing. In addition,
friction in a moving part, such as in orthopedic or dental composites, can cause abrasion of the matrix and produce new voids at the interface, exposing the reinforcing material to the host. The interaction of materials at the interface is integral to composite performance, and this can be affected by the tissue response in various ways, such as filling and swelling of interfacial voids with fluid and fibrous tissue, altering the interfacial adhesion strength between matrix and reinforcement, and delamination of laminate composites. Such effects can lead to failure of a composite, particularly in structural applications.

Thermosetting polymers, although uncommon in biomedical implants, may contain unreacted monomer and cross-linking agents, particularly in laminated composites made from prepreg layers. In both thermosetting and thermoplastic polymer composites, the sizing applied to glass and carbon fibers is another compound that may be present, and some residual solvents may also leach from the matrix if they are not completely removed during processing. These trace amounts may not be an issue if the application is external to the body, as in prosthetic limbs.

### 12.8 BIOMEDICAL APPLICATIONS

The use of composite materials in biomedical implants and devices is illustrated by the following examples of structural applications.

#### 12.8.1 Orthopedic

Composite materials have found wide use in orthopedic applications, as summarized by Evans, particularly in bone fixation plates, hip joint replacement, bone cement, and bone grafts. In total hip replacement, common materials for the femoral-stem component such as 316L stainless steel, CoCr alloys, and Ti-6Al-4V titanium alloy have very high stiffness compared with the bone they replace. Cortical bone has a stiffness of 15 GPa and tensile strength of 90 MPa. Corresponding values for titanium are 110 GPa and 800 MPa, which are clearly very high. This produces adverse bone remodeling and stress shielding, which over the long term leads to reduction in bone mass and implant loosening, specially in the proximal region. Fiber composites can be tailored to match the specific mechanical properties of the adjacent bone. Carbon-fiber composites in PEEK or polysulfone matrices can be fabricated with stiffness in the range 1 to 170 GPa and tensile strength from 70 to 900 MPa. Examples are press-fit femoral stems made from laminated unidirectional carbon fibers in PEEK, polysulfone, liquid crystalline polymer (LCP), and polyetherimide (PEI). These composites are difficult to fabricate and have not had very encouraging durability, but they continue to be developed for the inherent advantages of tailorability, flexibility, noncorrosiveness, and radioucency. Problems with biocompatibility due to particulate carbon debris from these composites have been addressed by polishing and coating with hydroxyapatite (Fig. 12.6) or carbon-titanium alloy.

For fracture fixation, a fully resorbable bone plate is desirable to avoid the need for a second operation to remove the implant after healing. This in the form of a tailored low-stiffness composite also avoids the problem of stress shielding described earlier. The rate of degradation must be controlled to maintain the mechanical properties such that strength loss in the implant mirrors strength increase in the healing. In addition, the degradation by-products must be nontoxic. A summary of the design of adsorbable fixation devices is provided by Pietrzak. Examples of composite bone plates include laminated continuous carbon fiber in a polylactide (PLA) matrix, which is partially adsorbable, and calcium-phosphate glass fibers also in PLA, which is fully resorbable. Continuous poly (L-lactide) fibers in a PLA matrix also produced a fully resorbable composite. These composites, however, did not have adequate mechanical properties and degraded quite rapidly. Nonresorbable carbon-epoxy bone plates with sufficient strength and fatigue properties are available from such manufacturers as Orthodesign, Ltd.
Bone cements used to fill the void and improve adhesion between implants and the host bone tissue have been reinforced with various fibers to prevent loosening and enhance shear strength. The typical bone cement is PMMA powder mixed with a methacrylate-type monomer that is polymerized during fixation. Low volume fractions of graphite, carbon, and Kevlar fibers have been added to PMMA matrices to increase fatigue life and reduce creep deformation.17

12.8.2 Dental

Composites have been by far the most successful in dental applications by meeting several stringent design requirements difficult to achieve with homogeneous materials such as ceramics and metal alloys. Whether it is preparation of crowns, repair of cavities, or entire tooth replacement, the product needs to be aesthetically matched in color and translucence with other teeth and retain its gloss. It must match the hardness of the opposing tooth and be resistant to wear or fatigue fracture. It must be dimensionally stable and withstand the largely varying thermal stresses in the mouth. It also has to
have short processing time and near-net shape. Particulate composites used to repair cavities have a polymer resin matrix filled with stiff inorganic or organic inclusions. The resin monomer is typically a methacrylate or a urethane dimethacrylate ester derivative such as bis-GMA cured on site by cross-linkers, ultraviolet light (UV), or light-emitting diodes. The stiff filler particles that increase strength and impart wear resistance can be glass ceramics, calcium silicate, calcium fluoride, crystalline quartz, and silicon nitride whiskers. These are usually silane treated or fused with silica particles to improve retention in the matrix, especially in stress-bearing restorations and to reduce water absorption. The filler can be from 50 percent to 80 percent by volume of the composite and have varying sizes from 20 nm to 50 µm. In a microfilled dental resin, fused silica particles 20 to 40 nm in size can be incorporated to modest volume fractions up to 40 percent to produce a composite that is translucent and can be polished to a high gloss but not mechanically strong enough for posterior teeth and difficult to handle because of low viscosity. Hybrid dental resins have particle sizes of different orders of magnitude from around 0.1 to around 10 µm, allowing for higher filler volume, up to 80 percent and higher viscosity for easier handling, as well as lower water absorption compared with microfilled resins. Commercial dental composite resins have polymerization shrinkages varying from 1.6 to 2.5 percent, followed by water absorption of up to 1.5 percent, causing dimensional changes. They also have poor adhesion to dentin, making it important to use bonding agents to prevent fitting and leakage problems.

All-ceramic dental composites are used for stress-bearing restorations of dental crowns and bridges. Fracture toughness is a very important concern and is addressed by designing crack deflection and bridging mechanisms into the composite. A common type is the alumina-glass composite known as In-Ceram, in which a skeleton of alumina particles is slip cast and sintered, followed by melt infiltration of glass into the porous core. The composition in one example is 75 percent by volume α-alumina particles of average 3 µm size and 25 percent glass. Thermal expansion mismatch between the alumina and glass was shown not to affect fracture toughness significantly. Recent development of aqueous tape-casting of the alumina core has made it easier to conform the composite to a tooth model. The composite can be many times harder than the enamel of the opposing teeth and can thus wear them out. They are coated with either alkali aluminosilicate dental porcelains or calcium phosphate composites to reduce the surface hardness.

Another application of dental composites is orthodontic archwires. One example is a unidirectional pultruded S2-glass-reinforced dimethacrylate thermoset resin. Depending on the yarn of glass fiber used, the fiber volume fraction varied from 32 to 74 percent. The strength and modulus were comparable with those of titanium wires. Orthodontic brackets were also made from composites with a polyethylene matrix reinforced with ceramic hydroxyapatite particles, resulting in isotropic properties and good adhesion to enamel.

### 12.8.3 External Prosthetics and Orthotics

Traditional prosthetic and orthotic materials such as wood, aluminum, and leather have been largely replaced by high-performance composites and thermoplastics. The requirements of low weight, durability, size reduction, safety, and energy conservation have made fiber-reinforced plastics very attractive in this area. This is one application where traditional composites design and manufacturing, particularly using thermosets, are common because the products are structural and external to the body. For transtibial (TT) and transfemoral (TF) prostheses, composites have been used for the socket-frame component that interfaces with the residual limb and transmits the load and for the shank component that supports the load over the ground. TT and TF prostheses have a target weight limit of 1 and 2 kg, respectively, which makes carbon-fiber-reinforced (CFR) composites ideal. Socket frames in the ISNY system have been made from carbon fiber tape and acrylic resin produced by laminate layup. The matrix used is a blend of rigid and flexible methyl methacrylate resins for tailoring the stiffness of the socket. CFR epoxy tubing has been used to replace stainless steel in artificial arms. Satin-weave carbon-fiber cloth in epoxy prepreg has been used to make the shank of the Endolite TF prosthesis. Hybrid composites for the shank with carbon and nylon fibers in polyester
resins had better impact resistance than just carbon- or nylon-only composites. Using thermoplastics, CFR Nylon 6,6 made easily by injection molding has excellent vibration-damping characteristics important for shock absorption. However, the part will need to be heavier because a simple analysis reveals that the wall thickness of a tubular molding in 30 percent discontinuous CFR Nylon 6,6 needs to be seven times that in 60 percent continuous CFR epoxy at constant tube radius. This can be overcome by using more advanced thermoplastics such as PEEK and longer fibers in injection molding. For the prosthetic foot unit, various composites have been used with the objective of storing energy and returning it during motion. The Flex-Foot unit has a long CFR epoxy composite beam that stores flexural energy along the entire length of the prosthesis rather than just the foot unit and is tailored to the individual patient characteristics and activity level. In the Carbon Copy 2 foot, the keel is made of a posterior Kevlar-reinforced nylon block and anterior CFR plastic leaf springs, providing two-stage resistance to flexion. Finally, a nylon-reinforced silicone elastomer has been used to make a durable cover for the flexible foam that encases the prosthesis. In the area of orthotics designed to support injured tissue, composites find use in new bandage-form splinting materials replacing the old cotton fabric and plaster of paris method. These are commonly laminated fiberglass or polyester knitted fabrics in partially cured polyurethane matrices. Besides strength, they have the advantages of better x-ray transmission and lower water adsorption. However, these casts also produce more dust during sawing and are harder to remove.

12.8.4 Soft-Tissue Engineering

Cross-linked hydrogel networks are suitable as a scaffold for skin regeneration due to their high water content and barrier properties, but they have poor mechanical properties. The tensile strength and break point of the hydrogel poly(2-hydroxyethyl methacrylate) (pHEMA) were dramatically enhanced by reinforcing it with Spandex and gauze fibers, resulting in gels that withstood greater forces before tearing. In cartilage repair, where high compressive and shear properties are desirable, low-density linear polyethylene was melt coated onto a woven three-dimensional fabric of UHMWPE fibers to produce a composite that had compressive behavior approximating that of natural cartilage. Fibrous poly(glycolic acid) (PGA) felts and poly(lactide-co-glycolide) (PLGA) fibers have been used as surfaces and scaffolds for cartilage cell growth, where the cells produce the bulk matrix when implanted at the site of the cartilage defect. The fiber diameter, interfiber distance, and biodegradation rate were important parameters that affected the quality of the neocartilage formed from such constructs. In the area of vascular grafts, woven-fiber tubes made from polyester (Dacron) have high permeability during implantation, resulting in severe blood leakage through the graft walls. To avoid the lengthy precolluting time needed to overcome this leakage problem, various impermeable materials are coated on such grafts to form a composite, where the matrix functions as the sealant rather than the load bearer. For example, alginate and gelatin have been used to thoroughly wet Dacron fibers and seal the vascular prosthesis, and over time they are biodegraded. For hemodialysis vascular access, where the graft has to be resilient to frequent needle puncture, a technique employed in the DIASTAT graft involves PTFE fibers sandwiched between layers of porous expanded PTFE. The fibers are pushed aside where the needle enters, and after needle withdrawal, the fibers create a baffle effect to reduce leaking blood velocity and improve resealing.

REFERENCES


