2 Carbon Fibers and Nanofillers

2.1 Carbons

Not included in the five categories mentioned in Sect. 1.1 is carbon, which can be found in the form of graphite (its most common form), diamond and fullerenes (a recently discovered form). Note that these are not ceramics, because they are not compounds.

Graphite (a semimetal) consists of carbon atom layers stacked in the *AB* sequence such that the bonding is covalent (due to sp^2 hybridization) and metallic (two-dimensionally delocalized $2p_z$ electrons) within a layer, and van der Waals between the layers. This bonding makes graphite very anisotropic, so it is a good lubricant (due to the ease with which the layers can slide past one another). Graphite is also used in pencils because of this property. Moreover, graphite is an electrical and thermal conductor within the layers but an insulator in the direction perpendicular to the layers. The electrical conductivity is valuable when using graphite for electrochemical electrodes. Graphite is chemically quite inert. However, due to its anisotropic structure, graphite can undergo a reaction (known as intercalation) in which foreign species (called the intercalate) are inserted between the carbon layers. Disordered carbon (called turbostratic carbon) also has a layered structure, but, unlike graphite, it does not have the *AB* stacking order and the layers are bent. Upon heating, disordered carbon becomes more ordered, as the ordered form (graphite) has the lowest energy. Graphitization refers to the ordering process that leads to graphite. Conventional carbon fibers are mostly disordered carbon such that the carbon layers lie preferentially along the fiber axis. A form of graphite called flexible graphite is formed by compressing a collection of intercalated graphite flakes that have been exfoliated (i.e., allowed to expand by over 100 times along the direction perpendicular to the layers, typically through heating after intercalation). The exfoliated flakes are held together by mechanical interlocking, as there is no binder. Flexible graphite is typically generated in the form of sheets that are resilient in the direction perpendicular to the sheet. This resilience allows flexible graphite to be used as a gasket for fluid sealing.

Diamond is a covalent network solid that exhibits the diamond crystal structure due to sp^3 hybridization (akin to silicon). It is used as an abrasive and as a thermal conductor. It has the highest thermal conductivity of any material. However, it is an electrical insulator. Due to its high material cost, diamond is typically used in the form of powder or thin-film coating. Diamond should be distinguished from diamond-like carbon (DLC), which is amorphous carbon with carbon that is sp^3-hybridized. Diamond-like carbon is mechanically weaker than diamond but also less expensive than it.

Fullerenes are molecules (C_{60}) with covalent bonding within each molecule. Adjacent molecules are held by van der Waals' forces. However, fullerenes are not polymers. Carbon nanotubes are a derivative of the fullerenes, as they are essentially fullerenes with extra carbon atoms at the equator. The extra atoms cause the fullerene to lengthen. For example, ten extra atoms (i.e., one equatorial band of atoms) exist in the molecule C_{70}. Carbon nanotubes can be singlewalled or multiwalled nanotubes, depending on the number of carbon layers in the wall of the nanotube.

2.2 Carbon Fibers

Since carbon fiber composites are important for both structural and functional applications, as covered in this book, this section provides an introduction to carbon fibers. The structural importance of carbon fibers stems from their high strength, high modulus and low density. The functional importance of carbon fibers stems from their high electrical conductivity.

There are three forms of carbon, namely graphite, diamond and fullerene. Carbon fibers belong to the graphite family, although they may not be crystalline. Graphite has a layered crystal structure, with the carbon layers stacked in the *AB* sequence (Fig. 2.1). Within a layer, the chemical bonding is a mixture of covalent bonding and metallic bonding. The covalent bonding, which results from the sp^2 hybridization of each carbon atom, is responsible for the high modulus and strength in the plane of the carbon layers. The metallic bonding, which is due to the delocalized p_z electrons, is responsible for the high electrical conductivity and high thermal conductivity in the plane of the carbon layers. Perpendicular to the carbon layers, the bonding involves van der Waals forces (secondary bonding). Due to the weak interlayer bonding, the carbon layers can easily slide with respect to one another, thus making graphite a good solid lubricant. Due to the difference between the in-plane and out-of-plane bonding, graphite is mechanically much stronger and stiffer and is electrically and thermally much more conductive in the plane of the carbon layers than in the direction perpendicular to them.

A carbon fiber is made from a polymer fiber by converting the polymer into carbon, using a process similar to that used for the fabrication of carbon-matrix composites, as described in Sect. 1.3.3. The diameter of a continuous carbon fiber is commonly around 7 μm. A carbon fiber can have various degrees of crystallinity, as controlled by the process of fabrication. For a given carbon precursor, e.g., pitch and polyacrylonitrile (PAN), the higher the heat treatment temperature, the greater the degree of crystallinity (also known as the degree of graphitization). After carbonization, a carbon fiber is noncrystalline (amorphous) and is said to be turbostratic. In the turbostratic form, there are still carbon layers, but the layers are not very extensive, not very flat and not very parallel, and they do not exhibit

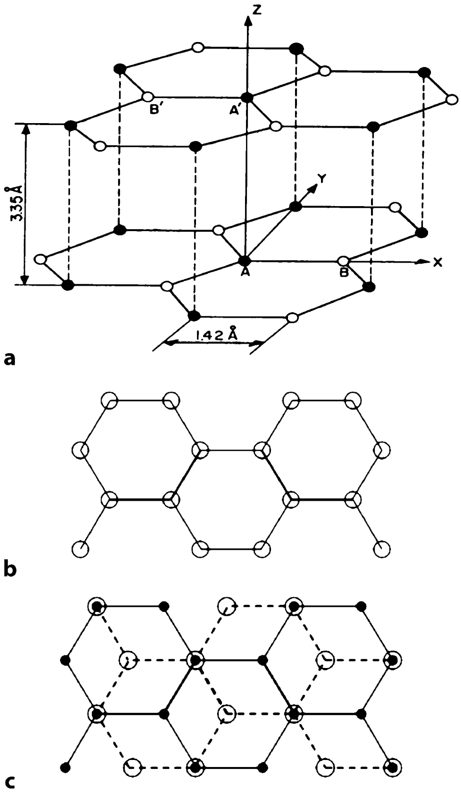

Figure 2.1. Crystal structure of graphite. **a** Three-dimensional view. **b** Two-dimensional view of a single carbon layer. **c** Two-dimensional view of two superimposed adjacent carbon layers. The *A* atoms (*solid circles*) constitute one carbon layer, whereas the *B* atoms (*open circles*) constitute the adjacent carbon layer

the *AB* stacking sequence. This means that turbostratic carbon has short-range order but no long-range order, as in the case of noncrystalline materials in general. In order for the carbon fiber to achieve a degree of crystallinity, the carbonization process needs to be followed by graphitization, which is heat treatment at a higher temperature, such as 2,300–3,000°C. Because the crystalline state is the thermodynamically stable state (i.e., the state of lowest energy), the carbon atoms would automatically move to approach the crystalline state if there was enough thermal energy for them to move. In other words, the crystallization process is spontaneous.

A carbon fiber has the carbon layers preferentially aligned with the fiber axis, even though the layers may not be flat (Fig.2.2). In other words, the layers are not randomly oriented; there is a distribution of orientations such that there is a degree of preference for the orientation parallel to the fiber axis. In general, the preferred orientation is known as the texture (or crystallographic texture). In the case of fibers, the preferred orientation is that in which the direction perpendicular to the carbon layers is preferentially in the cross-sectional plane of the fiber, such that

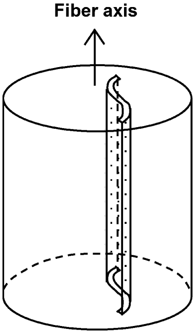

Figure 2.2. Preferential orientation of a carbon layer along the axis of a carbon fiber

this direction is two-dimensionally random in this plane. This is a type of texture known as the fiber texture, which in general refers to a texture involving preferential orientation of a certain crystallographic direction in a particular physical direction such that there is two-dimensional randomness of the crystallographic direction perpendicular to this direction. The fiber texture is a natural consequence of the fiber fabrication, which typically involves flow of the carbon precursor during the formation of the precursor fiber. This texture causes the modulus, strength, electrical conductivity and thermal conductivity of carbon fibers along the fiber axis to be high, in spite of the crystallographic anisotropy. This also means that the properties of a fiber in the transverse direction are inferior to those in the axial direction. Since a composite is typically designed to exploit the axial properties of the fiber (e.g., a composite is designed with the fibers aligned along the direction of the composite that needs to be strong), the inferior transverse properties are usually not an issue.

Carbon fibers are electrically and thermally conductive, in contrast to the non-conducting 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 a near-zero coefficient of thermal expansion, so they can also serve as an additive to lower the thermal expansion. This 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 graphitic fibers such as high-modulus pitch-based fibers and 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 a 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 (above 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 a composite 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.

The conductivity of carbon fiber and the nonconductivity of the polymer matrix enable carbon fiber polymer-matrix composites to be tailored for functional properties. For example, the electrical resistivity of a carbon fiber polymer-matrix composite is sensitive to the damage in the composite, thereby allowing the composite to be a sensor of its own damage. Damage in the form of fiber breakage increases the resistivity in the fiber direction of the composite. Damage in the form of delamination increases the resistivity in the through-thickness direction of the composite, since delamination diminishes the extent of fiber–fiber contact across the interlaminar interface. In other words, the fibers of one lamina cannot contact those of an adjacent lamina in the area where the two laminae are separated by a delamination crack. Damage monitoring, also known as structural health monitoring, is practically important, due to the aging and deterioration of aircraft made of composites.

A high degree of graphitization is attractive due to the resulting high values of modulus, electrical conductivity and thermal conductivity along the fiber axis. Although a high degree of crystallization enhances the modulus, it is detrimental to the strength of the fiber. This is because high crystallinity facilitates the sliding of a carbon layer relative to another layer, thus resulting in easy shear of the layers and hence low strength in the fiber. Therefore, there are two main grades of carbon fiber, namely high-modulus fiber (with a relatively high degree of graphitization, as in the case of a fiber that involves both carbonization and graphitization in its fabrication process) and high-strength fiber (with a relatively low degree of graphitization, as in the case of a fiber that involves carbonization but no graphitization in its fabrication process).

A high degree of graphitization enhances the oxidation resistance of the fiber. The oxidation of carbon refers to the reaction of carbon with oxygen to form carbon monoxide or carbon dioxide gas, which vanishes. This reaction occurs only at an elevated temperature. As a result, carbon fiber cannot withstand a high temperature in the presence of oxygen, although it can withstand extremely high temperatures in the absence of oxygen. This oxidation problem also applies to the matrix of a carbon-matrix composite. In general, the more crystalline the carbon, the higher the onset temperature for oxidation.

2.3 Nanofillers

Nanocomposites refer to composites with nanometer-scale structure. This structure can relate to the grain size, the filler size, the pore size, etc. A small pore size helps to improve the mechanical strength of a porous material. A small grain size is attractive since it leads to a high yield strength in metals and a high toughness in ceramics. A small filler size provides a large filler–matrix interface area per unit volume. The large area can be advantageous or disadvantageous, depending on the type of property. For example, it may result in a composite of low strength (in spite of the possibly high strength within a single unit of the nanofiller, e.g., within a single nanofiber) due to the mechanical weakness of the interface; it may also result in a composite of high electrical resistivity (in spite of the possibly low electrical resistivity within a single unit of the nanofiller, e.g., within a single nanofiber) due to the electrical resistance associated with the interface. On the other hand, the high interface area may be good for the performance of electrochemical electrodes due to the fact that the electrochemical reaction occurs at the interface between the electrode and the electrolyte, as in a battery; it may also be good for shielding from electromagnetic interference (abbreviated to "EMI") that occurs in the near-surface region of a conductive filler unit, due to the skin effect (the phenomenon in which high-frequency electromagnetic radiation penetrates only the near-surface region of an electrical conductor). Thus, nanocomposites are not necessarily superior to conventional composites.

A nanofiller refers to a filler in the nanometer size range (0.5–500 nm, typically 1–100 nm) along at least one of its dimensions. For example, a nanoplatelet is in the nanometer size range in the direction perpendicular to the plane of the platelet, but

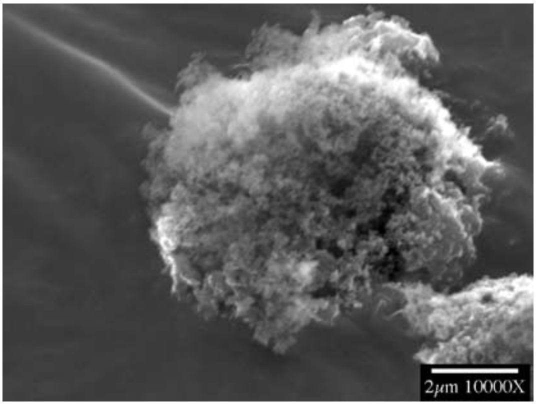

Figure 2.3. A scanning electron microscope photograph of fumed alumina, which takes the form of porous agglomerates of nanoparticles around 13 nm in size

is considerably larger in the plane of the platelet; a nanofiber is in the nanometer size range in its diameter, but is much larger along its length.

Nanofillers take the form of nanoparticles (e.g., carbon particles around 30 nm in size in carbon black, and alumina particles around 13 nm in size in fumed alumina, which is shown in Fig. 2.3), nanofibers (e.g., carbon nanofibers of diameter 150 nm, as shown in Fig. 2.4, with carbon layers oriented like a fishbone, as illustrated in Fig. 2.5), nanotubes (e.g., carbon nanotubes with one or more concentric carbon layers along the tube axis in the wall of the tube, which has a hollow channel at its center), nanoplatelets (e.g., graphite nanoplatelets, as shown in Fig. 2.6, and nanoclay), and other shapes. The porous agglomerate structure of carbon black and fumed alumina (Fig. 2.3) results in squishability (high compressibility), meaning that a small compressive force causes an agglomerate to become a sheet. Figure 2.7 shows carbon black before and after compression. The squishability enables it to conform to the topography of a surface or an interface, thus allowing the filler to be effective for interface or surface nanostructuring. Figure 2.8 illustrates interfacial microstructures corresponding to good and bad conformability of the interfacial filler. Conformability is also helped by the nanometer size of the carbon black particles, as the small particles can fill the small valleys in the surface

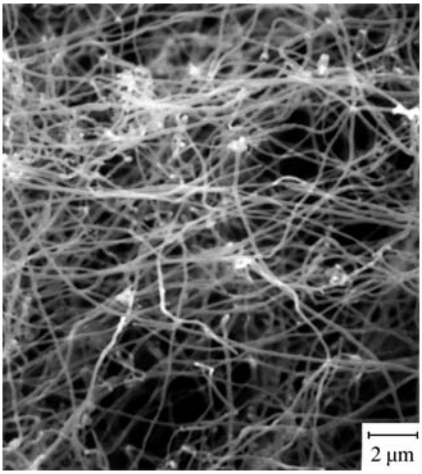

Figure 2.4. A scanning electron micrograph of carbon nanofibers with an intertwined morphology

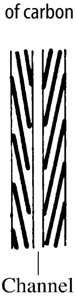

Figure 2.5. Carbon nanofiber with the carbon layers oriented like a fishbone. The structure is like a stack of ice cream cones with the tip of each cone cut off, thus resulting in a hollow channel at the center

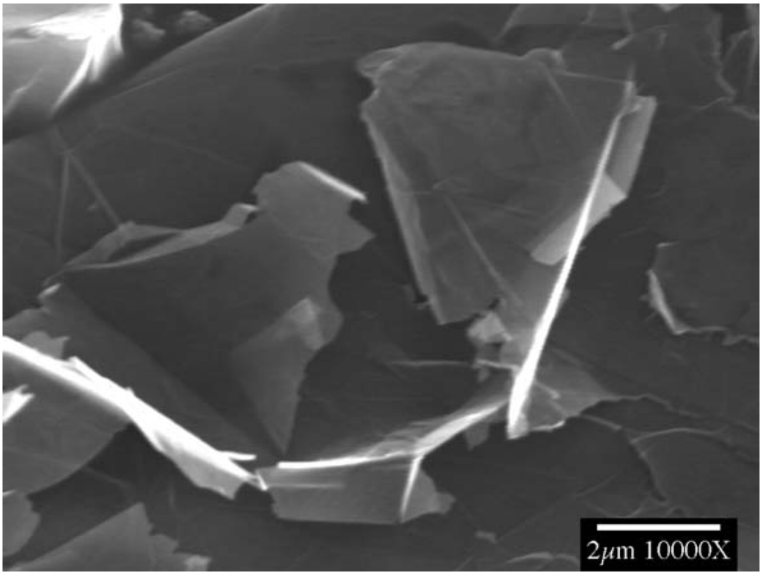

Figure 2.6. A scanning electron micrograph of graphite nanoplatelets

topography. However, conformability is dependent on not only the particle size but also the aggregate size. Each aggregate consists of a number of particles. Figure 2.9 illustrates three types of carbon black, as distinguished by the aggregate size. A small aggregate size tends to facilitate conformability.

Carbon nanotubes are classified according to the number of concentric cylindrical carbon layers within them. They can be single-walled, double-walled or multiwalled, corresponding to nanotubes with one, two and multiple carbon layers, respectively. Carbon nanotubes are also described in terms of their chirality, which relates to the crystallographic direction of the axis of the tube. This direction can be one of numerous directions in the plane of a flat carbon layer (Fig. 2.1b). The electrical behavior of a carbon nanotube depends strongly on the chirality; it may act as a metal or a semiconductor.

Nanofillers are all discontinuous. Although discontinuous carbon nanotubes can be connected (usually with the aid of a small amount of binder) to form a continuous yarn, the nanotubes in the yarn remain discontinuous. This discontinuity contributes to the limited effectiveness of carbon nanotubes when used as a reinforcement. In addition, the degree of alignment of carbon nanotubes is low compared to that of continuous carbon fibers. This poor alignment also contributes to the limited effectiveness of carbon nanotubes when used as a reinforcement. Due to the poor alignment, the maximum volume fraction of carbon nanotubes in a composite is much lower than that of continuous carbon fibers in a composite. For example, the maximum volume fraction of carbon nanotubes is around 10%, whereas that of continuous carbon fibers is around 60%. For these various reasons, it is difficult for carbon nanotubes to compete with continuous carbon fibers as load-bearing components in structural composites.

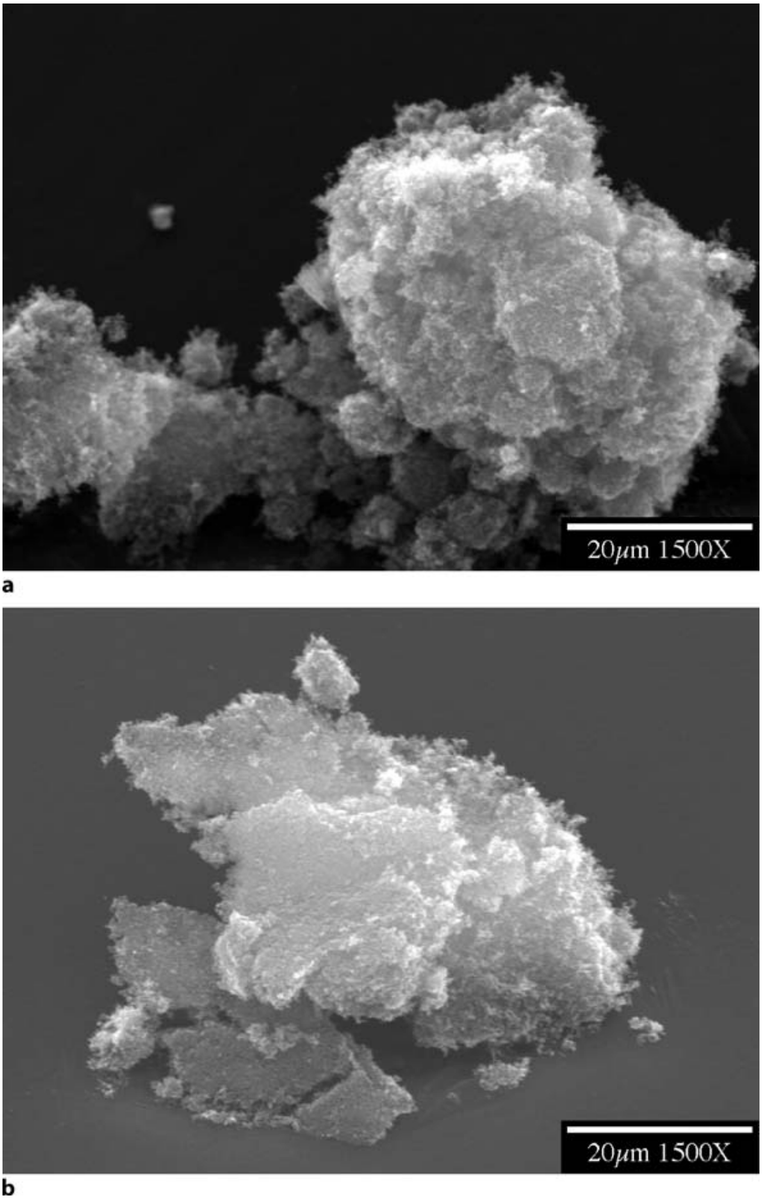

Figure 2.7. Carbon black in the form of a porous agglomerate of nanoparticles. **a** Before compression. **b** After compression

Carbon nanofibers commonly have an intertwined morphology (Fig. 2.4) akin to cotton wool. This means that the nanofibers tend to clump together, making it difficult to disperse them. Figure 2.10 illustrates a nonuniform filler distribution due to clumping and a uniform filler distribution in the absence of clumping. A relatively high degree of mechanical agitation, as achieved in high-shear mixing, is typically needed during composite fabrication in order to alleviate the clumping problem.

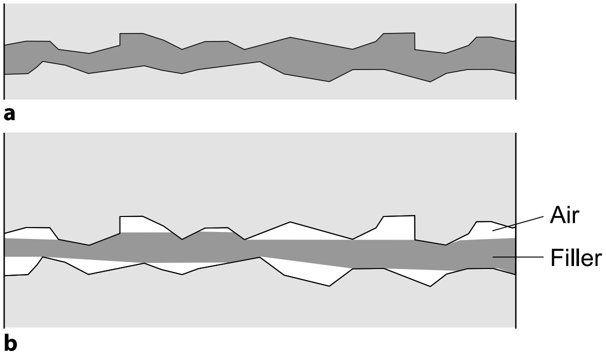

Figure 2.8. Interfacial microstructures for: **a** a conformable interfacial filler; **b** a nonconformable interfacial filler

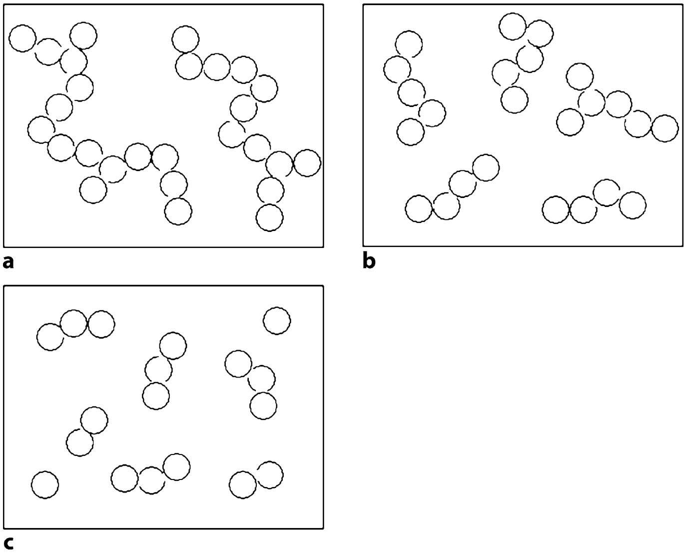

Figure 2.9. Schematic illustration of carbon black structures. **a** High structure (with a large aggregate size). **b** Medium structure (with a medium aggregate size). **c** Low structure (with a small aggregate size)

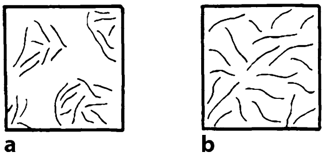

Figure 2.10. The distribution of discontinuous fibers in a composite. **a** Nonuniform distribution due to fiber clumping. **b** Uniform distribution in the absence of clumping

Due to the small thicknesses of composite interfaces, nanofillers are useful for interface modification. For example, silica fume (nanoparticles around 0.1 µm in size) added to a concrete mix aids bonding between the concrete and steel rebars,

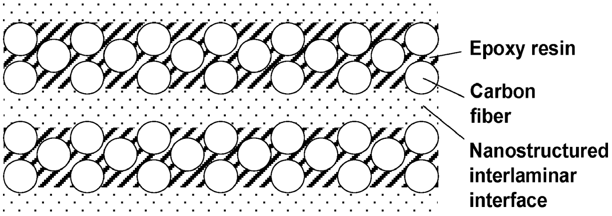

Figure 2.11. Schematic illustration of interlaminar interface nanostructuring

since the nanoparticles cause the pore structure in the concrete to be relatively fine, thereby reducing the porosity at the interface between the concrete and the steel rebars. In another example, the addition of carbon black (nanoparticles around 30 nm in size) to the interlaminar interface of a continuous carbon fiber polymer-matrix composite (Figs. 1.1 and 2.8) improves the through-thickness compressive modulus of the composite. Nanofillers are also useful for surface modification, such as the modification of the surface of a composite material for the purpose of increasing the wear resistance. Figure 2.11 illustrates both surface nanostructuring and interlaminar interface nanostructuring. In surface nanostructuring, the nanofiller is positioned on the surface rather than at the interlaminar interface.

Nanofillers are attractive for use as secondary fillers in composites that contain primary fillers (e.g., continuous carbon fibers) that serve as the load-bearing component in the composite. The secondary filler serves to enhance certain properties other than the load-bearing ability. For example, it may enhance the vibration damping capacity due to the large amount of nanofiller–matrix interface area per unit volume; the slight slippage at these interfaces during vibration causes mechanical energy dissipation. The nanofiller can be mixed with the matrix (e.g., the epoxy resin) prior to using the matrix in composite fabrication, though this approach suffers from increased viscosity of the resin (due to the presence of the nanofiller), which makes it more difficult for the resin to penetrate the small space between adjacent continuous fibers. Alternatively, the nanofiller is positioned at the interlaminar interface between the laminae of continuous fibers (Figs. 1.1 and 2.11).

Review Questions

1. Describe the crystallographic texture of a carbon fiber.
2. From the viewpoint of the chemical bonding, explain why graphite is a good lubricant.
3. From the viewpoint of chemical bonding, explain why diamond is mechanically very hard.
4. What are the three forms of carbon?
5. What is meant by turbostratic carbon?

6. Describe a process for making carbon fiber from pitch.
7. How is graphite nanoplatelet fabricated from graphite flakes?
8. Describe a method for nanostructuring the interlaminar interface of a continuous fiber polymer-matrix composite.
9. How is a carbon nanofiber fabricated?
10. What is the difference in structure between diamond and diamond-like carbon?
11. How is flexible graphite fabricated from graphite flakes?
12. Why is carbon black highly compressible?

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