6 Tailoring Composite Materials

The techniques that are used to tailor composite materials in order to achieve improved properties – as needed for a variety of applications – are covered in this chapter. These techniques include the selection and modification of the components and the engineering of the interfaces in the composite. An example of an interface is that between the reinforcement and the matrix. Interfaces can greatly affect the properties of a composite.

6.1 Tailoring by Component Selection

6.1.1 Polymer-Matrix Composites

Epoxy is by far the most widely used polymer matrix for structural composites. This is due to the strong adhesiveness of epoxy, in addition to the long history of its use in composites. Tradenames of epoxy include Epon, Epi-rez, and Araldite. Epoxy displays 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 resin 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, for example.

Epoxy resins are characterized by having two or more epoxide groups per molecule. The chemical structure of an epoxide group is shown in Fig. 6.1.

An epoxy is a thermosetting polymer that cures upon mixing with a catalyst (also known as a hardener). This curing process is a reaction that involves polymerization and crosslinking.

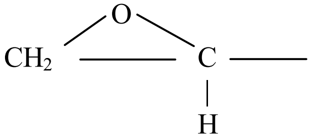

Figure 6.1. Chemical structure of an epoxide group

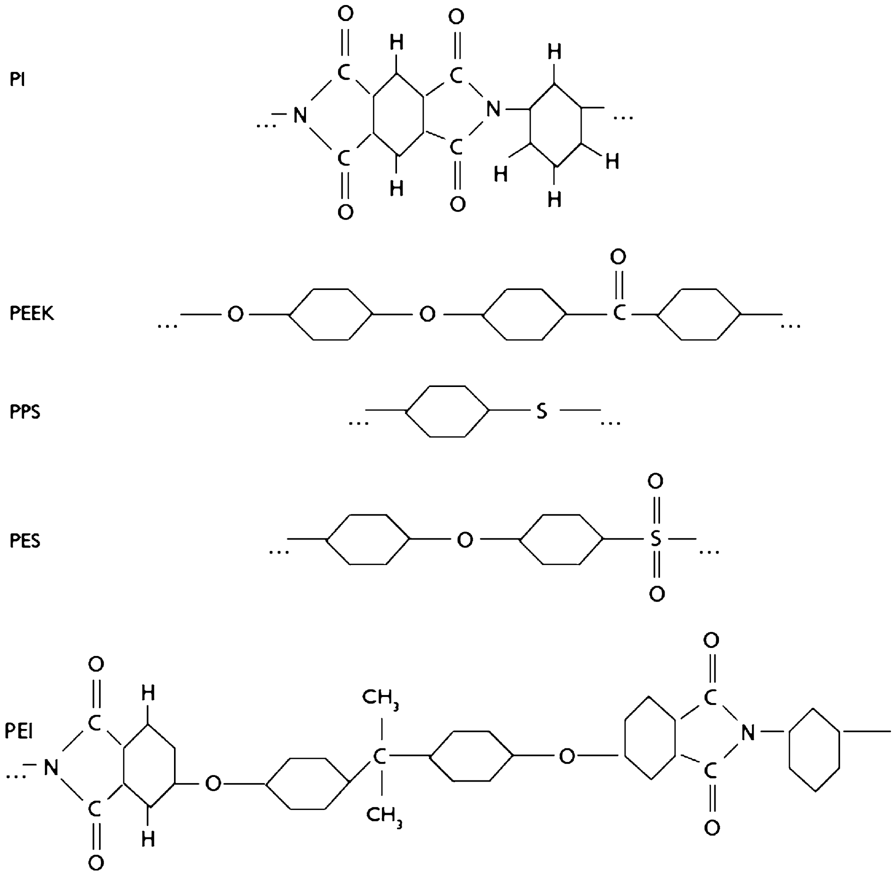

Figure 6.2. The mers (repeating units) of thermoplastic polymers typically used in structural composites

There are many types of epoxy. The most common epoxy resin is produced by a reaction between epichlorohydrin and bisphenol A. The mers (repeating units) of thermoplastic polymers that are typically used in structural composites are shown in Fig. 6.2.

The properties of these thermoplastics are listed in Table 6.1. In contrast, epoxies have a tensile strength of 103 MPa, an elastic modulus of 3.4 GPa, a ductility (elongation at break) of 6%, and a density of 1.25 g/cm^3 [1]. Thus, epoxies are stronger, stiffer and more brittle than most thermoplastic polymers. Another major difference between thermoplastics and epoxies is the higher processing temperatures of thermoplastics (300–400°C).

6.1.2 Cement-Matrix Composites

Component selection for cement-matrix composites involves the use of admixtures, which are additives included in the cement mix. These additives serve various functions, as described below:

Table 6.1. Properties of thermoplastics

	PES	PEEK	PEI	PPS	PI
T_g (°C)	230[a]	170[a]	225[a]	86[a]	256[b]
Decomposition temperature (°C)	550[a]	590[a]	555[a]	527[a]	550[b]
Processing temperature (°C)	350[a]	380[a]	350[a]	316[a]	304[b]
Tensile strength (MPa)	84[d]	70[d]	105[c]	66[d]	117[d]
Modulus of elasticity (GPa)	2.4[d]	3.8[d]	3.0[c]	3.3[d]	2.1[d]
Ductility (% elongation)	80[d]	150[d]	50–65[c]	2[d]	10[d]
Izod impact (ft lb/in.)	1.6[d]	1.6[d]	1[c]	0.5[d]	1.5[d]
Density (g/cm^3)	1.37[d]	1.31[d]	1.27[c]	1.30[d]	1.39[d]

Data from: [a] [2]; [b] [3]; [c] [4]; [d] [5]

- Water reducing agent – a minor additive to increase the workability of the mix
- Polymer (such as latex) – to decrease liquid permeability and bond strength
- Fine particles (such as silica fume) – to decrease liquid permeability, bond strength and drying shrinkage, and to increase the modulus and the abrasion resistance
- Short fiber (such as steel fiber) – to increase the flexural toughness.

Continuous fibers are not suitable for inclusion in a cement mix, although they can be applied prior to cement pouring and can serve as a reinforcement. Both processing and material costs are high. In addition, penetration of the cement mix into the small spaces between microfibers is difficult. On the other hand, macroscopic steel rebars are similar in shape to continuous microfibers and are commonly used to reinforce concrete.

6.1.2.1 Polymers in Cement-Matrix Composites

Polymer particles used as admixtures can take the form of a dry powder or an aqueous dispersion of particles. The latter form is more common. The inclusion of either form as an admixture results in improved joining of the mix constituents (e.g., sand), due to the presence of interweaving polymer films. The improved joining leads to superior mechanical and durability characteristics. Aqueous dispersions of polymer particles are more effective than dry polymer powder for the development and uniform distribution of polymer films. The most common form of polymer in aqueous dispersions is latex, particularly butadiene-styrene copolymer. The dispersions are stabilized by the use of surfactants.

In polymer-modified cement-based material, polymer particles are partitioned between the interiors of hydrates and the surfaces of anhydrous cement grains. The presence of the polymer results in an improved pore structure, thereby decreased porosity. Furthermore, the workability is enhanced and the water absorption is decreased. This enhanced workability allows the use of lower values of the water/cement ratio.

The rate of hydration is reduced by the presence of the polymer. The addition of a polymer tends to increase the flexural strength and toughness, but lower the compressive strength, modulus of elasticity, and hardness. Furthermore, polymer addition is effective at enhancing the vibration damping capacity, the frost resistance, and the resistance to biogenic sulfuric acid corrosion (relevant to sewer systems). In addition, polymer addition imparts stability and thixotropy to grouts and enables control over the rheology and the stabilization of the cement slurry against segregation. Dry polymer particles used as an admixture can be water-redispersible polymer particles, such as those obtained by spray drying aqueous dispersions. Examples are acrylic and poly(ethylenevinyl acetate). Redispersibility may be attained through the use of functional monomers. The effectiveness of redispersible polymer particles depends on the cement used. One special category of polymer particles is superabsorbent particles (hydrogel), which serve to provide the controlled formation of water-filled macropore inclusions (i.e., water entrainment) in the fresh concrete. The consequence of this is control over self-dessication. Another kind of superabsorbent polymer barely absorbs alkaline water in fresh/hardened concrete, but absorbs a great deal of neutral/acid water and creates a gel. Thus, when neutral water is poured onto the concrete after setting, the concrete is coated with the gel and can thus be kept without drying.

Organic liquid admixtures can be polymer solutions (involving water-soluble polymers such as methylcellulose, polyvinyl alcohol and polyacrylamide) or resins (such as epoxy and unsaturated polyester resin). The liquid form is attractive due to the ease with which it can be uniformly spatially distributed, and hence its effectiveness in even small proportions. In contrast to polymer solutions, particles (including particle dispersions) tend to require a higher proportion in order to be comparably effective. Polymer solutions used as admixtures can serve to optimize the air void distribution and rheology of the wet mix, thereby improving workability with low air contents.

Short fibers rather than continuous ones are used because they can be incorporated in the cement mix, thereby facilitating processing in the field. Furthermore, short fibers are less expensive than continuous ones. Polypropylene, polyethylene and acrylic fibers are particularly common due to the requirements of low cost and resistance to the alkaline environment in cement-based materials. Compared to carbon, glass and steel fibers, polymer fibers are attractive due to their high ductility, which results in high flexural toughness in the cement-based material. The combined use of short polymer fibers and a polymer particle dispersion (e.g., latex) results in superior strength (tensile, compressive, and flexural) and flexural toughness compared to the use of fibers without a polymer particle dispersion.

6.1.2.2 Silica Fume in Cement-Matrix Composites

Silica fume is very fine noncrystalline silica produced by electric arc furnaces as a by-product of the production of metallic silicon or ferrosilicon alloys. It is a powder with particles that have diameters that a hundredfold smaller than those of anhydrous Portland cement particles (i.e., the mean particle size is between 0.1 and 0.2 μm). The SiO_2 content ranges from 85 to 98%. Silica fume is pozzolanic – it has a limited ability to serve as a cementitious binder.

Silica fume used as an admixture in a concrete mix has significant positive effects on the properties of the resulting material. These effects pertain to the strength, modulus, ductility, vibration damping capacity, sound absorption, abrasion resistance, air void content, shrinkage, bonding strength with reinforcing steel, permeability, chemical attack resistance, alkali-silica reactivity reduction, corrosion resistance of embedded steel reinforcement, freeze–thaw durability, creep rate, coefficient of thermal expansion (CTE), specific heat, thermal conductivity, defect dynamics, dielectric constant, and degree of fiber dispersion in mixes containing short microfibers. However, silica fume addition degrades the workability of the mix. This problem can be alleviated by using more water-reducing agent or by treating the surfaces of the silica fume particles with silane.

6.1.2.3 Short Fibers in Cement-Matrix Composites

Short fibers are used as admixtures in cement-based materials in order to decrease the drying shrinkage, increase the flexural toughness, and in some cases to increase the flexural strength too. When the fibers are electrically conductive, they may also provide nonstructural functions, such as self-sensing (sensing the strain, damage, or temperature), self-heating (for deicing), and electromagnetic reflection (for electromagnetic interference shielding; i.e., EMI shielding).

Although continuous fibers are more effective than short fibers when used as a reinforcement, they are not amenable to incorporation in a concrete mix and they are relatively expensive. Low cost is critical to the practical viability of cement-based materials.

Although macroscopic steel fibers that are around 1 mm in diameter are used, the most effective fibers are usually microfibers with diameters ranging from 5 to 100 μm. For example, carbon fibers are typically around 10 μm in diameter. Nanofibers with diameters that are typically around 0.1 μm are less effective than microfibers as a reinforcement, although they are more effective than microfibers at providing EMI shielding (due to their small diameters and the skin effect, which refers to the phenomenon in which high-frequency electromagnetic radiation only interacts with the near-surface region of an electrical conductor). In general, the smaller the fiber diameter (and thus the higher the aspect ratio), the more difficult it is to disperse the fibers. Similarly, the smaller the fiber length (which relates to a lower aspect ratio), the easier it is to disperse the fibers. This is due to the tendency for fibers with small diameters or long lengths to cling to one another. The effectiveness of a fiber admixture at improving the structural or functional properties of cement-based materials is greatly affected by the degree of fiber dispersion. The attainment of a high degree of fiber dispersion is particularly critical when the fiber volume fraction is low. A low fiber volume fraction is usually preferred because the material cost increases, the workability decreases, the air void content increases, and the compressive strength decreases as the fiber content increases. The fiber dispersion is enhanced by improving the hydrophilicity (i.e., the wettability by water) of the fibers, as the cement mix is water-based. The hydrophilicity can be controlled by treating the surfaces of the fibers prior to incorporating the fibers into the cement mix. Furthermore, the fiber dispersion is affected by the admixtures that may be used along with the fibers. These admixtures may be fine particles (such as silica fume, which has a typical particle size of around 0.1 μm), the presence of which helps the fibers to break loose from one another as mixing occurs. Other admixtures may be polymers such as latex particle dispersions, which help fiber–cement bonding as well as fiber dispersion.

6.1.3 Metal-Matrix Composites

Aluminum is the most common matrix material used in metal-matrix composites because of (i) its low melting temperature, which allows casting to be conducted at relatively low temperatures, and (ii) its low density. Copper's high density makes it unattractive for lightweight composites, but its high thermal conductivity and low electrical resistivity make it attractive for electronic applications (Table 6.2).

Metals and ceramics tend to have very different in their properties, as shown in Table 6.2. Metals are electrically and thermally conductive. The thermal conductivities of aluminum and copper (Table 6.2) are higher than those of any of the ceramics listed, while the electrical resistivities of aluminum and copper are much lower (by many orders of magnitude) than those of any of the ceramics listed. However, most metals exhibit a high coefficient of thermal expansion (CTE) and a low elastic modulus compared to ceramics. The CTE values of aluminum and copper are higher than those of any of the ceramics listed, and the elastic moduli of aluminum and copper are lower than those of any of the ceramics listed. The density of aluminum is comparable to those of ceramics, but the density of copper is higher than those of ceramics.

Among the metals, molybdenum, tungsten, Kovar (Fe-Ni29-Co17) and Invar (Fe-Ni36) have exceptionally low CTE values (Table 6.2). Their CTE values are comparable to those of ceramics; indeed, the CTE of Invar is even lower than those of ceramics. Thus, Invar is used for precision instruments, such as clocks, physical laboratory devices, seismic creep gauges, and valves in motors. Guillaume received the Nobel Prize in Physics in 1920 for discovering Invar (which means "invariability in relation to the essential absence of thermal expansion"). However, all of these metals/alloys have low values of thermal conductivity. In addition, their densities are high. Furthermore, molybdenum and tungsten are refractory metals (i.e., metals that are extraordinarily resistant to heat and wear; a group that also includes niobium, tantalum, and rhenium). For example, the melting point of tungsten is 3,410°C. Such high melting temperatures make metal processing that involves casting (melting and subsequent solidification) difficult.

Carbon fibers exhibit slightly negative CTE values, so they are highly effective CTE-reducing fillers. The electrical resistivities of carbon fibers (all grades) are lower than those of metals, but their thermal conductivities can be lower or higher than those of metals, depending on the fiber grade. High-modulus carbon fiber can be more thermally conductive than metals (and even more thermally conductive than copper for the grade of high-modulus carbon fiber shown in Table 6.2), whereas high-strength carbon fiber is less thermally conductive than metals.

The incorporation of a carbon or ceramic filler into a metal to form a metal-matrix composite is attractive for attaining a low CTE (although not as low as that

Table 6.2. Properties of metals, carbons and ceramics

Material	Density (g/cm^3)	Thermal conductivity (W/(m K))	Electrical resistivity (Ωcm)	Elastic modulus (GPa)	CTE ($10^{-6}/K$)
Aluminum[a]	2.70	237	2.65×10^{-6}	70	23.1
Copper[a]	8.96	401	1.68×10^{-6}	110–128	16.5
Molybdenum[a]	10.22	142	5.2×10^{-6}	320	4.9
Tungsten[a]	19.3	155	5.3×10^{-6}	400	4.5
Kovar[a] (Fe-Ni29-Co17)	8.35	17	4.9×10^{-5}	159	5.2
Invar[a] (Fe-Ni36)	8.05	10.5	8.2×10^{-5}	141	1.2
Carbon fiber[b] (high strength)	1.76	8	1.8×10^{-3}	231	−0.60
Carbon fiber[b] (high modulus)	2.17	640	2.2×10^{-4}	827	−1.45
Silicon carbide (SiC)[c]	3.1	120	10^2–10^6	410	4.0
Silicon nitride (Si_3N_4)[c]	3.29	30	/	310	3.3
Aluminum nitride (AlN)[c]	3.26	140–180	$> 10^{14}$	330	4.5
Aluminum oxide (Al_2O_3)[c]	3.89	35	$> 10^{14}$	375	8.4
Boron nitride[c] (hexagonal)	1.9	121	$> 10^{14}$	/	−0.46
Titanium diboride (TiB_2)[c]	4.50	96	10^{-5}	565	6.4
Zirconium oxide (ZrO_2)[c], Y_2O_3 stabilized	6	2	$> 10^{10}$	200	10.3

[a] Metal; [b] carbon; [c] ceramic

of the carbon or ceramic filler) and a high elastic modulus (although not as high as that of the carbon or ceramic filler), in addition to high thermal and electrical conductivities (although not as high as those of the metal matrix). When copper is used as the matrix, the composite also allows a reduction in density (although the density does not become as low as that of the carbon or ceramic filler).

The combination of low CTE and high thermal conductivity is particularly attractive for electronic packaging, such as heat sinks, housings, substrates, lids, etc. The combination of high electrical and thermal conductivity and hardness is particularly attractive for welding electrodes, motor brushes, and sliding contacts.

Among the ceramic fillers listed in Table 6.2, titanium diboride and silicon carbide are most attractive due to their high elastic moduli. This is an important factor for strengthening the composite. Among the ceramic fillers listed, aluminum nitride is most attractive due to its high thermal conductivity, although silicon carbide and hexagonal boron nitride have quite high thermal conductivities. One drawback of aluminum nitride is its reactivity with water to form aluminum oxynitride, which has a much lower thermal conductivity than aluminum nitride. Aluminum oxide and zirconium oxide have particularly low thermal conductivities.

Among the ceramic fillers, titanium diboride is most attractive because of its low electrical resistivity, which allows it to be used as an anode material for aluminum smelting (the extraction of aluminum from its oxide, alumina) and to be machined by electrical discharge machining (abbreviated to EDM, and also called spark machining; this refers to the removal of material using electric arcing discharges between an electrode, which is the cutting tool, and the workpiece in the presence of an energetic electric field). EDM requires that the workpiece is electrically conductive.

Due to its low cost and high elastic modulus, silicon carbide is the filler most commonly used to reinforce metals. SiC is also used as an abrasive (e.g., in sandpaper). There are numerous polymorphs of SiC, but the most common polymorph is α-SiC, which has a hexagonal crystal structure (similar to wurtzite). A less common polymorph is β-SiC, which exhibits the zinc blende crystal structure.

Silicon carbide is available in particle and whisker forms. A whisker is a short fiber that can be essentially a single crystal. The SiC particle is typically α-SiC, with a size of 1–10 μm. The SiC whisker is typically β-SiC, with a diameter of about 1 μm and a length of about 20 μm. Figure 6.3 shows an SEM photograph of β-SiC whiskers of diameter 1.4 μm and length 18.6 μm. Figure 6.4 shows SEM photographs of an aluminum-matrix composite containing 10 vol% SiC whiskers of the type shown in Fig. 6.3. The composite is fabricated by liquid metal infiltration at an infiltration pressure of 13.8 MPa. The porosity in the composite is $< 0.5\%$.

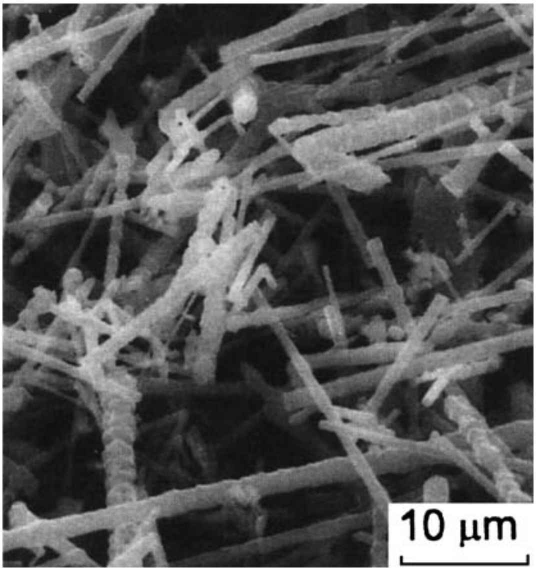

Figure 6.3. SEM photograph of silicon carbide whiskers without a matrix (from [6])

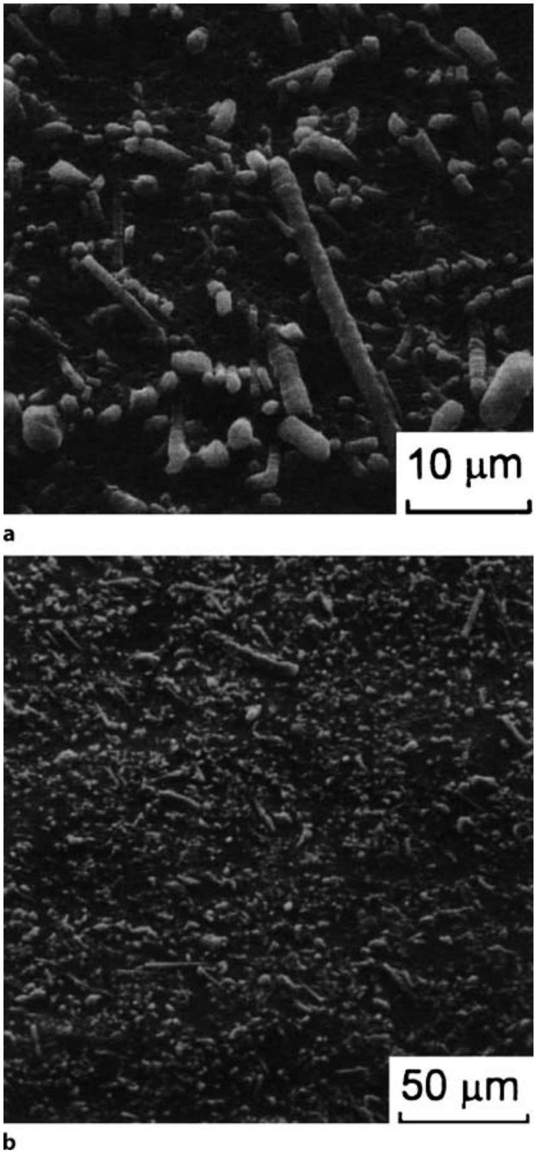

Figure 6.4. SEM photographs of mechanically polished sections of aluminum-matrix composites containing 10 vol% silicon carbide whiskers. **a** High-magnification view, **b** low-magnification view. The whiskers are essentially randomly oriented; the whisker diameter is 1.4 µm and the whisker length is 18.6 µm. (From [6])

Compared to silicon carbide, titanium diboride has a higher modulus but a lower thermal conductivity (Table 6.2). The high modulus makes titanium diboride a highly effective reinforcing material. The addition of TiB_2 to a metal greatly increases the stiffness, hardness and wear resistance and decreases the CTE, while it reduces the electrical and thermal conductivity much less than the addition of

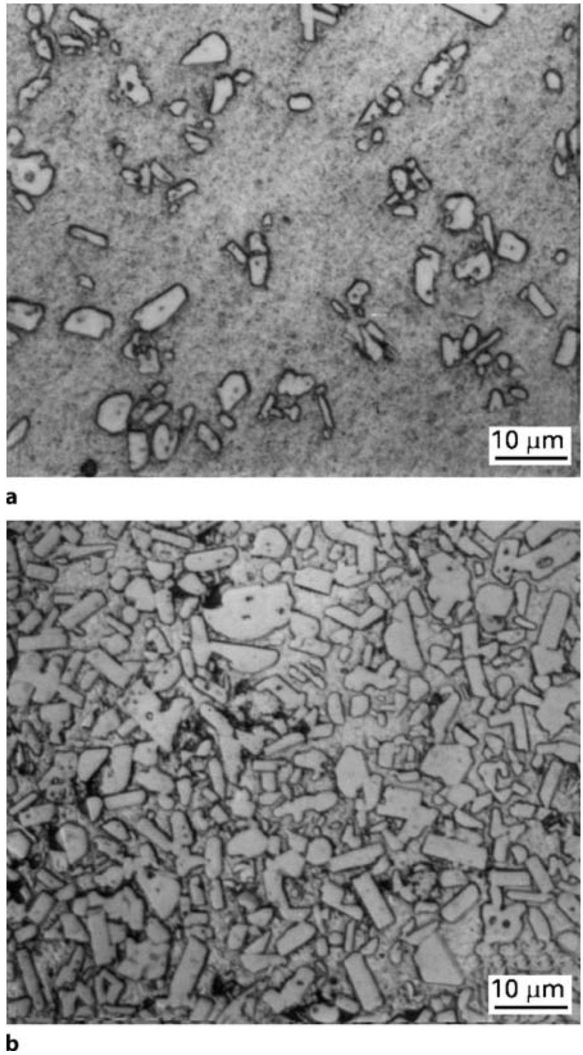

Figure 6.5. Optical microscope photographs of a copper-matrix composite containing: **a** 15 vol% TiB_2 platelets; **b** 60 vol% TiB_2 platelets. (From [7])

most other ceramic fillers. Figure 6.5 shows optical microscope photographs of copper-matrix composites containing TiB_2 platelets with diameters 3–5 µm and aspect ratios of about 3. The composites are made by the coated filler method (Fig. 1.9) of powder metallurgy. The CTE decreases monotonically with increasing TiB_2 volume fraction (Fig. 6.6) such that the coated filler method gives slightly lower CTE than the admixture method (Fig. 1.7) for the same TiB_2 volume fraction. However, even for the coated filler method, a high TiB_2 volume fraction of 60% is needed in order to reduce the CTE of copper from 17×10^{-6} to 8.5×10^{-6}/°C (Fig. 6.6). The thermal conductivity decreases monotonically with increasing TiB_2

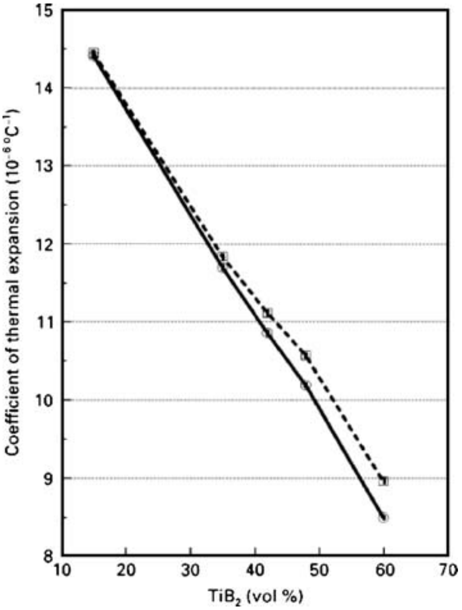

Figure 6.6. Effect of TiB_2 volume fraction on the coefficient of thermal expansion (CTE) of copper-matrix composites. *Circles* – coated filler method of powder metallurgy; *squares* – admixture method of powder metallurgy. (From [7])

volume fraction (Fig. 6.7). The electrical resistivity increases monotonically with increasing TiB_2 volume fraction (Fig. 6.8). Both the compressive yield strength (Fig. 6.9) and the hardness (Fig. 6.10) increase with increasing TiB_2 volume fraction up to a certain TiB_2 volume fraction, beyond which they decrease with increasing TiB_2 volume fraction. This behavior of the compressive yield strength and hardness is due to the porosity (Fig. 6.11), which increases abruptly with increasing TiB_2 volume fraction when this volume fraction exceeds a certain value. The coated filler method gives a slightly lower CTE, a higher thermal conductivity, a lower electrical resistivity, a higher compressive yield strength, a higher hardness, and a lower porosity than the admixture method for the same TiB_2 volume fraction.

In general, the difficulty involved in getting molten metal to wet the surface of a ceramic or carbon reinforcement complicates the fabrication of metal-matrix composites. This difficulty is particularly severe for high-modulus carbon fibers (e.g., Amoco's Thornel P-100) which have graphite planes that are mostly aligned parallel to the fiber surface. The edges of the graphite planes are more reactive with the molten metal than the graphite planes themselves, so low-modulus carbon fibers are more reactive and are thus wetted more easily by the molten metals. Although this reaction between the fibers and the metal aids the wetting, it produces a brittle carbide and degrades the strength of the fibers.

The wetting of a reinforcement by molten metal can be improved by adding alloying elements to the molten metal. When aluminum is used as the matrix and carbon fiber as the reinforcement, effective alloying elements include Mg, Cu, and Fe.

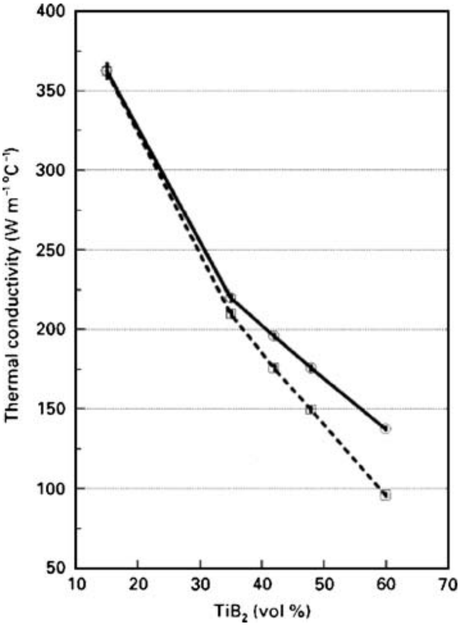

Figure 6.7. Effect of TiB_2 volume fraction on the thermal conductivity of copper-matrix composites. *Circles* – coated filler method of powder metallurgy; *squares* – admixture method of powder metallurgy. (From [7])

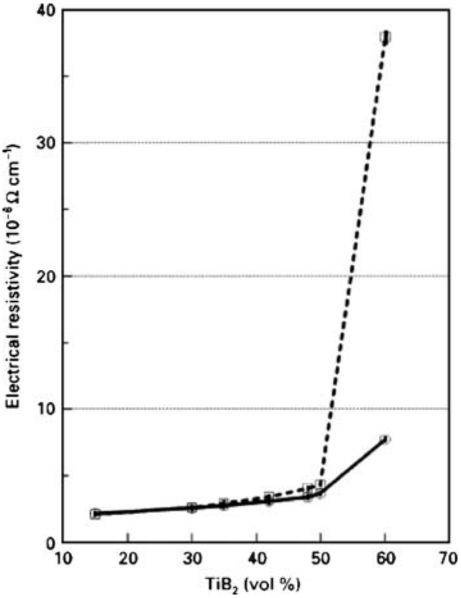

Figure 6.8. Effect of TiB_2 volume fraction on the electrical resistivity of copper-matrix composites. *Circles* – coated filler method of powder metallurgy; *squares* – admixture method of powder metallurgy. (From [7])

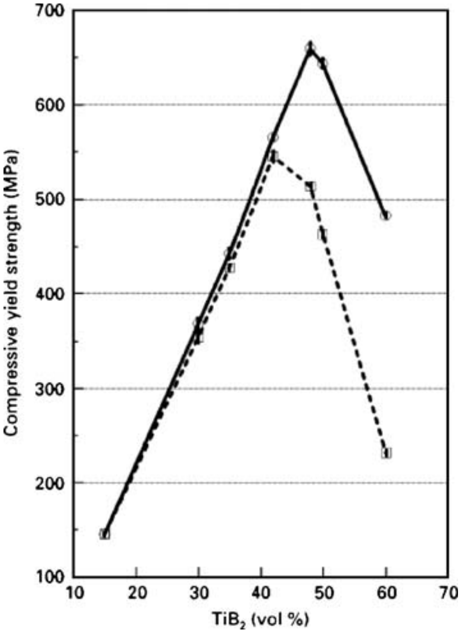

Figure 6.9. Effect of TiB_2 volume fraction on the compressive yield strength of copper-matrix composites. *Circles* – coated filler method of powder metallurgy; *squares* – admixture method of powder metallurgy. (From [7])

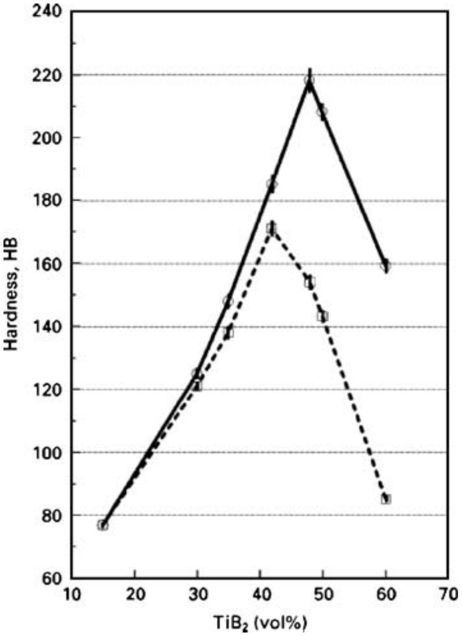

Figure 6.10. Effect of TiB_2 volume fraction on the hardness of copper-matrix composites. *Circles* – coated filler method of powder metallurgy; *squares* – admixture method of powder metallurgy. (From [7])

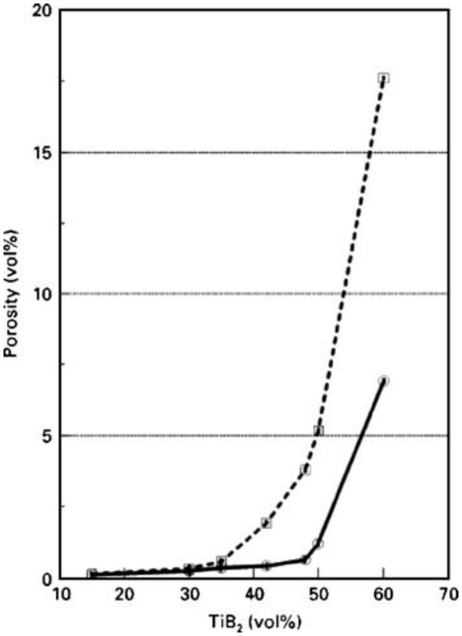

Figure 6.11. Effect of TiB_2 volume fraction on the porosity of copper-matrix composites. *Circles* – coated filler method of powder metallurgy; *squares* – admixture method of powder metallurgy. (From [7])

6.2 Tailoring by Interface Modification

6.2.1 Interface Bond Modification

6.2.1.1 General Concepts

Effective reinforcement requires good bonding between the filler and the matrix, especially for short fibers. For an ideally unidirectional composite (i.e., one containing continuous fibers all aligned in the same direction) containing fibers with a modulus that is 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 the 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 (e.g., carbon and ceramics) to become more brittle, as the strong fiber–matrix bonding causes cracks to propagate linearly 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 (e.g., 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 (i.e., 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. In particular, the fiber–matrix bond strength in carbon–carbon composites must be optimal. If the bond strength is too high, the resulting composite may be extremely brittle, exhibiting catastrophic failure and poor strength. If it is too low, the composites fail in pure shear, with poor transfer of the load to the fiber.

The mechanisms involved in filler–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 filler–matrix interface is sufficiently high and that a brittle reaction product is absent from the filler–matrix interface. The density of chemical bonds can be increased by (i) chemically treating the filler, (ii) using a suitable sizing (coating) on the filler, and (iii) using a molecular coupling agent. Interdiffusion at the filler–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 filler should have a rough surface in order to allow a small degree of mechanical interlocking to take place.

Chemical bonding, interdiffusion and van der Waals bonding require the filler 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 filler during the infiltration of the matrix or matrix precursor into the filler 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 involves adding 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 to use a high pressure during infiltration.

The occurrence of a reaction between the filler and the matrix aids the wetting and bonding between the filler and the matrix. However, an excessive reaction degrades the filler, and the reaction product(s) may have an undesirable effect on the mechanical, thermal, or moisture resistance properties of the composite. Therefore, an optimum amount of reaction is preferred.

An example relates to the reaction between silicon carbide and aluminum during the fabrication of a silicon carbide aluminum-matrix composite by infiltrating molten aluminum into a heated SiC preform. The reaction is

$$4\mathrm{Al} + 3\mathrm{SiC} \rightarrow \mathrm{Al}_4\mathrm{C}_3 + 3\mathrm{Si}\,, \tag{6.1}$$

which consumes a part of the SiC, produces silicon (Si) that dissolves in the molten aluminum, and also produces the Al_4C_3 compound at the interface between the SiC and the aluminum matrix. The fraction of SiC consumed increases with decreasing SiC volume fraction in the composite. The amount of silicon produced by the reaction increases with increasing SiC volume fraction. The extent of the reaction increases with increasing infiltration temperature. The fraction of SiC whiskers consumed is inversely proportional to the volume fraction of SiC whiskers in the composite. The product of these two fractions provides a scale (called the reactivity index) that describes the Al-SiC reactivity. The index decreases with decreasing infiltration temperature and is higher for SiC whiskers than SiC particles. At an infiltration temperature of 670°C, the fraction of SiC whiskers consumed is 26% for a SiC volume fraction of 0.10. In contrast, the fraction of SiC consumed is only 8.4% for a 55 vol% SiC particle composite made at an infiltration temperature of 800°C [6].

6.2.1.2 Filler Surface Treatment

The surface treatment of a filler is usually a valuable method of improving the bonding between the filler and the matrix. If the filler is carbon fiber, surface treatments involve oxidation treatments and the use of coupling agents, wetting agents, and/or sizings (coatings). Carbon fibers need treatment for both thermosetting and thermoplastic polymers. As the processing temperature is usually higher for thermoplastic polymers than for thermosetting polymers, the treatment must be stable to a higher temperature (300–400°C) when a thermoplastic polymer is used.

Oxidation treatments can be applied by gaseous, solution, electrochemical, and plasma methods. Oxidizing plasmas include those involving oxygen, CO_2 and air. The resulting oxygen-containing functional groups on the fiber surface cause improvements in the wettability of the fiber and the fiber–matrix adhesion. The result of this is enhanced interlaminar shear strength (ILSS) and flexural strength. Other plasmas (not necessarily oxidizing) that are also effective involve nitrogen, acrylonitrile, and trimethyl silane. Ion beam treatment is somewhat similar to plasma treatment, but it involves oxygen or nitrogen ions. Plasma treatments are useful for epoxy as well as thermoplastic matrices. Oxidation by gaseous methods includes the use of oxygen gas containing ozone. Oxidation by solution methods involves wet oxidation, such as acid treatments. Oxidation by electrochemical methods (i.e., anodic treatment) includes the use of ammonium sulfate solutions, a diammonium hydrogen phosphate solution containing ammonium rhodanide, ammonium bicarbonate solutions, a phosphoric acid solution, and other aqueous electrolytes. In general, the various treatments chemically modify the fiber surface and remove a loosely adhering surface layer. More severe oxidation treatments also serve to roughen the fiber surface, thereby enhancing the mechanical interlocking between the fibers and the matrix.

In the case of cement-matrix composites, it is important for the filler to be wettable by water, which is an important component of the cement mix. Inadequate wettability makes fiber dispersion more difficult and increases the amount of fiber–matrix interfacial voids in the resulting composite. The interfacial voids reduce the fiber–matrix bond strength. Thus, surface treatment of the filler is conducted to improve the wettability, whether the filler is fibrous (e.g., carbon fiber) or particulate (e.g., silica fume). Examples of surface treatment include ozone treatment of carbon fibers and silane treatment of carbon fibers and silica fume. Figure 6.12 shows that the drying shrinkage of cement paste containing silica fume is reduced by using silane-treated silica fume in place of as-received silica

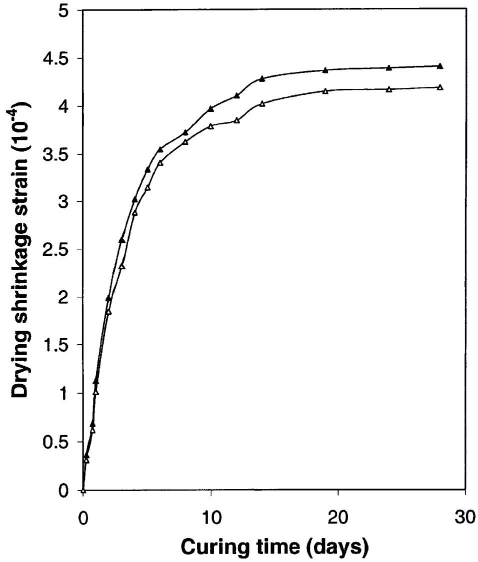

Figure 6.12. Drying shrinkage strain versus curing time for cement paste containing silica fume. *Filled triangles* – as-received silica fume; *unfilled triangles* – silane-treated silica fume. (From [8])

fume. This effect of silane treatment is due to the improved bonding between the silica fume and the cement matrix, facilitated by the improved wettability of the silica fume by water.

The surface treatment of the carbon fibers has a significant effect on the mechanical properties of the resulting carbon–carbon composites. Surface-treated fibers that bond strongly with the polymer exhibit high flexural strength in polymer composites, but result in carbonized composites of poor flexural strength. For graphitized composites, the flexural strength increases monotonically with increasing treatment time. Graphitization causes composites with surface-treated fibers to increase in flexural strength and interlaminar shear strength and those with untreated fibers to decrease in flexural strength and interlaminar shear strength. Hence, the fiber–matrix bonding is very poor in graphitized composites containing untreated fibers and is stronger in graphitized composites containing treated fibers.

6.2.1.3 Use of an Organic Coupling Agent

6.2.1.3.1 Organic Coupling of Inorganic Components

The use of an organic molecule (known as a coupling agent; also known as a molecular tether) to covalently link an inorganic particle and an inorganic matrix enhances the bonding between the inorganic particle and the matrix, thus resulting in a nanocomposite of increased strength. The chosen molecule must have functional groups at its two ends that are able to react with the surface of the inorganic particle and the matrix material. Silane coupling agents are most commonly used as the organic molecules.

An example is a nanocomposite with cement as the matrix and silica fume as the inorganic particles. The effectiveness of silane for cement is due to the reactivity of its molecular ends with –OH groups and the presence of –OH groups on the surfaces of both the silica and the cement.

One method of introducing the silane coupling agent involves coating the silica fume particles with the silane prior to incorporating the particles into the cement mix. An effective silane coupling agent for this situation is a 1:1 (by mass) mixture of $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$ (referred to as S_1, available as product Z-6020 from Dow Corning, Midland, MI, USA) and $OCH_2CHCH_2OCH_2CH_2CH_2Si(OCH_3)_3$ (referred to as S_2, available as product Z-6040 from Dow Corning). The amine (NH_2) group in S_1 serves as a catalyst for the curing of epoxy and consequently allows the S_1 molecule to attach to the epoxy (OCH_2) end of the S_2 molecule. The trimethylsiloxy (OCH_3) ends of the S_1 and S_2 molecules then connect to the –OH functional group on the surface of silica fume. The silane can be dissolved in ethylacetate. The introduction of the silane can involve immersion of the silica fume in the silane solution, heating to 75°C while stirring, and holding at 75°C for 1 h, followed by filtration, washing with ethylacetate, and drying. After this, the silica fume can be heated in a furnace at 110°C for 12 h for the purpose of drying. Table 6.3 shows that silane coupling results in increases in the strength, modulus, and ductility of cement mortar both under tension and in compression, and also slightly increases the density. In particular, the tensile strength is increased by 31% and the compressive strength is increased by 27%. Moreover, the hydrophilic nature of silane improves the workability of the mixture and also probably enhances the dispersion of silica fume in the cement mix.

Another method of introducing a silane coupling agent into silica fume cement involves adding the silane to the cement mix rather than coating the silica fume with silane. In this situation, the silane must be stable in water. An effective silane in this situation is aqueous amino vinyl silane (Hydrosil 2781, Sivento, Piscataway, NJ, USA). In contrast, the silane used to coat silica fume that was

Table 6.3. Effect of silane coupling of silica fume particles on the mechanical properties of cement mortar containing silica fume (from [9])

Property	Without silane coupling	With silane coupling
Tensile strength (MPa)	2.35 ± 0.11	3.09 ± 0.13
Tensile modulus (GPa)	10.2 ± 0.07	14.57 ± 0.08
Tensile ductility (%)	0.0141 ± 0.0003	0.0150 ± 0.0004
Compressive strength (MPa)	61.95 ± 2.3	78.4 ± 3.2
Compressive modulus (GPa)	21.1 ± 0.54	28.7 ± 0.46
Compressive ductility (%)	0.138 ± 0.002	0.145 ± 0.003
Density (g/cm^3)	2.13	2.20

mentioned in the last paragraph is not sufficiently stable in aqueous systems. The silane admixture is added at levels of 0, 0.20, 0.50, 0.75, 1.0, 1.5, and 2.0% by mass of cement. The corresponding amount of water-reducing agent is 1.0, 0.10, 0.10, 0.05, 0.05, 0.025, and 0.025% by mass of cement, respectively. Adding more silane means that less water-reducing agent is needed to maintain workability. The surfactant, added at the level of 1% by mass of cement to help distribute the silane, can be polyoxyethylene lauryl ether, $C_{12}H_{25}(OCH_2CH_2)_nOH$, (Aldrich Chemicals, Milwaukee, WI, USA). The defoamer can be Rhodoline 1010 (Rhodia, Cranbury, NJ, USA), added at the level of 0.13 vol%.

The use of silane as an admixture that is added directly to the cement mix involves slightly more silane material but less processing cost than the use of silane in the form of a coating on silica fume. Both methods of introducing silane result in increases in the tensile and compressive strengths. The network produced by the admixture method of silane introduction is not achieved with the silane coating method due to the localization of the silane in the coating, which nevertheless provides chemical coupling between the silica fume and cement. This network, which is formed by the hydrolysis and polymerization (condensation) reactions of silane during the hydration of cement, also causes the ductility to decrease.

6.2.1.3.2 Organic Coupling of an Inorganic filler and a Polymer Matrix

An organic coupling agent can be used to improve the bond between an inorganic filler and a polymer matrix. For example, a silane coupling agent is effective at enhancing the bond between boron nitride particles and an epoxy matrix. Boron nitride (BN) is a ceramic material, with some ionic character in the covalent bond between boron and nitrogen. Its thermal conductivity is one of the highest among electrical insulators. Polymer-matrix composites that exhibit high thermal conductivity are valuable for electronic packaging due to the importance of heat dissipation from microelectronics.

Two materials are said to be isoelectronic if they have the same number of valence electrons per unit cell and the same structure (i.e., the same number and connectivity of atoms), even though the two materials may be different in composition. Boron nitride is isoelectronic with carbon. Boron nitride with a cubic crystal structure and boron nitride with a hexagonal crystal structure are different polymorphs (also called allotropes – two different crystal forms with the same composition) of boron nitride. Diamond and graphite are different polymorphs of carbon. The cubic form of boron nitride is analogous to diamond, whereas the hexagonal form of boron nitride is analogous to graphite. The hexagonal form is made up of layers of hexagonal sheets, with the boron atom directly above the nitrogen atoms in the crystal structure. Cubic boron nitride, like diamond, is one of the hardest materials known. Hexagonal boron nitride, like graphite, is a lubricant.

Equiaxed hexagonal boron nitride particles of size 5–11 µm and thermal conductivity 280 W/m K (Product Polartherm 180, Advanced Ceramic Corporation, Cleveland, OH, USA) can be surface treated with silane ($O\ CH_2\ CH\ CH_2O\ CH_2CH_2CH_2\ Si\ (OCH_3)_3$, Product Z-6040, Dow Corning Corp.). The epoxy structure at one end of the silane molecule allows coupling to the epoxy matrix in the composite. The silane treatment process can involve (i) making a silane–water solution at a selected concentration, (ii) adding BN to the solution and stirring with a magnetic stirrer, (iii) heating at 60–70°C for 20 min, (iv) rinsing with water by filtration, and (v) drying at 110°C for 12 h.

The effects of the silane surface treatment of boron nitride have been compared with those of acid treatment. The acid treatment process involves (i) immersing the BN in acid in a beaker, (ii) stirring for 2 h with a magnetic stirrer, (iii) adding water and stirring for 2 min, (iv) rinsing with water by filtration until the water is neutral, and (v) drying at 110°C for 12 h.

The effects of the silane surface treatment of boron nitride have also been compared with those of acetone treatment. The surface treatment of BN particles using acetone involves (i) immersing BN in acetone, (ii) stirring for 2 h, (iii) filtering, and (iv) drying at 110°C for 12 h.

The polymer used in this example is epoxy, namely Epon (R) Resin 813 and EPI-Cure (R) 3234 Curing Agent from Shell Chemical Co. (Houston, TX, USA). The BN epoxy-matrix composites are fabricated by (i) mixing the epoxy resin and curing agent in the mass ratio 100:13, (ii) adding BN and mixing, (iii) pressing at room temperature and 10.5 MPa for 2 h, and (iv) heating at 45°C and 10.5 MPa for 1 h to complete polymerization.

Since the organic coupling is volatile compared to BN, the fractional loss in weight of the silane-treated BN particles after heating to a high temperature relates to the amount of silane present. Thus, BN particles with and without surface treatment are tested by measuring the weight loss upon heating to 600°C at 20°C/min under nitrogen gas flow (30 ml/min) protection, using a thermogravimetric analyzer (abbreviated TGA).

The fractional loss in weight of treated BN upon heating to 600°C is shown in Table 6.4. The amounts of volatile or decomposable material on the as-received, acetone-treated and acid (HNO_3 or H_2SO_4)-treated BN particles are negligible, indicating that treatments involving acetone and acid do not result in a coating on the BN particle. However, the weight losses for the silane-treated BN particles are much higher, indicating that the silane treatment results in a coating on the BN particle, since the weight loss results from the decomposition of the coating

Table 6.4. Fractional loss of mass from BN particles upon heating to 600°C (from [10])

Treatment	Fractional loss of mass (%)
As received	0.15
Acetone treated	0.14
Nitric acid (HNO_3) treated	0.10
Sulfuric acid (H_2SO_4) treated	< 0.10
Silane (low concentration) treated	0.7
Silane (medium concentration) treated	0.8
Silane (high concentration) treated	2.4

Table 6.5. Specific surface area of BN particles (from [10])

Treatment	Specific surface area (m^2/g)
As received	10.8
Acetone treated	16.4
Nitric acid (HNO_3) treated	14.9
Sulfuric acid (H_2SO_4) treated	12.5
Silane (high concentration) treated	10.5

at high temperature. Silane-water solutions of three different concentrations yield different amounts of coating. The higher the silane concentration in the solution, the greater the amount of coating.

Surface roughening that causes an increase in the surface area may result from acid treatment, due to the reaction between the acid and BN. Thus, the specific surface area (surface area per unit mass) of the BN particles with and without surface treatment is determined by nitrogen adsorption at 77 K and by measuring the pressure of the gas during adsorption using a surface area analyzer, such as the Micromeritics ASAP 2010 instrument. Nitrogen gas is commonly used for adsorption on the surface, due to its low reactivity and low cost. Adsorption of nitrogen gas on the BN surface causes a decrease in the pressure of the nitrogen gas in the chamber, so measuring the pressure allows the amount of nitrogen adsorbed to be determined. The surface area relates to the amount of nitrogen required to cover completely the surface with a monolayer of nitrogen.

Table 6.5 shows the specific (BET) surface areas of BN particles with and without surface treatment. Acetone treatment increases the specific surface area from 10.8 to 16.4 m^2/g due to its cleansing function and the consequent exposure of the true surface of the particle. Treatment with either acid also increases the specific surface area, but only by small amounts. Nitric acid treatment results in a slightly higher specific surface area than sulfuric acid treatment. However, both acid treatments result in lower specific surface areas than acetone treatment. The acid treatments also have a cleansing function, but acids are reactive and can change the surface morphology. On the other hand, the acid treatments do not have much effect on the surface, as shown by the fact that low specific surface areas are retained after the acid treatments. Silane (high concentration) treatment results in essentially no change in the specific surface area compared to the as-received case. However, the specific surface area is decreased compared to the acetone-washed case, since acetone washing allows the true surface to be exposed and the silane treatment coats the surface.

The composition of a surface tends to be affected by surface treatment. Thus, the surface elemental compositions of BN particles with and without surface treatment were analyzed by electron spectroscopy (electron spectroscopy for chemical analysis, abbreviated to ESCA).

The surface carbon, oxygen, and silicon concentrations were much higher after silane (high concentration) treatment than for the as-received, acetone-treated or H_2SO_4-treated particles (Table 6.6). This is because of the presence of these three elements in silane. The silane-treated BN particle surface has less

Table 6.6. Surface elemental compositions (in at.%) of as-received and treated BN particles (from [10])

Element	As received	Acetone treated	Sulfuric acid (H_2SO_4) treated	Silane (high concentration) treated
B	44.2	44.6	42.7	34.8
N	41.5	40.2	38.2	31.2
C	11.1	12.5	13.6	19.8
O	3.2	2.8	4.4	11.0
Si	–	–	1.1	3.2

boron and nitrogen compared to the as-received, acid-treated, and acetone-treated BN particles (Table 6.6), because the treated particles are partially covered by silane.

Table 6.7 shows the fractional increases in thermal conductivity following various treatments of epoxy-matrix composites with two BN volume fractions. At either volume fraction of BN, silane (high concentration) treatment gives the greatest fractional increase in thermal conductivity; the lower the silane content, the lower the fractional increase in thermal conductivity, except for the silane treatment with an extra high concentration, which corresponds to a weight loss of 3.2% upon heating to 600°C. At 57 vol% BN, silane (medium concentration) is more effective than H_2SO_4, whereas at 44 vol% BN, silane (medium concentration) is less effective than H_2SO_4. H_2SO_4 is more effective than HNO_3 at either volume fraction of BN, though the difference is small at 57 vol% BN. Silane (low concentration) is less effective than HNO_3 or H_2SO_4. Silane (extra high concentration) is less effective than silane (high concentration) or silane (medium concentration) at either volume fraction of BN, though this is not shown in Table 6.7. Acetone treatment is less effective than most of the other treatments at either volume fraction of BN.

The fractional increase in thermal conductivity due to surface treatment is much higher at 57 vol% BN than at 44 vol% BN for any BN condition. As shown in Table 6.7, at a low BN volume fraction, none of the treatments have a significant effect. However, their effects do become important at a high BN volume fraction, probably because of the increased tendency for adjacent particles to touch one

Table 6.7. Fractional increases in the thermal conductivity of a BN epoxy-matrix composite due to various BN particle surface treatments (from [10])

	44 vol% BN	57 vol% BN
Acetone treated	4.9%	48%
Nitric acid (HNO_3) treated	5.6%	62%
Sulfuric acid (H_2SO_4) treated	12%	63%
Silane (low concentration) treated	−5.6%	46%
Silane (medium concentration) treated	8.0%	72%
Silane (high concentration) treated	13%	96%

another at the higher BN volume fraction and the positive effect of the treatments on the filler–filler interface quality. HNO_3 treatment results in a higher specific surface area than H_2SO_4 treatment (Table 6.5), but it results in a lower fractional increase in thermal conductivity. This indicates that a high specific surface area is not needed to attain a high thermal conductivity. The effectiveness of the acid treatments at enhancing the thermal conductivity is probably due to certain surface functional groups that result from the treatments.

All silane treatments are effective at increasing the thermal conductivity. As the amount of silane coating on the particles increases, the thermal conductivity is enhanced until the silane concentration reaches the high concentration corresponding to a weight loss of 2.4% at 600°C. Further increasing the silane concentration to the extra high concentration corresponding to a weight loss of 3.2% at 600°C causes the thermal conductivity to decrease. Silane (high concentration) treatment is therefore the most effective. This means that the coating resulting from the silane treatment must be sufficiently thick in order for the treatment to be fully effective. The coating serves as an interlayer at the filler–matrix interface, thereby improving the quality of the interface. However, if the coating is too thick, the interlayer will become less effective or even a thermal barrier, thereby decreasing the thermal conductivity. Acetone treatment is effective due to its cleansing function. However, it is only moderately effective.

6.2.2 Interface Composition Modification

6.2.2.1 Filler–Matrix Interface Composition Modification

6.2.2.1.1 Ceramic–Metal and Carbon–Metal Interface Composition Modification

Due to the low CTEs of ceramics compared to metals, ceramic fillers are commonly used in metal-matrix composites in order to achieve a composite with a low CTE. However, liquid metals tend not to wet ceramic surfaces well (i.e., a liquid metal tends to ball up on a ceramic surface), thus making the liquid metal infiltration process difficult. To alleviate this problem, the ceramic surface may be modified by applying a coating that the liquid metal can wet sufficiently well.

In order to enhance the wetting of a reinforcement by a molten metal, the reinforcement can be coated by a metal or a ceramic. The metals used as coatings may be formed by plating and include Ni, Cu, and Ag; these generally result in lower strength composites than those predicted by the rule of mixtures (ROM). In the case of nickel-coated and copper-coated carbon fibers in an aluminum matrix, metal aluminides (Al_3M) form and embrittle the composites. In the case of nickel-coated carbon fibers in a magnesium matrix, nickel reacts with magnesium to form Ni-Mg compounds and a low-melting (508°C) eutectic. On the other hand, copper-coated fibers are suitable for matrices of copper, tin, or other metals. A metal coating that is particularly successful involves sodium, which wets carbon fibers and coats them with a protective intermetallic compound by reacting with one or more other molten metals (e.g., tin). This is called the sodium process. A related process immerses the fibers in liquid NaK. However, these processes involving sodium suffer from sodium contamination of the fibers, probably due to the intercalation of sodium into graphite. Nevertheless, aluminum-matrix composites containing unidirectional carbon fibers treated by the sodium process exhibit tensile strengths close to those calculated using the rule of mixtures, indicating that the fibers are not degraded by the sodium process.

Examples of ceramics used as coatings on carbon fibers include TiC, SiC, B_4C, TiB_2, TiN, K_2ZrF_6, and ZrO_2. Methods used to deposit the ceramics include (i) reaction of the carbon fibers with a molten metal alloy, called the liquid metal transfer agent (LMTA) technique, (ii) chemical vapor deposition (CVD), and (iii) solution coating.

The LMTA technique involves immersing the fibers in a melt of copper or tin (called a liquid metal transfer agent, which must not react with carbon) in which a refractory element (e.g., W, Cr, Ti) is dissolved, and subsequent removal of the transfer agent from the fiber surface by immersion in liquid aluminum (suitable for fabricating an aluminum-matrix composite). For example, to form a TiC coating, the alloy can be Cu-10% Ti at 1,050°C or Sn-1% Ti at 900–1,055°C. In particular, by immersing the fibers in Sn-1% Ti at 900–1,055°C for 0.25–10 min, a 0.1 μm layer of TiC is formed on the fibers, although they are also surrounded by the tin alloy. Subsequent immersion for 1 min in liquid aluminum causes the tin alloy to dissolve in the liquid aluminum. The result of this is a wire preform suitable for fabricating aluminum-matrix composites. Other than titanium carbide, tungsten carbide and chromium carbide have been formed on carbon fibers by the LMTA technique.

The CVD technique has been used to form coatings of TiB_2, TiC, SiC, B_4C, and TiN. The B_4C coating is formed by reactive CVD on carbon fibers, using a BCl_3/H_2 mixture as the reactant. The TiB_2 deposition uses $TiCl_4$ and BCl_3 gases, which are reduced by Zn vapor. The TiB_2 coating is particularly attractive because of the exceptionally good wetting between TiB_2 and molten aluminum. During composite fabrication, the TiB_2 coating is displaced and dissolved in the matrix, while an oxide (γ-Al_2O_3 for a pure aluminum matrix, $MgAl_2O_4$ spinel for a 6,061 aluminum matrix) is formed between the fiber and the matrix. The oxygen for the oxide formation comes from the sizing on the fibers; the sizing is not completely removed from the fibers before processing. The oxide layer serves as a diffusion barrier to aluminum, but allows the diffusion of carbon, thereby limiting Al_4C_3 growth to the oxide–matrix interface. Moreover, the oxide provides bonding between the fiber and the matrix. Because of the reaction at the interface between the coating and the fiber, the fiber strength is degraded after coating. To alleviate this problem, a layer of pyrolytic carbon is deposited between the fiber and the ceramic layer. The CVD process involves high temperatures (e.g., 1,200°C for SiC deposition using CH_3SiCl_4); this high temperature degrades the carbon fibers. Another problem with the CVD process is the difficulty involved in obtaining a uniform coating around the circumference of each fiber. Moreover, it is expensive and requires the scrubbing and disposal of most of the corrosive starting material, as most of it does not react at all. The most serious problem with the TiB_2 coating is that it is not air stable; it cannot be exposed to air before immersion in the molten metal or wetting will not take place. This problem limits the shapes of the materials that can be fabricated, especially since the wire preforms are not very flexible.

A high compliance (or a low modulus) is preferred for the coating in order to increase the interface strength. An increase in the interface (or interphase) strength results in an increase in the transverse strength. The modulus of SiC coatings can be varied by controlling the plasma voltage in plasma-assisted chemical vapor deposition (PACVD). Modulus values in the range from 19 to 285 GPa have been obtained in PACVD SiC, which should be compared to a value of 448 GPa for CVD SiC. Unidirectional carbon fiber (Thornel P-55) aluminum-matrix composites in which the fibers are coated with SiC exhibit interface and transverse strengths that increase with decreasing modulus of the SiC coating.

The most attractive coating technique developed to date is the solution coating method. When using an organometallic solution, fibers are passed through a toluene solution containing an organometallic compound, followed by hydrolysis or pyrolysis of the organometallic compounds to form the coating. Thus, the fibers are passed sequentially through a furnace in which the sizing on the fibers is vaporized, followed by an ultrasonic bath containing an organometallic solution. The coated fibers are then passed through a chamber containing flowing steam in which the organometallic compound on the fiber surface is hydrolyzed to oxide, and finally through an argon atmosphere drying furnace in which any excess solvent or water is vaporized and any unhydrolyzed organometallic is pyrolyzed. In contrast to the TiB_2 coatings, the SiO_2 coatings formed by organometallic solution coating are air stable.

The organometallic compounds used are alkoxides in which metal atoms are bound to hydrocarbon groups by oxygen atoms. The general formula is $M(OR)_x$, where R is any hydrocarbon group (e.g., methyl, ethyl, propyl) and x is the oxidation state of the metal atom M. When exposed to water vapor, these alkoxides hydrolyze:

$$M(OR)_x + \tfrac{x}{2}H_2O \rightarrow MO_{x/2} + x\mathrm{ROH} \qquad (6.2)$$

For example, the alkoxide tetraethoxysilane (also called tetraethylorthosilicate) is hydrolyzed by water as follows:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH\ . \qquad (6.3)$$

Alkoxides can also be pyrolyzed to yield oxides; for example:

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + 2C_2H_5OH + 2C_2H_4\ . \qquad (6.4)$$

Most alkoxides can be dissolved in toluene. By controlling the solution concentration and the time and temperature of immersion, it is possible to control the uniformity and thickness of the resulting oxide coating. The thickness of the oxide coatings on the fibers varies from 700 to 1,500 Å. The oxide is amorphous and contains carbon, which originates in the carbon fiber.

Liquid magnesium wets SiO_2-coated low-modulus carbon fibers (e.g., T-300) and infiltrates the fiber bundles due to reactions between the molten magnesium and the SiO_2 coating. The reactions include the following:

$$2Mg + SiO_2 \rightarrow 2MgO + Si \qquad \Delta G^\circ_{670^\circ C} = -76\,\text{kcal} \tag{6.5}$$

$$MgO + SiO_2 \rightarrow MgSiO_3 \qquad \Delta G^\circ_{670^\circ C} = -23\,\text{kcal} \tag{6.6}$$

$$2Mg + 3SiO_2 \rightarrow 2MgSiO_3 + Si \qquad \Delta G^\circ_{670^\circ C} = -122\,\text{kcal} \tag{6.7}$$

$$2MgO + SiO_2 \rightarrow Mg_2SiO_4 \qquad \Delta G^\circ_{670^\circ C} = -28\,\text{kcal} \tag{6.8}$$

$$2Mg + 2SiO_2 \rightarrow Mg_2SiO_4 + Si \qquad \Delta G^\circ_{670^\circ C} = -104\,\text{kcal}\,. \tag{6.9}$$

The interfacial layer between the fiber and the Mg matrix contains MgO and magnesium silicates. However, immersion of SiO_2-coated high-modulus fibers (e.g., P-100) in liquid magnesium causes the oxide coating to separate from the fibers due to the poor adherence of the oxide coating to the high-modulus fibers. This problem with the high-modulus fibers can be solved by first depositing a thin amorphous carbon coating onto the fibers by passing the fiber bundles through a toluene solution of petroleum pitch, and then evaporating the solvent and pyrolyzing the pitch.

The most effective air-stable coating for carbon fibers used in aluminum-matrix composites is a mixed boron-silicon oxide applied from organometallic solutions.

Instead of SiO_2, TiO_2 can be deposited onto carbon fibers by the organometallic solution method. For TiO_2, the alkoxide can be titanium isopropoxide.

SiC coatings can be formed by using polycarbosilane (dissolved in toluene) as the precursor, which is pyrolyzed to SiC. These coatings are wetted by molten copper containing a small amount of titanium due to a reaction between SiC and Ti to form TiC.

Instead of using an organometallic solution, another kind of solution coating method uses an aqueous solution of a salt. For example, the salts potassium zirconium hexafluoride (K_2ZrF_6) or potassium titanium hexafluoride (K_2TiF_6) are used to deposit microcrystals of K_2ZrF_6 or K_2TiF_6 on the fiber surface. These fluoride coatings are stable in air. The following reactions supposedly take place between K_2ZrF_6 and the aluminum matrix:

$$3K_2ZrF_6 + 4Al \rightarrow 6KF + 4AlF_3 + 3Zr \tag{6.10}$$

$$3Zr + 9Al \rightarrow 3Al_3Zr \tag{6.11}$$

$$Zr + O_2 \rightarrow ZrO_2\,. \tag{6.12}$$

When an Al-12 wt.% Si alloy (rather than pure Al) is used as the matrix, the following reaction may also occur:

$$Zr + 2Si \rightarrow ZrSi_2\,. \tag{6.13}$$

The fluorides KF and AlF_3 are thought to dissolve the thin layer of Al_2O_3 on the liquid aluminum surface, thus helping the liquid aluminum to wet the carbon fibers. Furthermore, reactions 6.10 and 6.11 are strongly exothermic and may therefore cause a local temperature increase near the fiber–matrix interface. The increased temperature probably gives rise to a liquid phase at the fiber–matrix interface.

Although the K_2ZrF_6 treatment causes the contact angle between carbon and liquid aluminum at 700–800°C to decrease from 160° to 60–75°, it causes the fiber tensile strength to degrade during aluminum infiltration.

Another example of a salt solution coating method involves the use of the salt zirconium oxychloride ($ZrOCl_2$). Dip coating the carbon fibers in the salt solution and then heating to 330°C causes the formation of a ZrO_2 coating less than 1 µm thick. The ZrO_2 coating serves to improve fiber–matrix wetting and reduce the fiber–matrix reaction in aluminum-matrix composites.

6.2.2.1.2 Reinforcement-Cement Interface Composition Modification

Due to the poor adhesiveness of cement compared to polymeric adhesives, the reinforcement–cement bond strength is low in cement-matrix composites. This problem exists whether the reinforcement is microscopic (such as with carbon, glass and polymer fibers) or macroscopic (such as for a steel rebar and an aggregate). The bond strength can be enhanced by adding polymeric admixtures such as latex (in the form of an aqueous particulate dispersion) and methylcellulose (in the form of an aqueous solution, since methylcellulose is water soluble) to the cement or concrete mix. The polymer not only resides in the cement matrix but it also lines the fiber–cement interface, thereby enhancing the fiber–matrix bond. The bond strength can also be enhanced by adding a fine particulate to the mix, such as silica fume, which is around 0.1 µm in particle size. The fine particles reduce the pore size in the cement matrix and at the reinforcement–cement interface. The pore size reduction at the interface results in the strengthening of the interface.

The bonding between carbon fiber and the cement matrix, as well as the wettability of the fiber by the cement matrix (water based), can be improved by ozone treatment of the carbon fiber prior to incorporation into the cement. The treatment involves surface oxidation, which results in surface oxygen-containing functional groups, thus increasing the surface oxygen concentration, and it changes the surface oxygen from C–O to C=O, as shown in Table 6.8. The improved bonding is shown in Fig. 3.11 by the adhesion of the cement matrix to a pulled-out fiber that has been ozone treated.

6.2.2.2 Interlaminar Interface Composition Modification

For continuous fiber polymer-matrix composites, the interface between adjacent laminae of fibers is a polymer-rich region. It is the weak link in the composite, as shown by the fact that delamination is a common type of damage in these composites. The composition of this interface can be modified by filling this region with

Table 6.8. Fractions of surface carbon atoms bonded as C–H, C–O and C=O (from [11])

Treatment	C–H	C–O	C=O
As received	86.5	13.5	0
After ozone exposure	76.0	0	24.0

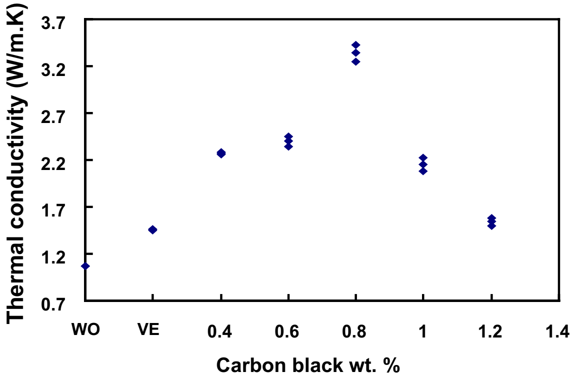

Figure 6.13. Thermal conductivity of crossply carbon fiber polymer-matrix composites with and without various interlaminar interface modifications. WO – without carbon black and without vehicle. VE – with vehicle and without carbon black. The vehicle is ethylene glycol monoethyl ether. The carbon black wt.% refers to the concentration of carbon black in the dispersion involving the vehicle. The dispersion is applied onto the fiber epoxy prepreg surface prior to consolidation of the laminae to form a composite. Three specimens of each composition are tested

a nanofiller, as illustrated in Fig. 6.13. Through such a modification, the through-thickness thermal conductivity and the compressive and flexural properties can be improved [12]. This improvement is due to the removal of some of the excess polymer at the interlaminar interface through the use of a solvent (the vehicle, namely ethylene glycol monoethyl ether, in the nanofiller dispersion), in addition to the filling of the interface region with the nanofiller, namely carbon black, which is introduced in the form of nanoparticles (30 nm).

The through-thickness thermal conductivity is enhanced by using the vehicle without carbon black for interlaminar interface modification and is further increased by using the vehicle with carbon black (Fig. 6.13). The optimum carbon black content for attaining the highest thermal conductivity is 0.8 wt.% (with respect to the dispersion). At the optimum carbon black content, the thermal conductivity increase (relative to the case of no interlaminar interface modification) is 212%. In contrast, the fractional increase attained by using aligned carbon nanotubes grown on continuous silicon carbide fibers is only 50% [13]. The increase in the thermal conductivity due to the use of the vehicle without carbon black is consistent with the fact that the vehicle dissolves away a part of the resin at the interface, thereby allowing greater proximity between the fibers of the adjacent laminae. The further increase in the thermal conductivity due to the use of the vehicle with carbon black is consistent with the fact that the carbon black is a conformable and conductive filler that improves the thermal contact across the interlaminar interface. An excessive content of carbon black decreases the thermal conductivity relative to the value at the optimum carbon black content because of the separation of the fibers of adjacent laminae when the carbon black content is excessive.

Nanoclay is a more effective interlaminar filler than carbon black when used to increase the flexural properties. It increases the flexural modulus by 30%, while carbon black increases it by only 10%. Nanoclay is more effective because of its nanoplatelet morphology, which contrasts with the particulate morphology of carbon black.

6.2.3 Interface Microstructure Modification

Mechanical interlocking is valuable for enhancing the cohesion between the reinforcement and the matrix, particularly when chemical bonding (whether covalent, van der Waals or other forces) is weak. Roughening an interface, typically by roughening the surface of the reinforcement, is commonly used to enhance the mechanical interlocking between the reinforcement and the matrix. The roughening can be achieved by mechanical or chemical methods. An example of a mechanical method is mechanical deformation of the surface region of the reinforcement by threading, like forming threads on a screw. An example of a chemical method is the use of an etchant (e.g., an acid) to react with the surface of the reinforcement. Chemical methods tend to provide microscopic roughness (low roughness, with a high density of hillocks in the resulting topography), whereas mechanical methods tend to provide macroscopic roughness (high roughness, with a low density of hillocks in the resulting topography). Both a high roughness and a high density of hillocks promote mechanical interlocking. Thus, both types of methods have their advantages and disadvantages. Chemical methods are usually used for microscopic reinforcements (e.g., carbon fiber), whereas mechanical methods are usually used for macroscopic reinforcements (e.g., steel rebars). Nonmechanical physical methods such as ion bombardment are costly and characterized by low productivity.

Due to the poor adhesiveness of cement compared to polymeric adhesives in addition to the high viscosity of the cement mix, voids tend to occur at the interface between a fiber and the cement matrix. One method of reducing the interfacial void content is to add silica fume to the cement mix. Due to the small size (around 0.1 μm) of the particles in silica fume, the void structure of the cement matrix becomes much finer and the fiber–matrix interfacial void content is lessened. As a consequence, the fiber–matrix bond strength is increased.

6.3 Tailoring by Surface Modification

The coating of carbon materials to protect them from oxidation is used in this section to illustrate methods of surface composition modification. In the absence of oxygen, carbon materials have excellent high-temperature resistance. For example, the carbon–carbon composites used for the nose cap of a Space Shuttle can withstand 1,600°C, whereas more advanced carbon–carbon composites can withstand 2,200°C. In contrast, superalloys can only withstand 1,200°C and also have high densities.

Carbon materials are highly susceptible to oxidation at temperatures above 320°C. The predominant reaction that occurs in air is

$$C + O_2 \rightarrow CO_2 \uparrow \tag{6.14}$$

This reaction converts carbon to a gas, thus causing carbon mass loss. The reaction is associated with a very large negative value of the Gibbs free energy change, so it proceeds with a large driving force, even at very low O_2 partial pressures. Thus, the rate of oxidation is controlled not by the chemical reaction itself, but by the transport of the gaseous species to and from the reaction front.

The oxidation of carbon–carbon composites preferentially occurs at the fiber–matrix interface and weakens the fiber bundles. The unoxidized material fails catastrophically by delamination cracking between plies and at bundle–bundle interfaces within plies. As oxidation progresses, failure becomes a multistep process with less delamination cracking and more cross-bundle cracking. This change of failure mode with oxidation is attributed to greater attack within bundles than at bundle–bundle interfaces. For a weight loss on oxidation of 10%, the reductions in elastic modulus and flexural strength are 30 and 50%, respectively.

Protecting carbon–carbon composites from oxidation up to 1,700°C involves the application of various combinations of the following methods:

1. SiC coating applied by pack cementation, reaction sintering, silicone resin impregnation/pyrolysis, or chemical vapor deposition (CVD) to the outer surface of the composite.
2. Oxidation inhibitors (oxygen getters and glass formers) introduced into the carbon matrix during lay-up and densification cycles, which provide additional oxidation protection from within by migrating to the outer surface and sealing cracks and voids during oxidation.
3. Application of a glassy sealant on top of the SiC conversion coating, mainly by brushing a slurry on, so that the sealants melt, fill voids and stop oxygen diffusion, and in some cases act as oxygen getters.
4. Dense SiC or Si_3N_4 overlayer applied by chemical vapor deposition (CVD) on top of the glassy sealant (if used) or the SiC conversion coating; this overlayer controls and inhibits the transfer of oxygen to the substrate, and controls the venting of reaction products to the outside.
5. Application of an aluminum metaphosphate coating by ozone treatment, followed by the impregnation of a liquid solution of aluminum hydroxide dissolved in phosphoric acid, and then heating in nitrogen gas at 800°C for 20 min. Without the ozone treatment, which increases the surface oxygen concentration, the impregnation is not effective for coating or for oxidation protection. Figure 6.14 shows the decrease in weight loss upon heating in air due to the coating.

The SiC coating in the first method described above, known as SiC conversion coating, is gradated in composition so that it changes gradually from pure silicon compounds on the outside surface to pure carbon on the inside. This gradation minimizes spallation resulting from the thermal expansion mismatch between SiC and the carbon–carbon composite. The conversion coating can also be made to be gradated in porosity so that it is denser near the outside surface. The coating is applied by pack cementation, which involves packing the composite into a mixture

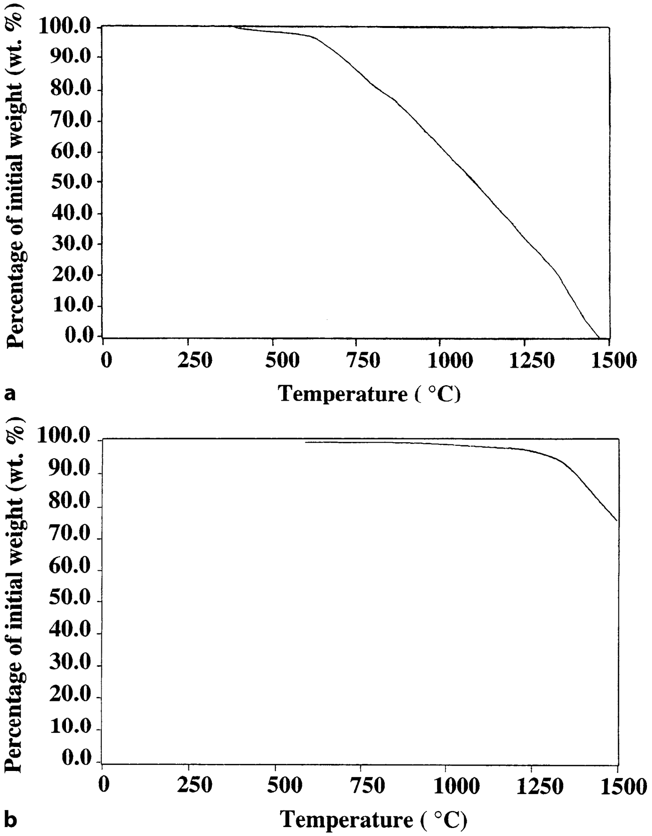

Figure 6.14. Percentage of initial weight versus temperature for graphite heated in air to 1,500°C at a heating rate of 10°C/min. **a** Untreated graphite, with 10% weight loss at 750°C. **b** Graphite coated with aluminum metaphosphate (weighing 20% of that of the graphite before coating), with 10% weight loss at 1,375°C. (From [14])

of silicon carbide and silicon powders and then heating this assembly up to 1,600°C. During this process, the following are the main reactions that take place:

$$\mathrm{Si_{(l)} + C \rightarrow SiC} \qquad (6.15)$$

$$\mathrm{Si_{(g)} + C \rightarrow SiC} \qquad (6.16)$$

$$\mathrm{SiO_{(g)} + 2C \rightarrow SiC + CO_{(g)}}\,. \qquad (6.17)$$

The net result is the chemical conversion of the outermost surfaces of the composite to silicon carbide. Typical thicknesses of pack cementation coatings range from 0.3 to 0.7 mm. One disadvantage of this process is that elemental silicon may be trapped in the carbon matrix under the conversion coating. The entrapped silicon tends to vaporize at elevated temperatures and erupt through the coating, leaving pathways for oxygen to migrate to the carbon–carbon substrate.

A second method of forming a SiC coating is reaction sintering, which involves dipping a carbon–carbon composite into a suspension of silicon powder (average 10 μm size) in an alcohol solution and then sintering at 1,600°C for 4 h in argon.

A third method of forming a SiC coating involves vacuum impregnation and cold isostatic pressing (30,000 psi or 200 MPa) of a silicone resin into the matrix of a carbon–carbon composite, with subsequent pyrolysis at 1,600°C for 2 h in argon.

The SiC overlayer described in method 4 above is denser (less porous) than the SiC conversion coating described in method1. It serves as the primary oxygen barrier. It is prepared by CVD, which involves the thermal decomposition/reduction of a volatile silicon compound (e.g., CH_3SiCl, CH_3SiCl_3) to SiC. The reaction takes the form:

$$CH_3SiCl_{3(g)} \xrightarrow{\text{Heat}/H_2} SiC + 3HCl_{(g)} \tag{6.18}$$

The decomposition occurs in the presence of hydrogen and heat (e.g., 1,125°C). If desired, the overlayer can be deposited so that it contains a small percentage of unreacted silicon that is homogeneously dispersed in the SiC. Upon oxidation, the excess silicon becomes SiO_2, which has a very low oxygen diffusion coefficient. This silicon-rich SiC is termed SiSiC. Instead of SiC, Si_3N_4 may be used as the overlayer; Si_3N_4 can also be deposited by CVD.

Among all high-temperature ceramics, silicon-based ceramics (SiC and Si_3N_4) have the best thermal expansion compatibilities with carbon–carbon composites and exhibit the lowest oxidation rates. Moreover, the thin amorphous SiO_2 scales that grow have low oxygen diffusion coefficients and can be modified with other oxides to control the viscosity. Above 1,800°C, these silicon-based ceramic coatings cannot be used because of the reactions at the interface between the SiO_2 scale and the underlying ceramic. Furthermore, the reduction of SiO_2 by carbon produces $CO_{(g)}$.

The glass sealants in method 3 take the form of glazes that usually contain silicates and borates. If desired, the glaze can be filled with SiC particles. The sealant is particularly important if the SiC conversion coating is porous. Moreover, when microcracks develop in the dense overlayer, the sealant fills the microcracks. Borate (B_2O_3) glazes wet C and SiC quite well, but they are useful up to 1,200°C due to volatilization. Moreover, B_2O_3 has poor moisture resistance at ambient temperatures, as it undergoes hydrolysis, which results in swelling and crumbling. In addition, B_2O_3 has a tendency to galvanically corrode SiC coatings at high temperatures. However, these problems with B_2O_3 can be alleviated by using multicomponent systems, such as $10TiO_2{\cdot}20SiO_2{\cdot}70B_2O_3$. TiO_2 has a high solubility in B_2O_3; it is used to prevent the volatilization of B_2O_3 and to increase the viscosity over a wide temperature range. The SiO_2 component acts to increase the moisture resistance at ambient temperatures, reduce the B_2O_3 volatility at high temperatures, increase the overall viscosity of the sealant, and prevent galvanic corrosion of the SiC at high temperatures by the B_2O_3.

The inhibitors used in method 2 are added to the carbon matrix by incorporating them as particulate fillers into the resin or pitch prior to prepregging. They function as oxygen getters and glass formers. These fillers can take the form of elemental silicon, titanium, and boron. Oxidation of these particles within the carbon matrix forms a viscous glass, which serves as a sealant that flows into the microcracks of the SiC coating, covering the normally exposed carbon–carbon surface to prevent oxygen ingress into the carbon–carbon. The mechanism of oxidation inhibition by boron-based inhibitors may involve B_2O_2, a volatile suboxide that condenses to B_2O_3 upon encountering a locally high oxygen partial pressure in coating cracks. Instead of using elemental Ti and Si, a combination of SiC, Ti_5Si_3, and TiB_2 may be used. For a more uniform distribution of the glass sealant, the filler ingredients can be prereacted to form alloys such as Si_2TiB_{14} prior to their addition to the resin or pitch. Yet another way to obtain the sealant is to use an organoborosilazane polymer solution.

The addition of glass-forming additives such as boron, silicon carbide and zirconium boride to the carbon matrix can markedly reduce the reactivity of the composite with air, but the spread of the glassy phase throughout the composite is slow and substantial fractions of the composite are gasified before the inhibitors become effective. Thus, in the absence of an exterior impermeable coating, the oxidation protection afforded at temperatures above 1,000°C by inhibitor particles in the carbon matrix is strictly limited.

The inhibition mechanism of B_2O_3 involves the blockage of active sites (such as the edge carbon atoms) for small inhibitor contents and the formation of a mobile diffusion barrier for oxygen when the B_2O_3 amount is increased. The inhibiting effect of B_2O_3 is most pronounced at the beginning of oxidation, as shown by the shallow slopes of the weight loss curves near time zero. Thereafter, a pseudolinear oxidation regime takes hold, just as for the untreated composite. The inhibition factor is defined as the ratio of the oxidation rate of the untreated carbon to that of the treated carbon.

For oxidation protection above 1,700°C, a four-layer coating scheme is available. This scheme consists of a refractory oxide (e.g., ZrO_2, HfO_2, Y_2O_3, ThO_2) used as the outer layer of erosion protection, an SiO_2 glass inner layer used as an oxygen barrier and sealant for cracks in the outer coating, followed by another refractory oxide layer for isolating the SiO_2 from the carbide layer underneath, and finally a refractory carbide layer (e.g., TaC, TiC, HfC, ZrC) to interface with the carbon–carbon substrate and to provide a carbon diffusion barrier to the oxide in order to prevent carbothermic reduction. The four-layer system is thus refractory oxide/SiO_2 glass/refractory oxide/refractory carbide. It should be noted that ZrO_2, HfO_2, Y_2O_3 and ThO_2 all have the required thermal stability for long-term use at $> 2{,}000$°C, but they have very high oxygen permeabilities; silica exhibits the lowest oxygen permeability and is the best candidate for use as an oxygen barrier other than iridium at $> 1{,}800$°C; however, iridium suffers from a relatively high thermal expansion coefficient, a high cost, and limited availability.

A ternary HfC-SiC-$HfSi_2$ system deposited by CVD has been reported to provide good oxidation protection up to 1,900°C. The HfC component is chemically compatible with carbon. Furthermore, HfO_2 is generated from HfC by the reaction:

$$HfC + \tfrac{3}{2}O_2 \rightarrow HfO_2 + CO \qquad (6.19)$$

Also, HfO_2 is a very stable oxide at high temperatures. However, HfO_2 undergoes a phase change from monoclinic to tetragonal at 1,700°C, with a volume change of 3.4%. To avoid catastrophic failure due to the volume change, HfO_2 is stabilized through the addition of $HfSi_2$. The SiC component acts as a diffusion barrier.

Pack cementation is a relatively inexpensive technique for coating carbon–carbon composites in large quantities. The quality of SiC coatings prepared by pack cementation can be improved by first depositing a 10 μm carbon film by CVD onto the surface of the carbon–carbon composite, because the carbon film improves the homogeneity of the carbon–carbon surface and eases the reaction with Si. Similarly, carbon CVD can be used to improve SiC films deposited by reaction sintering or resin impregnation. Carbon CVD involves the pyrolysis of methane in a tube furnace at 1,300°C.

Pack cementation has been used to form chromium carbide coatings in addition to SiC coatings for the oxidation protection of carbon–carbon composites. For chromium carbide coatings, the carbon–carbon composite sample is packed into a mixture of chromium powder, alumina powder, and a small quantity of NH_4Cl (an activator) and reacted at 1,000°C in argon. The chromium powder produces chromium carbide by reacting with the carbon–carbon composite. At the same time, HCl dissociated from NH_4Cl reacts with the chromium powder to form chromous halide liquid, which reacts with the carbon–carbon composite to form chromium carbide. This latter type of chromium carbide permeates into the openings in the former kind of chromium carbide. Upon oxidation of the chromium carbide coating, a dense layer of Cr_2O_3 is formed that serves to prevent the oxidation of the carbon–carbon composite.

Another form of oxidation protection can be provided by treating the carbon–carbon composites with various acids and bromine.

The fundamental approaches to the oxidation protection of carbons can be categorized into four groups: (i) preventing catalysis; (ii) blocking the access of gas to the carbon; (iii) inhibiting carbon–gas reactions, and; (iv) improving the carbon crystallite structure. Approach (ii) is the main one applied to carbon–carbon composites, as it provides the greatest degree of oxidation protection. However, the other approaches need to be exploited as well. In particular, Approach (iv) means that pitch and CVI carbon are preferred to resins as precursors for carbon–carbon matrices, as pitch and CVI carbon are more graphitizable than resins. Nevertheless, the stress applied to the matrix by the adjacent fibers during carbonization causes the alignment of the matrix molecules near the fibers. Furthermore, the microstructure of the carbon fibers strongly affects the microstructure of the carbon matrix, even when the fiber fraction is only about 50 wt.%, and the microstructure of the carbon matrix affects the amount of accessible porosity, thereby affecting the oxidation behavior.

The application of coatings to carbon–carbon composites can deteriorate their room-temperature mechanical properties. For example, after the application of a 0.25–0.50 mm thick SiC conversion coating, the flexural strength decreases by 29%. On the other hand, the oxidation of a carbon–carbon composite to a burn-off of 20% causes the flexural strength to decrease by 64%.

6.4 Tailoring by Microstructure Control

6.4.1 Crystallinity Control

6.4.1.1 Polymer-Matrix Composites

The ductility of a semicrystalline thermoplastic decreases with increasing crystallinity, though the ability to resist elevated temperatures increases with increasing crystallinity.

For thermoplastic-matrix composites, increasing the cooling rate after lamination decreases the crystallinity of the polymer matrix. Because the fibers act as nucleation sites for polymer crystallization when the polymer melt is sheared, the presence of fibers enhances the polymer crystallinity to a level above that of the neat polymer. Greater crystallinity is associated with a higher level of fiber–matrix interaction. The crystallinity can be increased by annealing; the presence of carbon fibers accelerates the annealing effect.

6.4.1.2 Carbon-Matrix Composites

The carbon matrix is derived from a pitch, a resin, or a carbonaceous gas. Depending on the carbonization/graphitization temperature, the resulting carbon matrix can range from being amorphous to being graphitic. The higher the degree of graphitization of the carbon matrix, the greater the oxidation resistance and the thermal conductivity, but the more brittle the material. As the carbon fibers used can be highly graphitic, it is usually the carbon matrix that limits the oxidation resistance of the composite.

The heat treatment temperature has a significant effect on the mechanical properties of carbon–carbon composites. Composites that are carbonized at 1,000°C before being graphitized at 2,700°C show a 54% increase in the flexural strength, a 40% decrease in the interlaminar shear strength, and a 93% increase in the flexural modulus. This suggests that the fiber–matrix interaction is different before and after graphitization. The increase in the flexural modulus is probably due to the further graphitization of the carbon fibers under the influence of the carbon matrix around them, even though the fibers have been graphitized prior to this. The choice of the graphitization temperature affects the toughness of the composite. For a pitch-based matrix, the optimum graphitization temperature is 2,400°C, since this is the temperature at which the microstructure is sufficiently ordered to accommodate some slip from shear forces but is disordered enough to prevent long-range slip. A similar graphitization temperature may be used for a polymer-based matrix.

The crystallinity of carbon fibers affects the quality of the resulting carbon–carbon composites. The use of graphitized fibers (fired at 2,200–3,000°C) with a carbon content in excess of 99% is preferred because their thermal stability reduces the part warpage during later high-temperature processing to form a carbon–carbon composite. Moreover, graphitized fibers lead to better densified carbon–carbon composites than carbon fibers that have not been graphitized. This is because the adhesion of the fibers to the polymer resin is weaker for graphitized fibers, so that the matrix can easily shrink away from the fibers during carbonization, leaving a gap which can be filled in during subsequent impregnation. In contrast, the polar surface groups on carbonized fibers make strong bonds with the resin, thus inhibiting the shrinking of the charred matrix away from the fibers and leading to the formation of fine microcracks in the carbon matrix.

The high-temperature resistance of carbon–carbon composites containing boron or zirconium diboride glass-forming oxidation inhibitors can be impaired by the reactions between the inhibitors and the carbonaceous components of the composite. These reactions, which probably form carbides, affect both fibers and matrix. They result in almost complete crystallization of the composite components. This crystallization transforms the microstructure of the composite, weakening it and producing brittle failure behavior. For boron, the reaction occurs at temperatures of between 2,320 and 2,330°C; for zirconium diboride, it occurs at temperatures of between 2,330 and 2,350°C.

6.4.2 Porosity Control

Porosity is detrimental to the strength of a material. The increase in the filler content may cause an increase in the porosity, especially when the filler–matrix bond is not strong or when the filler volume fraction is so high that the matrix is insufficient.

For carbon fiber reinforced cement paste, as shown in Fig. 6.15, the air void content (i.e., the porosity) increases significantly with increasing fiber content, even though the fiber volume fraction is less than 5%. This is due to the poor bonding between carbon fiber and the cement matrix, in addition to the decrease in workability (i.e., the paste gets thicker) with increasing fiber content.

For copper-matrix silicon carbide whisker composites fabricated by powder metallurgy, the porosity increases when the whisker volume fraction exceeds 30%, as shown in Fig. 1.10. Microscope photographs of the porosity are shown in Fig. 1.11 for copper-matrix titanium diboride platelet (60 vol%) composites made by powder metallurgy. The detrimental effect of the porosity on the mechanical properties is also shown in Fig. 1.10.

The porosity can be reduced by tailoring the process and composition. For silicon carbide whisker copper-matrix composites, the use of the coated filler method of powder metallurgy in place of the admixture method of powder metallurgy for composite fabrication reduces the porosity at a given filler volume fraction, as shown in Fig. 1.10.

In the case of carbon fiber cement-matrix composites, the use of appropriate admixtures can reduce the porosity. The use of a combination of methylcellulose (a water-soluble polymer that helps fiber dispersion, at the level of 0.4% by mass of cement) and silica fume (size about 0.1 μm, at the level of 15% by mass of cement) as admixtures gives lower porosity than the use of methylcellulose (0.4% by mass of cement) at the same fiber volume fraction, as shown in Fig. 6.15. This is because the silica fume (nanoparticles) causes a finer microstructure and enhances the

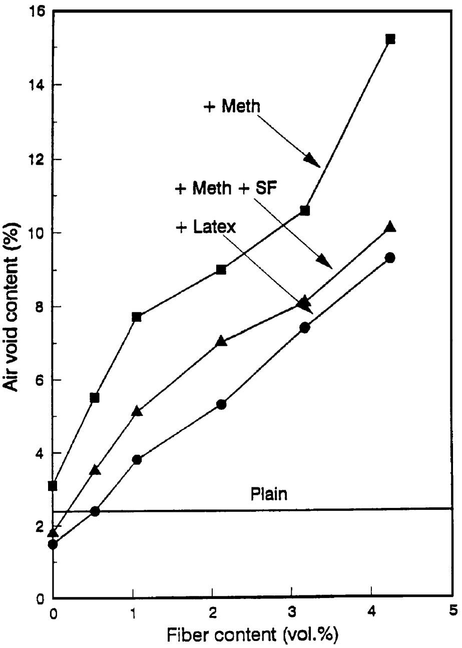

Figure 6.15. Dependence of the air void content on the fiber content in a carbon fiber cement-matrix composite. Meth – methylcellulose (0.4% by mass of cement); SF – silica fume (15% by mass of cement); Latex – aqueous latex particle dispersion (20% by mass of cement). (From [15])

dispersion of the fiber in the cement matrix. Since fiber clumping gives rise to porosity within the clump, improved fiber dispersion reduces the porosity. The use of latex (an aqueous dispersion of latex particles; the amount of dispersion used is 20% by mass of cement) as an admixture gives even lower porosity than the use of methylcellulose and silica fume, as also shown in Fig. 6.15, due to the ability of the fine latex particles in the dispersion to fill the voids (at least the relatively large ones). Figure 6.16 shows that the average air void size is diminished by using the abovementioned admixtures. A lower air void content and a smaller average air void size are associated with a higher tensile strength, as shown in Fig. 6.17.

Figure 6.18 shows that the air void content decreases monotonically with increasing latex content in the absence of fiber, but, in the presence of fiber, it decreases with increasing latex content up to a latex content of 15% by mass of cement, and increases with further increase in the latex content. This means that an excess amount of latex is not desirable in the presence of fiber. This is because the degree of fiber dispersion is reduced as the latex content increases, as shown by electrical resistivity measurements (Sect. 6.5.1). At any latex content, the addition of fiber increases the air void content, as shown in Fig. 6.18.

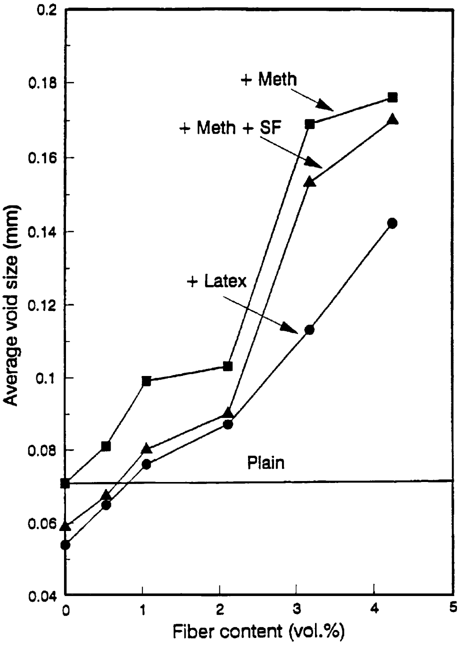

Figure 6.16. Dependence of the average air void size on the fiber content in a carbon fiber cement-matrix composite. Meth – methylcellulose (0.4% by mass of cement); SF – silica fume (15% by mass of cement); Latex – aqueous latex particle dispersion (20% by mass of cement). (From [15])

6.5 Tailoring by Organic–Inorganic Nanoscale Hybridization

Due to the large difference in properties between organic and inorganic materials, the combined use of these materials in a composite is often attractive for composite tailoring. The use of glass fiber (not a nanofiber) in a polymer matrix is an example of such a combined use. In general, neither the organic component nor the inorganic component needs to have a particular shape. Another example of such a combined use is a nanoscale organic–inorganic hybrid. The nanoscale allows the hybrid to serve as the matrix of a composite that contains a filler, such as a fiber. This section covers nanoscale organic–inorganic hybrids; i.e., nanocomposites involving organic and inorganic components.

6.5.1 Nanocomposites with Organic Solid Nanoparticles Dispersed in an Inorganic Matrix

Nanocomposites with dispersed organic nanoparticles in an inorganic matrix can be attractive for toughening and porosity reduction, since the organic component is relatively tough and its nanosize may allow it to fill the pores that tend to be present in an inorganic material.

An example of such a nanocomposite is cement with dispersed polymer particles that are used as an admixture. An example of the polymer is latex (styrene-

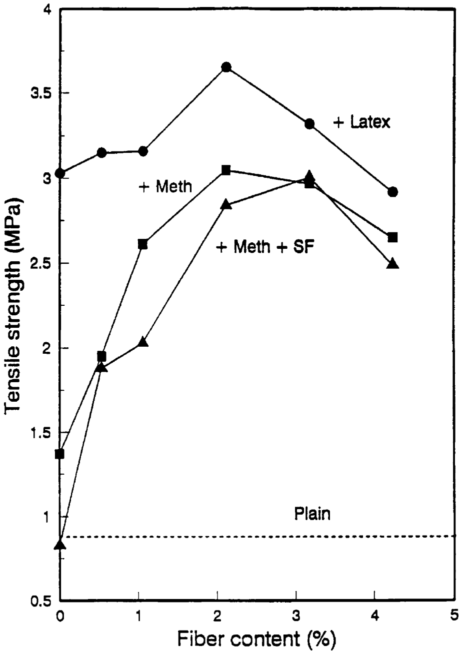

Figure 6.17. Dependence of the tensile strength on the fiber content in a carbon fiber cement-matrix composite. Meth – methylcellulose (0.4% by mass of cement); SF – silica fume (15% by mass of cement); Latex – aqueous latex particle dispersion (20% by mass of cement). (From [15])

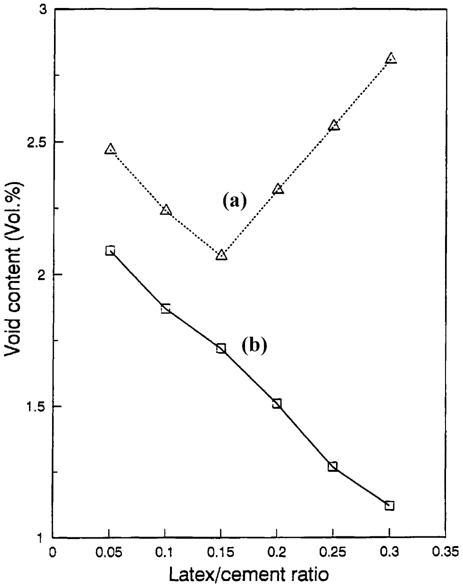

Figure 6.18. Effect of latex/cement ratio on the air void content of cement paste. *a* With 0.53 vol% carbon fibers, *b* without fibers. (From [15])

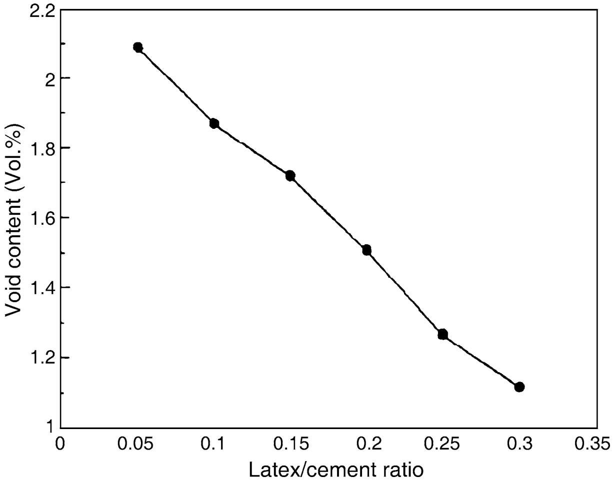

Figure 6.19. Decrease in the air void content with increasing latex/cement ratio (from [16])

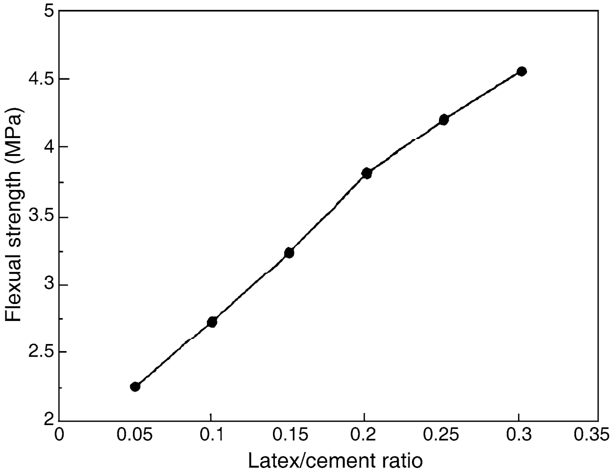

Figure 6.20. Increase in the flexural strength with increasing latex/cement ratio (from [16])

butadiene copolymer) particles of size 0.2 μm (e.g., Latex 460NA of Dow Chemical Corp., Midland, MI, USA, where the styrene:butadiene mass ratio is 66:34 and the copolymer solid amounts to 48 wt.% of the product, which is a water-based dispersion). This means that a latex dispersion proportion of 0.05 by mass of cement is equivalent to a latex solid proportion of 0.024 (i.e., 0.05 × 0.48) by mass of cement. Figure 6.19 shows the monotonic decrease in the air void content (porosity) with increasing latex content in the nanocomposite. The decrease in porosity results in an increase in the flexural strength, as shown in Fig. 6.20. Due to the toughness of the polymer compared to cement, the flexural toughness increases with increasing latex content in the nanocomposite (Fig. 6.21). Due to the high

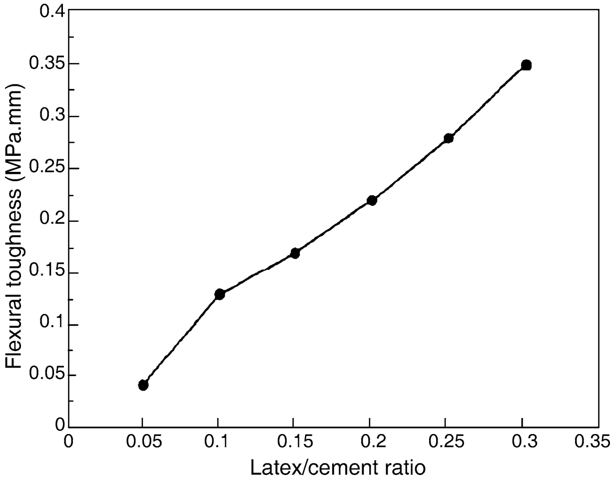

Figure 6.21. Increase in the flexural toughness with increasing latex/cement ratio (from [16])

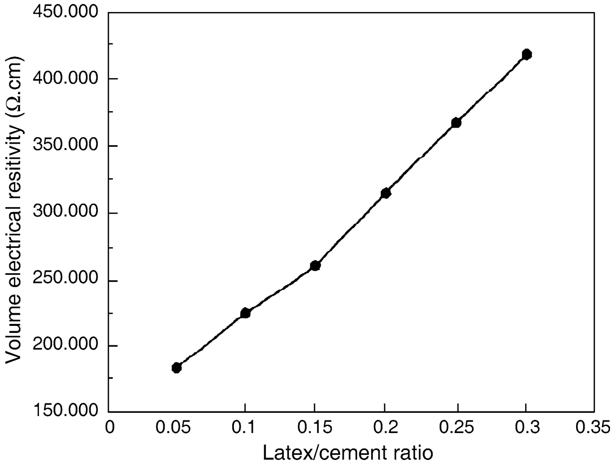

Figure 6.22. Increase in the volume electrical resistivity with increasing latex/cement ratio (from [16])

electrical resistivity of the polymer compared to cement, the electrical resistivity increases with increasing latex content in the nanocomposite (Fig. 6.22).

6.5.2 Nanocomposites with an Organic Component Dispersed in an Inorganic Matrix Where the Organic Component is Added as a Liquid

Instead of using an organic component in the form of particles, one can use an organic component in the form of a liquid solution obtained by dissolving the organic component in a solvent. The dispersion of a liquid solution is usually easier than that of solid particles, due to the greater fluidity of a liquid than a solid particle dispersion. Furthermore, the spatial distribution of the organic component

Table 6.9. Effect of organic component (methylcellulose) on the tensile properties of cement paste (from [17])

Methylcellulose (% by mass of cement)	Strength (MPa)	Modulus (GPa)	Ductility (%)
0	0.89 (±3.1%)	11.13 (±2.9%)	0.0052 (±0.9%)
0.4	1.38 (±3.2%)	6.89 (±1.9%)	0.0213 (±0.8%)
0.6	1.42 (±2.3%)	5.95 (±2.5%)	0.0254 (±1.1%)
0.8	1.53 (±2.4%)	4.74 (±2.3%)	0.0375 (±1.2%)

tends to be more uniform when the component takes the form of a solution rather than solid particles, especially when the proportion of organic component is low. The greater spatial uniformity allows a relatively small proportion of the organic component to be needed to achieve a similar level of property enhancement.

Methylcellulose is a water-soluble polymer and water is needed for a cement mix anyway. Thus, the water used to dissolve the methylcellulose can be counted as some or all of the water in the cement mix. The addition of a methylcellulose solution to cement paste results in a slight increase in the tensile strength (due to the decreased porosity), a decrease in the tensile modulus (due to the low modulus of the methylcellulose compared to cement), and a significant increase in the tensile ductility (due to the high ductility of the methylcellulose compared to cement), as shown in Table 6.9. The highest methylcellulose (solid) proportion of 0.008 by mass of cement in Table 6.9 is much lower than the lowest latex solid proportion of 0.024 by mass of cement in Figs. 6.19–6.22. Due to the low methylcellulose proportion, the tensile strength is increased only slightly by methylcellulose addition (Table 6.9), whereas it is increased substantially by latex addition (Fig. 6.17). However, due to the uniform distribution of the methylcellulose (because the methylcellulose is introduced in the form of a solution) and the consequent high degree of continuity of the organic component, the small proportion of methylcellulose (0.8% by mass of cement) results in increases in ductility and shear bond strength (between steel rebars and concrete) that are as large as those due to 20% latex solid dispersion by mass of cement (i.e., 9.5% latex solid by mass of cement). The increase in bond strength is due to the presence of a layer of the polymer component at the bond interface. However, due to the uniform distribution and the consequent continuity of the methylcellulose in the nanocomposite, the modulus is decreased by the addition of methylcellulose much more severely than that of latex at a much higher proportion.

6.5.3 Nanocomposites Made by Inorganic Component Exfoliation and Subsequent Organic Component Adsorption

Inorganic components (e.g., clay) that form loosely bonded layers in the crystal structure may be exfoliated. Exfoliation is a chemical and/or physical process that results in the separation of the material into platelets, such that each platelet consists of a small number of atomic layers. The resulting platelets are known as nanoplatelets. Subsequent adsorption of an organic component onto the surface of the nanoplatelets results in a nanocomposite with the organic component as the matrix and the inorganic nanoplatelets as the filler. [In general, adsorption is a process that occurs when a gas or liquid accumulates on the surface of a solid (adsorbent), forming a film of molecules or atoms (the adsorbate).] The overall process is known as exfoliation–adsorption. When clay (such as montmorillonite) is used as the inorganic component, the platelets are known as nanoclay, and each nanoplatelet tends to consist of a silicate monolayer. The exfoliation of clay is preceded by the intercalation of the clay with an organic modifier (such as a quaternary ammonium salt) that contains ions. [In general, intercalation refers to the chemical process of inserting a foreign species, typically in the form of a monolayer of atoms, ions or molecules, between the layers of a host material.] The modified clay is known as organoclay, which is then immersed in a liquid solution of the organic component (or its resin) that serves as the matrix for the resulting composite. Interaction of the solution with the salt in the modified clay, along with sonication (e.g., using an ultrasonic cleaner for, say, 2 h, perhaps supplemented by minor heating to, say, 35–45°C), results in exfoliation of the clay and adsorption of the solution onto the exfoliated silicate platelets. Subsequent evaporation of the solvent in the solution allows the organic component to adsorb onto the exfoliated silicate platelets, thus rendering a nanocomposite. The evaporation can be hastened by heating (at, say, 100°C for 4 h) and/or evacuation.

Review Questions

1. What is special about the behavior of the alloy known as Invar?
2. What is the difference between the admixture method and the coatedfiller method of power metallurgy?
3. Why is it undesirable to have an excessively strong bond between the fiber and the matrix in a composite with a brittle matrix?
4. Describe a method of improving the thermal conductivity of a boron nitride particle epoxy-matrix composite.
5. Describe a method for coating a carbon–carbon composite with silicon carbide.
6. What is the advantage of having silica fume, which is used as an admixture in cement, coated with silane?
7. What is the advantage of adding methylcellulose to cement?
8. What is attractive about having a high degree of graphitization in the carbon matrix of a carbon-matrix composite?

References

[1] D.R. Askeland and P.P. Phule, *The Science and Engineering of Materials*, 5th edn., PWS-Kent, Boston, 2006, p. 597.

[2] W.-T. Whang and W.-L. Liu, *SAMPE Q.* 22(1), 3–9 (1990).

[3] D.C. Sherman, C.-Y. Chen and J.L. Cercena, *Proc. Int. SAMPE Symp. and Exhib., 33, Materials: Pathway to the Future*, ed. by G. Carrillo, E.D. Newell, W.D. Brown, and P. Phelan, 1988, pp. 538–539.

[4] D.R. Askeland, *The Science and Engineering of Materials*, 2nd edn., PWS-Kent, Boston, 1989, pp. 538–539.

[5] D.R. Askeland and P.P. Phule, *The Science and Engineering of Materials*, 5th edn., PWS-Kent, Boston, 2006, p. 574.

[6] S.-W. Lai and D.D.L. Chung, "Consumption of SiC Whiskers by the Al-SiC Reaction in Aluminum-Matrix SiC Whisker Composites", *J. Mater. Chem.* 6(3), 469–477 (1996).

[7] P. Yih and D.D.L. Chung, "Titanium Diboride Copper-Matrix Composites," *J. Mater. Sci.* 32(7), 1703–1709 (1997).

[8] Y. Xu and D.D.L. Chung, "Silane-Treated Carbon Fiber for Reinforcing Cement", *Carbon* 39 (ER13), 1995–2001 (2001).

[9] Y. Xu and D.D.L. Chung, "Cement-Based Materials Improved by Surface Treated Admixtures", *ACI Mater. J.* 97(3), 333–342 (2000).

[10] Y. Xu and D.D.L. Chung, "Increasing the Thermal Conductivity of Boron Nitride and Aluminum Nitride Particle Epoxy-Matrix Composites by Particle Surface Treatment", *Compos. Interfaces* 7(4), 243–256 (2000).

[11] X. Fu, W. Lu and D.D.L. Chung, "Ozone Treatment of Carbon Fiber for Reinforcing Cement," *Carbon* 36(9), 1337–1345 (1998).

[12] S. Han, J.T. Lin, Y. Aoyagi and D.D.L. Chung, "Enhancing the Thermal Conductivity and Compressive Modulus of Carbon Fiber Polymer-Matrix Composites in the Through-Thickness Direction by Nanostructuring the Interlaminar Interface with Carbon Black", *Carbon* 46(7), 1060–1071 (2008).

[13] V.P. Veedu, A. Cao, X. Li, K. Ma, C. Soldano, S. Kar, P.M. Ajayan and M.N. Ghasemi-Nejhad. Multifunctional Composites Using Reinforced Laminae with Carbon-Nanotube Forests. *Nat. Mater.* 5(6), 457–462 (2006).

[14] W. Lu and D.D.L. Chung, "Oxidation Protection of Carbon Materials by Acid Phosphate Impregnation", *Carbon* 40(8), 1249–1254 (2002).

[15] P.-W. Chen, X. Fu, and D.D.L. Chung, "Microstructural and Mechanical Effects of Latex, Methylcellulose and Silica Fume on Carbon Fiber Reinforced Cement", *ACI Mater. J.* 94(2), 147–155 (1997).

[16] X. Fu and D.D.L. Chung, "Degree of Dispersion of Latex Particles in Cement Paste, as Assessed by Electrical Resistivity Measurement," *Cem. Concr. Res.* 26(7), 985–991 (1996).

[17] X. Fu, and D.D.L. Chung, "Improving the Bond Strength of Concrete to Reinforcement by Adding Methylcellulose to Concrete," *ACI Mater. J.* 95(5), 601–608 (1998).

Further Reading

D.D.L. Chung, "Interface Engineering for Cement-Matrix Composites", *Compos. Interfaces* 8(1), 67–82 (2001).

D.D.L. Chung, "Applications of Polymers in Cement-Based Structural Materials", *Annu. Tech. Conf. Soc. Plast. Eng.*, 2004, pp. 3845–3858.

C.-K. Leong and D.D.L. Chung, "Improving the Electrical and Mechanical Behavior of Electrically Conductive Paint by Partial Replacement of Silver by Carbon Black", *J. Electron. Mater.* 35(1), 118–122 (2006).

C. Lin, Timothy A. Howe and D.D.L. Chung, "Electrically Nonconductive Thermal Pastes with Carbon as the Thermally Conductive Component", *J. Electron. Mater*. 36(6), 659–668 (2007).

W. Lu and D.D.L. Chung, "Preparation of Conductive Carbons with High Surface Area", *Carbon* 39(1), 39–44 (2000).

W. Lu and D.D.L. Chung, "A Comparative Study of Carbons for Use as an Electrically Conducting Additive in the Manganese Dioxide Cathode of an Electrochemical Cell", *Carbon* 40 (ER3), 447–449 (2002).

W. Lu and D.D.L. Chung, "Oxidation Protection of Carbon Materials by Acid Phosphate Impregnation", *Carbon* 40(8), 1249–1254 (2002).

W. Lu and D.D.L. Chung, "A Comparative Study of Carbons for Use as an Electrically Conducting Additive in the Manganese Dioxide Cathode of an Electrochemical Cell", *Carbon* 40 (ER3), 447–449 (2002).

S. Wen and D.D.L. Chung, "Pitch-Matrix Composites for Electrical, Electromagnetic and Strain-Sensing Applications", *J. Mater. Sci.* 40(15), 3897–3903 (2005).