Chapter 3
Matrix Materials

A brief description of the various matrix materials, polymers, metals, and ceramics, is given in this chapter. We emphasize the characteristics that are relevant to composites. The reader should consult the references listed under Further Reading for greater details regarding any particular aspect of these materials.

3.1 Polymers

Polymers are structurally much more complex than metals or ceramics. They are cheap and can be easily processed. On the other hand, polymers have lower strength and modulus and lower use temperature limits. Prolonged exposure to ultraviolet light and some solvents can cause the degradation of polymer properties. Because of predominantly covalent bonding, polymers are generally poor conductors of heat and electricity. Polymers, however, are generally more resistant to chemicals than are metals. Structurally, polymers are giant chainlike molecules (hence the name *macromolecules*) with covalently bonded carbon atoms forming the backbone of the chain. The process of forming large molecules from small ones is called *polymerization*; that is, polymerization is the process of joining many monomers, the basic building blocks, together to form polymers. There are two important classes of polymerization:

1. *Condensation polymerization*. In this process a stepwise reaction of molecules occurs and in each step a molecule of a simple compound, generally water, forms as a by-product.
2. *Addition polymerization*. In this process monomers join to form a polymer without producing any by-product. Addition polymerization is generally carried out in the presence of catalysts. The linear addition of ethylene molecules (CH_2) results in polyethylene (a chain of ethylene molecules), with the final mass of polymer being the sum of monomer masses.

K.K. Chawla, *Composite Materials: Science and Engineering*,
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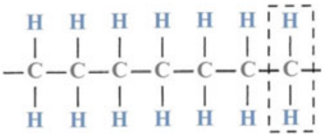

Based on their behavior, there are two major classes of polymers, produced by either condensation or addition polymerization, i.e., thermosetting and thermoplastic polymers. Thermosets undergo a curing reaction that involves cross-linking of polymeric chains. They harden on curing, hence the term *thermoset*. The curing reaction can be initiated by appropriate chemical agents or by application of heat and pressure, or by exposing the monomer to an electron beam. Thermoplastics are polymers that flow under the application of heat and pressure, i.e., they soften or become plastic on heating. Cooling to room temperature hardens thermoplastics. Their different behavior, however, stems from their molecular structure and shape, molecular size or mass, and the amount and type of bond (covalent or van der Waals). We first describe the basic molecular structure in terms of the configurations of chain molecules. Figure 3.1 shows the different chain configuration types.

1. *Linear polymers*. As the name suggests, this type of polymer consists of a long chain of atoms with attached side groups. Examples include polyethylene, polyvinyl chloride, and polymethyl methacrylate (PMMA). Figure 3.1a shows the configuration of linear polymers; note the coiling and bending of chains.
2. *Branched polymers*. Polymer branching can occur with linear, cross-linked, or any other type of polymer; see Fig. 3.1b.
3. *Cross-linked polymers*. In this case, molecules of one chain are bonded with those of another; see Fig. 3.1c. Cross-linking of molecular chains results in a three-dimensional network. Cross-linking makes sliding of molecules past one another difficult; thus such polymers are strong and rigid.
4. *Ladder polymers*. If we have two linear polymers linked in a regular manner (Fig. 3.1d) we get a ladder polymer. Not unexpectedly, ladder polymers are more rigid than linear polymers.

3.1.1 Glass Transition Temperature

Pure crystalline materials have well-defined melting temperatures. The melting point is the temperature at which crystalline order is completely destroyed on heating. Polymers, however, show a range of temperatures over which crystallinity vanishes. Figure 3.2 shows specific volume (volume/unit mass) vs. temperature curves for amorphous and semicrystalline polymers. When a polymer liquid is cooled, it contracts. The contraction occurs because of a decrease in the thermal vibration of molecules and a reduction in the free space; that is, the molecules occupy the space less loosely. At certain temperature, called the melting point, T_m,

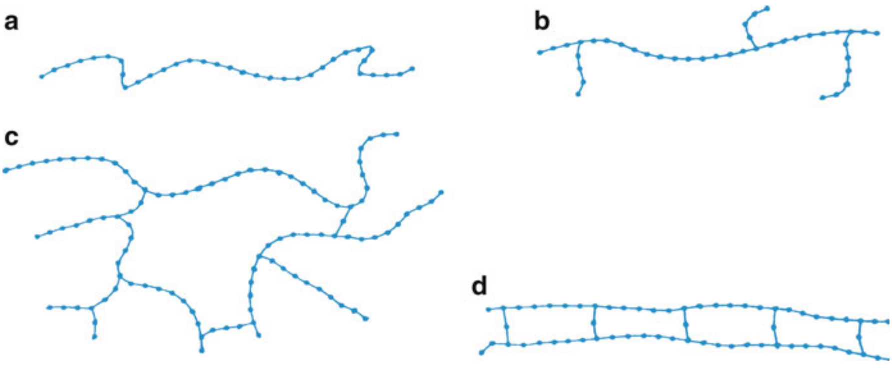

Fig. 3.1 Different molecular chain configurations: (**a**) linear, (**b**) branched, (**c**) cross-linked, (**d**) ladder

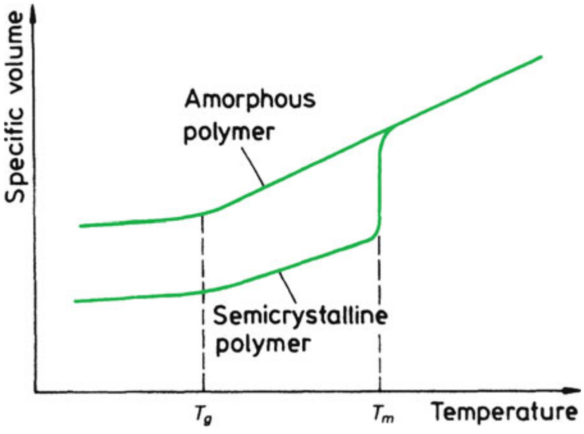

Fig. 3.2 Specific volume vs. temperature for an amorphous and a semicrystalline polymer

there occurs a thermodynamic phase transformation and the material assumes an orderly crystalline structure. In the case a semicrystalline polymer consists of a crystalline and an amorphous phase, the crystalline part undergoes this transformation. In the case of amorphous polymers, there is no fixed melting point, T_m. The polymer liquid continues to contract, below what would be the melting point for the crystalline phase. It does so down to a less well-defined temperature called the glass transition temperature, T_g. Below T_g, it becomes a supercooled liquid polymer that is quite rigid and solidlike because of very high viscosity. Unlike the crystalline phase, the structure of a glassy or amorphous material below T_g is essentially that of a liquid (highly disordered), albeit a very viscous one. Such a phenomenon is commonly observed in silica-based inorganic glasses. In the case of amorphous polymers, we are dealing with a glassy structure made of organic molecules.

The glass transition temperature T_g, although it does not represent a thermodynamic phase transformation, is in many ways akin to the melting point for the crystalline solids. Many physical properties (e.g., viscosity, heat capacity, elastic modulus, and expansion coefficient) change quite rapidly at T_g. Polystyrene, for example, has a T_g of about 100 °C and is therefore rigid at room temperature. Rubber, on the other hand, has a T_g of about -75 °C and therefore is flexible at room temperature. T_g is a function of the chemical structure of the polymer. For example, if a polymer has a rigid backbone structure and/or bulky branch groups, then T_g will be quite high.

Although both amorphous polymers and inorganic silica-based glasses have a glass transition temperature T_g, generally, the T_g of inorganic glasses is several hundred degrees Celsius higher than that of polymers. The reason for this is the different types of bonding and the amount of cross-linking in the polymers and glasses. Inorganic glasses have mixed covalent and ionic bonding and are highly cross-linked. This gives them a higher thermal stability than polymers, which have covalent and van der Waals bonding and a lesser amount of cross-linking than found in inorganic glasses.

3.1.2 Thermoplastics and Thermosets

Polymers that soften or melt on heating are called thermoplastic polymers and are suitable for liquid flow forming. Examples include low- and high-density polyethylene, polystyrene, and PMMA. When the structure is amorphous, there is no apparent order among the molecules and the chains are arranged randomly; see Fig. 3.3a. Small, platelike single crystalline regions called *lamellae* or *crystallites* can be obtained by precipitation of the polymer from a dilute solution. In the lamellae, long molecular chains are folded in a regular manner; see Fig. 3.3b. Many crystallites group together and form spherulites, much like grains in metals.

When the molecules in a polymer are cross-linked in the form of a network, they do not soften on heating. We call such cross-linked polymers *thermosetting*

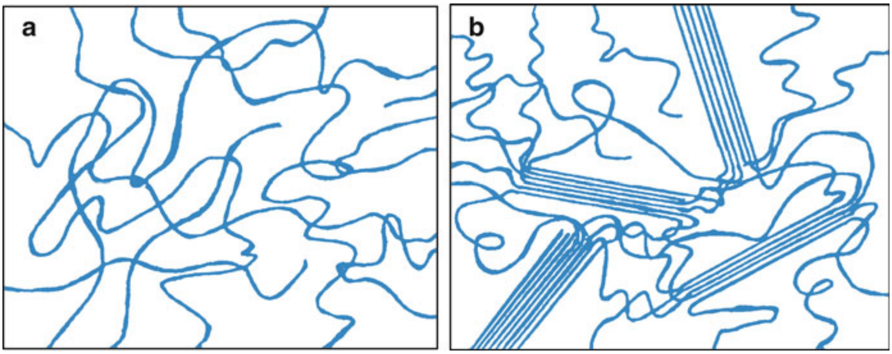

Fig. 3.3 Possible arrangements of polymer molecules: (**a**) amorphous, (**b**) semicrystalline

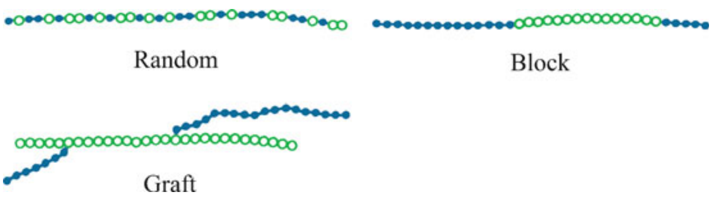

Fig. 3.4 Different types of copolymers

polymers. Thermosetting polymers decompose on heating. Cross-linking makes sliding of molecules past one another difficult, making the polymer strong and rigid. A typical example is that of rubber cross-linked with sulfur, that is, vulcanized rubber. Vulcanized rubber has ten times the strength of natural rubber. Common examples of thermosetting polymers include epoxy, phenolic, polyester, and vinyl ester.

3.1.3 Copolymers

There is another type of classification of polymers based on the type of repeating unit. When we have one type of repeating unit forming the polymer chain, we call it a *homopolymer*. *Copolymers*, on the other hand, are polymer chains with two different monomers. If the two different monomers are distributed randomly along the chain, we have a *regular*, or *random*, *copolymer*. If, however, a long sequence of one monomer is followed by a long sequence of another monomer, we have a *block copolymer*. If we have a chain of one type of monomer and branches of another type, we have a *graft copolymer*. Figure 3.4 shows schematically the different types of copolymers.

3.1.4 Molecular Weight

Molecular weight (MW) is a very important parameter for characterization of polymers. Generally, strength increases but strain-to-failure decreases with increasing molecular weight. Of course, concomitant with increasing molecular weight, the processing of polymers becomes more difficult. The degree of polymerization (DP) indicates the number of basic units (mers) in a polymer. These two parameters are related as follows:

$$\mathrm{MW} = \mathrm{DP} \times (\mathrm{MW})_\mathrm{u},$$

where $(\mathrm{MW})_\mathrm{u}$ is the molecular weight of the repeating unit. In general, polymers do not have exactly identical molecular chains but may consist of a mixture of different species, each of which has a different molecular weight or DP. Thus, the molecular weight of the polymer is characterized by a distribution function. Clearly, the narrower this distribution function is, the more homogeneous the polymer is. That is why one speaks of an average molecular weight or degree of polymerization.

It is instructive to compare the molecular weights of some common polymeric materials vis à vis monomeric materials. A molecule of water, H_2O, has a molecular weight of 18. Benzene, a low-molecular-weight organic solvent, has a molecular weight of 78. Compared to these, natural rubber can have a molecular weight of about 10^6. Polyethylene, a common synthetic polymer, can have molecular weights greater than 10^5. The molecular size of these high-molecular-weight solids is also very large. The molecular diameter of water, for example, is 40 nm, while that of polyethylene can be as large as 6,400 nm (Mandelkern 1983).

3.1.5 Degree of Crystallinity

Polymers can be amorphous or partially crystalline; see Fig. 3.3. A 100 % crystalline polymer is difficult to obtain. In practice, depending on the polymer type, molecular weight, and crystallization temperature, the amount of crystallinity in a polymer can vary from 30 to 90 %. The inability to attain a fully crystalline structure is mainly due to the long chain structure of polymers. Some twisted and entangled segments of chains that get trapped between crystalline regions never undergo the conformational reorganization necessary to achieve a fully crystalline state. Molecular architecture also has an important bearing on the polymer crystallization behavior. Linear molecules with small or no side groups crystallize easily. Branched chain molecules with bulky side groups do not crystallize as easily. For example, linear high-density polyethylene can be crystallized to 90 %, while branched polyethylene can be crystallized to only about 65 %. Generally, the stiffness and strength of a polymer increase with the degree of crystallinity. It should be mentioned that deformation processes such as slip and twinning, as well as phase transformations that take place in monomeric crystalline solids, can also occur in polymeric crystals.

3.1.6 Stress–Strain Behavior

Characteristic stress–strain curves of an amorphous polymer and of an elastomer (a rubbery polymer) are shown in Fig. 3.5a, b, respectively. Note that the elastomer does not show a Hookean behavior; its behavior is characterized as nonlinear elastic. The characteristically large elastic range shown by elastomers results from an easy reorganization of the tangled chains under the action of an applied stress.

Yet another point in which polymers differ from metals and ceramics is the extreme temperature dependence of their elastic moduli. Figure 3.6 shows schematically the variation of the elastic modulus of an amorphous polymer with temperature. In the temperature range below T_g, the polymer is hard and a typical value of elastic modulus would be about 5 GPa. Above T_g, the modulus value drops significantly and the polymer shows a rubbery behavior. Above T_f (the temperature at which the polymer becomes fluid), the modulus drops abruptly. It is in this region of temperatures above T_f that polymers are subjected to various processing operations.

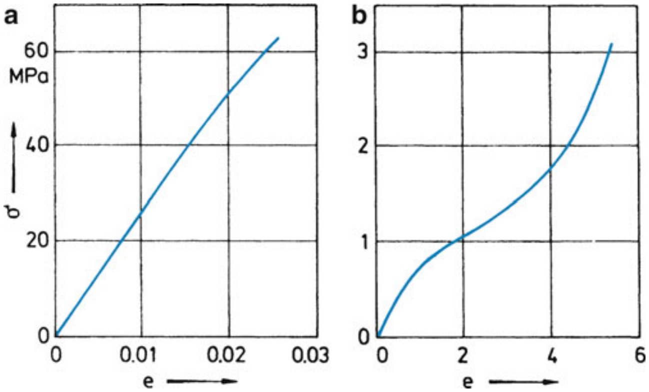

Fig. 3.5 (**a**) Hookean elastic behavior of a glassy polymer. (**b**) Nonlinear elastic behavior of an elastomer

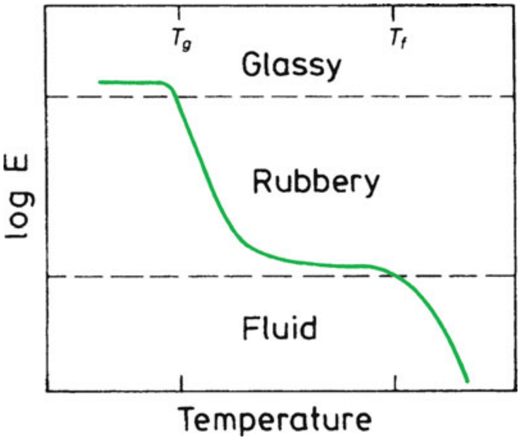

Fig. 3.6 Variation of elastic modulus of an amorphous polymer with temperature (schematic)

3.1.7 Thermal Expansion

Polymers generally have higher thermal expansivities than metals and ceramics. Furthermore, their thermal expansion coefficients are not truly constants; that is, the polymers expand markedly in a nonlinear way with temperature. Epoxy resins have coefficient of linear expansion values between 50×10^{-6} and $100 \times 10^{-6}\ \mathrm{K}^{-1}$ while polyesters show values between 100×10^{-6} and $200 \times 10^{-6}\ \mathrm{K}^{-1}$. Small compositional changes can have a marked influence on the polymer expansion characteristics.

3.1.8 Fire Resistance or Flammability

Fire performance of any polymer depends on a number of variables, such as surface spreading of flame, fuel penetration, and oxygen index. The limiting oxygen index (LOI) is the minimum amount of oxygen that will support combustion.

The degree of flammability of a polymer or a PMC is a function of the following parameters:

- Matrix type and amount (dominant!)
- Quantity of fire-retardant additives
- Type and amount of reinforcement (if any)

The order of increasing fire resistance of common polymer matrix materials is as follows: polyester, vinyl ester, epoxy, phenolic. Phenolic has very low smoke emission and gives out no toxic by-products. An added advantage of phenolic is that when it burns, it leaves behind char which is a good thermal insulator. In the case of thermosets, such as polyester, it is common practice to add fire-retardant additives. Addition of large amount of glass fiber also helps.

3.1.9 Common Polymeric Matrix Materials

Thermosets and thermoplastic polymers are common matrix materials. A brief description of important polymer matrix materials is provided here.

3.1.9.1 Common Thermoset Matrix Materials

Among the common polymer matrices used with continuous fibers are polyester and epoxy resins. We provide a summary of thermosetting resins commonly used as matrix materials.

Epoxy

This is one of the major thermoset matrix materials. An epoxy is a polymer that contains an epoxide group (one oxygen atom and two carbon atoms) in its chemical structure; see Fig. 3.7. Diglycidyl ether of bisphenol A (DGEBA) is an example. DGEBA, containing two epoxide groups, is a low-molecular-weight organic liquid. Frequently, one uses various additives to modify the characteristics of epoxies. For example, diluents are used to reduce the viscosity. Flexibilizing agents are used to make the epoxy flexible. Other agents are used for protection against ultraviolet radiation. Curing agents are organic amino or acid compounds, and cross-linking is obtained by introducing chemicals that react with the epoxy and hydroxy groups between adjacent chains. A common curing agent for DGEBA epoxy is diethylenetriamine (DETA). The extent of cross-linking is a function of the amount of curing agent added. Generally, 10–15 % by weight of amines or acid anhydrides is added, and they become part of the epoxy structure. An accelerator, if added, can speed up the curing process. In general, characteristics such as stiffness, strength, and glass transition temperature increase with increased cross-linking, but toughness decreases.

Epoxy resins are more expensive than polyesters, but they have better moisture resistance, lower shrinkage on curing (about 3 %), a higher maximum use temperature, and good adhesion with glass fibers. Many proprietary formulations of epoxies are available, and a very large fraction of high-performance polymer matrix composites has thermosetting epoxies as matrices.

The curing reaction of an epoxy can be slowed by lowering the reaction temperature. An epoxy before it is fully cross-linked is said to be in stage B. In stage B, an epoxy has a characteristic *tackiness*. This B-stage resin is used to make a fiber prepreg, which is shipped to the manufacturer where it can be fully cured into a hard solid. The type and extent of curing agent addition will control the total curing time (also called the *shelf life* or *pot life*). In order to increase the shelf life, such B-stage cured epoxy matrix prepregs are transported in refrigerated trucks and stored in refrigerated storage. Table 3.1 gives some important characteristics of epoxy at room temperature. Epoxy matrix composites were originally formulated to withstand prolonged service at 180 °C (~350 °F). In the 1970s, it came to be recognized that they are prone to hygrothermal effects and their service temperature limitation is 120 °C (250 °F). A detailed account of structure–property relationships of epoxies used as composite matrices is provided by Morgan (1985).

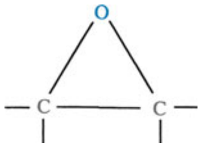

Fig. 3.7 Chemical structure of the epoxide group

Table 3.1 Some important characteristics of epoxy

Density, ρ (g/cm^3)	Strength, σ (MPa)	Modulus, E (GPa)	Poisson's ratio, ν	CTE, α (10^{-6} K^{-1})	Cure shrinkage (%)	Use temp. (°C)
1.2–1.3	50–125	2.5–4	0.2–0.33	50–100	1–5	150

Polyester

An unsaturated polyester resin contains a number of C=C double bonds. A condensation reaction between a glycol (ethylene, propylene, or diethylene glycol) and an unsaturated dibasic acid (maleic or fumaric) results in a linear polyester that contains double bonds between certain carbon atoms. The term *unsaturated* means that there are reactive sites in the molecule. Diluents such as styrene are used to reduce the viscosity of polyester. Styrene contains C=C double bonds and cross-links the adjacent polyester molecules at the unsaturation points. Hardening and curing agents and ultraviolet absorbents are usually added. Frequently, a catalyst such as an organic peroxide is added to initiate the curing action. One can hasten the curing process by raising the temperature; this increases the decomposition rate of the catalyst. This can also be accomplished by using an accelerator such as cobalt napthalate. Unsaturated polyester has adequate resistance to water and a variety of chemicals, weathering, aging, and, last but not least, it is very cheap. It can withstand temperatures up to about 80 °C and combines easily with glass fibers. Polyester resins shrink between 4 and 8 % on curing. Table 3.2 gives some important room temperature properties of polyester.

There is an unfortunate confusion about the term polyester. The same term is used for two very different polymers. Unsaturated polyester is a thermoset resin commonly used as a matrix material in polymer composites. Commonly referred to just as polyester, it is very different from the thermoplastic polyester (see below). As pointed out above, unsaturated polyester resin is amorphous in structure and is obtained by condensation polymerization of an unsaturated dibasic acid and a glycol (commonly polypropylene glycol). For use in composites, one starts with a very viscous liquid unsaturated polyester resin. Styrene is used to control the viscosity of the resin. The resin undergoes a curing reaction involving cross-linking of chains that leads to hardening. A catalyst (commonly, methyl ethyl ketone peroxide, MEKP) is used to start the curing reaction. The cured thermoset is amorphous in structure. This thermoset polymer finds extensive uses in products such as glass fiber reinforced boats, pipes, shower stalls, etc.

Table 3.2 Some important characteristics of polyester

Density, ρ (g/cm^3)	Strength, σ (MPa)	Modulus, E (GPa)	Poisson's ratio, ν	CTE, α (10^{-6} K^{-1})	Cure shrinkage (%)	Use temp. (°C)
1.1–1.4	30–100	2–4	0.2–0.33	50–100	5–12	80

There is another resin which is also commonly referred to as polyester, but it is very different from the unsaturated polyester described above. The full name of this thermoplastic polyester is polyethylene terephthalate or PET (sometimes PETE). It is one of the three major commodity thermoplastics—PE, PP, and PET. PET is made by an esterification reaction between terephthalic acid and ethylene glycol to produce the monomer PET, with water as a by-product. The PET monomer is subjected to polymerization via a polycondensation reaction of monomers. Interestingly, ethylene glycol is a by-product of this reaction, which is of course recycled. PET, or polyester as it is commonly called, is used extensively to make fibers, films, and bottles for water and soda pop. The bottle variety has a higher molecular weight. PET is a semicrystalline material. PET-based fibers form about 60 % of the market while bottles make up 30 %. Common trade names of PET-based fibers include Tergal, Terylene, and Dacron fibers.

Other Thermosets

Polyimides are thermosetting polymers that have a relatively high service temperature range, 250–300 °C. However, like other thermosetting resins, they are brittle. Their fracture energies are in the 15–70 J/m^2 range. A major problem with polyimides is the elimination of water of condensation and solvents during processing. There is a considerable interest in developing polymeric materials that can withstand high temperatures. Polyimides represent a class of resins that can have a higher service temperature than epoxies. PMR resins are based on aromatic dianhydride ester acid and aromatic diamine. They are polymerized via solvent-addition. The acronym PMR stands for polymerized monomeric reactant. PMR-15 and PMR-II-50 are two trade names. Their service temperature can be around 250 °C. Their use has been limited, mainly because PMR resins contain a toxic compound methylene dianiline (MDA) and emit volatile organic compounds (VOCs) during processing. A polyimide developed by NASA is called DMBZ-15, wherein MDA is replaced with a noncoplanar diamine, 2,2′-dimethylbenzidine (DMBZ). The DMBZ-15 composition has a glass transition temperature of 414 °C, an increase in use temperature of 55 °C over PMR-15 composites. Carbon fiber reinforced DMBZ-15 has an operational temperature range up to 335 °C and good thermo-oxidative stability in aircraft engine or missile environments.

Some newer resins can extend the use temperature range to 300 °C. An example is phenylethynyl-terminated imide (PETI) oligomers. PET 15, PETI-298, PETI-330, and PETI-365 are the designations with the numbers indicating the glass transition temperature in °C. In particular, PETI-330 is a high-temperature resin (PETI resins were developed at NASA) that is suitable for infusion and resin-transfer molding (RTM) processes. This resin has high-temperature mechanical properties coupled with low melt viscosity ($<$10 Pa s at 288 °C) and melt stability which allow it to be processed by relatively low-cost RTM. The resin has a high glass transition temperature of 330 °C, and it can be processed without the use of solvents, i.e., no VOCs are generated during processing.

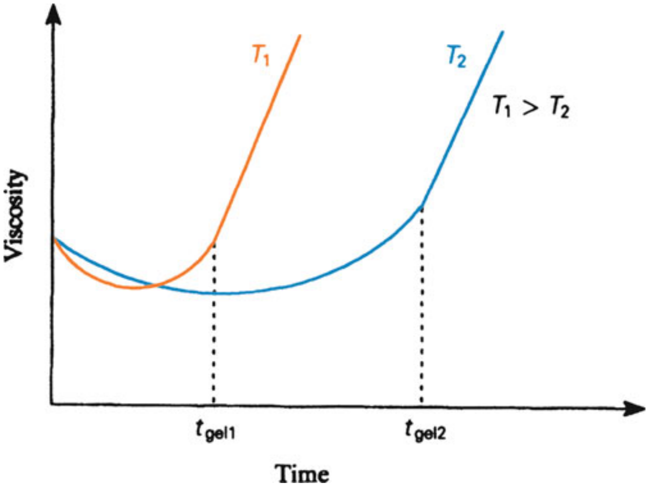

Fig. 3.8 Viscosity (η) vs. time (t) for a thermoset for two different temperatures, $T_1 > T_2$

Bismaleimides (BMI), thermosetting polymers, can have service temperatures between 180 and 200 °C. They have good resistance to hygrothermal effects. Because they are thermosets, they are quite brittle and must be cured at higher temperatures than conventional epoxies.

Curing

Figure 3.8 shows schematically the variation of viscosity of a thermoset as a function of time at two different temperatures ($T_1 > T_2$). There occurs a slight decrease in viscosity in the beginning because of the heat generated by the exothermic curing reaction. As the cross-linking progresses, the molecular mass of the thermoset increases; viscosity increases at first slowly and then very rapidly. At the time corresponding to a perceptible change in viscosity, t_{gel}, a gel-like lump appears. At times greater than t_{gel}, viscosity tends to infinity and the thermoset can be treated as a solid. Figure 3.9 shows the variation of mechanical properties as a function of curing time. After a time marked t_{cure}, the mechanical properties of a thermoset essentially do not change with time.

Electron Beam Curing

An electron beam (1–10 MeV) is a good source of ionizing radiation that can be used to initiate polymerization or the curing reaction in a polymer. Parts up to 25 mm thick can be cured. Higher energy beams are required for parts thicker than 25 mm. It turns out that one needs to modify the resin formulation for electron beam curing.

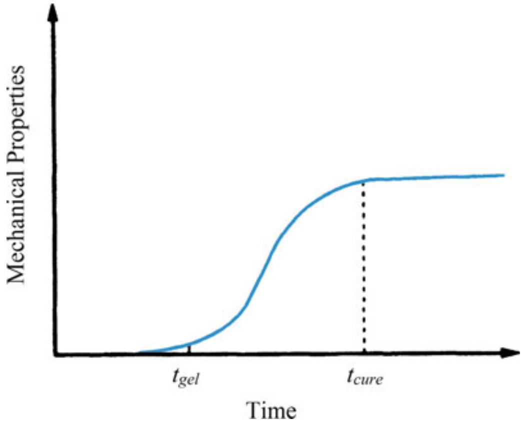

Fig. 3.9 Variation of mechanical properties with curing time

Addition of 1–3 parts per hundred of a cationic photo-initiator can do the job. No hardener is required. However, other conventional additives, such as toughening agents or diluents, can be used to improve the processability of the resin. Among the advantages of electron beam curing, one may list the following:

- Shorter cure times (minutes rather than the hours required by conventional thermal processes).
- Curing can be accomplished at a selected temperature (room temperature or near the service temperature).
- Lower energy consumption than in thermal curing.
- Removal of hardener means elimination of the undesirable VOCs. It also allows the use of thermoset resins with unlimited shelf life.

Among the limitations, one may list the following:

- Only a few electron beam curing facilities are available, especially for large and complex structures. This is especially so in the 5–15 MeV range.
- Shipping parts to outside accelerator facilities can be problematic.
- Long-term testing and experience in the field are missing; that is, customer confidence needs to be built.

3.1.9.2 Common Thermoplastic Matrix Materials

Thermoplastics are characterized by linear chain molecules and can be repeatedly melted or reprocessed. It is important to note that in this regard the cool-down time affects the degree of crystallinity of the thermoplastic. This is because the polymer chains need time to get organized in the orderly pattern of the crystalline state; too quick a cooling rate will not allow crystallization to occur. Although repeated melting and processing are possible with thermoplastics, it should be recognized that thermal exposure (too high a temperature or too long a dwell time at a given temperature) can degrade the polymer properties such as, especially, impact properties.

Linear molecules in a thermoplastic result in higher strain-to-failure values compared to those of thermosets, i.e., thermoplastics are tougher than the cross-linked thermosets. Thermoplastic matrix materials can have failure strains ranging from 30 to 100 %, while the thermosets typically range from 1 to 3 %. The large range of failure strains in thermoplastics stems from the rather large variations in the amount of crystallinity.

Common thermoplastic resins used as matrix materials in composites include some conventional thermoplastics such as polypropylene, nylon, thermoplastic polyesters (PET, PBT), and polycarbonates. Some of the new thermoplastic matrix materials include polyamide imide, polyphenylene sulfide (PPS), polyarylsulfone, and polyetherether ketone (PEEK). Figure 3.10 shows the chemical structure of some of these thermoplastics. PEEK is an attractive matrix material because of its toughness and impact properties, which are a function of its crystalline content and morphology. It should be pointed out that crystallization kinetics of a thermoplastic matrix can vary substantially because of the presence of fibers (Waddon et al. 1987). In order to make a thermoplastic matrix flow, heating must be done to a temperature above the melting point of the matrix. In the case of PEEK, the melting point of the crystalline component is 343 °C. In general, most thermoplastics are harder to flow vis à vis thermosets such as epoxy! Their viscosity decreases with increasing temperature, but at higher temperatures the danger is decomposition of resin.

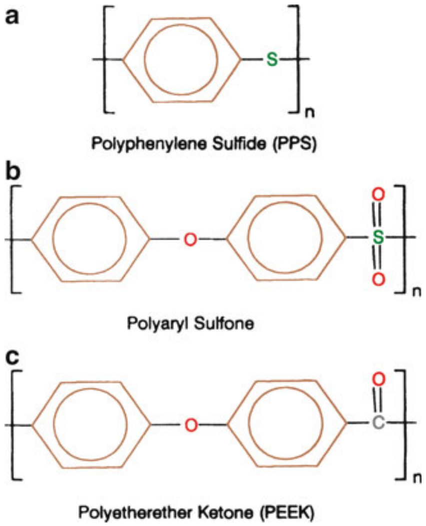

Fig. 3.10 Chemical structure of (**a**) PPS, (**b**) polyaryl sulfone, and (**c**) polyetherether ketone (PEEK)

PPS is a linear polymer of "modest" molecular weight (~150) and low mold shrinkage (0.1–0.5 % range). It can be injection molded, and the scrap can be ground and reused without much effect on processability and performance of a part. Polyethersulfone (PES) belongs to the polysulfone group of thermoplastics. Its chemical structure has an aromatic sulfone unit, which imparts high thermal stability and mechanical strength. It is completely amorphous and can withstand loads for long periods up to 190 °C. Both PEEK and PES are wholly aromatic polymers suitable for high temperatures, and both can be processed as conventional thermoplastics. PEEK, however, is partially crystalline, while PES is amorphous. The deactivated nature of PEEK results in a high melting point (343 °C) and good oxidative stability. PEEK has a long-term use temperature of 250 °C and a short use temperature of 300 °C.

Polyimides are among the most temperature-resistant engineering polymers. They can be linear or cross-linked, aromatic polymers. Processing problems and high cost have limited their use. Avimid K is the trade name of Du Pont Co. for an amorphous, linear, thermoplastic polyimide resin that is used to make fibrous prepregs. These prepregs are processed by a vacuum bag lay-up technique in an autoclave. Avimid K resin is made by condensation. An aromatic diethyl ester diacid is reacted with an aromatic diamine in *n*-methyl pyrrolidone (NMP) solvent. The by-products of the reaction are water, ethanol, and the solvent.

Thermoplastic resins have the advantage that, to some extent, they can be recycled. Heat and pressure are applied to form and shape them. More often than not, short fibers are used with thermoplastic resins but in the late 1970s continuous fiber reinforced thermoplastics began to be produced. The disadvantages of thermoplastics include their rather large expansion and high viscosity characteristics.

An important problem with polymer matrices is associated with environmental effects. Polymers can degrade at moderately high temperatures and through moisture absorption. Absorption of moisture from the environment causes swelling in the polymer as well as a reduction in its T_g. In the presence of fibers bonded to the matrix, these hygrothermal effects can lead to severe internal stresses in the composite. The presence of thermal stresses resulting from thermal mismatch between matrix and fiber is, of course, a general problem in all kinds of composite materials; it is much more so in polymer matrix composites because polymers have high thermal expansivities.

Typical properties of some common polymeric matrix materials are summarized in Table 3.3 (English 1985).

Matrix Toughness

Thermosetting resins (e.g., polyesters, epoxies, and polyimides) are highly cross-linked and provide adequate modulus, strength, and creep resistance, but the same cross-linking of molecular chains causes extreme brittleness, that is, very low fracture toughness. By *fracture toughness*, we mean resistance to crack propagation. It came to be realized in the 1970s that matrix fracture characteristics (strain

Table 3.3 Representative properties of some polymeric matrix materials

Property	Epoxy	Polyimide	PEEK	Polyamideimide	Polyetherimide	Polysulfone	Polyphenylene sulfide	Phenolics
Tensile strength (MPa)	35–85	120	92	95	105	75	70	50–55
Flexural modulus (GPa)	15–35	35	40	50	35	28	40	–
Density (g/cm^3)	1.38	1.46	1.30	1.38	–	1.25	1.32	1.30
Continuous-service temperature (°C)	25–85	260–425	310	–	170	175–190	260	150–175
Coefficient of thermal expansion (10^{-5} °C^{-1})	8–11	9	–	6.3	5.6	9.4–10	9.9	4.5–11
Water absorption (24 h %)	0.1	0.3	0.1	0.3	0.25	0.2	0.2	0.1–0.2

Source: Adapted with permission from English (1985)

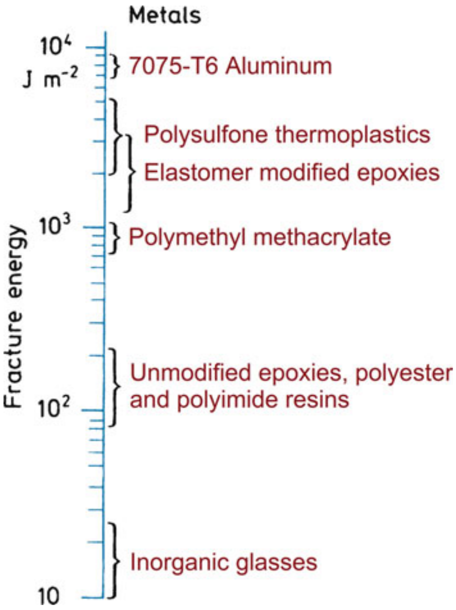

Fig. 3.11 Fracture energy for some common materials [adapted from Ting (1983), used with permission]

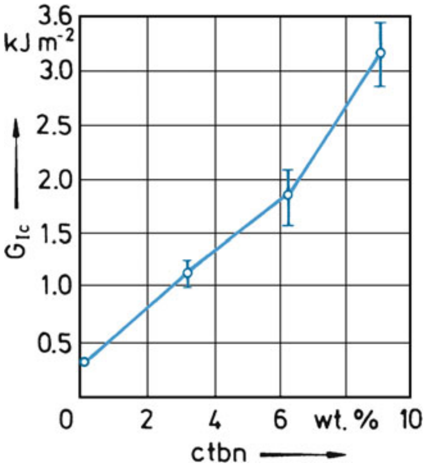

Fig. 3.12 Fracture surface energy of an epoxy as a function of weight % of carboxyl-terminated butadiene-acrylo-nitrile (ctbn) [adapted from Scott and Phillips (1975), used with permission]

to failure, work of fracture, or fracture toughness) are as important as lightness, stiffness, and strength properties. Figure 3.11 (note the log scale) compares some common materials in terms of their fracture toughness as measured by the fracture energy in J/m^2 (Ting 1983). Note that thermosetting resins have values that are only slightly higher than those of inorganic glasses. Thermoplastic resins such as PMMA have fracture energies of about 1 kJ/m^2, while polysulfone thermoplastics have fracture energies of several kJ/m^2, almost approaching those of the 7075-T6 aluminum alloy. Amorphous thermoplastic polymers show higher fracture energy values because they have a large free volume available that absorbs the energy associated with crack propagation. Among the well known modified thermoplastics are the acrylonitrile-butadiene-styrene (ABS) copolymer and high-impact polystyrene (HIPS). One class of thermosetting resins that comes close to polysulfones is the elastomer-modified epoxies. Elastomer-modified or rubber-modified thermosetting epoxies form multiphase systems, a kind of composite in their own right. Small (a few micrometers or less), soft, rubbery inclusions distributed in a hard, brittle epoxy matrix enhance its toughness by several orders of magnitude (Sultan and McGarry 1973; Riew et al. 1976; Bascom and Cottington 1976; St. Clair and St. Clair 1981; Scott and Phillips 1975).

Epoxy and polyester resins are commonly modified by introducing carboxyl-terminated butadiene-acrylonitrile copolymers (ctbn). The methods of manufacture can be simple mechanical blending of the soft, rubbery particles and the resin or copolymerization of a mixture of the two. Figure 3.12 shows the increase in fracture surface energy of an epoxy as a function of weight % of ctbn elastomer (Scott and Phillips 1975).

Toughening of glassy polymers by elastomeric additions involves different mechanisms for different polymers. Among the mechanisms proposed for explaining this enhanced toughness are triaxial dilation of rubber particles at the crack tip, particle elongation, and plastic flow of the epoxy. Ting (1983) studied such a rubber-modified epoxy containing glass or carbon fibers. He observed that the mechanical properties of rubber-modified composite improved more in flexure than in tension. Scott and Phillips (1975) obtained a large increase in matrix toughness by adding ctbn in unreinforced epoxy. But this large increase in toughness could be translated into only a modest increase in carbon fiber reinforced modified epoxy matrix composite. Introduction of a tough elastomeric phase, for example, a silicone rubber with good thermal resistance in a polyimide resin, produced a tough matrix material: a three- to fivefold gain in toughness, G_{Ic} without a reduction in T_g (St. Clair and St. Clair 1981).

Continuous fiber reinforced thermoplastics show superior toughness values owing to superior matrix toughness. PEEK is a semicrystalline aromatic thermoplastic (Hartness 1983; Cogswell 1983; Blundell et al. 1985) that is quite tough. PEEK can have 20–40 % crystalline phase. At 35 % crystallinity, the spherulite size is about 2 μm (Cogswell 1983). Its glass transition temperature T_{g} is about 150 °C, and the crystalline phase melts at about 350 °C. It has an elastic modulus of about 4 GPa, a yield stress of 100 MPa, and a relatively high fracture energy of about 500 J/m^2. In addition to PEEK, other tough thermoplastic resins are available, for example, thermoplastic polyimides and PPS, which is a semicrystalline aromatic sulfide. PPS is the simplest member of a family of polyarylene sulfides (O’Connor et al. 1986). PPS (trade name Ryton), a semicrystalline polymer, has been reinforced by chopped carbon fibers and prepregged with continuous carbon fibers (O’Connor et al. 1986).

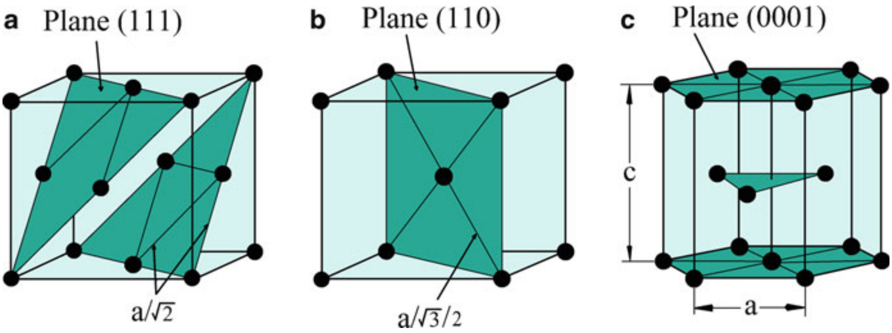

Fig. 3.13 Three crystalline forms of metals: (**a**) Face-centered cubic, (**b**) body-centered cubic, (**c**) hexagonal close packed. *a* is the side of the cube in (**a**) and (**b**), while it is the side of the hexagon base in (**c**)

3.2 Metals

Metals are very versatile engineering materials. They are strong and tough. They can be plastically deformed, and they can be strengthened by a wide variety of methods, mostly involving obstruction of movement of lineal defects called *dislocations*.

3.2.1 Structure

Metals, with the exception of metallic glasses, are crystalline materials. Most metals exist in one of the following three crystalline forms:

- Face-centered cubic (fcc)
- Body-centered cubic (bcc)
- Hexagonal close packed (hcp)

Figure 3.13 shows these three structures. The black dots mark the centers of the atomic positions, and some of the atomic planes are shown shaded. In real metals, the atoms touch each other and all the space is filled up. Some important metals with their respective crystalline structures are listed in Table 3.4. Metals are crystalline materials; however, the crystalline structure is never perfect. Metals contain a variety of crystal imperfections. We can classify these as follows:

1. Point defects (zero dimensional)
2. Line defects (unidimensional)
3. Planar or interfacial defects (bidimensional)
4. Volume defects (tridimensional)

Table 3.4 Crystal structure of some important metals

fcc	bcc	hcp
Iron (910–1,390 °C)	Iron ($T < 910$ °C and $T > 1{,}390$ °C)	Titanium[a]
Nickel	Beryllium ($T > 1{,}250$ °C)	Beryllium ($T < 1{,}250$ °C)
Copper	Cobalt ($T > 427$ °C)	Cobalt ($T < 427$ °C)
Aluminum	Tungsten	Cerium (-150 °C $< T < -10$ °C)
Gold	Molybdenum	Zinc
Lead	Chromium	Magnesium
Platinum	Vanadium	Zirconium[a]
Silver	Niobium	Hafnium[a] ($T < 1{,}950$ °C)

[a]Undergoes bcc ↔ hcp transformation at different temperatures

Point defects can be of three types. A *vacancy* is created when an atomic position in the crystal lattice is vacant. An *interstitial* is produced when an atom of material or a foreign atom occupies an interstitial or nonlattice position. A *substitutional point defect* comes into being when a regular atomic position is occupied by a foreign atom. *Intrinsic point defects* (vacancies and self-interstitials) in metals exist at a given temperature in equilibrium concentrations. Increased concentrations of these defects can be produced by quenching from high temperatures, bombarding with energetic particles such as neutrons, and plastic deformation. Point defects can have a marked effect on the mechanical properties.

Line imperfections, called dislocations, represent a critically important structural imperfection that plays a very important role in the area of physical and mechanical metallurgy, diffusion, and corrosion. A dislocation is defined by two vectors: a dislocation line vector, t, (tangent to the line) and its Burgers vector, b, which gives the magnitude and direction of atomic displacement associated with the dislocation. There are two types of dislocations: in an edge dislocation b and t vectors are perpendicular to each other, while in a screw dislocation, b and t are parallel. The dislocation has a kind of lever effect because its movement allows one part of metal to be sheared over the other without the need for simultaneous movement of atoms across a plane. It is the presence of these line imperfections that makes it easy to deform metals plastically. Under normal circumstances then, the plastic deformation of metals is accomplished by the movement of these dislocations. Figure 3.14a shows an edge dislocation. The two vectors, defining the dislocation line and the Burgers vector, are designated as t (not shown) and b, respectively (see Fig. 3.14a). The dislocation permits shear in metals at stresses much below those required for simultaneous shear across a plane. Figure 3.14b shows this in an analogy. A carpet, of course, can be moved by pushing or pulling. However, a much lower force is required to move the carpet by a distance b if a defect (a bump in the carpet) is introduced into it and made to move the whole extension of the carpet. Figure 3.15 shows dislocations as seen by transmission electron microscopy in a thin foil of steel. This is a dark field electron micrograph; dislocation lines appear as white lines. Dislocations become visible in the transmission electron microscope because of the distortion of the atomic planes owing to the presence of dislocations. Also visible in this micrograph are equiaxial precipitate particles pinning the dislocations at various points.

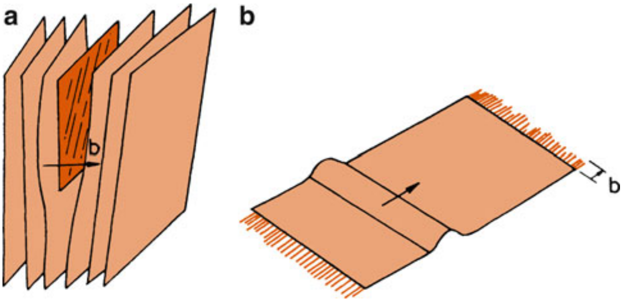

Fig. 3.14 (**a**) Edge dislocation, (**b**) dislocation in a carpet

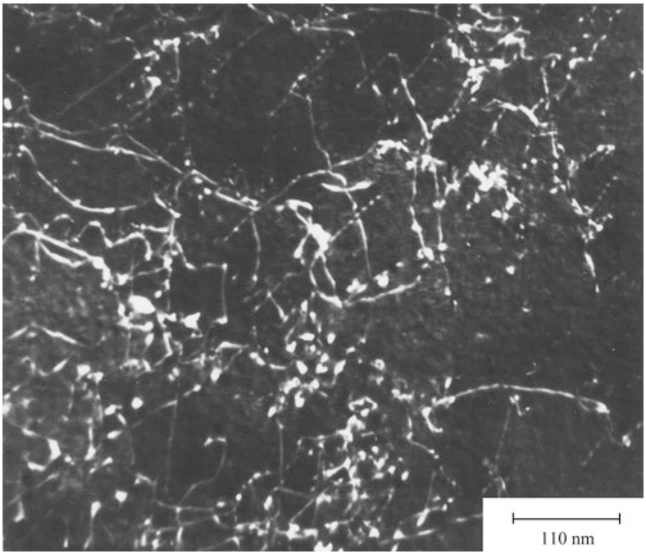

Fig. 3.15 Dislocations (*white lines*) in a steel sample: dark field transmission electron micrograph. Also visible are equiaxial precipitate particles

The interfacial or planar defects occupy an area or surface of the crystal, for example, grain boundaries, twin boundaries, domain or antiphase boundaries. Grain boundaries are, by far, the most important of these planar defects from the mechanical behavior point of view. Among the volumetric or tridimensional defects we can include large inclusions and porosity and preexisting cracks.

3.2.2 Conventional Strengthening Methods

Experimental results show that work hardening (or strain hardening), which is the ability of a metal to become more resistant to deformation as it is deformed, is related in a singular way to the dislocation density (ρ) after deformation. There exists a linear relationship between the flow stress in shear, τ and $\sqrt{\rho}$ (Meyers and Chawla 2009):

$$\tau = \tau_0 + \alpha G b \sqrt{\rho}, \tag{3.1}$$

where G is the shear modulus, b is the Burgers vector, α is an adjustable parameter, and τ_0 is the shear stress required to move a dislocation in the absence of any other dislocations. Basically, work hardening results from the interactions among dislocations moving on different slip planes. A tangled dislocation network results after a small plastic deformation, which impedes the motion of other dislocations. This, in turn, requires higher loads for further plastic deformation. Various theories (Seeger 1957; Kuhlmann-Wilsdorf 1977) explain the interactions of dislocations with different kinds of barriers (e.g., dislocations, grain boundaries, solute atoms, and precipitates) that result in characteristic strain hardening of metals. All these theories arrive at the relationship between τ and ρ given in Eq. (3.1), indicating that a particular dislocation distribution is not crucial and that strain hardening in practice remains the same for various dislocation distributions and configurations. Cold working of metals, which leads to the strengthening of metals as a result of increase in dislocation density and work hardening, is a routinely used strengthening technique.

A similar relationship exists between the flow stress τ and the mean grain size (or dislocation cell size) to an undetermined level

$$\tau = \tau_0 + \frac{\alpha' G b}{D^{1/2}}, \tag{3.2}$$

where D is the mean grain diameter. This relationship is known as the *Hall–Petch relationship* after the two researchers who first postulated it (Hall 1951; Petch 1953). Again, various models have been proposed to explain this square root dependence on grain size. Earlier explanations involved a dislocation pileup bursting through the boundary owing to stress concentrations at the pileup tip and activation of dislocation sources in adjacent grains (Cottrell 1958). Later theories involved the activation of grain boundaries as sources of dislocations (Li 1963). An important aspect of strengthening by grain refinement is that, unlike other strengthening mechanisms, it results in an improvement in toughness concurrent with that in strength (again to an undefined lower grain size). Another easy way of strengthening metals by impeding dislocation motion is that of introducing heterogeneities such as solute atoms or precipitates or hard particles in a ductile matrix. When we introduce solute atoms (e.g., carbon, nitrogen, or manganese in iron) we obtain solid solution hardening. Interstitial solutes such as carbon and nitrogen are much more efficient strengthening agents than substitutional solutes such as manganese and silicon. This is because the interstitials cause a tetragonal distortion in the lattice and thus interact with both screw and edge dislocations, while the substitutional atoms cause a spherical distortion that interacts only with edge dislocations, because the screw dislocations have a pure shear stress field and no hydrostatic component. Precipitation hardening of a metal is obtained by decomposing a supersaturated solid solution to form a finely distributed second phase. Classical examples of precipitation strengthening alloys are Al–Cu and Al–Zn–Mg alloys, which are used in the aircraft industry (Fine 1964). Oxide dispersion strengthening involves artificially dispersing rather small volume fractions (0.5–3 vol.%) of strong and inert oxide particles (e.g., Al_2O_3, Y_2O_3, and ThO_2) in a ductile matrix by internal oxidation or powder metallurgy blending techniques (Ansell 1968). Both the second-phase precipitates and dispersoids act as barriers to dislocation motion in the ductile matrix, thus making the matrix more deformation resistant. Dispersion hardened systems (e.g., Al + Al_2O_3) show high strength levels at elevated temperatures while precipitates (say, $CuAl_2$ in aluminum) tend to dissolve at those temperatures. Precipitation hardening systems, however, have the advantage of enabling one to process the alloy in a soft condition and give the precipitation treatment to the finished part. The precipitation process carried out for long periods of time can also lead to overaging and solution; a weakening effect.

Quenching a steel to produce a martensitic phase has been a time-honored strengthening mechanism for steels. The strength of the martensite phase in steel depends on a variety of factors, the most important being the amount of carbon. The chemical composition of martensite is the same as that of the parent austenite phase from which it formed, but it is supersaturated with carbon (Roberts and Owen 1968). Carbon saturation and the lattice distortion that accompanies the transformation lead to the high hardness and strength of martensite.

Another approach to obtaining enhanced mechanical performance is rapid solidification processing (Grant 1985). By cooling metals at high rates, 10^4 to 10^9 K/s, it is possible to produce unique microstructures. Very fine powders or ribbons of rapidly solidified materials are processed into bulk materials by hot pressing, hot isostatic pressing, or hot extrusion. The rapidly solidified materials can be amorphous (noncrystalline), nanocrystalline (grain size in the nm range), or microdendritic solid solutions containing solute concentrations vastly superior to those of conventionally processed materials. Effectively, massive second-phase particles are eliminated. These unique microstructures lead to very favorable mechanical properties.

3.2.3 Properties of Metals

Typical values of elastic modulus, yield strength, and ultimate strength in tension and fracture toughness of some common metals and their alloys are listed in Table 3.5, while typical engineering stress–strain curves in tension are shown in Fig. 3.16. Note the large plastic strain range.

3.2.4 Why Reinforcement of Metals?

Precipitation or dispersion hardening of a metal can result in a dramatic increase in the yield stress and/or the work hardening rate. The influence of these obstacles on the elastic modulus is negligible. This is because the intrinsic properties of the strong particles (e.g., the high elastic modulus) are not used. Their only function is to impede dislocation movements in the metal. The improvement in stiffness can be profitably obtained by incorporating the high-modulus fibers or particles in a metal matrix. It turns out that most of these high-modulus reinforcements are also lighter than the metallic matrix materials; the only exception is tungsten, which has a high modulus and is very heavy. Table 3.6 lists some common metals and their densities, ρ. The densities of various fibers are given in Chap. 2.

Table 3.5 Mechanical properties of some common metals and alloys

Property	E (GPa)	σ_y (MPa)	$\sigma_{\max}$ (MPa)	K_{Ic} (MPa $\mathrm{m}^{1/2}$)
Aluminum	70	40	200	100
Copper	120	60	400	65
Nickel	200	70	400	350
Ti–6Al–4V	110	900	1,000	120
Aluminum alloys				
(Low strength–high strength)	70	100–380	250–480	40–23
Plain carbon steel	210	250	420	140
Stainless steel (304)	195	240	365	200

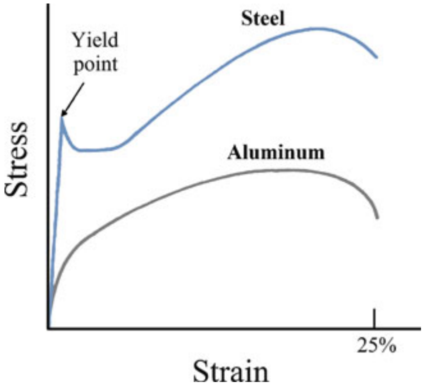

Fig. 3.16 Stress–strain curves of two common metals. Note the large plastic strain range

Table 3.6 Density of some common metals

Metal	Density (g/cm^3)	Metal	Density (g/cm^3)
Aluminum	2.7	Lead	11.0
Beryllium	1.8	Nickel	8.9
Copper	8.9	Silver	10.5
Gold	19.3	Titanium	4.5
Iron	7.9	Tungsten	19.3

Although one generally thinks of a high Young's modulus, E, as something very desirable from a structural point of view, it turns out that for structural applications involving compression or flexural loading of beams (for example, in an airplane, rocket, or truck), it is the E/ρ^2 value, ρ being the density, that should be maximized. Consider a simple square section cantilever beam, of length l and thickness t under an applied force P. The elastic deflection of this beam, ignoring self-weight, is given by (Fitzgerald 1982)

$$\delta = \frac{Pl^3}{3EI},$$

where I is the moment of inertia; in this case it is equal to $t^4/12$.

Therefore,

$$\delta = \frac{4l^3 P}{Et^4}. \tag{3.3}$$

The mass of this beam is

$$M = \text{volume} \times \text{density} = lt^2\rho$$

or

$$t = \left(\frac{M}{l\rho}\right)^{1/2}. \tag{3.4}$$

From Eqs. (3.3) and (3.4), we have

$$\delta = \left(\frac{4l^3 P}{E}\right)\left(\frac{l^2\rho^2}{M^2}\right)$$

or

$$M = \left(\frac{4l^5 P}{\delta}\right)\left(\frac{\rho^2}{E}\right)^{1/2}.$$

Thus, for a given rigidity or stiffness P/δ, we have a minimum of mass when the parameter E/ρ^2 is a maximum. What this simple analysis shows is that it makes good sense to use high modulus fibers or particles to reinforce metals in a structural application and it makes eminently more sense to use reinforcements that are not only stiffer than metallic matrices but also lighter. Continuous ceramic fibers or particles such as SiC, Al_2O_3, and B (see chap. 2) would meet these requirements.

3.3 Ceramic Matrix Materials

Ceramic materials are very hard and brittle. Generally, they consist of one or more metals combined with a nonmetal such as oxygen, carbon, or nitrogen. They have strong covalent and ionic bonds and very few slip systems available compared to metals. Thus, characteristically, ceramics have low failure strains and low toughness or fracture energies. In addition to being brittle, they lack uniformity in properties, have low thermal and mechanical shock resistance, and have low tensile strength. On the other hand, ceramic materials have very high elastic moduli, low densities, and can withstand very high temperatures. The last item is very important and is the real driving force behind the effort to produce tough ceramics. Consider the fact that metallic superalloys, used in jet engines, can easily withstand temperatures up to 800 °C and can go up to 1,100 °C with oxidation-resistant coatings. Beyond this temperature, one must use ceramic materials if they are available with the requisite toughness.

By far, the major disadvantage of ceramics is their extreme brittleness. Even the minutest of surface flaws (scratches or nicks) or internal flaws (inclusions, pores, or microcracks) can have disastrous results. One important approach to toughen ceramics involves fiber reinforcement of brittle ceramics. We shall describe the ceramic matrix composites in Chap. 7. Here we make a brief survey of ceramic materials, emphasizing the ones that are commonly used as matrices.

3.3.1 Bonding and Structure

Ceramic materials, with the exception of glasses, are crystalline, as are metals. Unlike metals, however, ceramic materials have mostly ionic bonding and some covalent bonding. Ionic bonding involves electron transfer between atomic species constituting the ceramic compound; that is, one atom gives up an electron(s) while another accepts an electron(s). Electrical neutrality is maintained; that is, positively charged ions (*cations*) balance the negatively charged ions (*anions*). Generally, ceramic compounds are stoichiometric; that is, there exists a fixed ratio of cations to anions. Examples are alumina (Al_2O_3), beryllia (BeO), spinels ($MgAl_2O_4$), silicon carbide (SiC), and silicon nitride (Si_3N_4). It is not uncommon, however, to have nonstoichiometric ceramic compounds, for example, $Fe_{0.96}O$. The oxygen ion (anion) is generally very large compared to the metal ion (cation). Thus, cations occupy interstitial positions in a crystalline array of anions.

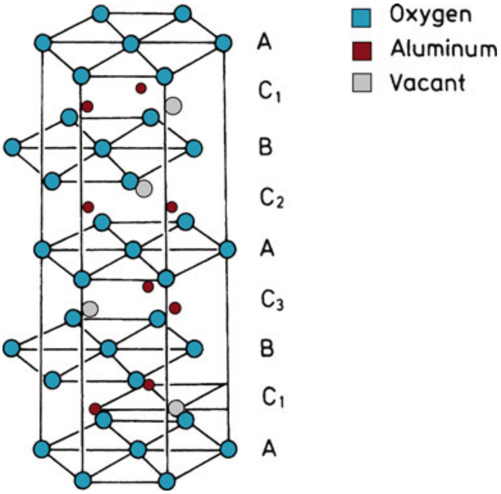

Fig. 3.17 Hexagonal close-packed structure of α-alumina. A and B layers contain oxygen atoms. C_1, C_2, and C_3 contain aluminum atoms. The C layers are only two-thirds full

Crystalline ceramics generally exhibit close-packed cubic and hcp structures. The simple cubic structure is also called the cesium chloride structure. It is, however, not very common. CsCl, CsBr, and CsI show this structure. The two species form an interpenetrating cubic array, with anions occupying the cube corner positions while cations go to the interstitial sites. Cubic close-packed is really a variation of the fcc structure described in Sect. 3.2. Oxygen ions (anions) make the proper fcc structure with metal ions (cations) in the interstices. Many ceramic materials show this structure, also called the NaCl or rock salt-type structure. Examples include MgO, CaO, FeO, NiO, MnO, and BaO. There are other variations of fcc close-packed structures, for example, zinc blende types (ZnS) and fluorite types (CaF). The hcp structure is also observed in ceramics. ZnS, for example, also crystallizes in the hcp form. Other examples are nickel arsenide (NiAs) and corundum (Al_2O_3). Figure 3.17 shows the hcp crystal structure of α-Al_2O_3. A and B layers consist of oxygen atoms while C_1, C_2, and C_3 layers contain aluminum atoms. The C layers are only two-thirds full.

Glass-ceramic materials form yet another important category of ceramics. They form a sort of composite material because they consist of 95–98 % by volume of crystalline phase and the rest glassy phase. The crystalline phase is very fine (grain size less than 1 μm in diameter). Such a fine grain size is obtained by adding nucleating agents (commonly TiO_2 and ZrO_2) during the melting operation, followed by controlled crystallization. Important examples of glass-ceramic systems include the following:

1. Li_2O-Al_2O_3-SiO_2: This has a very low thermal expansion and is therefore very resistant to thermal shock. Corningware is a well-known trade name of this class of glass-ceramic.
2. MgO-Al_2O_3-SiO_2: This has high electrical resistance coupled with high mechanical strength.

Ceramic materials can also form solid solutions. Unlike metals, however, interstitial solid solutions are less likely in ceramics because the normal interstitial sites are already filled. Introduction of solute ions disrupts the charge neutrality. Vacancies accommodate the unbalanced charge. For example, FeO has a NaCl-type structure with an equal number of Fe^{2+} and O^{2-} ions. If, however, two Fe^{3+} ions were to replace three Fe^{2+} ions we would have a vacancy where an iron ion would form.

Glasses, the traditional silicate ceramic materials, are inorganic solidlike materials that do not crystallize when cooled from the liquid state. Their structure (see Fig. 2.6) is not crystalline but that of a supercooled liquid. In this case we have a specific volume vs. temperature curve similar to the one for polymers (Fig. 3.2) and a characteristic glass transition temperature T_g. Under certain conditions, crystallization of glass can occur with an accompanying abrupt decrease in volume at the melting point because the atoms take up ordered positions.

3.3.2 *Effect of Flaws on Strength*

As in metals, imperfections in crystal packing of ceramics do exist and reduce their strength. The difference is that important defects in ceramic materials are surface flaws and vacancies. Dislocations do exist but are relatively immobile. Grain boundaries and free surfaces are important planar defects. As in metals, small grain size improves the mechanical properties of ceramics at low to medium temperatures.

Surface flaws and internal pores (Griffith flaws) are particularly dangerous for strength and fracture toughness of ceramics. Fracture stress for an elastic material having an internal crack of length $2a$ is given by the Griffith relationship:

$$\sigma_f = \left(\frac{2E\gamma}{a}\right)^{1/2},$$

where E is the Young's modulus and γ is the surface energy of the crack surface. Linear elastic fracture mechanics treats this problem of brittle fracture in terms of a parameter called the *stress intensity factor, K*. The stresses at a radius, r from the crack tip are given by

$$\sigma_{ij} = \left[\frac{K}{(2\pi r)^{1/2}}\right] f_{ij}(\theta),$$

where $f_{ij}(\theta)$ is a geometric function. Fracture occurs when K attains a critical value K_{Ic}. Yet another approach is based on the energy viewpoint, a modification of the Griffith idea. Fracture occurs, according to this approach, when the crack extension force G reaches a critical value G_{Ic}. For ceramic materials, $G_{\mathrm{Ic}} = 2\gamma$. It can also be shown that $K^2 = EG$ for opening failure mode and plane stress; that is, the stress intensity factor and the energy approaches are equivalent.

3.3.3 Common Ceramic Matrix Materials

Silicon carbide has excellent high-temperature resistance. The major problem is that it is quite brittle up to very high temperatures and in all environments. Silicon nitride is also an important nonoxide ceramic matrix material. Among the oxide ceramics, alumina and mullite are quite promising. Silica-based glasses and glass-ceramics are other ceramic matrices. With glass-ceramics one can densify the matrix in a glassy state with fibers, followed by crystallization of the matrix to obtain high-temperature stability.

Ceramic matrices are used to make fiber reinforced composites to achieve gains in fracture toughness. Gains in strength and stiffness are less important except in glass matrix composites. Table 3.7 summarizes some of the important characteristics of common ceramic matrix materials (Phillips 1983).

Table 3.7 Properties of some ceramic matrix materials

Material	Young's modulus (GPa)	Tensile strength (MPa)	Coefficient of thermal expansion ($10^{-6}\,K^{-1}$)	Density (g/cm^3)
Borosilicate glass	60	100	3.5	2.3
Soda lime glass	60	100	8.9	2.5
Lithium aluminosilicate glass-ceramic	100	100–150	1.5	2.0
Magnesium aluminosilicate glass-ceramic	120	110–170	2.5–5.5	2.6–2.8
Mullite	143	83	5.3	
MgO	210–300	97–130	13.8	3.6
Si_3N_4	310	410	2.25–2.87	3.2
Al_2O_3	360–400	250–300	8.5	3.9–4.0
SiC	400–440	310	4.8	3.2

Source: Adapted with permission from Phillips (1983)

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Problems

3.1. Ductility, the ability to deform plastically in response to stresses, is more of a characteristic of metals than it is of ceramics or polymers. Why?
3.2. Ceramic materials generally have some residual porosity. How does the presence of porosity affect the elastic constants of ceramic materials? How does it affect the fracture energy of ceramics?

3.3. Explain why it is difficult to compare the stress–strain behavior of polymers (particularly thermoplastics) with that of metals.

3.4. The mechanical behavior of a polymer can be represented by an elastic spring and a dashpot in parallel (Voigt model). For such a model we can write for stress

$$\sigma = \sigma_{\mathrm{el}} + \sigma_{\mathrm{visc}} = E_{\varepsilon} + \eta\,\mathrm{d}\varepsilon/\mathrm{d}t,$$

where E is the Young's modulus, ε is the strain, η is the viscosity, and t is the time. Show that

$$\varepsilon = \sigma/E[1 - \exp(-E/\eta)t].$$

3.5. What is the effect of the degree of crystallinity on fatigue resistance of polymers?

3.6. Discuss the importance of thermal effects (hysteretic heating) on fatigue of polymers.

3.7. Glass-ceramics combine the generally superior mechanical properties of crystalline ceramics with the processing ease of glasses. Give a typical thermal cycle involving the various stages for producing a glass-ceramic.

3.8. Silica-based glasses and many polymers have amorphous structure. An amorphous structure is characterized by a glass transition temperature. Explain why silica-based glasses have a much higher glass transition temperature than polymers.