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Materials

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12.1 Metals

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Introduction — Nature and Properties of Pure Metals

Metals achieve engineering importance because of their abundance, variety, and unique properties as conferred by metallic bonding. Twenty-four of the 26 most abundant elements in the Earth's crust are

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metals, with only two nonmetallic elements, oxygen and silicon, exceeding metals in frequency. The two most abundant metallic elements, iron (5.0%) and aluminum (8.1%), are also the most commonly used structural metals. Iron is the most-used metal, in part because it can be extracted from its frequently occurring, enriched ores with considerably less energy penalty than aluminum, but also because of the very wide range of mechanical properties its alloys can provide (as will be seen below). The next 15 elements in frequency, found at least in parts per thousand, include most common engineering metals and alloys: calcium (3.6%), magnesium (2.1%), titanium (0.63%), manganese (0.10), chromium (0.037%), zirconium (0.026%), nickel (0.020%), vanadium (0.017%), copper (0.010%), uranium (0.008%), tungsten (0.005%), zinc (0.004%), lead (0.002%), cobalt (0.001%), and beryllium (0.001%). The cost of metals is strongly affected by strategic abundance as well as secondary factors such as extraction/processing cost and perceived value. Plain carbon steels and cast irons, iron alloys with carbon, are usually most cost-effective for ordinary mechanical applications. These alloys increase in cost with alloying additions.

A variety of metal properties are unique among materials and of importance technologically. These properties are conferred by metallic bonding, in which the “extra” outer valence electrons are “shared” among all metal ion cores. This bonding is different from other types of solids in that the electrons are free to acquire energy, and the metallic ions are relatively mobile, and quite interchangeable with regard to their positions in the crystal lattice, the three-dimensional repeating arrangement of atoms in a solid. This section of the chapter will concentrate on the mechanical properties of metals, for which metallic bonding provides ductile deformation, i.e., shows substantial permanent shape change under mechanical load prior to fracture. The ductility of metals at low and moderate temperature makes them formable as solids and also confers safety (fracture toughness) in mechanical applications, in that under impact loading the metal will absorb energy rather than break catastrophically.

Metals are good conductors of heat and electricity because thermal and electrical energy can be transferred by the free electrons. These two properties tend to parallel each other. For example, the pure noble metals (e.g., copper, silver, gold, platinum) are among the best electrical and thermal conductors. As a broad generalization, metallic elements with an odd number of valence electrons tend to be better conductors than those with an even number. These behaviors can be seen in Table C.6A of the Appendix. Thermal conductivity and electrical resistivity (inverse conductivity) have a reciprocal relationship and follow the indicted trends. As metals are alloyed with other elements, are deformed, contain multiple phases, and contain crystalline imperfections, their electrical and thermal conductivity usually decreases significantly from that of the pure, perfect, unalloyed metal. The specific values of thermal conductivity and electrical resistivity for several common engineering alloys is given in Table C.6B of the Appendix. Electrical and thermal conductivities tend to decrease proportionately to each other with increasing temperature for a specific metal. These conductivities may be altered if heating introduces metallurgical change during annealing (see subsection on mechanical forming).

Metals are opaque to and reflective of light and most of the electromagnetic spectrum, because electromagnetic energy is transferred to the free electrons and immediately retransmitted. This gives most metals a characteristic reflective “metallic color” or sheen, which if the metal is very smooth yields a mirror surface. At very short wavelengths (high energies) of the electromagnetic spectrum, such as X rays, the radiant energy will penetrate the material. This is applied in radiographic analysis of metals for flaws such as cracks, casting porosity, and inclusions.

Metals are almost always crystalline solids with a regular repeating pattern of ions. A number of atomic-level defects occur in this periodic array. A large number of atomic sites are “vacancies” (point defects) not occupied by atoms (Figure 12.1.1). The number and mobility of vacant sites increase rapidly with temperature. The number and mobility of vacancies in metals are quite high compared with other materials because there are no charge balance or local electron bond considerations. This means that solid metal can undergo significant changes with only moderate thermal excitation as vacancy motion (diffusion) provides atom-by-atom reconstruction of the material. Vacancies allow solid metals to homogenize in a “soaking pit” after casting and permit dissimilar metals to diffusion bond at moderate temperatures and within short times. In the process, substitutional metallic atoms (ions) shown in Figure

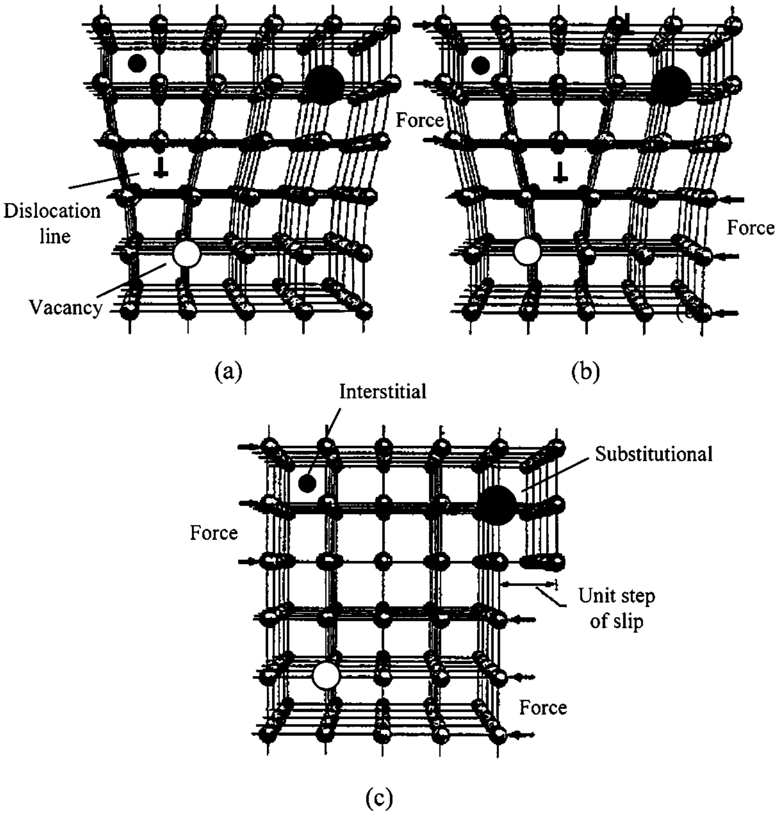

FIGURE 12.1.1 Point defects exist in the metal crystal structure: vacancies, substitutional atoms (ions), ions, and interstitial atoms (ions). A dislocation (⊥) line moves under an applied shear force until a surface step of plastic deformation is produced on the surface.

12.1.1 move via vacancy jumps while small interstitial atoms such as carbon (Figure 12.1.1) move from interstice to interstice. Vacancy mobility gives rise to major changes in mechanical properties during annealing (see subsection on mechanical forming) and is an important mechanism in creep deformation under load at elevated temperature (see subsection on corrosion and environmental effects).

At a slightly larger level, linear atomic packing defects known as dislocations, give rise to the ability of metallic materials to deform substantially under load. When a plane of atoms in the lattice ends, it gives rise to an edge "dislocation" such as that shown in Figure 12.1.1a. Such a dislocation can break and remake bonds relatively easily in a metal and thereby shift an atomic distance (Figure 12.1.1b). The process can continue until a surface step results. Many dislocations moving in this fashion can give rise to significant shape change in the material at moderate stresses. The onset of such massive dislocation motion in a metal is termed *yield* and occurs at the "yield stress" or "elastic limit" (see subsection on strength and deformation). Dislocations explain why the yield stress can be as low as about 100 Pa (10 psi) in a pure, pristine, single crystal of metal. Dislocations also explain how a fine-grained polycrystalline metal containing many microstructural features which interfere with dislocation motion may have a yield stress as great as 10 gPa (1000 ksi). Dislocations interact with each other in three dimensions and multiply. Therefore, dislocation motion can cause a major increase in dislocation density and yield stress, termed *cold work*. Vacancies can rearrange these dislocation tangles, restoring the metal to a condition closer to its original state, thereby lowering the yield stress. This can occur at moderate annealing temperatures (see subsection on mechanical forming).

The interaction of deformation, alloying elements, temperature, and time can cause a wide variety of microstructures in a solid metal down to near atomic levels with mechanical (and other) properties which can vary over a very wide range. It is possible to manipulate the properties of a single metal composition over a very wide range in the solid state — a behavior which can be used to mechanically form a particular metal and then use it in a demanding load-bearing application. The use of minor alloying additions can provide a yet wider range of properties with appropriate thermal and mechanical treatment.

Casting

One of the important technological advantages of metals is their ability to incorporate a wide variety of secondary elements in a particular metal and thereby create alloys of the metal. Alloying can increase the strength of a metal by several orders of magnitude and permit the strength and ductility to be varied over a wide range by thermal and/or mechanical treatment, resulting in ease of mechanical forming or resistance to deformation.

Several metal phases may exist together in the solid as grains (crystals), or secondary phases may occur as smaller entities on grain (intercrystal) boundaries or within grains. Often the strengthening phase is submicroscopic and cannot be detected by optical metallography (reflection optical microscopy). The size and distribution of secondary phases is manipulated by thermomechanical (thermal and/or mechanical) treatment of the solid metal as well as the original casting procedure.

Casting methods include expendable mold casting (investment/precision, plaster mold, dry sand, and wet sand casting), permanent mold casting (ingot, permanent mold, centrifugal, and die casting), and continuous casting (direct chill and “splat” casting). These are listed in approximate order of cooling rate in Figure 12.1.2. As cooling rate increases, the grain (crystal) size tends to be smaller and the strength increases while compositional segregation decreases, providing more uniform properties. At the extremely high casting rates (10^5 to 10^6/sec) of continuous splat casting, it is possible to produce homogeneous metals not possible in terms of phase diagrams, and many metals have been produced in the amorphous state, yielding unusual metallic glasses. Ingot casting and continuous direct chill casting are primarily used to produce solid metal which will be extensively mechanically formed to final shape. The other casting methods are used to produce shapes near final dimensions, but to varying extends may receive extensive machining, forming, or finishing prior to use. For the latter group, grain refiners are frequently added to reduce solidification grain size. Metal tends to solidify directionally, with grains elongated in the direction of heat flow. This gives rise to directional mechanical properties which should be accounted for in design.

Comparison of Casting Methods

	Solidification Rate	Grain Size	Strength	Segregation
Expendable mold	Slow	Coarse	Low	Most
Investment	↓	↑	↓	↑
Plaster mold	↓	↑	↓	↑
Dry sand	↓	↑	↓	↑
Green sand	↓	↑	↓	↑
Reusable mold	↓	↑	↓	↑
Ingot	↓	↑	↓	↑
Permanent mold	↓	↑	↓	↑
Centrifugal	↓	↑	↓	↑
Die cast	↓	↑	↓	↑
Continuous — direct chill	↓	↑	↓	↑
Continuous — splat cast	Fast	Fine	High	Least

FIGURE 12.1.2 The effects of casting speed (solidification rate) are compared.

To obtain optimum properties and prevent flaws which may cause failure, the casting procedure must avoid or control compositional segregation, shrinkage cavities, porosity, improper texture (grain directionality), residual (internal) stresses, and flux/slag inclusions. This can be accomplished with good casting practice. With the exception of investment (lost wax, precision) casting and to a lesser extent die casting, it is difficult to achieve very exacting tolerances and fine surface finish without postfinishing or forming of a casting.

Strength and Deformation, Fracture Toughness

Figure 12.1.3 shows a typical stress–strain diagram for a metal. The first portion is a linear, spring-type behavior, termed *elastic*, and attributable to stretching of atomic bonds. The slope of the curve is the "stiffness" (given for various metals in Table C.3 of the Appendix). The relative stiffness is low for metals as contrasted with ceramics because atomic bonding is less strong. Similarly, high-melting-point metals tend to be stiffer than those with weaker atomic bonds and lower melting behavior. The stiffness behavior is frequently given quantitatively for uniaxial loading by the simplified expressions of Hooke's law:

$$\varepsilon_x = \sigma_x / E \qquad \varepsilon_y = \varepsilon_z = -\upsilon \sigma_x / E \tag{12.1.1}$$

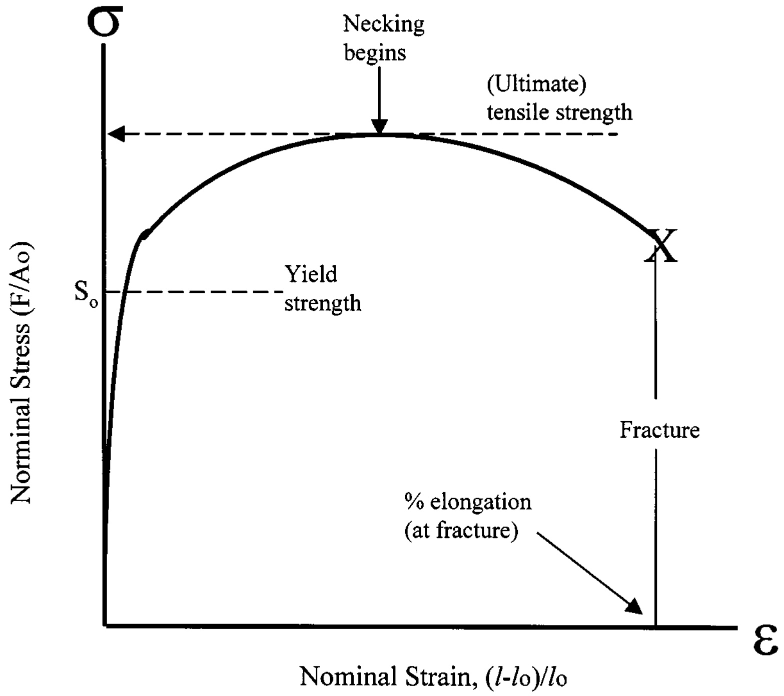

FIGURE 12.1.3 Typical engineering stress–strain curve for a metal.

Where σ_x is the stress (force per unit area, psi or Pa) in the x direction of applied unidirectional tensile load, ε_x is the strain (length per unit length or percent) in the same direction ε_y and ε_z are the contracting strains in the lateral directions, E is Young's modulus (the modulus of elasticity), and υ is Poisson's ratio. Values of the modulus of elasticity and Poisson's ratio are given in Table C.6A of the Appendix for pure metals and in C.6B for common engineering alloys. It may be noted that another property which depends on atomic bond strength is thermal expansion. As the elastic modulus (stiffness) increases with atomic bond strength, the coefficient of linear expansion tends to decrease, as seen in Table C.6.

The relationship of Equation (12.1.1) is for an isotropic material, but most engineering metals have some directionality of elastic properties and other structure-insensitive properties such as thermal expansion coefficient. The directionality results from directional elongation or preferred crystal orientation, which result from both directional solidification and mechanical forming of metals. In most cases two elastic moduli and a Poisson's ratio are required to fully specify behavior. A principal modulus might be given in the rolling direction of sheet or plate with a secondary modulus in the transverse direction. A difference of 2 to 5% should ordinarily be expected, but some metals can show an elastic modulus difference as great as a factor of 2 in the principal directions of heavily formed material. Such directional differences should be accounted for when spring force or dimensional tolerance under load (or change of temperature) is critical in a design.

At a critical stress the metal begins to deform permanently, as seen as a break in the straight-line behavior in the stress-strain diagram of Figure 12.1.3. The stress for this onset is termed the yield stress or elastic limit. For engineering purposes it is usually taken at 0.2% plastic strain in order to provide a predictable, identifiable value. An extensive table of yield values and usual applications for commercial metals and alloys is given in Appendix C.5. In the case of steel a small yield drop allows for clear identification of the yield stress and this value is used. The onset of yield is a structure-sensitive property. It can vary over many orders of magnitude and depends on such factors as grain size and structure, phases present, degree of cold work, and secondary phases in grains or on grain boundaries as affected by the thermal and mechanical treatment of the alloy. The extension to failure, the ductility, and maximum in the stress–strain curve, the "ultimate stress" or "tensile strength" (see Appendix C.5) are also structure-sensitive properties. The strength and specific strength (strength-to-weight ratio) generally decrease with temperature.

The ductility usually decreases as the strength (yield or ultimate) increases for a particular metal. Reduction in the grain size of the metal will usually increase yield stress while decreasing ductility (Figure 12.1.4). Either yield or ultimate strength are used for engineering design with an appropriate safety factor, although the former may be more objective because it measures the onset of permanent deformation. Ductility after yield provides safety, in that, rather than abrupt, catastrophic failure, the metal deforms.

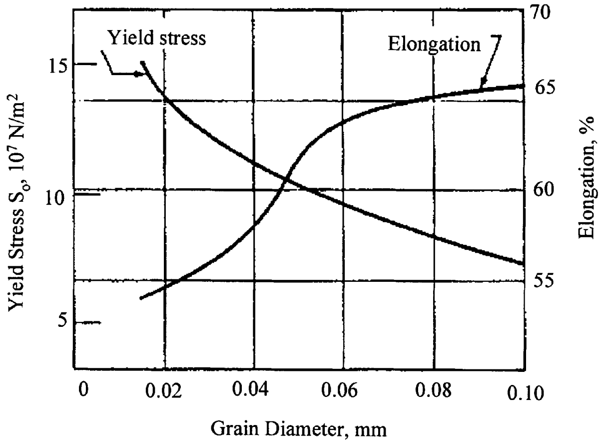

FIGURE 12.1.4 The effect of grain (crystal) size on yield stress and elongation to failure (ductility) for cartridge brass (Cu–30 Zn) in tension.

A different, independent measure is needed for impact loads — "toughness." This is often treated in design, materials selection, and flaw evaluation by extending Griffith's theory of critical flaw size in a brittle material:

$$\sigma_f = K_{1c}/\gamma c^{1/2} \qquad (12.1.2)$$

where σ_f is the failure stress, K_{Ic} is a structure-sensitive materials property, the "fracture toughness" or "stress intensity factor" for a normal load, γ is a constant depending on orientation, and c is the depth of a long, narrow surface flaw or crack (or half that of an internal flaw). This is a separate design issue from that of strength. It is of particular importance when a metal shows limited ductility and catastrophic failure must be avoided. In some applications the growth of cracks, c is monitored to prevent catastrophic failure. Alternatively, as a performance test sufficient energy absorption as characteristic of a metal is determined when it is fractured in a Charpy or Izod impact test. Many metals will show a rapid decline in such energy absorption below a nil ductility temperature (NDT), which may establish a lowest use temperature for a particular metal in a particular state and for a particular application. Welds are often qualified by impact tests as well as strength testing. Care must be taken to apply the impact test appropriate to an application.

Hardness, the resistance of the near surface of a metal to penetration by an indentor, is also employed as a mechanical test. Increased hardness can often be correlated with an increase in yield and ultimate strengths. Typical hardness values for a large number of commercial metals and alloys are provided in Appendix C.5. A hardness indent is frequently done to "determine" the strength of a steel, using "equivalency" tables. Great caution must be taken in applying such tables because while hardness is an easy test to perform, it measures a complex and interactive set of properties, increasing with strength, elastic modulus, and work hardening rate. It is also an observation of surface properties which may not be characteristic of the bulk metal — particularly thick-gauge steel used in tension. Surface-hardening treatments can make the simplistic use of an "equivalency" table particularly dangerous. Application to nonferrous metals is also problematic. If a hardness tested part is to be put into service, the placement of hardness indents (surface flaws) can cause permanent failure.

A summary of important engineering metals can be found in Appendix C.5. This extensive table provides strength, hardness, and applications information for many commercial metals in varied heat treatments.

Mechanical Forming

Hot working is used when major shape change, cross-section reduction, or texture (directional) properties are desired. Cold working is preferred when close tolerances and fine surface finish are needed. The cold-worked form of a metal typically shows higher yield and tensile strength, as can be seen for several alloys listed in Appendix C.5. Rolling, forging, and extrusion are primarily done hot, while shape drawing, extrusion, deep drawing, stretching, spinning, bending, and high-velocity forming are more commonly performed cold. Hot rolling between parallel rollers is used to reduce ingots to plates, sheets, strips, and skelp, as well as structural shapes, rail, bar, round stock (including thick-walled pipe), and wire. Sheet metal and threads on round or wire stock may be rolled to shape cold. Closed die hot forging employs dies with the final part shape, while open die forging (including swaging and roll forging) uses less-shaped dies. Coining, embossing, and hobbing are cold-forging operations used to obtain precision, detailed surface relief or dimensions. Generally, extrusion and die drawing require careful control of die configuration and forming rate and, in the latter case, lubricant system. Impact extrusion, hydrostatic extrusion, and deep drawing (thin-walled aluminum cans) permit very large precise dimensional and cross-section changes to be made cold in a single pass. Stretching, spinning, bending are usually used to shape sheet or plate metal and the spring-back of the metal due to elastic modulus must be accounted for to obtain a precise shape.

Solute, Dispersion, and Precipitation Strengthening and Heat Treatment

Alloying additions can have profound consequences on the strength of metals. Major alloying additions can lead to multiphase materials which are stronger than single-phase materials. Such metal alloys may also give very fine grain size with further strengthening of material. Small alloying additions may also substantially increase strength by solute strengthening as solid solution substitutional or interstitial atoms and or by particle strengthening as dispersion or precipitation hardening alloys.

Substitutional solute strengthening of copper by various atoms is shown in Figure 12.1.5. As the amount of an alloying element in solution increases, the strength increases as disloctions are held in place by the "foreign" atoms. The greater the ionic misfit (difference in size — Sn is a much larger ion than Ni), the greater the strengthening effect. The strength increase can be quite dramatic — as much as a 20-fold increase with a 1.5% addition to copper. Alternatively, a large addition of a very soluble element such as nickel can give major strengthening — monel, the Cu–70Ni alloy is more than four times stronger than pure copper (Figure 12.1.6). Interstitial solid solution carbon contributes to the strength of iron and is one contributor to strength in steels and cast irons. Solute strengthening can become ineffective in strengthening at elevated temperature relative to the absolute melting point of a metal as a result of rapid diffusion of substitutional and interstitial elements. The addition of more than one solute element can lead to synergistic strengthening effects, as this and other strengthening mechanisms can all contribute to the resistance of a metal to deformation.

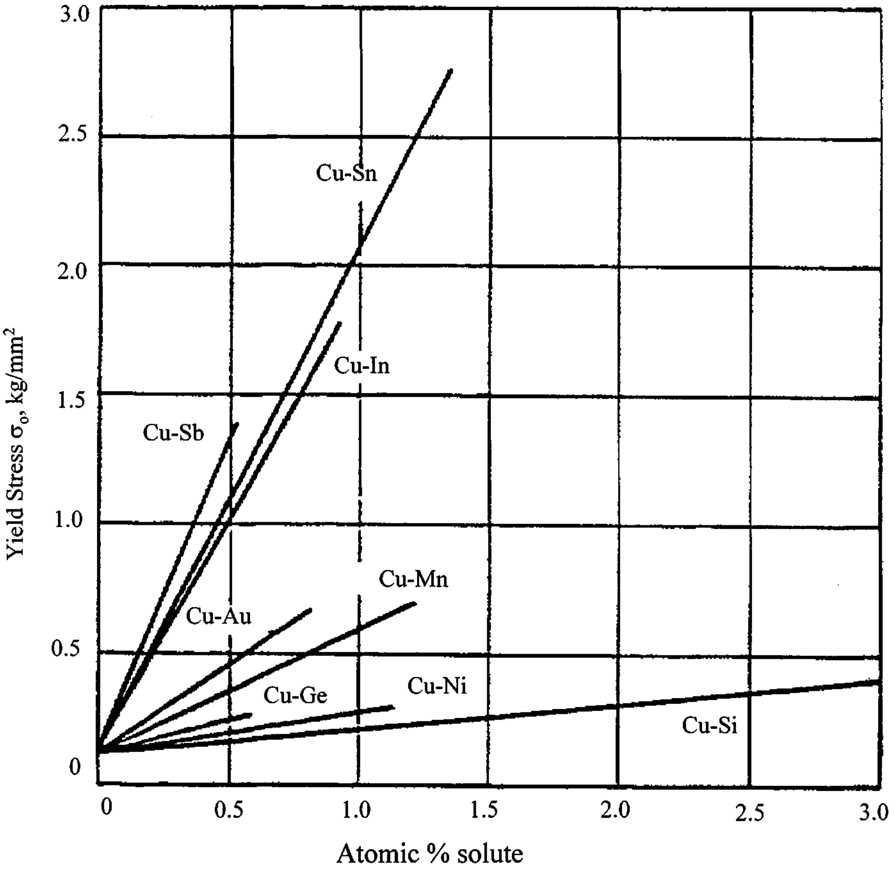

FIGURE 12.1.5 Effect of various substitutional atoms on the strength of copper. Note that as the ionic size of the substitutional atom becomes larger the strengthening effect becomes greater.

Ultrafine particles can also provide strengthening. A second phase is introduced at submicroscopic levels within each crystal grain of the metal. This may be done by a variety of phase-diagram reactions, the most common being precipitation. In this case the solid alloy is heated to a temperature at which the secondary elements used to produce fine second-phase particles dissolve in the solid metal — this is termed *solution heat treatment*. Then the metal is usually quenched (cooled rapidly) to an appropriate

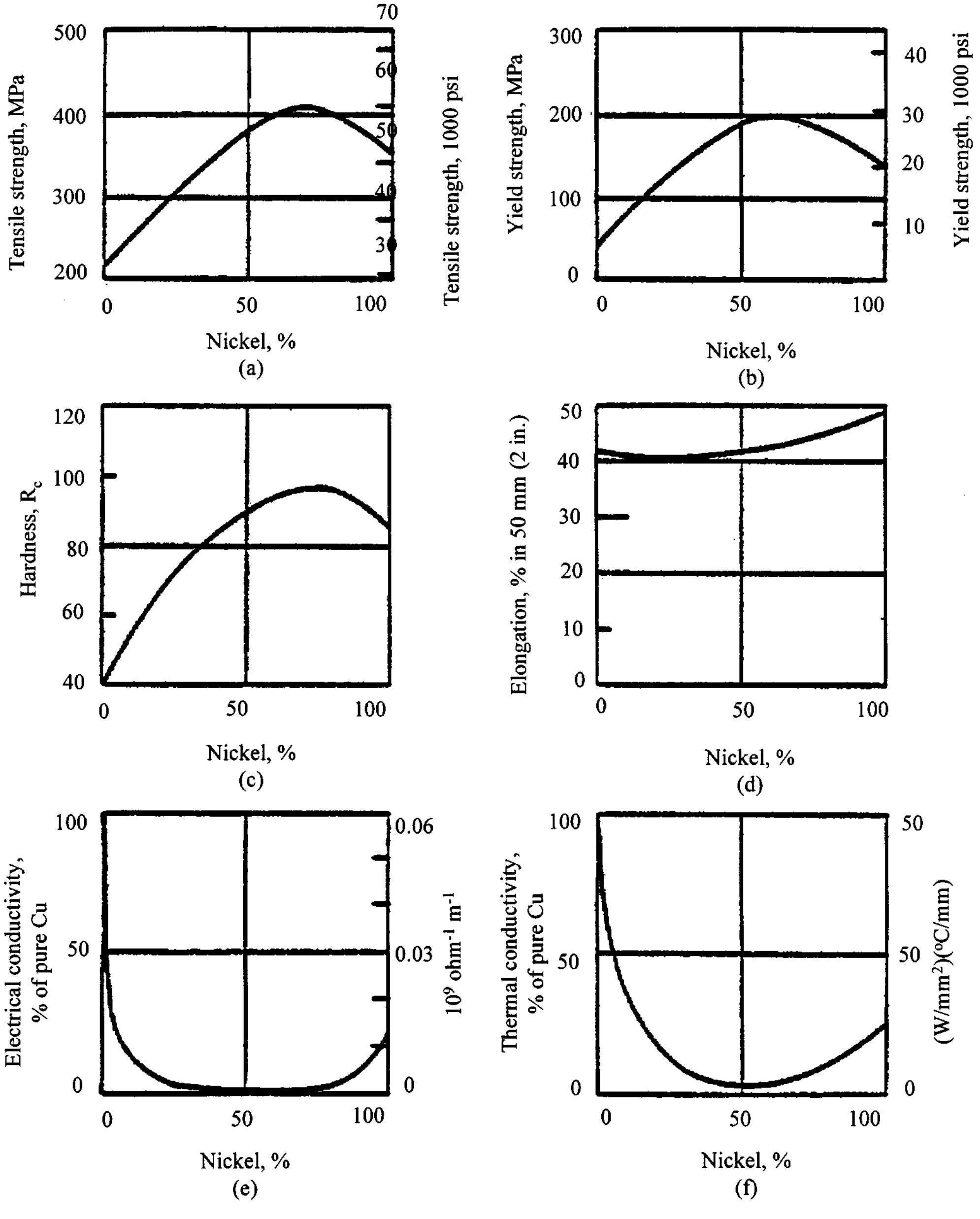

FIGURE 12.1.6 Variation in properties for copper–nickel random solid solution alloys. Note that over time at low temperature alloys (monel) may become nonrandom with significant strength increases.

temperature (e.g., room temperature or ice brine temperature) and subsequently held at an elevated temperature for a specified "aging" time during which particles precipitate and grow in size at near atomic levels throughout the solid metal. Temperature, time, alloy composition, and prior cold work affect the size and distribution of second-phase particles. The combination of treatments can be quite complex, and recently "thermomechanical treatments" combining temperature, time, and dynamic working have resulted in substantial property improvements. Heat treatment can be performed by the user, but it is difficult to achieve the optimum properties obtained by a sophisticated metallurgical mill. The heat treatment can manipulate structure and properties to obtain maximum strength or impact resistance. When metal is to be cold worked, a "softening treatment" can be employed which provides low yield stress and high ductility. The difference between the “dead soft” and maximum strength conditions can be over an order of magnitude — a useful engineering property change.

Alternative surface diffusion methods such as nitriding and carburizing, which introduce particles for fracture and wear resistance, are presented in the subsection on metal surface treatments.

In the case of dispersion strengthening (hardening), the fine strengthening particles are a discontinuous second phase without atomic continuity with the matrix. The behavior of such particles is shown schematically in Figure 12.1.7a as a function of increasing aging time or aging temperature (fixed time) which result in larger, more widely spaced dispersed-phase particles. Under stress, dislocations must move around (bypass) such particles, so that yield strength decreases with increased aging. Long aging times may be used to decrease yield strength (“soften”) of the metal for fabrication. A short aging time, would be used for maximum strength. The dispersed phase can also provide some enhancement of ductility. A dispersion-strengthened metal for which the dispersed phase is stable at elevated temperatures can provide both high-temperature strength and creep resistance (subsection on high-temperature effects). Surface diffusion treatments usually produce dispersion hardening.

Precipitation strengthening (hardening) employs particles which have at least some atomic continuity with the matrix metal. Thus, when the metal is deformed, dislocations can either bypass or pass through (cut) the particles. The resulting behavior is shown in Figure 12.1.7b. As aging time or temperature increases (particles grow larger and more widely spaced), the yield stress increases to a maximum and then decreases. The maximum is termed *critically aged*, and when this designation is part of an alloy treatment, precipitation strengthening may be assumed. For fabrication by cold working, the lower-strength, higher-ductility *underaged* condition is usually employed. There are different possible combinations of thermal and mechanical treatment which will provide a maximum critical aging treatment. Usually the best optimum for strength is given in handbooks and data sheets. However, improved treatments may be available, particularly of the combined thermomechanical type.

Strengthening of Steels and Steel Heat Treatment

Steels, perhaps the most important of all engineering metals, are alloys of iron and carbon usually containing about 0.02 to 1.0 $^w/_o$ carbon. The binary Fe–C phase diagram is important in describing this behavior and is shown in Figure 12.1.8. This diagram shows what phases and structures will occur in quasi equilibrium at various carbon contents and temperatures (under atmospheric pressure). Steel forming and heat treatment center on the transformation from austenite, γ phase, at elevated temperature to ferrite (α phase) plus cementite (iron carbide, Fe_3C) below 727°C (1340°F), the Ac_1 temperature, a eutectoid transformation. If there are no other intentional alloying elements, the steel is a “plain carbon” steel and has an AISI (American Iron and Steel Institute) designation 1002 to 10100. The first two characters indicate that it is a plain carbon steel, while the latter characters indicate the “points” of carbon.* Alloy steels, containing intentional alloying additions, also indicate the points of carbon by the last digits and together with the first digits provide a unique designation of alloy content. In the phase diagram (Figure 12.1.8) iron carbide (Fe_3C, cementite) is shown as the phase on the right. This is for all practical purposes correct, but the true thermodynamically stable phase is graphite (C) — relevant when the eutectic at 1148°C (2048°F) is used to produce cast irons (alloys greater than 2 $^w/_o$ C).

The solid-state eutectoid transformation is promoted by the magnetic effect in iron as nonmagnetic austenite transforms below the eutectoid (Ac_1) temperature to the two magnetic solid phases ferrite (iron with solid solution carbon) and cementite solid phase.** At the eutectoid composition, 0.77 $^w/_o$ carbon,

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* Plain carbon steels contain about 0.2 $^w/_o$ Si, 0.5 $^w/_o$ Mn, 0.02 $^w/_o$ P, and 0.02 $^w/_o$ S.

** It should be noted that austenitic stainless steels (300 and precipitation hardening, PH, series designations), nonmagnetic alloys with considerable chromium and nickel content to provide corrosion resistance, do not ordinarily transform from austenite to the lower-temperature phases. They are not intentionally alloyed with carbon, are not magnetic, and do not show the phase transformation strengthening mechanisms of steels. The term *steel* is something of a misnomer for these alloys.

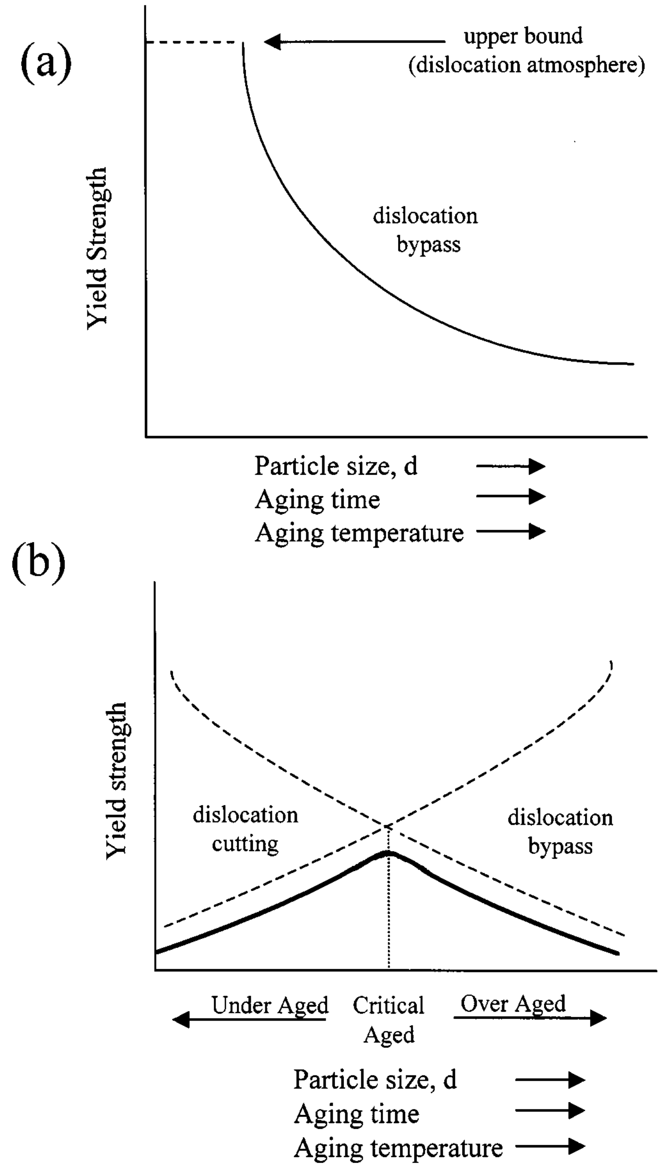

FIGURE 12.1.7 Effect of aging on dispersion- and precipitation-strengthened alloys for a fixed second–phase addition. (a) Dispersion strengthening: as aging time or temperature increases (dispersed phase particles larger and more separated), yield strength increases. A lower bound exists for near atomic size particles. (b) Precipitation hardening: two behaviors can occur giving a composite curve with a maximum at the critical aging time or temperature (optimum size and spacing of particles).

the two phases form as a fine alternating set of plates (lamellae) termed *pearlite* because of their pearllike appearance in a metallographic microscope. This two-phase structure of metal (ferrite) and carbide (cementite) provides strength (very slowly cooled — about 65 ksi, 14% tensile elongation), which increases as a more-rapid quenching yields a finer pearlite microstructure (to about 120 ksi). As strength increases, ductility and fracture toughness decrease. With yet more rapid quenching and more local atomic diffusion, the austenite transforms to bainite, a phase of alternating carbon and iron-rich atomic planes. This has yet higher strength (to about 140 ksi) and lower ductility. When the metal is quenched so rapidly that carbon diffusion is prevented, the austenite becomes unstable. Below a critical temperature,

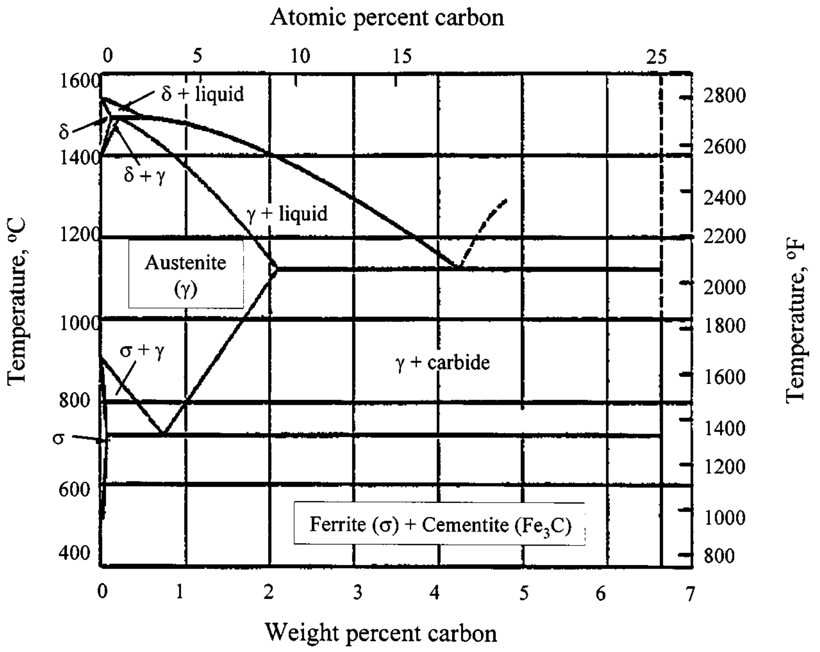

FIGURE 12.1.8 Iron–carbon phase diagram relevant for steel. The steel composition range is from about 0.02 to 1.00 ${}^{w}/_{o}$ carbon. Steel strengthening treatments require heating into the austenite region (above the Ac_3) and then quenching.

the martensitic start temperature (M_s), the metal transforms spontaneously by shear to martensite. Full transformation occurs below the martensite finish temperature (M_f). The formation of this hard phase introduces enormous microscopic deformation and residual stress. The strength is very much higher (about 300 ksi) but there is almost no ductility. This rapidly cooled material can spontaneously fail from “quench cracking,” which results from residual stresses and the martensite acting as an internal flaw. To relieve stresses and provide some fracture toughness, martensitic steel is “tempered” at an intermediate temperature such as 500°C for about an hour to provide some ductility (about 7%) while sacrificing some strength (about 140 ksi). Tempering for shorter times or at lower temperatures can give intermediate properties. High-carbon steels are often used for cutting tools and forming dies because of their surface hardness and wear resistance. When a high-carbon steel (>0.7 ${}^{w}/_{o}$ C) requires fabrication at lower temperature, it may be held at a temperature just under the eutectoid for an extended time (e.g., for 1080 steel: 700°C, 1300°F — 100 hr) either after or without quenching to provide a soft condition (<60 ksi, 20% extension). A variety of different quenching temperatures, media, and procedures can be used to vary required combinations of the microstructures above and mechanical properties. The discussion above centered on eutectoid steel and holds for other high-carbon steels. Increasing carbon content favors the formation of martensite in steels, thereby providing increased strength, hardness, and wear resistance. However, such steels can be quite brittle.

At lower carbon content, “primary ferrite” forms (Figure 12.1.8) as the steel is quenched from above the boundary of austenitic (γ) region, the Ac_3. Subsequently, pearlite (ferrite and cementite), bainite, and/or martensite can form. Lower carbon content increases the amount of primary ferrite, a weaker/ductile phase, and decreases the tendency to form martensite, a stronger/brittle phase. The result is a more fracture tough, ductile (“safer”) steel, but strength is lower. Such steels are also mechanically more forgiving if welded. Thus, a 1010 steel (0.10 ${}^{w}/_{o}$ C) might be used for applications where extreme “formability” and “weldability” are required, such as for car bodies and cans, while a 1020 steel (0.20 ${}^{w}/_{o}$ C) might be used for construction materials for which some increased strength is desired while maintaining safety. A medium-carbon steel such as a 1040 would be used when a balance of strength and toughness (and ease of welding) is needed.

In order to quench (and temper) steels continuous cooling transformation (CCT) diagrams are used such as that in Figure 12.1.9 for a 1040, medium-carbon steel. The steel is quenched from above the Ac_3. Vertical lines indicate quenching rates as shown in the lower left inset of the diagram. The cooling rate for the center of a round bar of given diameter quenched in air, oil, and water is given below the diagram. Solid lines on the diagram indicate percent transformation (start, 10%, 50%, 90%, finish of transformation), and a dotted line separates the region where primary ferrite forms from that of transformation to pearlite. The lower diagram shows the indentation hardness to be expected, as this and other mechanical behavior can be predicted from the CCT curve. As an example, the center of a 15 mm ($\sim ^1/_2$ in.) diameter bar quenched in air would be about 25% primary ferrite and 75% fine pearlite, with a Rockwell C hardness (HRC) of about 15. If quenched in oil, the bar center would be chiefly bainite with a small amount of martensite (HRC $\cong$ 25). The same bar quenched in water would be all martensite (HRC $\cong$ 55) before tempering. The transformation at other positions in the bar and for other engineering shapes (sheet, pipe, square rod, etc.) can be obtained from conversion curves.

It should be noted that layers in the steel closer to the quenched surface cool more quickly and are therefore displaced toward the left of the CCT diagram. There is a variation in structure and mechanical properties from the quenched surface to the center. One result is that the surface of the steel tends to be stronger, harder, and more wear resistant than the center. A steel beam undergoing bending has maximum strength at the near surface which undergoes the greatest stresses, while the center provides safety because of its relative fracture toughness and ductility. A thin knife edge cools quickly and can be resistant to deformation and wear, while the thick back prevents the blade from snapping in half when bent.

Many elements may be incorporated in steels to promote specific properties. Almost all common additions (other than cobalt) tend to promote strengthening by the formation of martensite (or bainite) instead of pearlite. When alloying additions tend to promote martensite throughout a thick section independent of cooling rate, the alloy is said to have *high hardenability.* Some elements such as chromium, molybdenum, and nickel also may help to provide high-temperature strength and environmental resistance. One class of alloys with relatively small alloying additions are termed *HSLA* steels (high strength, low alloy) and usually show somewhat superior mechanical properties to their plain carbon steel equivalents. As steel is alloyed, the relative cost increases substantially. A useful strategy in steel selection (and steels are usually the first engineering candidate on a cost basis) is to start by determining if a medium-carbon steel will do. If greater safety and formability are needed, a lower carbon content may be used (with slightly lower cost); alternatively, a higher-carbon steel would be chosen for greater strength and wear resistance. Heat treatment would be used to manipulate the properties. If plain carbon steels prove unsatisfactory, the HSLA steels would be the next candidate. For very demanding applications, environments, and long-term operations, specialty alloy steels would be selected insofar as they are cost-effective.

Fatigue

Fatigue is the repeated loading and unloading of metal due to direct load variation, eccentricity in a rotating shaft, or differential thermal expansion of a structure. Even substantially below the yield point (elastic limit) of a metal or alloy this repeated loading can lead to failure, usually measured in terms of the number of cycles (repeated load applications) to failure. Some studies have suggested that well over 80% of all mechanical failures of metal are attributable to fatigue.

High-stress, low-cycle fatigue usually occurs at stresses above the yield point and lifetimes are tens or hundreds of cycles (to about a thousand cycles). Failure occurs as a result of the accumulation of plastic deformation, that is, the area (energy) under the stress–strain curve (Figure 12.1.3). A simple lifetime predictive equation can be used to predict lifetime:

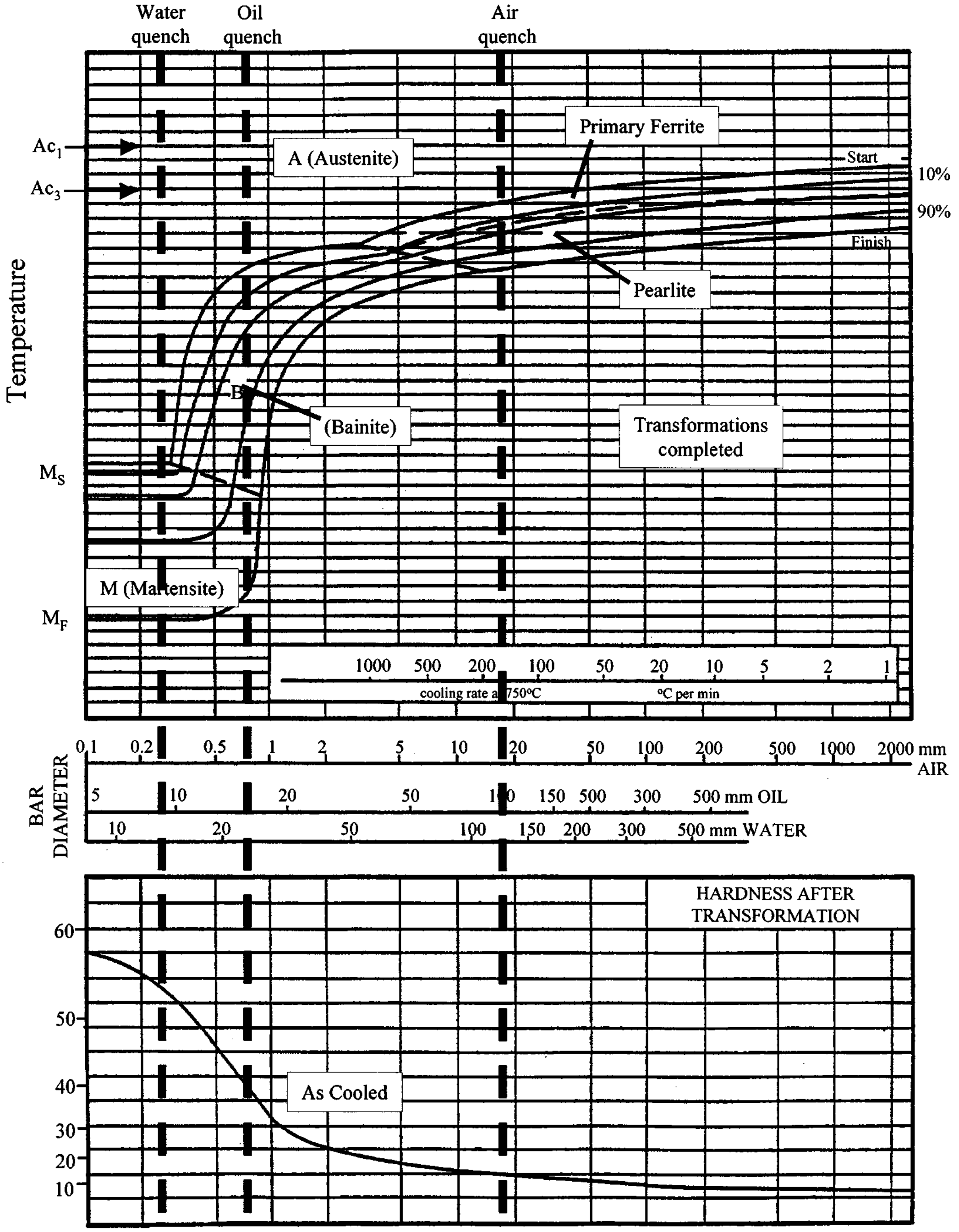

FIGURE 12.1.9 CCT diagram for 1040 steel. A 15-mm round bar air quenched from above the Ac_3 will be chiefly fine pearlite (ferrite and iron carbide, cementite) with about a quarter of the structure primary ferrite at the center. Quenching in oil will yield bainite with about 10% martensite. Water quenching will produce wholly martensite at the center. (After Atkins, M., *Atlas of Continuous Cooling Transformation Diagrams for Engineering Steels,* ASM International, Materials Park, OH, 1980.)

$$N \approx \left[\varepsilon_u / 2\varepsilon_{\mathrm{pf}}\right]^2 \tag{12.1.3}$$

where N is the number of cycles to failure, ε_u is total strain from the stress–strain curve, and $\varepsilon_{\mathrm{pf}}$ is the plastic strain amplitude in each fatigue cycle.

More commonly, metals are used well below their yield point and fail after many, many cycles of repeated loading in low-stress, high-cycle fatigue. There is microscopic, local plastic deformation (cold working) and vacancy generation (recovery effects) during such cyclic loading which result in "fatigue hardening" (strengthening) of unworked metal and "fatigue softening" of unworked metal. Some have even found success relieving residual stressed with a vibratory anneal. Early in the fatigue process surface flaws or in some cases severe internal flaws begin to propagate. The fatigue crack propagates in areas of high stress a small, usually submicroscopic, distance with each tensile loading. The propagation on each cycle frequently leaves identifiable marking on the failure surface termed *fatigue striations* which mark the progress of the subcritical crack. When the crack becomes so large that the fracture toughness criterion is exceeded (Equation 12.1.2), catastrophic overload failure occurs. When the future fatigue loading can be predicted and the cyclic crack propagation rate is known, fatigue cracks can be inspected or monitored in different applications such as aircraft structures and pressure vessels to decommission or replace parts before fatigue failure. This must be done cautiously because a change to a more aggressive (corrosive, oxidative, elevated temperature) environment can increase the crack propagation rate. If a harmonic resonance occurs in the metal part, vibratory maxima can cause premature fatigue failure. Harmonics can change as fatigue cracks propagate. Harmonic vibration can be prevented with vibratory (dynamic) design concepts and/or direct monitoring.

Figure 12.1.10 shows typical metal *S–N* curves (stress vs. number of cycles to failure) for a high-strength aluminum and for a titanium alloy. Note that the convention is to make stress the vertical axis and to plot the number of cycles to failure on a logarithmic scale. For high-stress, low-cycle fatigue ($<10^3$ cycles) the curve is flat and linear, consistent with the model of Equation12.1.3. For high cycle fatigue the lifetime is a rapidly varying function of stress until very low stresses (long lifetimes occur). The actual fatigue life varies statistically about the mean value shown in approximate proportion to the number of cycles to failure. These curves are for testing in ambient air. Fatigue life would be longer in an inert environment and may be shortened drastically in an aggressive environment. Iron- and titanium-based alloys, such as the example shown, usually have an "endurance limit," a stress below which lifetime is ostensibly infinite. In air, at room temperature, the endurance limit is about half the tensile strength for most iron and titanium alloys. Other metals appear to show no stress below which they last indefinitely. Therefore, a "fatigue limit" is designated — usually the stress at which the fatigue life is 10^8 cycles. This may be a long lifetime or not depending on the frequency of loading and engineering lifetime. The fatigue limit is generally about 0.3 times the tensile strength for metals with strengths below about 100 ksi (700 MPa). The factor is somewhat poorer for higher-strength metals. It is apparent that on a relative strength basis, iron- and titanium-based alloys are fatigue-resistant metals when compared with others. Dispersion-strengthened alloys have been seen to provide some lifetime advantage in fatigue.

A number of mathematical relationships have been proposed to predict fatigue life, but none works with complete success and all require experimental data. Perhaps the most successful of the so-called fatigue "laws" are the "cumulative damage" laws. The simplest is Miner's law:

$$\sum i\left[n_i / N_i\right] = 1 \tag{12.1.4}$$

where n_i is the number of cycles applied and N_i is the number of cycles for failure at a particular stress level, σ_i. The conceptual basis is that the number of fatigue cycles at a stress level uses up its relative fraction of total fatigue lifetime and may be correlated to fatigue crack propagation (striation spacing). Modifications of this model account for the order and relative magnitude of loads. Several techniques

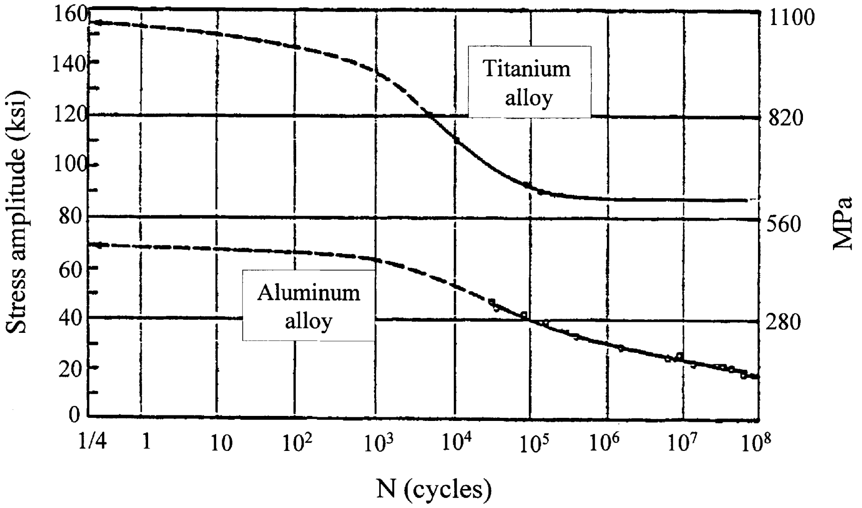

FIGURE 12.1.10 *S–N* (fatigue) curves for high-strength titanium (upper curve) and aluminum alloys. Note that titanium (and iron) alloys show an endurance limit, a stress below which the metal lasts indefinitely.

have met with partial success in increasing fatigue lifetime beyond that predicted by the cumulative damage models:

1. Coaxing — intermittent or continuous, superimposed vibration at very low stress,
2. Overstressing — intermittent or superimposed compressive loading,
3. Surface compression — intermittent shot peening or surface rolling,
4. Surface removal — chemical or mechanical surface polishing.

All but 1 are thought to close or eliminate fatigue cracks and surface damage. Coaxing has been said to introduce more of the vacancy-related recovery effects associated with fatigue.

High-Temperature Effects — Creep and Stress Rupture

Elevated temperature can cause a significant loss of strength and elastic modulus, so that a metal part may fail as a result of overheat even at loads which appear small at room temperature. High temperature is a relative matter and is usually judged as a fraction of the melting point measured on the absolute temperature scale. Thus, even moderate temperature excursions can be important for low-melting-point metals and alloys. As indicated in several sections above, many alloying and cold work strengthening methods depend upon heat treatment; an alloy can undergo metallurgical change due to overheat or to long-term holds at moderate temperatures and thereby alter properties significantly. Thus, the thermal stability of the microstructure should be determined. For example, metallographic replica techniques have been developed for determining in the field if microstructure has coarsened, making the metal weak.

Creep deformation is the continued deformation of a metal under load at elevated temperature, usually at a design stress well below the yield point. While measurable creep can occur at low temperatures over very long times or at very high (compressive) loads, creep usually becomes of engineering importance above about two thirds the melting point (absolute) of an alloy. Thus, both lead, which creeps at room temperature, and tungsten, which creeps in an incandescent light bulb at white heat, require a mechanical support or creep-resistant alloying additions. Figure 12.1.11 shows a schematic creep curve plotting creep strain* vs. time, *t*, at a particular tensile load and temperature. After the immediate elastic

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* If a constant extension is applied to an object, the force it generates will decline over time due to creep. This is called *stress relaxation* and can be treated in a similar way.

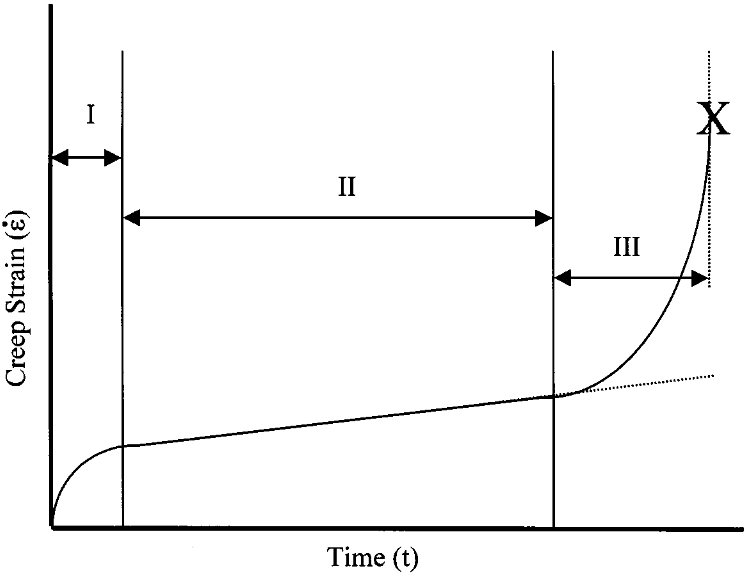

FIGURE 12.1.11 Schematic creep curve showing transient creep (I), steady-state creep (II), and tertiary creep (III). Note that the slope of the straight-line portion is the steady-state creep rate (minimum creep rate).

strain (t = 0), "transient creep" occurs in Region I. At elevated temperature this usually follows a $t^{1/3}$ behavior (Andrade creep). The majority of the curve has a straight-line behavior (Region II) in which the extension with time is constant. The slope of this part of the curve is termed the *steady-state strain rate* or *minimum creep rate*. It is used to calculate the creep extension which could cause functional failure when dimensional tolerances are exceeded. A simplified predictive model is

$$\varepsilon' = A\sigma^m e^{-h/kT} \tag{12.1.5}$$

where ε' is the minimum creep rate, A is a constant, σ is the applied stress, m is the stress dependence exponent (often 4 to 8), h is the activation enthalpy for creep, and T the absolute temperature.

In Region III the creep rate accelerates as the metal necks down severely in a local area, thereby increasing the local stress. The steady-state rate would continue (dotted line) if the load were adjusted to give constant load at the minimum cross section. Since loads do not readjust to compensate for necking in real applications, a final accelerated stage can be experienced. For example, a blowout can occur in late creep of a pressurized high-temperature piping system. The time to failure is termed the *stress rupture lifetime*. Predictive models are developed from Equation (12.1.5) to provide lifetime information.

Lowering use temperature or applied stress decreases susceptibility to creep deformation and increases stress rupture lifetime. Frequently, a moderate temperature decrease is most effective in this regard. Higher-melting-point metals are more creep resistant, so that the refractory metals tungsten and molybdenum can be used but require an inert atmosphere or protective coating to prevent rapid oxidation. In air or other active atmosphere, niobium-, nickel-, titanium-, and iron-based alloys may be used for creep resistance. Dispersion hardening, particularly with a high-temperature stable phase, such as an oxide, nitride, or carbide, can confer a degree of creep resistance.

Corrosion and Environmental Effects

Corrosion usually involves the slow removal of metal due to chemical and/or electrochemical reaction with an environment. Most metallic corrosion involves a galvanic, that is, electrochemical, component and localized attack in the form of pitting, attack in crevices, grain boundary attack, selective leaching of one phase, and exfoliation (attack parallel to the surface causing layers to peel away). Uniform corrosion is less common and also less of a concern as long as the rate of material removal is gradual and predictable.

Galvanic corrosion requires a medium, usually liquid (water), often containing a specific agent which promotes corrosion, a potential difference, and a complete electrical circuit, as well as an anode and a cathode. The anode will be the attacked, corroded, portion of the system. One cause for potential corrosion is dissimilar metals. For example, the galvanic series in seawater shows magnesium alloys as most anodic followed by zinc, aluminum, iron, nickel, brass, and copper alloys which are progressively more cathodic. When coupled electrically, the more-anodic metal would be corroded and the more cathodic would promote corrosion. One way of preventing corrosion is to isolate with insulator material the metal parts electrically so that a circuit is interrupted. The surfaces can be isolated from the corroding medium with paint, protective metal, conversion coatings, or a corrosion inhibitor additive to the liquid. In this situation it is more important to coat the cathode (noncorroding metal) since it impresses corrosion on the anodic metal dependent on exposed area. When in doubt, all parts should be painted repeatedly to prevent pinholes. Other possibilities include cathodic protection with an impressed electrical counterpotential or use of a sacrificial anode which is attacked instead of the metal components. Some metals such as stainless steels and aluminum alloys provide protection via an oxide coating, a *passive film*, which will form under specific, controlled electrochemical conditions providing *anodic protection*.

Another source for an anode and cathode can be the solution itself. Differences in temperature, ion concentration, oxygen content, and pH can all lead to a potential difference which results in corrosion. Often corrosion occurs far more rapidly for a specific range of solution concentration — indeed, sometimes dilution may accelerate corrosive attack. An oxygen deficiency cell under dirt or in a crevice frequently causes attack at the resulting anode. Potential differences can also exist in the metal itself: between different phases, inclusions, or grain chemistries; between grains and grain boundaries; between surface films and metal; and between different grain orientations. Selective leaching such as dezincification of high-zinc brasses (Cu–Zn) is an example for composition differences, while exfoliation corrosion of aluminum alloys and sensitized stainless steel are examples of grain boundary attack. Cold-worked metal tends to be anodic to annealed material so that a heavily formed part of a metal part may corrode preferentially.

Another important environmental cause of failure is stress corrosion cracking (SCC). A combination of applied or residual tensile stress and environmental attack results in progressive slow crack propagation over a period of time. Eventually, the crack becomes critical in size (Equation 12.1.2) and catastrophic failure occurs. There need be no evidence of corrosion for SCC to occur. When the loading is of a cyclic nature the effect is termed *corrosion fatigue*. To prevent these long-term crack propagation effects the environment and/or the source of tensile load may be removed. Considerable effort has been made to identify an ion concentration below which stress corrosion cracking will not occur (e.g., Cl for austenitic stainless steels), but there may be no level for complete immunity, merely a practical maximum permissible level.

Hydrogen embrittlement and hydrogen cracking can occur in the presence of stress and a hydrogen source. Embrittlement results when hydrogen diffuses into the metal and/or acts on the crack tip altering the fracture toughness. Hydrogen cracking may be regarded as a special case of stress corrosion cracking. Either environmental effect can lead to catastrophic failure. The source of hydrogen can be an acid solution, hydrogen evolved during corrosion, electrochemical treatment (plating, electropolishing), or hydrocarbons. Often isolation from the hydrogen source is difficult because hydrogen diffuses quickly through most materials and barrier coatings. Glass coating has met with some success.

Metal Surface Treatments

A number of treatments are employed to strengthen the surface of steels and make them more resistant to failure or wear. Some of the techniques may also be applied to selected nonferrous alloys. Flame, induction, and laser hardening provide intense heat to the outer surface of a medium- or high-carbon (hardenable) steel bringing it into the austenitic region, above Ac_3 (see subsection on fatigue). The bulk of the metal is not heated so that the surface can then be quenched rapidly forming hardening phases and a compressive surface stress. This provides strength and wear resistance. Another surface-hardening technique is carburizing. This can also be used on steels with lower carbon content. The metal is exposed to a controlled balance of carbon monoxide and carbon dioxide or is packed in graphite. At elevated temperature (usually above the Ac_3) carbon diffuses into the surface, converting it to a high-carbon steel. The steel is then either quenched directly from the carburizing temperature or reaustenitized and quenched. The result is similar to flame hardening, but higher hardness and surface compression can be accomplished compared with flame hardening. The center of the piece, with much lower carbon content, can provide fracture toughness, ductility, and safety. Nitriding exposes steel containing appropriate alloying elements (chromium, aluminum, vanadium, …) to monatomic nitrogen in the form of cracked ammonia, cyanide, or high-energy dissociated nitrogen gas. This is done below the eutectoid (lower transformation) temperature. Dispersed-phase nitrides are formed as nitrogen diffuses into the surface which harden the surface without a need for further heat treatment. The effects of both carburizing and nitriding can be introduced by carbonitriding above the transformation temperature and quenching or nitrocarburizing below the transformation to austenite.

Suggested Reading

ASM International, 1985, *Metals Handbook Desk Edition,* ASM International, Materials Park, OH.
ASM International, *Metals Handbook, 8th–10th ed.,* ASM International, Materials Park, OH.

12.2 Polymers

James D. Idol and Richard L. Lehman

Introduction

Polymers constitute a wide range of materials which are derived at least in part from organic, usually petroleum-based, raw materials; they consist of repeating molecular units and have special properties obtained by engineering the form of the molecular structures. The term *polymer* is derived from Greek roots and means “having many parts,” a term which aptly describes the infinite number of compounds which can be synthesized from a relatively limited number of monomer units. The term *plastic* is often used in describing polymers, although this term is not in current usage since it is a general descriptive which refers to the forming rheology of many polymers but is too general to accurately describe this group of materials.

Polymers are used as engineering materials in the neat form, i.e., as the pure material, or in combination with a large diversity of additives, both organic and inorganic. These additives may be, among others, plasticizers which reduce the rigidity or brittleness of the material, fillers which increase strength and load deflection behavior under load, or stabilizers which protect the polymer against ultraviolet radiation.

The following discussion will separate polymers into two groups, thermoplastic and thermosetting, based on the distinctly different thermal processing behavior of these two broad classes of polymers. Thermoplastic polymers soften when heated and can be reshaped, the new shape being retained on cooling. The process can be repeated many times by alternate heating and cooling with minimal degradation of the polymer structure. Thermosetting polymers (or thermosets) cannot be softened and reshaped by heating. They are plastic and moldable at some state of processing, but finally set to a rigid solid and cannot be resoftened. Thermosets are generally stronger and stiffer than thermoplastic.

Table 12.2.1 of this section gives an overview of the physical properties of the most commonly used industrial polymers. Table 12.2.2 provides an overview of properties such as chemical resistance, ease of machining, and compressive strength for thermoplastic and thermosetting plastics, while Table 12.2.3 is a selection guide for polymers by application. A detailed summary of polymer properties, including electrical properties, thermal properties, optical properties, and fabrication, is presented in Table 12.2.4.

Thermoplastic Polymers

Acetal and Polyacetal

These combine very high strength, good temperature and abrasion resistance, exceptional dimensional stability, and low coefficient of thermal expansion. They compete with nylon (but with many better properties) and with metal die castings (but are lighter). Chemical resistance is good except for strong acids. Typical applications are water-pump parts, pipe fittings, washing machines, car instrument housings, bearings, and gears.

Acrylics (Methylmethacrylate, PMMA)

These are noted for their optical clarity and are available as sheet, rod, tubings, etc., as Perspex (U.K.) and Plexiglas (U.S., Germany, etc.). They are hard and brittle and quite resistant to discoloring and, especially, weathering. Applications include outdoor display signs, optical lenses and prisms, transparent coverings, drafting instruments, reflectors, control knobs, baths, and washbasins. They are available in a wide range of transparent and opaque colors.

Acrylonitrile-Butadiene-Styrene (ABS)

This combination of three monomers gives a family of materials which are strong, stiff, and abrasion resistant with notable impact-resistance properties and ease of processing. The many applications include

TABLE 12.2.1 Physical Properties of Polymers

Properties of Plastics	ρ (kg m^{-3})	Tensile Strength (N mm^{-2})	Elongation (%)	*E* (GN m^{-2})	BHN	Machinability
Thermoplastics						
PVC rigid	1330	48	200	3.4	20	Excellent
Polystyrene	1300	48	3	3.4	25	Fair
PTFE	2100	13	100	0.3	—	Excellent
Polypropylene	1200	27	200–700	1.3	10	Excellent
Nylon	1160	60	90	2.4	10	Excellent
Cellulose nitrate	1350	48	40	1.4	10	Excellent
Cellulose acetate	1300	40	10–60	1.4	12	Excellent
Acrylic (methacrylate)	1190	74	6	3.0	34	Excellent
Polyethylene (high density)	1450	20–30	20–100	0.7	2	Excellent
Thermosetting plastics						
Epoxy resin (glass filled)	1600–2000	68–200	4	20	38	Good
Melamine formaldehyde (fabric filled)	1800–2000	60–90	—	7	38	Fair
Urea formaldehyde (cellulose filled)	1500	38–90	1	7–10	51	Fair
Phenol formaldehyde (mica filled)	1600–1900	38–50	0.5	17–35	36	Good
Acetals (glass filled)	1600	58–75	2–7	7	27	Good

Note: BHN = Brinell hardiness number, ρ = density, *E* = Young's modulus.

TABLE 12.2.2 Relative Properties of Polymers

Material	Tensile Strength[a]	Compressive Strength[b]	Machining Properties	Chemical Resistance
Thermoplastics				
Nylon	E	G	E	G
PTFE	F	G	E	O
Polypropylene	F	F	E	E
Polystyrene	E	G	F	F
Rigid PVC	E	G	E	G
Flexible PVC	F	P	P	G
Thermosetting plastics				
Epoxy resin (glass-fiber filled)	O	E	G	E
Formaldehyde (asbestos filled)	G	G	F	G
Phenol formaldehye (Bakelite)	G	G	F	F
Polyester (glass-fiber filled)	E	G	G	F
Silicone (asbestos filled)	O	G	F	F

Note: O = outstanding, E = excellent, G = good, F = fair, P = poor.

[a] Tensile strength (typical): E = 55 Nmm^{-2}; P = 21 Nmm^{-2}.

[b] Compressive strength (typical): E = 210 Nmm^{-2}; P = Nmm^{-2}.

pipes, refrigerator liners, car-instrument surrounds, radiator grills, telephones, boat shells, and radio and television parts. Available in medium, high, and very high impact grades.

Cellulosics

"Cellulose nitrate" is inflammable and has poor performance in heat and sunlight. Its uses are therefore limited. Cellulose acetate has good strength, stiffness, and hardness and can be made self-extinguishing. Glass-filled grades are made. Cellulose acetate-butyrate (CAB) has superior impact strength, dimensional stability, and service temperature range and can be weather stabilized. Cellulose proprionate (CP) is similar to CAB, but has better dimensional stability and can have higher strength and stiffness. Ethyl cellulose has better low-temperature strength and lower density than the others. Processing of cellulose

TABLE 12.2.3 Selection Guide for Polymers by Application

Application or Service	Properties Required	Suitable Plastics
Chemical and thermal equipment	Resistance to temperature extremes and to wide range of chemicals; minimum moisture absorption; fair to good strength	Fluorocarbons, chlorinated polyether, polyvinylidene fluoride, polypropylene, high-density polyethylene, and epoxy glass
Heavily stressed mechanical components	High-tensile plus high-impact strength; good fatigue resistance and stability at elevated temperatures; machinable or moldable to close tolerance	Nylons, TFE-filled acetals, polycarbonates, and fabric-filled phenolics
Electrostructural parts	Excellent electrical resistance in low to medium frequencies; high-strength and -impact properties; good fatigue and heat resistance; good dimensional stability at elevated temperatures	Allylics, alkyds, aminos, epoxies, phenolics, polycarbonates, polyesters, polyphenylene oxides, and silicones
Low-friction applications	Low coefficient of friction, even when nonlubricated; high resistance to abrasion, fair to good form stability and heat and corrosion resistance	Fluorocarbons (TFE and FEP), filled fluorocarbons (TFE), TFE fabrics, nylons, acetals, TFE-filled acetals, and high-density polyethylenes
Light-transmission components, glazing	Good light transmission in transparent or translucent colors; good to excellent formability and moldability; shatter resistance; fair to good tensile strength	Acrylics, polystyrenes, cellulose acetates, cellulose butyrates, ionomers, rigid vinyls, polycarbonates, and medium-impact styrenes
Housings, containers, ducts	Good to excellent impact strength and stiffness; good formability and moldability; moderate cost; good environmental resistance; fair to good tensile strength and dimensional stability	ABS, high-impact styrene, polypropylene, high-density polyethylene, cellulose acetate butyrate, modified acrylics, polyester–glass and epoxy–glass combinations

plastics is by injection molding and vacuum forming. Applications include all types of moldings, electrical insulation, and toys.

Ethylene-Vinyl Acetate (EVA)

This material gives tough flexible moldings and extrusions suitable for a wide temperature range. The material may be stiffened by the use of fillers and is also specially formulated for adhesives. Applications include all types of moldings, disposable liners, shower curtains, gloves, inflatables, gaskets, and medical tubing. The material is competitive with polyvinyl chloride (PVC), polyethene, and synthetic rubbers, and is also used for adhesives and wax blends.

Fluorocarbons

This class of polymers, characterized by fluorine substitution, has outstanding chemical, thermal, and electrical properties and is characterized by the following four main classes of structures.

Polytetrafluoroethylene (PTFE), known commercially as Teflon or Fluon, is the best-known material and resists all known chemicals, weather, and heat, has an extremely low coefficient of friction, and is “non-stick.” These materials are inert with good electrical properties. They are nontoxic, nonflammable, and have a working temperature range of –270 to 260°C. They may be glass filled for increased strength and rigidity. They do not melt and they must be formed by sintering of powders. Applications include chemical, mechanical, and electrical components, bearings (plain or filled with glass and/or bronze), tubing, and vessels for “aggressive” chemicals.

Fluoroethylenepropylene (FEP), unlike PTFE, can be processed on conventional molding machines and extruded, but thermal and chemical resistance properties are not quite as good.

Ethylenetetrafluoroethylene (ETFE) possess properties similar to but not as good as those of PTFE. However, the material exhibits a thermoplastic character similar to that of polyethylene which gives it a very desirable molding behavior.

TABLE 12.2.4 Properties of Polymers

Chemical class	Cellulose acetate	Cellulose acetate	Cellulose acetate butyrate	Cellulose acetate butyrate	Nylon	Polycarbonates	Polyethylene	Polyethylene
	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic
	Soft	Hard	Soft	Hard	6/6	Unfilled	Low Density	Medium Density
ELECTRICAL PROPERTIES								
D.C. resistivity, ohm-cm	10^{10}-10^{13}	10^{10}-10^{13}	10^{10}-10^{12}	10^{10}-10^{12}		2×10^{16}	$>10^{15}$	$>10^{15}$
Dielectric constant, 60 cps	3.5-7.5	3.5-7.5	3.5-6.4	3.5-6.4	4.0-4.6	3.17	2.3-2.35	2.3
Dielectric constant, 10^6 cps	3.2-7.0	3.2-7.0	3.2-6.2	3.2-6.2	3.4-3.6	2.96	2.3-2.35	2.3
Dissipation factor, 60 cps	0.01-0.06	0.01-0.06	0.01-0.04	0.01-0.04	0.014-0.04	0.0009	<0.0005	<0.0005
Dissipation factor, 10^6 cps	0.01-0.10	0.01-0.10	0.01-0.04	0.01-0.04	0.04	0.01	<0.0005	<0.0005
MECHANICAL PROPERTIES								
Modulus of elasticity, 10^3 psi	86-250	190-400	74-126	150-200		290-325	14-38	35-90
Tensile strength, psi	1,900-4,700	4,600-8,500	1,900-3,800	5,6800	9,000-12,000	8,000-9,500	1,000-1,400	1,200-3,500
Ultimate elongation, %	32-50	6-40	60-74	38-54	60-300	20-100	400-700	50-600
Yield stress, psi	2,200-4,200	4,100-7,600	1,200-2,600	3,600-6,100		8,000-10,000	1,100-1,700	1,500-2,600
Yield strain, %							20-40	10-20
Rockwell hardness	R 49-R 103	R 101-R 123	R 59-R 95	R 108-R 117	R 108-R 120	M 70-M 180		
Notched Izod impact strength, ft lb/in.	2.0-5.2	0.4-2.7	2.5-5.4	0.7-2.4	1.0-2.0	8-16	No break	0.5->16
Specific gravity	1.27-1.34	1.27-1.34	1.15-1.22	1.19-1.25	1.13-1.15	1.2	0.91-0.925	0.926-0.941
THERMAL PROPERTIES								
Burning rate	Medium	Medium	Medium	Medium	Self-extinguishing	Self-extinguishing	Very slow	Slow
Heat distortion, 264 psi. C	44-57	60-113	49-58	70-99		135-145		
Specific heat, cal/g	0.3-0.42	0.3-0.42	0.3-0.4	0.3-0.4	0.4	0.3	0.55	0.55
Linear thermal expansion coefficient, 10^{-5}, C	8-16	8-16	11-17	11-17	8.0	6.6	10-20	14-16
Maximum continuous service temperature, C					80-150	138-143	60-77	71-93
CHEMICAL RESISTANCE								
Mineral acids, weak	Fair to good	Fair to good	Good	Good	Very good	Excellent	Good	Excellent
Mineral acids, strong	Poor	Poor	Fair to good	Fair to good	Poor	Fair	Good	Excellent
Oxidizing acids, concentrated	Very poor	Very poor			Poor		Good to poor	Good to poor
Alkalies, weak	Poor	Poor	Good	Good	No effect	Poor	Good	Excellent
Alkalies, strong	Very poor	Very poor	Poor	Poor	No effect	Poor	Good	Excellent
Alcohols	Poor	Poor	Poor	Poor	Good	Poor	Excellent to poor	Excellent to poor
Ketones	Poor	Poor	Poor	Poor	Good	Poor	Excellent to poor	Excellent to poor
Esters	Poor	Poor	Poor	Poor	Good	Poor	Excellent to poor	Excellent to poor
Hydrocarbons, aliphatic	Fair to good	Fair to good	Fair to good	Fair to good	Very good	Poor	Fair	Fair
Hydrocarbons, aromatic	Poor to fair	Poor to fair	Poor	Poor	Fair to good	Poor	Fair	Good
Oils: vegetable, animal, mineral	Fair to good	Fair to good	Good	Good	Good	Poor	Good	Excellent
MISCELLANEOUS PROPERTIES								
Clarity	Excellent	Excellent	Good to excellent	Good to excellent	Clear	Clear	Translucent	Translucent
Color	Pale to colorless	Pale to colorless	Pale to colorless	Pale to colorless	Pale amber to colorless	Colorless	Colorless	Colorless
Refractive index, n_D	1.46-1.50	1.46-1.50	1.46-1.49	1.46-1.49	1.53	1.60	1.50-1.54	1.52-1.54
FABRICATION								
Cl—calendering, Cs—casting, E—extrusion, F—hot forming or drawing, I—impregnation, MC—blow molding, MC—compression molding, MI—injection molding, S—spreading	Cs, E, F, MB, MC, MI, S	Cs, E, F, MB, MC, MI, S	Cs, E, F, MB, MC, MI, S	Cs, E, F, MB, MC, MI, S	E, F, MB, MC, MI	Cs, E, F, MB, MC, MI	Cl, E, F, MB, MC, MI	Cl, E, F, MB, MC, MI

TABLE 12.2.4 Properties of Polymers (continued)

Polyethylene	Polymethylmethacrylate	Polypropylene	Polypropylene	Polystyrene	Polystyrene-acrylonitrile	Polytetrafluoroethylene	Polytrifluorochloroethylene	Polyvinylchloride and vinylchloride acetate	Polyvinylchloride and vinylchloride acetate	Epoxy
Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermoplastic	Thermosetting
High Density	Unmodified	Unmodified	Copolymer	Unmodified	Unmodified	Unmodified	Unmodified	Unmodified, rigid	Plasticized, non-rigid	Unfilled
$>10^{15}$	$>10^{14}$	$>10^{15}$	$>10^{17}$	$>10^{16}$	10^{13}-10^{17}	10^{18}	10^{18}	10^{12}-10^{16}	10^{11}-10^{14}	10^{12}-10^{14}
2.3-2.35	3.5-4.5	2.2-2.6	2.3	2.5-2.65	2.6-3.4	2.	2.2-2.8	3.2-4.0	5.0-9.0	3.5-5.0
2.3-2.35	3.0-3.5	2.2-2.6	2.3	2.5-2.65	2.5-3.1	2.	2.3-2.5	3.0-4.0	3.0-4.0	3.4-4.4
<0.0005	0.04-0.06	<0.0005	0.0001-0.0005	0.0001-0.0003	0.006-0.008	0.0002	0.001	0.01-0.02	0.03-0.05	0.001-0.005
<0.0005	0.02-0.03	0.0005-0.002	0.0001-0.002	0.0001-0.0004	0.008-0.01	0.0002	0.005	0.006-0.02	0.06-0.1	0.03-0.05
85-160	350-500	1.4-1.7		400-600	$>10^{16}$	33-65	150	200-600		>300
3,100-5,500	7,000-11,000	4,300-5,500	2,900-4,500	5,000-10,000	9,000-12,000	2,000-4,500	4,500-6,000	5,000-9,000	1,500-3,000	4,000-13,000
15-100	2.0-10	>220	200-700	1.0-2.5	1.0-2.5	200-400	250	2.0-40	200-400	2.0-6.0
2,400-5,000		4,900				1,600-2,000	4,200			
5-10		15				50-75	10	1.0-5.0		
R 30-R 50	M 80-M 105	93	R 50-R 96	M 65-M 85	M 75-M 90	D 50-D 65	J 75-J 95	R 110-R 120		M 75-M 110
1.5-20	0.3-0.6	1.0	1.1-12	0.25-0.60	0.3-0.6	2.5-4.0	2.5-4.0	0.4-2.0		0.2-1.0
0.941-0.965	1.18-1.20	0.90	0.90	1.04-1.08	1.05-1.1	2.1-2.3	2.1-2.3	1.36-1.4	1.15-1.35	1.115
Slow	Slow	Medium	Medium	Medium to slow	Slow	Self-extinguishing	Self-extinguishing	Self-extinguishing	Slow to self-extinguishing	Slow
	66-99				91-104	60		60-80		Up to 120
0.55	0.35	0.5	0.5	0.32-0.35	0.32-0.35	0.25	0.22	0.2-0.28	0.36-0.5	0.25-0.4
11-13	5.0-9.0	5.8-10	8-10	6.0-8.0	3.6-3.8	10	7.0	5.0-18	7.0-25	4.5-9.0
92-200	60-93		190-240	66-82	77-88	260	200	70-74	80-105	80
Excellent	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Fair to good	Excellent
Excellent	Fair to poor	Excellent	Excellent	Excellent	Good to excellent	Excellent	Excellent	Good to excellent	Fair to good	Fair to good
Good to poor	Attacked	Good to poor	Poor	Poor	Poor	Excellent	Excellent	Fair to good	Poor to fair	Excellent
Excellent	Good	Excellent to good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Fair to good	Excellent
Excellent	Poor	Excellent to good	Good	Excellent	Good to excellent	Excellent	Excellent	Good	Fair to good	Excellent
Excellent to poor		Excellent to good	Good below 80 C	Excellent	Good to excellent	Excellent	Excellent	Excellent	Fair	Poor
Excellent to poor	Dissolves	Excellent to good	Good below 80 C	Dissolves	Dissolves	Excellent	Excellent	Poor	Poor	
Excellent to poor	Dissolves	Excellent to good	Good below 80 C	Poor	Dissolves	Excellent	Excellent	Poor	Poor	Excellent
Fair	Good	Good to fair	Good below 80 C	Poor	Good	Excellent	Excellent	Excellent	Poor	Excellent
Fair	Softens	Good to fair	Good below 80 C	Dissolves	Fair to good	Excellent	Excellent	Poor	Poor	Excellent
Good	Good	Good		Fair to poor	Good to excellent	Excellent	Excellent	Excellent	Poor	
Translucent		Transparent	Transparent	Transparent	Transparent	Translucent	Transparent	Transparent	Transparent	Transparent
Colorless	Colorless	Colorless to sl. yellow	Colorless to sl. yellow	Colorless	Colorless to amber	Colorless to gray	Colorless to pale	Colorless to amber	Colorless to amber	Colorless
1.54	1.48-1.50	1.49		1.59-1.60	1.56-1.57	1.30-1.40	1.43	1.54	1.50-1.55	1.58
Cl, E, F, MB, MC, MI	Cs, E, F, Lq, MB, MC, MI		Cl, E, F, MB, MC, MI	E, F, MB, MC, MI	Cl, E, F, MB, MC, MI	E, F, MC, MI	Cs, E, F, I, MC, MI, S	Cl, Cs, E, F, I, MB, MC, MI, S	Cl, Cs, E, MB, MC, MI, S	Cs, I, S

TABLE 12.2.4 Properties of Polymers (continued)

Properties of Polymers [continued]

Melamine-formaldehyde	Melamine-formaldehyde	Phenol-formaldehyde	Phenol-formaldehyde	Phenol-formaldehyde	Polyester (styrene-alkyd)	Silicones	Urea Formaldehyde	Acrylonitrile-butadiene-styrene (ABS)	Acetal	Alkyd resins
Thermosetting	Thermosetting	Thermosetting	Thermosetting	Thermosetting	Thermosetting	Thermosetting	Thermoplastic	Thermoplastic	Thermoplastic	Thermosetting
-Cellulose filled	Mineral filled (electrical	Cord filled	Cellulose filled	Unfilled cast phenolic, mechanical and chemical grade	Glassfiber mat reinforced	Mineral filled	-Cellulose filled	High-heat resistant	Homopolymer	Synthetic-fiber filled
10^{12}-10^{14}	10^{13}-10^{14}	10^{11}-10^{12}	10^{11}-10^{13}	$1.0\text{-}7.0 \times 10^{12}$	10^{11}	$>10^{12}$	0.5-5.0	2.4-5.0		3.8-5.0
7.9-9.4	10.2	7.0-10.0	5.0-9.0	6.5-7.5	4.0-5.5	3.5-3.6	7.7-9.5	2.4-3.8	3.7	3.6-4.7
7.2-8.4	6.1	5.0-6.0	4.0-7.0	4.0-5.5	4.0-5.5	3.4-3.6	6.7-8.0	0.003-0.008		0.012-0.026
0.03-0.08	0.10	0.1-0.3	0.04-0.3	0.10-0.15	0.01-0.04	0.004	0.036-0.043	0.007-0.015	0.004	0.01-0.016
0.03-0.043	0.051	0.04-0.09	0.03-0.07	0.04-0.05	0.01-0.06	0.005-0.007	0.025-0.035			
1,300	1,950	900-1,300	800-1,200	4.0-5.0	500-1,500		1,300-1,400	7,000-8,000	10,000-12,000	4,500-6,500
7,000-13,000	5,500-6,500	6,000-9,000	6,500-8,500	6,000-9,000	30,000-50,000	3,000-4,000	5,500-13,000	1.0-20	15-75	
0.6-0.9		0.5-1.0	0.6-1.0	1.5-2.0	0.5-1.5		0.6	4,000-9,000		10,000-13,000
M 110-M 124	E 90		M 110-M 120	M 93-M 120	M 80-M 120	M 85-M 95	E 94-E 97	R 110-R 115	M 94, R 120	E 76
0.24-0.35	0.3-0.4	4.0-8.0	0.24-0.34	0.25-0.4	7.0-30	0.25-0.35	0.24-0.40	2.0-4.0	1.4-2.3	0.50-4.5
1.47-1.52	1.78	1.36-1.43	1.32-1.55	1.307-1.318	1.5-2.1	1.8-2.8	1.47-1.52	1.06-1.08	1.43	1.24-2.6
Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Slow	Slow	Self-extinguishing
204	130	121-127	143-171	74-80	93-288	>260	130	115-118		
0.4			0.35-0.40		0.2-0.4	0.2-0.3	0.6	0.3-0.4	0.35	
2.0-5.7	2.1-4.3		3.0-4.5	6.0-8.0	1.8-3.0	2.0-4.0	2.2-3.6	6.0-6.5	8.1	4.0-5.5
99.0	149	121	149-177		121-204	288	77	88-110	84	149-220
Good	Fair	Variable	Variable	Fair to good	Good	Fair to good	Poor	Good	Fair	Good
Poor	Poor	Poor	Poor	Poor to good	Poor	Poor to good	Poor	Good	Poor	Fair
Poor	Poor	Poor	Poor	Poor	Poor		Poor	Poor	Poor	
Good	Fair	Variable	Variable	Poor to good	Good	Fair	Fair	Good	Poor	Good
Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Good	Poor	Fair
Good	Good	Good	Good to excellent	Good to excellent	Good	Poor	Good	Good	Good	Fair to good
Good	Good	Poor to fair	Fair	Fair	Poor	Poor	Good	Poor	Good	Fair to good
Good	Good	Fair to good	Fair to good	Fair to good	Good		Good	Poor	Good	Fair to good
Good	Good	Fair to good	Excellent	Good to excellent	Good	Fair to good	Good	Fair	Good	Fair to good
Good	Good	Fair to good	Excellent	Good	Poor to fair	Poor	Good	Fair	Good	Fair to good
Good	Good	Good	Excellent	Excellent	Good	Good	Good	Good	Good	
Translucent	Opaque	Opaque	Opaque	Clear	Translucent	Opaque	Translucent	Translucent to opaque	Translucent to opaque	Opaque
Colorless	Dark			Colorless to amber	Colorless	Pale to dark	Colorless	Colorless	Colorless	Colorless
							1.54-1.56		1.48	
MC	MC	MC	MC	Cs, F	I	MC	MC	CI, E, MB, MI	MI, E	Cs MC, MI

TABLE 12.2.4 Properties of Polymers (continued)

Properties of Polymers [continued]

Chemical class	Polyketone							
	aliphatic thermoplastic							
	neat resin							
ELECTRICAL PROPERTIES								
D.C. resistivity, ohm-cm	103							
Dielectric constant, 60 cps	5-6							
Dielectric constant, 10^6 cps								
Dissipation factor, 60 cps								
Dissipation factor, 10^6 cps	0.04							
MECHANICAL PROPERTIES								
Modulus of elasticity, 10^3 psi	250							
Tensile strength, psi	>9000							
Ultimate elongation, %	300							
Yield stress, psi	9000							
Yield strain, %	2.2							
Rockwell hardness								
Notched Izod impact strength, ft lb/in.	4							
Specific gravity	1.24							
THERMAL PROPERTIES								
Burning rate								
Heat distortion, 264 psi. C	105-110							
Specific heat, cal/g								
Linear thermal expansion coefficient, 10^{-5}, C	9-11							
Maximum continuous service temperature, C								
CHEMICAL RESISTANCE								
Mineral acids, weak	Good							
Mineral acids, strong	Fair							
Oxidizing acids, concentrated	Fair							
Alkalies, weak	Good							
Alkalies, strong	Good							
Alcohols	Excellent							
Ketones	Excellent							
Esters	Excellent							
Hydrocarbons, aliphatic	Excellent							
Hydrocarbons, aromatic	Excellent							
Oils: vegetable, animal, mineral								
MISCELLANEOUS PROPERTIES								
Clarity	translucent							
Color	white crystals							
Refractive index, n_D								
FABRICATION								
Cl—calendering, Cs—casting, E—extrusion, F—hot forming or drawing, I—impregnation, MC—blow molding, MC—compression molding, MI—injection molding, S—spreading	E, MI							

Perfluoroalkoxy (PFA) is the fourth group of fluorinated polymers. These materials have the same excellent properties as PTFE, but the compound is melt processible and, therefore, suitable for linings for pumps, valves, pipes, and pipe fittings.

Ionomers

These thermoplastics are based on ethylene and have high melt strength, which makes them suitable for deep forming, blowing, and other similar forming processes. They are used for packaging, bottles, moldings for small components, tool handles, and trim. They have a high acceptance of fillers.

Polymethylpentene

Polymethylpentene (TPX) is a high-clarity resin with excellent chemical and electrical properties and the lowest density of all thermoplastics. It has the best resistance of all transparent plastics to distortion at high temperature — it compares well with acrylic for optical use, but has only 70% of its density. It is used for light covers, medical and chemical ware, high-frequency electrical insulation, cables, microwave oven parts, and radar components. It can withstand soft soldering temperatures.

Polyethylene Terephthalate

Polyethylene terephthalate (PETP) and modified versions thereof have high strength, rigidity, chemical and abrasion resistance, impact resistance in oriented form, and a low coefficient of friction. It is attacked by acetic acid and concentrated nitric and sulfuric acids. It is used for bearings, tire reinforcement, bottles, automotive parts, gears, and cams.

Polyamides (Nylons)

The polyamides are a family of thermoplastics, e.g., Nylon 6, Nylon 66, and Nylon 610, which are among the toughest engineering plastics with high vibration-damping capacity, abrasion resistance, inherent lubricity, and high load capacity for high-speed bearings. They have a low coefficient of friction and good flexibility. Pigment-stabilized types are not affected by ultraviolet radiation and chemical resistance is good. Unfilled nylon is prone to swelling due to moisture absorption. Nylon bearings may be filled with powdered molybdenum disulfide or graphite. Applications include bearings, electrical insulators, gears, wheels, screw fasteners, cams, latches, fuel lines, and rotary seals.

Polyethylene

Low-density polyethylene (orinally called *polythene*) is used for films, coatings, pipes, domestic moldings, cable sheathing, and electrical insulation. High-density polyethylene is used for larger moldings and is available in the form of sheet, tube, etc. Polyethylene is limited as an engineering material because of its low strength and hardness. It is attacked by many oxidizing chemical agents and some hydrocarbon solvents.

Polyketone, Aliphatic

Aliphatic polyketones are relatively strong, tough, ductile polymeric resins derived from equal proportions of ethylene and carbon monoxide with an additional few percent of higher olefin for property and processibility adjustment. Their physical, thermal, and mechanical properties are similar to polyamides and polyacetals. Mechanical properties are characterized by preservation of high levels of stiffness, toughness, and strength over a broad temperature range. Resistance to hydrolysis, swelling, and permeation provides broad chemical resistance. Relatively new in commercial supply, they find application in gears, machine components, and similar engineering applications. Tribological performance is very good, and in particular they have a low coefficient of friction and a low wear factor against steel. The electrical properties of the neat polyketone are typical of those of polar, semicrystalline thermoplastics.

Polyethersulfone

Polyethersulfone is a high-temperature engineering plastic — useful up to 180°C in general and some grades have continuous operating ratings as high as 200°C. It is resistant to most chemicals and may be extruded or injection molded to close tolerances. The properties are similar to those of nylons. Applications are as a replacement for glass for medical needs and food handling, circuit boards, general electrical components, and car parts requiring good mechanical properties and dimensional stability.

Polystyrene

This polymer is not very useful as an engineering material because of brittleness in unmodified forms, but it is well known for its use in toys, electrical insulation, refrigerator linings, packaging, and numerous commercial articles. It is available in unmodified form as a clear transparent resin and also in clear and opaque colors. High-impact forms are achieved by compounding with butadiene or other rubbery resins and heat-resistant forms are achieved by the use of fillers. Polystyrene can be stabilized against ultraviolet radiation and also can be made in expanded form for thermal insulation and filler products. It is attacked by many chemicals, notably aromatic hydrocarbon solvents, and by ultraviolet light.

Polysulfone

Polysulfone has properties similar to nylon, but these properties are retained up to 180°C compared with 120°C for nylon, which greatly expands the range of applications. Its optical clarity is good and its moisture absorption lower than that of nylon. Applications are as a replacement for glass for medical needs and chemistry equipment, circuit boards, and many electrical components.

Polyvinyl Chloride

This is one of the most widely used of all plastics. With the resin mixed with stabilizers, lubricants, fillers, pigments, and plasticizers, a wide range of properties is possible from flexible to hard types, in transparent, opaque, and colored forms. It is tough, strong, with good resistance to chemicals, good low-temperature characteristics and flame-retardant properties. PVC does not retain good mechanical performance above 80°C. It is used for electrical conduit and trunking, junction boxes, rainwater pipes and gutters, decorative profile extrusions, tanks, guards, ducts, etc.

Polycarbonate

Polycarbonate is an extremely tough thermoplastic with outstanding strength, dimensional stability, and electrical properties, high heat distortion temperature and low-temperature resistance (down to –100°C). It is available in transparent optical, translucent, and opaque grades (many colors). Polycarbonates have only fair resistance to chemicals as evidenced by the stress cracking caused by many solvents. The weathering tendencies can be stabilized against ultraviolet radiation by the use of proper additives. Polycarbonate compounds are used for injection moldings and extrusions for glazing panels, helmets, face shields, dashboards, window cranks, and gears. Polycarbonate is an important engineering plastic.

Polypropylene

Polypropylene is a low-density, hard, stiff, creep-resistant plastic with good resistance to chemicals, good wear resistance, low water absorption, and is relatively low cost. Polypropylene can be spun into filaments, converted into weaves, injection molded, and is commonly produced in a large variety of forms. Glass-filled polypropylene is widely used for its enhanced mechanical properties. It is used for food and chemical containers, domestic appliances, furniture, car parts, twine, toys, tubing, cable sheath, and bristles.

Polyphenylene Sulfide

Polyphenylene sulfide is a high-temperature plastic useful up to 260°C. Ambient temperature properties are similar or superior to those of nylon. It has good chemical resistance and is suitable for structural components subject to heat. Glass filler improves strength and enables very high heat resistance to 300°C. Uses are similar to those of nylon, but for higher temperatures.

Polyphenylene Oxide

This is a rigid engineering plastic similar to polysulfone in uses. It can be injection molded and has mechanical properties similar to those for nylon. It is used for automotive parts, domestic appliances, and parts requiring good dimensional stability. Frequently, the commercially available product is blended (or “alloyed”) with polystyrene which acts as a cost-effective extender.

Thermosetting Polymers

Alkyds

There are two main groups of alkyds: diallyphthalate (DAP) and diallylisopthalate (DIAP). These have good dimensional stability and heat resistance (service temperature 170°C; intermittent use 260°C), excellent electrical properties, good resistance to oils, fats, and most solvents, but limited resistance to strong acids and alkalis. The mechanical properties are improved by filling with glass or minerals. The main uses are for electrical components and encapsulation. A wide range of colors and fast-curing grades are available.

Amino Resins

These are based on formaldehyde reacted with urea or melamine and are formulated as coatings and adhesives for laminates, impregnated paper textiles, and molding powders. The resins are usually compounded with fillers of cellulose, wood flour, and/or other extenders. As composites with open-weave fabric, they are used for building panels. Uses also include domestic electrical appliances and electric light fittings; the melamine type is used for tableware. The strength is high enough for use in stressed components, but the material is brittle. Electrical, thermal, and self-extinguishing properties are good.

Epoxies

Epoxy resins are used extensively across industry as engineering polymers and as adhesives. They can be cold cured without pressure using a “hardener” or may be heat cured. Inert fillers, plasticizers, flexibilizers, and extenders give a wide range of properties from soft flexible to rigid solid materials. Bonding to nearly all materials, e.g., wood, metal, glass, is excellent as are the mechanical, electrical, and chemical properties. Epoxies are used in all branches of engineering, including large castings, electrical parts, circuit boards, potting, glass and carbon fiber structures, flooring, protective coatings, and adhesives. Importantly, they exhibit little or no shrinkage on cure.

Phenolics (Phenol Formaldehyde, PF)

PF, the original “Bakelite,” is usually filled with 50 to 70% wood flour for molded nonstressed or lightly stressed parts. Other fillers are mica for electrical parts, asbestos for heat resistance, glass fiber for strength and electrical properties, nylon, and graphite. Phenolics represent one of the best polymers for low-creep applications. Moldings have good strength, good gloss, and good temperature range (150°C wood filled; intermittent use 220°C), but are rather brittle. Applications include electrical circuit board, gears, cams, and car brake linings (when filled with asbestos, glass, metal powder, etc.). The cost is low and the compressive strength very high.

Polyester

Polyester resins can be cured at room temperature with a hardener or alone at 70 to 150°C. It is used unfilled as a coating, for potting, encapsulation, linings, thread locking, castings, and industrial moldings. It is used mostly for glass-reinforced-plastic (GRP) moldings.

Polyimides

Polyimides are noted for their unusually high resistance to oxidation and service temperatures up to 250°C (400°C for intermittent use). The low coefficient of friction and high resistance to abrasion make them ideal for nonlubricated hearings. Graphite or molybdenum disulfide filling improves these properties. They are used for high-density insulating tape. Polyimides have high strength, low moisture absorption, and resist most chemicals, except strong alkalis and ammonia solutions.

Silicones

These may be cold or heat cured and are used for high-temperature laminates and electrical parts resistant to heat (heat distortion temperature 450°C). Unfilled and filled types are used for special-duty moldings. Organosilicones are used for surface coatings and as a superior adhesive between organic and nonorganic materials.

Laminated Polymer Structures

A wide range of composite structures are prepared from polymer resins combined with fibers. The reader is referred to Section 12.6 for a more extensive discussion of polymer composites. Laminated polymer structures consist of layers of fibrous material impregnated with and bonded together usually by a thermosetting resin to produce sheets, bars, rods, tubes, etc. The laminate may be “decorative” or “industrial,” the latter being of load-bearing mechanical or electrical grade.

Phenolics

Phenolic plastics can be reinforced with paper, cotton fabric, asbestos paper fabric or felt, synthetic fabric, or wood flour. They are used for general-purpose mechanical and electrical parts. They have good mechanical and electrical properties.

Epoxies

These are used for high-performance mechanical and electrical duties. Fillers used are paper, cotton fabric, and glass fiber.

Tufnol

“Tufnol” is the trade name for a large range of sheet, rod, and tube materials using phenolic resin with paper and asbestos fabric and epoxy resin with glass or fabric.

Polyester

This is normally used with glass fabric (the cheapest) filler. The mechanical and electrical properties are inferior to those of epoxy. It can be rendered in self-colors.

Melamine

Fillers used for melamine are paper, cotton fabric, asbestos paper fabric, and glass fabric. Melamines have a hard, nonscratch surface, superior electrical properties, and can be rendered in self-colors. They are used for insulators, especially in wet and dirty conditions, and for decorative and industrial laminates.

Silicone

Silicone is used with asbestos paper and fabric and glass fabric fillers for high-temperature applications (250°C; intermittent use 300°C). It has excellent electrical but inferior mechanical properties.

Polyimide

Polyimide is most often used with glass fabric as filler. Polyimides have superior thermal and electrical properties with a service temperature similar to that for silicones but with two to three times the strength and flexibility.

Foam and Cellular Polymers

Thermoplastics

Polyurethane Foams. The “flexible” type is the one most used. It is “open cell” and used for upholstery, underlays, thermal and vibration insulation, and buoyancy. It can be generated *in situ*. The rigid type has “closed cells” and is used for sandwich construction, insulation, etc. Molded components may be made from rigid and semirigid types.

Expanded Polystyrene. This material is produced only in rigid form with closed cells. It can be formed *in situ*. The density is extremely low, as is the cost. Chemical resistance is low and the service temperature is only 70°C. It is used for packaging, thermal and acoustic insulation, and buoyancy applications.

Cellular Polyvinyl Chlorides. The low-density type is closed cell and flexible. It is used for sandwich structures, thermal insulation, gaskets, trim, to provide buoyancy, and for insulating clothing. The moderate- to high-density open-cell type is similar to latex rubber and is used as synthetic leather cloth. The rigid closed-cell type is used for structural parts, sandwich construction, thermal insulation, and buoyancy. Rigid open-cell PVC (microporous PVC) is used for filters and battery separators. In general, cellular PVC has high strength, good flame resistance, and is easy to work.

Polyethylene Foams. The flexible type is closed cell and has low density with good chemical resistance and color availability, but is a poor heat insulator and is costly. The flexible foams are used for vibration damping, packaging, and gaskets. The rigid type has high density and is used for filters and cable insulation. A structural type has a solid skin and a foam core.

Ethylene Vinyl Acetates. These are microcellular foams similar to microcellular rubber foam, but are much lighter with better chemical resistance and color possibilities.

Other Types. Other types of thermoplastics include cellular acetate, which is used as a core material in constructions; expanded acrylics, which have good physical properties, thermal insulation, and chemical resistance; expanded nylon (and expanded ABS), which are low-density, solid-skin constructions; expanded PVA, which has similar properties to expanded polystyrene; and expanded polypropylene, which gives high-density foams.

Thermosets

Phenolics. These can be formed *in situ*. They have good rigidity, thermal insulation, and high service temperature, but are brittle.

Urea Formaldehyde (UF) Foam. This is readily formed *in situ* and has good thermal insulation. It has open pores and is used for cavity-wall filling.

Expanded Epoxies. These have limited use because of their high cost. They give a uniform texture and good dimensional stability and are used for composite forms, e.g., with polystyrene beads.

Silicon Foams. These are rigid and brittle with a high service temperature (300°C; 400°C intermittent use). Their use is limited to high-temperature-resistant sandwich constructions. The flexible closed-cell type is costly but will operate up to 200°C and is used for high-temperature seals and gaskets.

Elastomers

Cellular Rubbers. There are three types: *sponge*, solid rubber blown to give an open-cell structure, *foam*, a liquid rubber expanded to form open or closed cells which is stiffer than sponge; and *expanded*, a solid rubber blown with mainly closed cells, also it is stiffer than sponge. Uses include gaskets, seals, thermal insulation, cushioning, shock absorption, sound and vibration damping, buoyancy, and sandwich constructions.

Elastomers

Elastomers, or rubbers, are essentially amorphous polymers with linear chain molecules with some cross-linking, which ensures elasticity and the return of the material to its original shape when a load is removed. They are characterized by large strains (typically 100%) under stress. The synthetic rubber styrene butadiene is the most-used elastomer, with natural rubber a close second. The following describes the commonly used elastomers and gives some applications and properties.

Natural Rubbers (Polyisoprene, NR)

These elastomers have high strength, flexibility, and resilience, but have poor resistance to fuels, oils, flame, and sunlight aging. They are more costly than synthetic rubbers, which often replace them. “Soft-rubber” contains 1 to 4% sulfur as a vulcanizer. Wear resistance is increased by inclusion of fillers such as carbon black, silicon dioxide, clay, and wood flour. “Hard rubber” may contain up to 25% sulfur. Applications include vehicle tires and tubes, seals, antivibration mountings, hoses, and belts. Full vulcanization of 45% produces ebonite. Shore hardness: 30 to 90. Temperature range: –55 to 82°C.

Synthetic Rubbers

Styrene Butadiene Rubbers (SBR, GRS, BUNAS). These are similar to natural rubbers in application, but are usually inferior in mechanical properties, although cheaper. They are used in car brake hydraulic systems and for hoses, belts, gaskets, and antivibration mountings. Shore hardness: 40 to 80. Temperature range: –50 to 82°C.

Butadiene Rubbers (Polynutadiene, BR). These are used as substitutes for natural rubber, but are generally inferior. They have similar applications as natural rubber. Shore hardness: 40 to 90. Temperature range: –100 to 93°C.

Butyl Rubbers (Isobutylene Isoprene, GR 1). These are extremely resistant to water, silicon fluids and grease, and gas permeation. They are used for puncture-proof tires, inner tubes, and vacuum seals. Shore hardness: 40 to 90. Temperature range: –45 to 150°C.

Nitrile Rubbers (Butadiene Acrylonitrile, BUNA, N.NBR). These have good physical properties and good resistance to fuels, oils, solvents, water, silicon fluids, and abrasion. They are used for O rings and other seals, petrol hoses, fuel-pump diaphragms, gaskets, and oil-resistant shoe soles. Shore hardness: 40 to 95. Temperature range: –55 to 82°C.

Neoprene Rubbers (Polychloroprene, Chloroprene). These are some of the best general-purpose synthetic rubbers. They have excellent resistance to weather aging, moderate resistance to oils, and good resistance to refrigerants and mild acids. Shore hardness: 40 to 95. Temperature range: –40 to 115°C.

Chlorosulfonated Polyethylene Rubbers (CSM). These have poor mechanical properties but good resistance to acids and heat with complete resistance to ozone. They are used in chemical plants, tank linings, and high-voltage insulation. Shore hardness: 45 to 100. Temperature range: –100 to 93°C.

Ethylene Propylene Rubbers (EP, FPM). These specialized rubbers are especially resistant to weather aging heat, many solvents, steam, hot water, dilute acids and alkalis, and ketones, but not petrol or mineral oils. They are used for conveyor belts, limited automotive applications, silicone fluid systems, and electrical insulation. Shore hardness: 40 to 90. Temperature hardness: –50 to 177°C.

Fluorocarbon Rubbers. These comprise a wide range of rubbers with excellent resistance to chemical attack, heat, acids, fuels, oils, aromatic compounds, etc. They have a high service temperature. They are particularly suitable for vacuum applications. Shore hardness: 60 to 90. Temperature hardness: –23 to 260°C.

Isoprenes (Polyisoprene, IR). These are chemically the same as natural rubber but are more costly. The properties and applications are similar to those of natural rubber. Shore hardness: 40 to 80. Temperature hardness: –50 to 82°C.

Polyacrylic Rubbers (ACM, ABR). This is a group of rubbers with properties midway between nitrile and fluorocarbon rubbers with excellent resistance to mineral oils, hypoid oils, and greases and good resistance to hot air and aging. The mechanical strength is low. They are often used for spark plug seals and transmission seals. Shore hardness: 40 to 90. Temperature hardness: –30 to 177°C.

Polysulfide Rubbers. These have poor physical properties and heat resistance, but good resistance to oils, solvents, and weathering and are impermeable to gases and moisture. They are used for caulking and sealing compounds and as a casting material. Shore hardness: 40 to 85. Temperature hardness: –50 to 121°C.

Polyurethane Rubbers. These have exceptional strength and tear and abrasion resistance (the best of all rubbers), low-temperature flexibility, and good resistance to fuels, hydrocarbons, ozone, and weather. Resistance to solutions of acids and alkalis, hot water, steam, glycol, and ketones is poor. They are used for wear-resistant applications such as floor coverings. Shore hardness: 35 to 100. Temperature hardness: –53 to 115°C.

Silicone Rubbers (SI). These have exceptionally high service-temperature ranges, but the mechanical properties and chemical resistance are poor. They cannot be used in applications which expose them to fuels, light mineral oils, or high-pressure steam. They are used for high- and low-temperature seals, high-temperature rotary seals, cable insulation, hydraulic seals, and aircraft door and canopy seals. Shore hardness: 30 to 90. Temperature hardness: –116 to 315°C (380°C for intermittent use).

Fluorosilicone Rubbers. These are similar to silicone rubbers but have better oil resistance and a lower temperature range. Shore hardness: 40 to 80. Temperature hardness: –64 to 204°C.

12.3 Adhesives

Richard L. Lehman

Introduction

Adhesives are substances capable of holding materials together in a useful manner by surface attachment. The principal attribute of adhesives is their ability to form strong bonds with surfaces of a wide range of materials and to retain bond strength under expected use conditions. Although most adhesives do not have excellent bulk properties and it is therefore important to keep adhesive films thin, some materials such as epoxies have bulk properties which qualify them as engineering materials and thus can be used in multifunctional applications.

Advantages and Limitations of Use

The principal advantages of adhesives are their ability to bond similar to dissimilar materials of different thickness; to enable the fabrication of complex shapes not feasible by other fastening means; to smooth external joint surfaces; to permit economic and rapid assembly; to distribute stresses uniformly over joined interfaces, to provide weight reduction in critical structures via the elimination of fasteners; to dampen vibrations; to prevent or reduce galvanic corrosion; and to provide thermal and electrical insulation.

The limitations of adhesives depend on the specific adhesive and application and may include the necessity of surface preparation, long curing times, service-temperature limitations, loss of properties during service, toxicity of flammability during assembly or use, and the tendency of many adhesives to creep under sustained load.

Classes of Adhesives

Thermoplastic adhesives are a general class of adhesives based upon long-chained polymeric structure, and are capable of being softened by the application of heat with subsequent hardening upon cooling (hot-melt adhesives). The softening process if reversible for numerous cycles, which facilitates assembly and disassembly of structures. Thermosetting adhesives are a general class of adhesives based upon cross-linked polymeric structures which develop strong bonds that cannot be reversibly broken once they are formed. Thus, the thermoset adhesives are incapable of being softened once solidified.

Thermoplastic and thermosetting adhesives are cured, a process often referred to as setting, by polymerization or solidification, by heat, catalysis, chemical reaction, free-radical activity, radiation, evaporation of solvent, or another process as governed by the chemical nature of the particular adhesive.

Elastomers are a special class of thermoplastic adhesive possessing the common quality of substantial flexibility or elasticity. Refer to Section 12.2 on polymers.

Anaerobic adhesives are a special class of thermoplastic adhesive, the polyacrylates, that set only in the absence of air (oxygen). The two basic types are (1) machinery — possessing shear strength only and (2) structural — possessing both tensile and shear strength.

Pressure-sensitive adhesives are permanently and aggressively tacky solids which form immediate bonds when two parts are brought together under pressure. They are available as films and tapes as well as hot-melt systems.

Performance of Adhesives

To obtain optimum mechanical performance of an adhesive, it is critical to select the proper compound for the target application. Table 12.3.1 illustrates compatibility of adhesives and five broad classes of common materials. Generally, for good adhesive bonds the chemistry of the adhesive must match or be

TABLE 12.3.1 Relative Performance of Adhesive Resins

	Adherence To:					Resistance			
Adhesive Resin	**Paper**	**Wood**	**Metal**	**Ceramics**	**Rubbers**	**Water**	**Solvents**	**Alkali**	**Acids**
Alkyd	6	7	5	6	7	7	2	2	5
Cellulose acetate	4	3	1	3	5	2	3	1	3
Cellulose acetate butyrate	3	1	4	5	2	3	1	3	3
Cellulose nitrate	5	1	5	5	3	2	2	4	4
Ethyl cellulose	3	1	3	5	2	3	3	3	3
Methyl cellulose	1	1	3	3	1	6	3	3	3
Carboxy methyl cellulose	1	2	3	2	1	6	1	4	4
Epoxy resin	10	8	8	8	8	7	8	8	8
Furane resin	7	2	8	7	8	9	7	8	8
Melamine resin	10	5	2	5	4	9	5	5	5
Phenolic resins	8	5	5	7	6	10	7	8	8
Polyeseter, unsaturated	8	4	5	7	7	6	2	5	7
Polyethylacrylate	4	3	5	6	8	4	6	7	7
Polymethylmethacrylate	4	4	3	6	6	5	6	7	7
Polystyrene	3	2	2	5	8	5	5	8	8
Polyvinylacetate	7	7	7	3	3	3	4	6	6
Polyvinyl alcohol	2	2	4	6	1	7	1	3	3
Polyvinyl acetyl	7	8	7	7	8	5	3	5	5
Polyvinyl chloride	7	6	7	6	8	6	10	9	9
Polyvinyl acetate chloride	8	6	7	5	8	5	8	8	5
Polyvinylidene copolymer	7	6	7	7	8	7	10	9	9
Silicone T.S.	6	7	7	8	10	7	6	6	6
Urethane T.S.	10	10	9	10	7	8	4	4	4
Acrylonitrile rubber	6	8	6	9	7	5	8	8	8
Polybutene rubber	3	6	2	8	8	3	10	9	9
Chlorinated rubber	5	7	4	7	6	3	10	9	9
Styrene rubber	7	6	5	8	7	3	8	9	9

Note: 1 = low performance; 10 = high performance.
Source: Adapted from Simonds, H.R. and Church, J.M., *A Concise Guide to Plastics*, 2nd ed., Reinhold, New York, 1963. With permission.

TABLE 12.3.2 High-Performance Engineering and Machine Part Adhesives

Thread locking	• Anaerobic acrylic
Hub mounting	• Anaerobic acrylic — compatible materials or flow migration unimportant • Modified acrylic — large gaps or migration must be avoided • Epoxy — maximum strength at high temperatures
Bearing mounting	• Anaerobic acrylic — compatible materials necessary and flow into bearing area to be prevented • Modified acrylic — for lowest cost
Structural joining	• Epoxies and modified epoxies — for maximum strength (highest cost) • Acrylics — anaerobic or modified cyanacrylates
Gasketing	• Silicones — primarily anaerobic

similar to the surface energy, polarity, and/or chemistry of the material being bonded. The elastic modulus of the adhesive should not be greater than the bonded material.

Adhesives are used in two classes of application, those requiring only shear strength and those requiring structural properties, often tensile and shear strength. Table 12.3.2 provides a quick reference for some typical applications. A much more detailed summary and classification of adhesives is given in Table 12.3.3.

Table 12.3.3 presents a sample of a number of adhesives (with practical information) that are available from various sources. The table is adapted from the rather extensive one found in J. Shields, *Adhesives Handbook*, CRC Press, Boca Raton, FL, 1970. For other extensive lists of trade sources, the reader is

TABLE 12.3.3 Properties and Applications of Adhesive Materials

Basic Type	Curing Cycle, Time at Temperature	Service Temperature Range, C	Adherends	Main Uses	Remarks
			Animal		
Animal (hide)	Melted at 70–75°C; sets on cooling	<70	Paper, wood, textiles	Woodworking, carpet materials, paper, bookbinding	May be thinned with water
Animal (hide) + plasticizers	Applied as a melt at 60°C	<60	Paper, cellulosic materials	Bookbinding, stationery applications	Cures to permanent flexible film
Fish glue	1 hr at 20°C	<60	Wood, chipboard, paper	General-purpose for porous materials	Rapid setting; good flexibility, moderate resistance to water; high tack
Casein	Cold setting after 20 min standing period on mixing	<50	Timber with moisture content	Laminated timber arches and beams, plybox beams, and engineering timber work	Full bond strength developed after seasoning period of 48 hr
Casein + 60% latex	Cold setting after 20 min standing period on mixing	<60	Aluminum, wood, phenolic formaldehyde (rigid, leather, rubber)	Bonding of dissimilar materials to give flexible, water-resistant bond	Flexible
			Vegetable		
Dextrine	Air drying		Paper, cardboard, leather, wood, pottery	General-purpose glue for absorbent materials	Medium drying period of 2–3 hr
Dextrine–starch blend	Applied above 15°C air drying	<48	Cellulosic materials, cardboard, paper	Labeling, carton sealing, spiral-tube winding	Fast setting; may be diluted with water
Gum arabic	Cold setting	<50	Paper, cardboard	Stationery uses	Fast drying
			Mineral		
Silicate	8 hr at 20°C	10–430	Asbestos, magnesia	Lagging asbestos cloth on high-temperature insulation	Unsuitable where moisture; not recommended for glass or painted surfaces

TABLE 12.3.3 Properties and Applications of Adhesive Materials (continued)

Basic Type	Curing Cycle, Time at Temperature	Service Temperature Range, C	Adherends	Main Uses	Remarks
Silicate with china-clay filler	Dried at 80°C before exposure to heat	–180–1500	Asbestos, ceramics, brickwork, glass, silver, aluminum, steel (mild)–steel	General purpose cement for bonding refractory materials and metals; furnace repairs and gastight jointing of pipe work; heat-insulating materials	Resistant to oil, gasoline, and weak acids
Sodium silicate	Dried at 20–80°C before exposure to heat	0–850	Aluminum (foil), paper, wood–wood	Fabrication of corrugated fiber board; wood bonding, metal foil to paper lamination	Suitable for glass-to-stone bonding
Aluminum phosphate + silica filler	Dried $^1/_2$ hr at 20°C, then $^1/_2$ hr at 70°C + $^1/_2$ hr at 100°C + 1 hr at 200°C + 1 hr at 250°C; repeat for two overcoatings and finally cure at 1 hr at 350°C	<750	Steels (low-alloy), iron, brass, titanium, copper, aluminum	Strain-gauge attachment to heat-resistant metals; heater-element bonding	Particularly suited to heat-resistant steels where surface oxidation of metal at high temperatures is less detrimental to adhesion
Bitumen/latex emulsion	Dried in air to a tacky state	0–66	Cork, polystyrene (foam), polyvinyl chloride, concrete, asbestos	Lightweight thermal-insulation boards, and preformed sections to porous and nonporous surfaces; building applications	Not recommended for constructions operated below 0°C
			Elastomers		
Natural rubber	Air dried 20 min at 20°C and heat-cured 5 min at 140°C	<60	Rubber (styrene butadiene), rubber (latex), aluminum, cardboard, leather, cotton	Vulcanizing cement for rubber bonding to textiles and rubbers	May be thinned with toluene
Natural rubber in hydrocarbon solvent	Air dried 10 min at 20°C and heat-cured for 20 min at 150°C	<100	Hair (keratin), bristle, polyamide fiber	Brush-setting cement for natural- and synthetic-fiber materials	Resistant to solvents employed in oil, paint and varnish industries, can be nailed without splitting
Rubber latex	Air drying within 15 min	<60	Canvas, paper, fabrics, cellulosic materials	Bonding textiles, papers packaging materials; carpet bonding	Resistant to heat; should be protected from frosts, oils

TABLE 12.3.3 Properties and Applications of Adhesive Materials (continued)

Basic Type	Curing Cycle, Time at Temperature	Service Temperature Range, C	Adherends	Main Uses	Remarks
Chlorinated rubber in hydrocarbon solvents	Air dried 10 min at 20°C and contact bonded	–20–60	Polyvinyl chloride, acrylonitrile butadiene styrene, polystyrene, rubber, wood	General-purpose contact adhesive	Resistant to aging, water, oils, petroleum
Styrene–butadene rubber lattices	Air drying	–20–60	Polystyrene (foam), wood, hardboard, asbestos, brickwood	Bonding polystyrene foams to porous surface	—
Neoprene/nitrile rubbers in (?)	Dried 30 min in air and bonded under pressure; tacky	–20–60	Wood, linoleum, leather, paper, metals, nitrile rubbers, glass, fabrics	Cement for bonding synthetic rubbers to metals, woods, fabrics	May be thinned with ketones
Acrylonitrile rubber + phenolic resin	Primer air dried 60 min at 20°C, film cured 60 min at 175°C under pressure; pressure released on cooling at 50°C	–40–130	Aluminum (alloy)–aluminum to DTD 746	Metal bonding for structural applications at elevated temperatures	Subject to creep at 150°C for sustained loading
Polysulfide rubber in ketone solvent and catalyst	3 days at 25°C	–50–130, withstands higher temperatures for short periods	Metals	Sealant for fuel tanks and pressurized cabins in aircraft, where good weatherproof and waterproof properties are required	Resistant to gasoline, oil, hydraulic fluids, ester lubricants; moderate resistance to acids and alkalis
Silicone rubber	24 hr at 20°C (20% R.H.); full cure in 5 days	–65–260	Aluminum, titanium, steel (stainless), glass, cork, silicone rubber, cured rubber–aluminum, cured rubber–titanium, cured rubber–steel (stainless), aluminum–aluminum (2024 Alclad), cork–cork (phenolic bonded)	General-purpose bonding and scaling applications; adhesive/sealant for situations where material is expected to support considerable suspended weight; high-pressure exposure conditions	Resistant to weathering and moisture
Reclaim rubber	Contact bonded when tacky	<50	Fabric, leather, wood, glass, metals (primed)	General industrial adhesive for rubber, fabric, leather, porous materials	May be thinned with toluene
Polychloroprene	Air dried 10–20 min at 20°C	<60	Rubber, steel, wood, concrete	Bonding all types of rubber flooring to metals, woods, and masonry	Good heat resistance

TABLE 12.3.3 Properties and Applications of Adhesive Materials (continued)

Basic Type	Curing Cycle, Time at Temperature	Service Temperature Range, C	Adherends	Main Uses	Remarks
Modified polyurethane	3 hr at 18°C to 16 hr at –15°C	–80–110	Concrete, plaster, ceramics, glass, hardboards, wood, polyurethane (foam), phenol formaldehyde (foam), polystyrene (foam), copper, lead, steel, aluminum	Bonding to rigid and semirigid panels to irregular wall surfaces, wall cladding and floor laying; building industry applications	Foam remains flexible on aging even at elevated temperatures; will withstand a 12% movement
			Thermoplastic		
Nitrocellulose in ester solvent	Heat set 1 hr at 60°C after wet bonding	60	Paper, leather, textiles, silicon carbide, metals	Labeling, general bonding of inorganic materials including metals	Good resistance to mineral oils
Modified methyl cellulose	Dries in air	<50	Vinyl-coated paper, polystyrene foam	Heavy-duty adhesive; decorating paper and plastics	Contains fungicide to prevent biodeterioration
Ethylene vinyl acetate copolymer + resins	Film transfer at 70–80°C followed by bonding at 150–160°C	60, or 1 hr at 90	Cotton (duck)–cotton, resin rubber–leather, melamine laminate–plywood, steel (mild)–steel, acrylic (sheet) acrylic	Metals, laminated plastics, and textiles; fabrication of leather goods; lamination work	Good electrical insulation
Polyvinyl acetate	Rapid setting	<60	Paper, cardboard	Carton sealing in packaging industry	Resistant to water
Synthetic polymer blend	Applied as a melt at 177°C	<70	Paper, cardboard, polythene (coated materials)	Carton and paperbag sealing; packaging	—
Polychloroprene/resin blend in solvent	Air dried 10 min at 20°C and cured 4 days at 20°C to 7 hr at 75°C	<70	Chlorosulfonated polythene, polychloroprene fabrics, polyamide fabrics, leather, wood, textiles	Bonding synthetic rubbers and porous materials; primer for polyamide-coated fabrics such as nylon, terylene	—
Polychloroprene	Air dried 10–20 min at 20°C	—	Rubber, steel, wood, concrete	Bonding all types of rubber flooring to metals, woods, and masonry	Good heat resistance
Saturated polyester + isocyanate catalyst in ethyl acetate	Solvent evaporation and press cured at 40–80°C when tacky	—	Cellulose, cellulose acetate, polyolefins (treated film), polyvinyl chloride (rigid), paper, aluminum (foil), copper (foil)	Lamination of plastic films to themselves and metal foils for packaging industry, printed circuits	Resistant to heat, moisture, and many solvents

TABLE 12.3.3 Properties and Applications of Adhesive Materials (continued)

Basic Type	Curing Cycle, Time at Temperature	Service Temperature Range, C	Adherends	Main Uses	Remarks
Cyanoacrylate (anaerobic)	15 sec to 10 min at 20°C substrate dependent	Melts at 165	Steel–steel, steel–aluminum, aluminum–aluminum, butyl rubber–phenolic	Rapid assembly of metal, glass, plastics, rubber components	Anaerobic adhesive. Curing action is based on the rapid polymerization of the monomer under the influence of basic catalysts; absorbed outer layer on most surfaces suffices to initiate polymerization and brings about bonding
Polyacrylate resin (anaerobic)	3 min at 120°C to 45 min at 65°C or 7 days at 20°C	–55–95	Aluminum–aluminum	Assembly requirements requiring high resistance to impact or shock loading; metals, glass and thermosetting plastics	Anaerobic adhesive
			Thermosetting		
Urea formaldehyde	9 hr at 10°C to 1 hr at 21°C after mixing powder with water (22%)	<90	Wood, phenolic laminate	Wood gluing and bonding on plastic laminates to wood; plywood, chipboard manufacture; boat building and timber engineering	Excess glue may be removed with soapy water
Phenolic formaldehyde + catalyst PX-12	Cold acting	<100	Wood	Timber and similar porous materials for outdoor-exposure conditions; shop fascia panels	Good resistance to weathering and biodeterioration
Resorcinol formaldehyde + catalyst RXS-8	Cured at 16–80°C under pressure	<100	Wood, asbestos, aluminum, phenolic laminate, polystyrene (foam), polyvinyl chloride, polyamide (rigid)	Constructional laminates for marine craft; building and timber applications; aluminum–plywood bonding; laminated plastics	Recommended for severe outdoor-exposure conditions
Epoxy resin + catalyst	24–48 hr at 20°C to 20 min at 120°C	100	Steel, glass, polyester–glass fiber composite, aluminum–aluminum	General-purpose structural adhesive	—

TABLE 12.3.3 Properties and Applications of Adhesive Materials (continued)

Basic Type	Curing Cycle, Time at Temperature	Service Temperature Range, C	Adherends	Main Uses	Remarks
Epoxy resin + catalyst	8 hr at 24°C to 2 hr at 66°C to 45 min at 121°C	65	Steel, copper, zinc, silicon carbide, wood, masonry, polyester–glass fiber composite, aluminum–aluminum	Bonding of metals, glass, ceramics, and plastic composites	Cures to strong, durable bond
Epoxy + steel filler (80% w/w)	1–2 hr at 21°C	120	Iron, steel, aluminum, wood, concrete, ceramics, aluminum–aluminum	Industrial maintenance repairs; metallic tanks, pipes, valves, engine castings, castings	Good resistance to chemicals, oils, water
Epoxy + amine catalyst (ancamine LT)	2–7 days at 20°C for 33% w/w catalyst content	–5–60	Concrete stonework	Repair of concrete roads and stone surfaces	Excellent pigment-wetting properties; effective underwater and suited to applications under adverse wet or cold conditions
Epoxy resin (modified)	4–5 hr at 149°C to 20 min at 230°C to 7 min at 280°C	150	Aluminum, steel, ceramics	One-part structural adhesive for high-temperature applications	Good gap-filling properties for poorly fitting joints; resistant to weather, galvanic action
Epoxy	45 sec at 20°C	—	Gem stones, glass, steel, aluminum–aluminum	Rapid assembly of electronic components, instrument parts, printed circuits; stone setting in jewelry and as an alternative to soldering	—
Epoxy resin in solvent + catalyst	8 hr at 52°C to $^{1}/_{2}$ hr at 121°C	–270–371	Aluminum and magnesium alloys for elevated-temperature service	Strain gauges for cryogenic and elevated-temperature use; micromeasurement strain gauges	Cured material resists outgassing in high vacuum
Epoxy polyamide	8 hr at 20°C to 15 min at 100°C	100	Copper, lead, concrete, glass, wood, fiberglass, steel–steel aluminum–aluminum	Metals, ceramics, and plastics bonding; building and civil engineering applications	Resists water, acids, oils, greases

TABLE 12.3.3 Properties and Applications of Adhesive Materials (continued)

Basic Type	Curing Cycle, Time at Temperature	Service Temperature Range, C	Adherends	Main Uses	Remarks
Epoxy/polysulfide	24 hr at 20°C to 3 hr at 60°C to 20 min at 100°C	<120	Asbestos (rigid), ceramics, glass–fiber composites, carbon, polytetrafluoroethylene (treated), polyester (film), polystyrene (treated), rubber (treated), copper (treated), tungsten carbide, magnesium alloys, aluminum–aluminum, steel (stainless)–steel	Cold-setting adhesive especially suitable for bonding materials with differing expansion properties	Cures to flexible material; resistant to water, petroleum, alkalis, and mild acids
Phenol furfural + acid catalyst	2 days at 21°C	90–140	Alumina, carbon (graphite)	Formulation of chemically resistant cements; bedding and joining chemically resistant ceramic tiles	Extremely resistant to abrasion and heat
			Pressure-sensitive		
	Heated by air drying for several hours or 15–30 min at 210°F	—	Teflon–Teflon, Teflon–metal	—	Good resistance to acids and alkalis; excellent electrical properties
			Miscellaneous		
Ceramic-based	Dried for 1/2 hr at 77°C and cured 1/2 hr at 200°C + 1 hr at 250°C; postcured, 1 hr at 350°C	816	Metals	Strain gauges, temperature sensors for elevated-temperature work	—

referred to Charles V. Cagle, Ed., *Handbook of Adhesive Bonding*, McGraw-Hill, New York, 1972, and Lerner et al., *Adhesives Red Book*, Palmerton Publishing Co., New York, 1968.

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12.4 Wood

Daniel J. Strange

Definition

Wood is the structural component of a tree. It is composed of dead cells which were originally formed near the cambium (just beneath the bark). As the tree grows, the cambium moves outward, leaving the dead cells behind to serve as structure.

The two broad classifications for types of wood and softwoods and hardwoods. Softwoods come from conifers while hardwoods come from deciduous trees, and as the name implies softwoods are generally softer and hence weaker and with lower elastic modulus than hardwoods, although this generalization is not universally true.

The wood closest to the bark is called sapwood, and this layer extends about an inch into the tree. Although most of the cells in this layer are dead, this is the layer which transports moisture to the rest of the tree by capillary action. Beneath the sapwood layer is the heartwood, which is almost totally inactive except to provide structural support.

Composition

Wood is a fibrous cellular material with the cell walls composed primarily of cellulose, hemicellulose, and lignin. Cellulose is a linear polymer of glucose units and is the single most common organic chemical in nature. It accounts for roughly 40 to 50% of the wood by weight. Hemicellulose is a modified form of cellulose comprising approximately 30% of the cell wall whose structure can vary depending upon the exact type of wood. Lignin is a complex three-dimensional phenolic polymer which composes 20 to 30% of the structure of the wood. The rest of the weight of the wood is composed primarily of extraneous extractive substances which reside within the cellular structure and affect properties such as specific gravity, moisture absorption, and durability.

Variations in the compositions, structures, and volumes of these four components can have dramatic effects on the properties of the wood. These properties are relatively constant within a species, although growing conditions can have a significant influence.

Mechanical Properties

The properties of wood can vary substantially depending upon moisture content. "Green" wood, wood taken directly from a living tree with associated high moisture level, is significantly weaker (lower Young's modulus, tensile strength, and compressive strength) than oven-dried wood. Typical ratios of dry to green wood strength properties vary from 1.2 to 1.8.

The failure modes of wood are more complex than one might expect. Because wood is essentially a composite material, it does not follow Hooke's law at high stresses but instead exhibits viscoelastic behavior. Figure 12.4.1 shows typical stress–strain curves for wood in tension and compression. At very high stresses, creep can occur. Wood is strongest in tension parallel to the grain, on the order of 100 MPa for a typical softwood. Perpendicular to the grain this value drops to about 4 MPa. In compression the strength values are approximately half the tension values, due to the collapse of the cellular structure and buckling of the wood fibers.

There are three principal shear failure modes in wood, six if one distinguishes between the radial and tangential directions. These modes are shear perpendicular to grain, shear parallel to grain, and rolling shear. Rolling shear occurs when the failure plane is parallel to the grain but the sliding direction is perpendicular to the grain, hence the fibers "roll" over each other. Wood is strongest when the shear is perpendicular to the grain, and weakest in rolling shear.

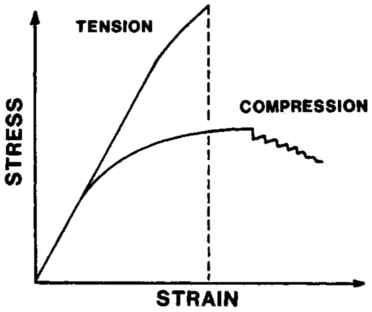

FIGURE 12.4.1 Stress–strain behavior of wood in tension and compression. Stress–strain curves for wood in tension and compression parallel to grain. Signs of stress and strain have been ignored so that both may be plotted together. Note particularly the difference in strength and in the extent of the nonlinear deformation prior to maximum stress.

Decay Resistance

Totally dry wood does not decay. Furthermore, wood kept completely submerged will not decay significantly. Wood decays most rapidly in warm, humid, low-altitude areas. Some species of wood are more decay resistant than others as a result of the presence of extractives. White oak, walnut, cherry, cedar, and yew are examples of highly decay-resistant woods. Pines, willows, elms, beeches, and spruces are examples of low decay-resistant woods.

Composites

By gluing wood plies, chips, fibers, or pulp together a composite material can be formed which has more isotropic and homogenous properties than regular timber. In addition, this technique creates a strong and durable product out of wood unsuitable for timber. In general, wood composites homogenize the extreme anisotropy of timber into a nearly isotropic material whose properties are an average of the properties in each direction of the original timber. Table 12.4.1 classifies the various wood composites based upon the constitutive particle and the binder.

The most common wood composite is paper. Paper is made from pulped and chemically treated cellulose fibers, which is then rolled into sheets, pressed, and dried. There is no glue involved, as the microfibrils of the cellulose interlock and form hydrogen bonds. Fiberboard is similar to paper, only thicker (by an arbitrary value, typically 0.012 in.) and with larger fiber bundles. *Hardboard* simply refers to a high-density fiberboard.

Wood chips and/or sawdust pressed and glued together is referred to as *particleboard*. Typically, the chips range in size from 10 to 300 mm long and are in the form of flakes or fibers. Particleboard is effectively isotropic, easily machineable, and inexpensive. It is often used in furniture and for floor underlayment. When larger wood chips are used the product is referred to as *flakeboard*.

Plywood is created by layering plies of radial-cut wood. Typically, the plies are oriented at 90° to each other, which results in a strong material when the stress in parallel or perpendicular to the grain of the face plies, but a lesser strength at any other angle. Some design strength specifications of plywood are given in Table 12.4.2. Plywood makes efficient use of timber due to its radial cut, minimizes the effects of imperfections, resists warping, and can be formed into large sheets. Plywood is also less expensive than clear lumber.

The reader is referred to Table C.14 in the Appendix for an overview of the physical properties and uses of American woods. The table also contains recommendations for appropriate applications. Table E.1 in the Appendix gives nominal sizes for lumber and timber, as well as allowable stresses in tension and compression and moduli of elasticity of various kinds of woods.

TABLE 12.4.1 Allowable Stresses for Plywood (Stresses in MPa)

Type of Stress	Species Group of Face Ply	Grade Stress Level				
		S-1		S-2		S-3
		Wet	Dry	Wet	Dry	Dry Only
Tension in plane of plies (at 45° to face use 1/6 value)	1	9.86	13.79	8.20	11.38	11.38
	2,3	6.76	9.65	5.65	8.27	8.27
	4	6.48	9.17	5.38	7.65	7.65
Compression in plane of plies (at 45° to face use 1/3 value)	1	6.69	11.31	6.21	10.62	10.62
	2	5.03	8.27	4.69	7.58	7.58
	3	4.21	7.31	4.00	6.83	6.83
	4	4.21	6.89	4.00	6.55	6.55
Shear in plane perpendicular to plies (45° use 2 × value)	1	1.41	1.72	1.41	1.72	1.45
	2,3	1.10	1.28	1.10	1.28	1.10
	4	1.00	1.21	1.00	1.21	1.07
Shear, rolling, in the plane of plies (at 45° to face grain use $1^1/_3$ value)	Marine and Structural I	0.43	0.52	0.43	0.52	—
	Structural II and 2.4.1	0.34	0.39	0.34	0.39	0.38
	All Other	0.30	0.37	0.30	0.37	0.33
Modulus of rigidity (shear in plane perpendicular to plies)	1	480	620	480	620	570
	2	410	520	410	520	470
	3	350	410	350	410	380
	4	310	350	310	350	310
Bearing (on face) (perpendicular to plane of plies)	1	1.45	2.34	1.45	2.34	2.34
	2,3	0.93	1.45	0.93	1.45	1.45
	4	0.72	1.10	0.72	1.10	1.10
Modulus of elasticity in bending in plane of plies (face grain parallel or ⊥ to span)	1	10,300	12,400	10,300	12,400	12,400
	2	9,000	10,300	9,000	10,300	10,300
	3	7,600	8,300	7,600	8,300	8,300
	4	6,200	6,900	6,200	6,900	6,900

Adapted from American Plywood Association, Plywood Design Specifications, 1976.

TABLE 12.4.2 Classification of Wood Composites

Material	Constitutive Particle	Binder
Wood flour molding	Wood flour	Plastic; synthetic resin
Fiber-reinforced plastic	Fiber	Plastic
Paper	Fiber segment; fiber	Cellulose; hemicellulose; synthetic resin
Fiberboard	Fiber segment; fiber; fiber bundle	Lignin; synthetic resin
Particleboard	Splinter; chip; flake; planer shaving	Synthetic resin
Plywood	Veneer	Synthetic resin; natural glue
Laminated wood	Lumber	Synthetic resin; natural glue; mechanical connector
Solid wood	Single fiber or earlywood–latewood and wood ray, etc.	Lignin; hemicellulose

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12.5 Portland Cement Concrete

Steven H. Kosmatka

Introduction

Portland cement concrete is a simple material in appearance with a very complex internal nature. In contrast to its internal complexity, versatility, durability, and economy of concrete have made it the most-used construction material in the world. This can be seen in the variety of structures it is used in, from highways and bridges to buildings and dams.

Concrete is a mixture of portland cement, water, and aggregates, with or without admixtures. The portland cement and water form a paste that hardens as a result of a chemical reaction between the cement and water. The paste acts as a glue, binding the aggregates (sand and gravel or crushed stone) into a solid rocklike mass. The quality of the paste and the aggregates dictate the engineering properties of this construction material. Paste qualities are directly related to the amount of water used in relation to the amount of cement. The less water that is used, the better the quality of the concrete. Reduced water content results in improved strength and durability and in reduced permeability and shrinkage. As the fine and coarse aggregates make up 60 to 75% of the total volume of the concrete (Figure 12.5.1), their selection is important. The aggregates must have adequate strength and resistance to exposure conditions and must be durable.

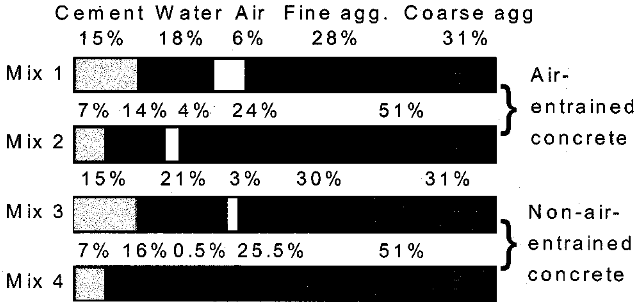

FIGURE 12.5.1 Range of proportions of materials used in concrete. (From *Design and Control of Concrete Mixtures,* EB001, Portland Cement Association, Skokie, IL, 1992. With permission.)

Fresh Concrete Properties

Freshly mixed concrete should be in a semifluid state capable of being molded by hand or mechanical means. All the particles of sand and coarse aggregate are encased and held in suspension. The ingredients should not segregate or separate during transport or handling. After the concrete hardens, it becomes a homogeneous mixture of all the components. Concrete of plastic consistency should not crumble, but flow sluggishly without segregation.

Concrete must be consolidated to form a homogeneous mass without the presence of large voids to achieve the desired strength and durability of the construction material. Internal and external vibration of concrete using vibrators allows stiff, slow-slump mixtures to be properly densified. The use of mechanical vibration provides an economical, practical method to quickly consolidate concrete without detrimentally affecting its properties.

Hardened Concrete Properties

Strength

Concrete gains strength by the reaction between cement and water — called hydration. Portland cement is primarily a calcium silicate cement. The calcium silicate combines with water and forms calcium silicate hydrate, which is responsible for the primary engineering properties of concrete, such as setting, hardening, strength, and dimensional stability. The compressive strength of concrete increases with age as long as an appropriate moisture content and temperature are available. This is illustrated in Figure 12.5.2. Compressive strength is usually specified at the age of 28 days; however, depending on the project, ages of 3 and 7 days can also be specified. For general-use concrete, a 28-day compressive strength between 20 and 40 MPa (3000 and 6000 psi) is used. 28 MPa (4000 psi) is most common. Higher-strength concrete, 50 to 140 MPa (7000 to 20,000 psi), is used in special applications to minimize structural dimensions, increase abrasion resistance and durability, and minimize creep (long-term deformation).

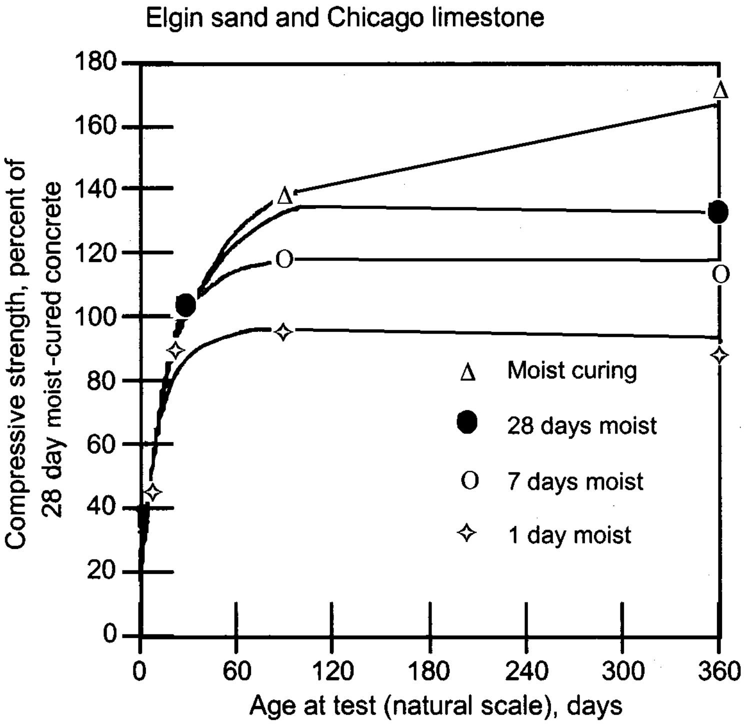

FIGURE 12.5.2 Concrete strength increases with age as long as moisture and a favorable temperature are present.

Increase in strength with age continues as long as any unhydrated cement is still present, the relative humidity in the concrete is approximately 80% or higher, and the concrete temperature is favorable. In order to maintain this increase in strength, concrete must be properly cured. Curing means that not only will a favorable temperature be present, but also moisture loss will not be permitted or extra water will be provided at the surface.

The compressive strength of concrete is directly related to the water/cement ratio. A decrease in water/cement ratio results in higher strength. Concrete achieves about 70 to 75% of its 28-day strength in 7 days. Although concrete is very strong in compression, it is weak in tensile strength. Tensile strength is about 8 to 12% of the compressive strength. Flexural strength is 0.7 to 0.8 times (for English units 5 to 7.5 times) the square root of the compressive strength. Shear strength is about 20% of the compressive strength. Modulus of elasticity ranges from 14,000 to 41,000 MPa and can be estimated as 5000 times the square root of the compressive strength (2 to 6 million psi or 57,000 times the square root of the compressive strength in English units). Refer to Tables 12.5.1, 12.5.2, and 12.5.3.

TABLE 12.5.1 Typical Properties of Normal-Strength Portland Cement Concrete

Compressive strength	20–40 MPa (3000–6000 psi)
Flexural strength	3–5 MPa (400–700 psi)
Tensile strength	2–5 MPa (300–700 psi)
Modulus of elasticity	14,000–41,000 MPa (2–6 million psi)
Permeability	1×10^{-10} cm/sec
Coefficient of thermal expansion	10^{-5}/°C (5.5×10^{-6}/°F)
Drying shrinkage	$4–8 \times 10^{-4}$
Drying shrinkage of reinforced concrete	$2–3 \times 10^{-4}$
Poisson's ratio	0.20–0.21
Shear strain	6000–17,000 MPa (1–3 million psi)
Density	2240–2400 kg/m^3 (140–150 lb/ft^3)

Density

Normal-weight concrete has a density of 2240 to 2400 kg/m^3 (140 to 150 lb/ft^3). The density of concrete varies with the relative density of the aggregate, the amount of air present in the paste, and the amount of water and cement in the mixture.

Permeability

Concrete permeability is a function of the permeability of the paste and aggregate and the interface between them. Decreased permeability improves the resistance of concrete to saturation, sulfate attack, chemical attack, and chloride penetration. Paste permeability has the greatest influence on concrete permeability. Paste permeability is directly related to the water/cement ratio and the degree of hydration or length of moist curing. A low water cement ratio and an adequate moist-curing period result in concrete with low permeability (Figure 12.5.3). The water permeability of mature, good-quality concrete, is approximately 1×10^{-10} cm/sec.

Abrasion Resistance

Abrasion resistance is directly related to the compressive strength of the concrete. The type of aggregate and the surface finish also have a strong influence on abrasion resistance. A hard aggregate, such as a granite, would provide more abrasion resistance than a soft limestone aggregate.

Volume Change and Crack Control

Concrete changes slightly in volume for various reasons. Understanding the nature of these changes is useful in planning concrete work and preventing cracks from forming. If concrete is free to move, normal volume changes would have very little consequence; but since concrete in service is usually restrained by foundations, subgrades, reinforcement, or connecting elements, significant stresses can develop. As the concrete shrinks, tensile stresses develop that can exceed the tensile strength of the concrete, resulting in crack formation.

The primary factors affecting volume change are temperature and moisture changes. Concrete expands slightly as temperature rises and contracts as temperature falls. The average value for the coefficient of thermal expansion of concrete is about 1.0×10^{-5}/°C (5.5×10^{-6}/°F). This amounts to a length change of 5 mm for a 10-m length (0.66 in. for 100 ft) of concrete subjected to a rise or fall of 50°C (100°F). The thermal coefficient of expansion for steel is about 1.2×10^{-5} per degree Celsius (6.5×10^{-6}/°F), comparable to that of concrete. The coefficient for reinforced concrete can be assumed as 1.1×10^{-5}/°C (6×10^{-6}/°F).

Concrete expands slightly with a gain in moisture and contracts with a loss in moisture. The drying-shrinkage of concrete specimens ranges from 4 to 8×10^{-4} when exposed to air at a 50% relative humidity. Concrete with a unit shrinkage of 5.5×10^{-4} shortens about the same amount as a thermal contraction caused by a decrease in temperature of 55°C (100°F). The shrinkage of reinforced concrete is less than that for plain concrete because of restraint offered by the reinforcement. Reinforced concrete structures with normal amounts of reinforcement have a drying-shrinkage in the range of 2 to 3×10^{-4}.

TABLE 12.5.2 Compressive Strength of Concrete Made from Type I Cement, psi[a]

Series	Mix Id.	w/c by Weight	1 Day	3 Days	7 Days	28 Days	3 Months	1 Year	3 Years	5 Years	10 Years	20+ Years
						Moist Curing						
308	1	0.37	2160	4430	5930	7080	8260	8410		10400		
308	2	0.51	1040	2690	4200	5890	6410		8520			
308	3	0.65	610	1770	2780	4320	5030	5020		6050		
308	4	0.82	330	990	1580	2700	3180	3290		3680		
308	5	0.36	2060	4300	5820	7010	7750	8930		10330		
308	6	0.50	990	2780	4110	5950	6440	7280		8180		
308	7	0.64	550	1710	2700	4420	5190	5390		6180		
308	8	0.83	500	1000	1690	2850	3330	3490		3790		
308	9	0.36	2010	4330	5770	6940	7940	8550		10170		
308	10	0.50	900	2600	4250	6210	6490	7280		8670		
308	11	0.64	530	1720	2810	4510	5130	5770		6470		
308	12	0.82	250	920	1670	2880	3570	3540		3750		
356	AV1	0.40		5650	7140	9020	9460	8870	10760	10070	11020	12700
356	AV2	0.53		3390	4760	6510	7480	6890	7780	7720	8900	9680
356	AV3	0.71		1770	2540	4160	4540	4540	4960	5030	5840	6130
356	DV1	0.40		5000	6710	7980	8530	8660	10240	10340	10540	12300
356	DV2	0.53		3070	4810	6720	7400	7840	8780	8720	9330	9980
356	DV3	0.71		1580	2610	4380	5060	5360	5680	5700	6470	6710
356	EV1	0.40		4670	6650	8530	9790	10090	9940	11330	10900	12460
356	EV2	0.53		2700	4580	6730	7690	7860	8240	8960	8580	10290
356	EV3	0.71		1470	2500	4290	5010	5070	5110	5770	6200	6420
356	XL1	0.40		4780	6300	8090		9470		10780	10740	11730
356	XL2	0.53		3170	4470	6040		7740		8070	8370	8060
356	XL3	0.71		1800	2650	4060		4990		5220	5280	5260
356	XV1	0.40		5220	6950	8520		9720		10550	10850	13100
356	XV2	0.53		3350	4870	6700		7950		8710	8760	9800
356	XV3	0.71		1680	2810	4120		5060		5610	6280	6590
356	XW1	0.40		4680	6200	7780		9840		10100	10310	11480
356	XW2	0.53		3100	4520	6270		7420		8180	8150	8760
356	XW3	0.71		1770	2680	4140		5290		5560	5630	5460
374	11	0.41	1550		5680	7390	7610	9160	9810		10070	10460
374	11	0.56	780		4210	5870	6390	7020	6910		6740	7410
374	12	0.41	1120		5920	7490	8770	9170	9710		9710	10900
374	12	0.55	580		3800	5710	6650	7010	7380		7010	7300
374	13	0.42	1520		4320	6280	7560	8280	8620		9100	9940
374	13	0.57	890		2740	4730	5760	6400	6750		6340	7360
374	14	0.41	1490		5020	6460	7160	8730	9280		9400	10140
374	14	0.55	800		3480	5190	5700	6540	7030		6560	7410
374	15	0.45	2230		6080	7180	7820	8530	9290		9520	10770
374	15	0.59	1260		4730	5830	6280	6440	6360		5980	
374	16	0.41	1820		6040	7230	8080	9540	10160		10400	
374	16	0.56	1020		4000	5820	6520	7060	7640		7230	6840
374	17	0.46	1340		5220	7040	7560	8700	9310		9280	
374	17	0.61	740		3480	5770	6410	6560	6890		6700	7190
374	18	0.49	1220		5290	7000	7600	8360	9110		10290	10630
374	18	0.58	670		3600	5600	6230	6540	6810		6660	
374	19A	0.45	770		3090	4810	6600	7350	7930		8610	9240
374	19A	0.54	410		1710	3100	4280	5060	5940		5950	6480
374	19B	0.45	1110		4350	6560	7450	7740	8850		9550	10550
374	19B	0.60	560		2640	4260	5140	5420	6000		6360	6730
374	19C	0.45	1540		5370	6860	7390	7960	9000		9520	
374	19C	0.59	890		3910	5520	6200	6580	6970		6640	7220
436	1	0.36	2640	4780	6460	8070	8890	9670	9840		11030	10710

TABLE 12.5.2 Compressive Strength of Concrete Made from Type I Cement, psi[a] (continued)

Series	Mix Id.	w/c by Weight	1 Day	3 Days	7 Days	28 Days	3 Months	1 Year	3 Years	5 Years	10 Years	20+ Years
436	2	0.49	1320	2780	4200	6110	7210	7920	7990		8990	8940
436	3	0.62	700	1620	2550	4170	5210	5840	5850		6010	5390
436	4	0.42	1760	3500	5080	7200	8100	8720	9640		10540	10820

[a] To convert to MPa, multiply by 0.00689476.

Source: From Wood, S.L., *Research and Development Bulletin RD102T*, Portland Cement Association, Skokie, IL, 1992. With permission.

The amount of shrinkage is directly related to the amount of water in the concrete. Higher water content results in higher shrinkage. Specimen size also has an effect. Larger specimens shrink less than small specimens.

Drying-shrinkage is an inherent and unavoidable property of concrete; therefore, properly positioned reinforcing steel is used to reduce crack widths or joints are used to predetermine or control the location of cracks. Shrinkage control joints should be spaced about 25 to 30 times the thickness of a concrete slab on ground.

Deformation and Creep

Concrete will deform a small amount when a load is placed on it. When concrete is loaded, the deformation caused by the load can be divided into two parts: a deformation that occurs immediately, such as elastic strain, and a time-dependent deformation that begins immediately but continues at a decreasing rate for as long as the concrete is loaded (Figure 12.5.4). This latter deformation is called creep. The amount of creep is dependent on the magnitude of the stress, the age and strength of the concrete when the stress is applied, and the length of time the concrete is stressed. Creep is of little concern for normal concrete pavements, bridges, and small buildings; however, creep should be considered in design for very tall buildings or very long bridges.

Concrete Ingredients

Portland Cements

Portland cements are hydraulic cements; that is, they set and harden by reacting with water. This reaction, called hydration, combines water and cement to form a stonelike mass. Portland cement was invented in 1824 by an English mason, Joseph Aspdin, who named his product portland cement because it produced a concrete that was of the same color as natural stone on the Isle of Portland in the English Channel.

Portland cement is produced by combining appropriate proportions of lime, iron, silica, and alumina and heating them. These raw ingredients are fed into a kiln that heats the ingredients to temperatures of 1450 to 1650°C (2600 to 3000°F) and changes the raw materials chemically into cement clinker. The clinker is cooled and then pulverized. During this operation a small amount of gypsum is added to control the setting of the cement. The finished pulverized product is portland cement. Portland cement is essentially a calcium silicate cement.

The American Society for Testing and Materials (ASTM) Standard C 150, Specification for Portland Cement, provides for the following types of portland cement:

Type I	General portland cement
Type II	Moderate-sulfate-resistant cement
Type III	High-early-strength cement
Type IV	Low–heat-of-hydration cement
Type V	High-sulfate-resistant cement

Types I, II, and III may also be designated as being air entraining. Type I portland cement is a general cement suitable for all uses where special properties of other cements are not required. It is commonly used in pavements, building, bridges, and precast concrete products.

TABLE 12.5.3 Flexural Strength of Concrete Made from Type I Cement, psi[a] (Third-Point Loading)

Series	Mix Id.	w/c by Weight	1 Day	3 Days	7 Days	28 Days	3 Months	1 Year	3 Years	5 Years	10 Years	20 Years
Moist Curing												
308	1	0.37	295	540	625	855	975	925		960		
308	2	0.51	160	415	570	765	805	845		780		
308	3	0.65	80	290	425	595	675	680		645		
380	4	0.82	40	155	285	450	505	485		480		
308	5	0.36	285	510	680	825	890	940		930		
308	6	0.50	165	445	545	720	810	760		815		
308	7	0.64	95	290	465	605	695	655		690		
308	8	0.83	45	180	310	450	530	525		470		
308	9	0.36	310	535	655	820	905	970		915		
308	10	0.50	175	410	570	710	860	815		830		
308	11	0.64	90	320	440	675	715	715		690		
308	12	0.82	40	180	330	490	575	555		495		
356	XL1	0.40			705	880						
356	XL2	0.53			555	720						
356	XL3	0.71			420	555						
356	XV1	0.40			625	725						
356	XV2	0.53			555	655						
356	XV3	0.71			385	490						
356	XW1	0.40			620	750						
356	XW2	0.53			515	665						
356	XW3	0.71			395	515						
374	11	0.41	240		640	765	840	905	855		945	1070
374	11	0.56	135		520	625	710	690	730		730	830
374	12	0.41	180		640	790	910	925	965		970	1030
374	12	0.55	100		530	705	785	755	770		795	850
374	13	0.42	260		525	690	845	885	915		995	1140
374	13	0.57	165		420	595	705	765	765		800	880
374	14	0.41	250		620	725	800	915	890		965	
374	14	0.55	150		490	630	740	765	745		780	890
374	15	0.45	320		660	755	865	865	870		945	970
374	15	0.59	215		580	650	710	710	665		735	830
374	16	0.41	265		675	755	890	920	935		1035	1110
374	16	0.56	165		535	655	760	770	775		820	930
374	17	0.46	210		600	685	855	870	935		905	
374	17	0.61	120		490	650	735	760	720		695	
374	18	0.49	220		585	720	830	915	895		965	1090
374	18	0.58	130		510	650	750	740	730		725	
374	19A	0.45	145		450	605	745	840	870		950	1000
374	19A	0.54	75		300	470	610	655	700		735	850
374	19B	0.45	195		555	670	810	835	875		955	1060
374	19B	0.60	105		415	580	680	725	715		785	840
374	19C	0.45	275		605	750	890	920	890		950	1050
374	19C	0.59	170		510	665	775	810	765		790	890
436	1	0.36	370	555	655	770	925	l980	955		960	1030
436	2	0.49	225	435	565	745	825	860	905		900	960
436	3	0.62	135	300	420	620	690	720	730		730	800
436	4	0.42	320	505	655	755	875	890	1005		1010	1060

[a] To convert to MPa, multiply by 0.00689476.

Source: From Wood, S.L., *Research and Development Bulletin RD102T,* Portland Cement Association, Skokie, IL, 1992. With permission.

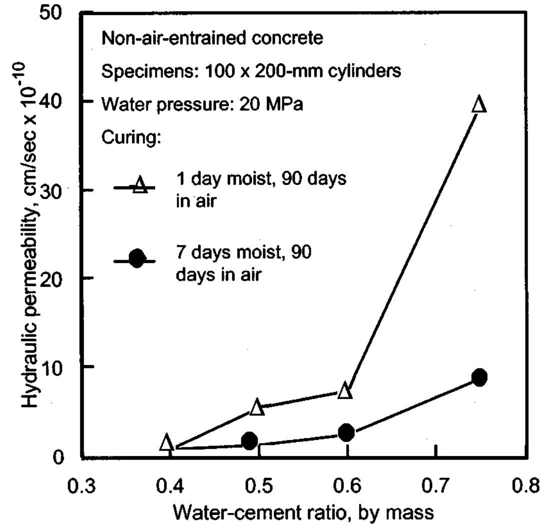

FIGURE 12.5.3 Water permeability of concrete as affected by water/cement ratio and curing. (From *Design and Control of Concrete Mixtures,* EB001, Portland Cement Association, Skokie, IL, 1992. With permission.)

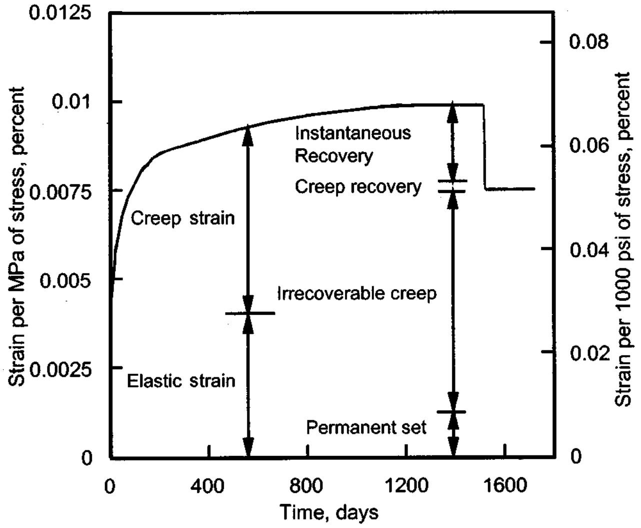

FIGURE 12.5.4 Combined curve of elastic and creep strains showing amount of recovery. (From *Design and Control of Concrete Mixtures,* EB001, Portland Cement Association, Skokie, IL, 1992. With permission.)

Type II portland cement is used where precaution against moderate sulfate attack is important where sulfate concentrations in groundwater or soil are higher than normal, but not severe. Type II cement can also be specified to generate less heat than Type I cement. This moderate heat of hydration requirement is helpful when placing massive structures, such as piers, heavy abutments, and retaining walls. Type II cement may be specified when water-soluble sulfate in soil is between 0.1 and 0.2%, or when the sulfate content in water is between 150 and 1500 ppm. Types I and II are the most common cements available.

Type III portland cement provides strength at an early age. It is chemically similar to Type I cement except that the particles have been ground finer to increase the rate of hydration. It is commonly used in fast-track paving or when the concrete structure must be put into service as soon as possible, such as in bridge deck repair.

Type IV portland cement is used where the rate and amount of heat generated from hydration must be minimized. This low heat of hydration cement is intended for large, massive structures, such as gravity dams. Type IV cement is rarely available.

Type V portland cement is used in concrete exposed to very severe sulfate exposures. Type V cement would be used when concrete is exposed to soil with a water-soluble sulfate content of 0.2% and higher or to water with over 1500 ppm of sulfate. The high sulfate resistance of Type V cement is attributed to its low tricalcium aluminate content.

Blended Hydraulic Cements

Blended hydraulic cements are produced by intimately blending two or more types of cementitious material. Primary blending materials are portland cement, ground granulated blast-furnace slag, fly ash, natural pozzolans, and silica fume. These cements are commonly used in the same manner as portland cements. Blended hydraulic cements conform to the requirements of ASTM C 595 or C 1157. ASTM C 5195 cements are as follows: Type IS — portland blast-furnace slag cement, Type IP and Type P — portland–pozzolan cement, Type S — slag cement, Type I (PM) — pozzolan-modified portland cement, and Type I (SM) — slag-modified portland cement. The most common blended cements available are Types IP and IS.

ASTM C 1157 blended hydraulic cements include the following: Type GU — blended hydraulic cement for general construction, Type HE — high-early-strength cement, Type MS — moderate-sulfate-resistant cement, Type HS — high-sulfate-resistant cement, Type MH — moderate-heat-of-hydration cement, and Type LH — low-heat-of-hydration cement.

Supplementary Cementing Materials (Mineral Admixtures)

Supplementary cementing materials, also called mineral admixtures, are sometimes added to concrete mixtures. They contribute to the properties of hardened concrete through hydraulic or pozzolanic activity. Typical examples are natural pozzolans, fly ash, ground granulated blast-furnace slag, and silica fume. These materials react chemically with calcium hydroxide released from the hydration of portland cement to form cement compounds.

Below is a summary of the specifications and classes of supplementary cementing materials:

1. Ground granulated iron blast-furnace slag—ASTM C 989

   Grade 80 — Slags with a low activity index
   Grade 100 — Slags with a moderate activity index
   Grade 120 — Slags with a high activity index
2. Fly ash and natural pozzolans — ASTM C 618
3. Class N — Raw or calcined natural pozzolans including diatomaceous earth, opaline cherts, shales, tuffs, volcanic ashes, and some calcined clays and shales
4. Class F — Fly ash with pozzolanic properties
5. Class C — Fly ash with pozzolanic and cementitious properties
6. Silica fume — ASTM C 1240

Mixing Water for Concrete

Almost any natural water that is drinkable can be used as mixing water for making concrete. However, some waters that are not fit for drinking may be suitable for concrete. Reference 1 provides guidance concerning the use of waters containing alkali carbonates, chlorides, sulfates, acids, oils, and other materials, and provides guidance as to allowable levels of contamination.

Aggregates for Concrete

The importance of using the right type and quality of aggregates cannot be overemphasized since the fine coarse aggregates occupy between 60 to 75% of the concrete volume and strongly influence the freshly mixed and hardened properties, mix proportions, and economy of the concrete. Fine aggregates consist of natural sand or crushed rock with particles smaller than 5 mm (0.2 in). Coarse aggregates consist of a combination of gravel or crushed aggregate with particles predominately larger than 5 mm (0.2 in.) and generally between 10 and 13 mm ($^3/_8$ and $^1/_2$ in.). The most common coarse aggregate size is 19 and 25 mm ($^3/_4$ and 1 in.) aggregate.

Normal weight aggregates should meet the requirements of ASTM C 33. This specification limits the amounts of harmful substances and states the requirements for aggregate characteristics, such as grading. The grading and maximum size of the aggregate affect the relative aggregate proportions as well as cement and water requirements, workability, pumpability, economy, shrinkage, and durability of the concrete.

Chemical Admixtures for Concrete

Admixtures are ingredients in concrete other than portland cement, water, and aggregates that are added to the mixture immediately before or during mixing. Common chemical admixtures include air-entraining, water-reducing, retarding, accelerating, and superplasticizing admixtures. The major reasons for using admixtures are to reduce the cost of concrete construction, achieve certain properties in concrete more effectively than by other means, or to ensure the quality of concrete during the states of mixing, transporting, placing, or curing in adverse weather conditions. Refer to Table 12.5.4.

Air-entraining admixtures are used purposely to entrain microscopic air bubbles in concrete. Air entrainment will dramatically improve the durability of concrete exposed to moisture during freezing and thawing. Air-entraining admixtures are commonly used to provide between 5 and 8% air content in concrete.

Water-reducing admixtures are used to reduce the quantity of mixing water required to produce concrete of a certain slump, reduce water/cement ratio, reduce cement content, or increase slump. Typical water-reducing admixtures reduce the water content by approximately 5 to 10%. High-range water reducers (superplasticizers) reduce the water content by approximately 12 to 30% and they can produce a highly fluid concrete.

Retarding admixtures are used to retard the rate of setting of concrete. An accelerating admixture is used to accelerate strength development of concrete at an early age.

Proportioning Normal Concrete Mixtures

The objective in proportioning concrete mixtures is to determine the most economical and practical combination of readily available materials to produce a concrete that will satisfy the performance requirements under particular conditions of use. To fulfill these objectives a properly proportioned concrete mix should possess these qualities: (1) acceptable workability of freshly mixed concrete, (2) durability, strength, and uniform appearance of hardened concrete, and (3) economy. Only with proper selection of materials and mixture characteristics can the above qualities be obtained in concrete production.

The key to designing a concrete mixture is to be fully aware of the relationship between the water/cement ratio and its effect on strength and durability. The specified compressive strength at 28 days and durability concerns dictate the water/cement ratio established for a concrete mixture. The water/cement ratio is simply the weight of water divided by the weight of cement. If pozzolans or slags are used, it would include their weights and would be referred to as the water/cementitious material ratio. The water/cement ratio can be established by a known relationship to strength or by durability requirements. For example, a concrete structure may require only 20 MPa (3000 psi) compressive strength, which would relate to a water/cement ratio of about 0.6; however, if the concrete is exposed to deicers, the maximum water/cement ratio should be 0.45 (Table 12.5.5). For corrosion protection or reinforced concrete exposed to deicers, the maximum water/cement ratio should be 0.40. When designing concrete mixtures, remember that where durability is concerned, water/cement ratio should be as low as practical. Entrained air must be used in all concrete that will be exposed to freezing and thawing and

TABLE 12.5.4 Concrete Admixtures by Classification

Type of Admixture	Desired Effect	Material
Accelerators (ASTM C 494, Type C)	Accelerate setting and early-strength development	Calcium chloride (ASTM D 98) Triethanolamine, sodium thiocyanate, calcium formate, calcium nitrite, calcium nitrate
Air detrainers	Decrease air content	Tributyl phosphate, dibutyl phthalate, octyl alcohol, water-insoluble esters of carbonic and boric acid, silicones
Air-entrained admixtures (ASTM C 260)	Improve durability in environments of freeze-thaw, deicers, sulfate, and alkali reactivity Improve workability	Salts of wood resins (Vinsol resin) Some synethic detergents Salts of sulfonated lignin Salts of petroleum acids Salts of proteinaceous material Fatty and resinous acids and their salts Alkylbenzene sulfonates Salts of sulfonated hydrocarbons
Alkali-reactivity reducers	Reduce alkali-reactivity expansion	Natural pozzolans, fly ash, silica fume, blast-furnace slag, salts of lithium and barium
Bonding admixtures	Increase bond strength	Rubber, polyvinyl chloride, polyvinyl acetate, acrylics, butadiene-styrene copolymers
Coloring agents	Colored concrete	Modified carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide, cobalt blue (ASTM C 979)
Corrosion inhibitors	Reduce steel corrosion activity in a chloride environment	Calcium nitrite, sodium nitrite, sodium benzoate, certain phosphates or fluorosilicates, fluoroaluminates
Dampproofing admixtures	Retard moisture penetration into dry concrete	Soaps of calcium or ammonium stearate or eleate Butyl stearate Petroleum products
Finely divided mineral admixtures		
Cementitious	Hydraulic properties Partial cement replacement	Ground granulated blast-furnace slag (ASTM C 989) Natural cement Hydraulic hydrated lime (ASTM C 141)
Pozzolans	Pozzolanic activity Improve workability, plasticity, sulfate resistance; reduce alkali reactivity, permeability, heat of hydration Partial cement replacement Filler	Diatomaceous earth, opaline cherts, clays, shales, volcanic tufts, pumicites (ASTM C 618, Class N); fly ash (ASTM C 618, Classes F and C), silica fume
Pozzolanic and cementitious	Same as cementitious and pozzolan categories	High calcium fly ash (ASTM C 618, Class C) Ground granulated blast-furnace slag (ASTM C 989)
Nominally inert	Improve workability Filler	Marble, dolomite, quartz, granite
Fungicides, germicides, and insecticides	Inhibit or control bacterial and fungal growth	Polyhalogenated phenols Dieldrin emulsions Copper compounds
Gas formers	Cause expansion before setting	Aluminum powder Resin soap and vegetables or animal glue Saponin Hydrolized protein
Grouting agents	Adjust grout properties for specific applications	See Air-entraining admixtures, Accelerators, Retarders, Workability agents
Permeability reducers	Decrease permeability	Silica fume (ASTM C 1240) Fly ash (ASTM C 618) Ground slag (ASTM C 989) Natural pozzolans (ASTM C 618)

TABLE 12.5.4 Concrete Admixtures by Classification (continued)

Type of Admixture	Desired Effect	Material
Pumping aids	Imnprove pumpability	Water reducers Latex Organic and synthetic polymers Organic flocculents Organic emulsions of paraffin, coal tar, asphalt, acrylics Bentonite and pyrogenic silicas Natural pozzolans (ASTM C 618, Class N) Fly ash (ASTM C 618, Classes F and C) Hydrated lime (ASTM C 141)
Retarders (ASTM C 494, Type B)	Retard setting time	Lignin Borax Sugars Tartaric acid and salts
Superplasticizers[a] (ASTM C 1017, Type 1)	Flowing concrete Reduce water/cement ratio	Sulfonated melamine formaldehyde condensates Sulfonated napthalene formaldehyde condensates Ligonsulfonates
Superplasticizer[a] and retarder (ASTM C 1017, Type 2)	Flowing concrete with retarded set Reduce water	See Superplasticizers and also Water reducers
Water reducer (ASTM C 494, Type A)	Reduce water demand at least 5%	Lignosulfonates Hydroxylated carboxylic acids Carbohydrates (Also tend to retard set so accelerator is often added)
Water reducer and accelerator (ASTM C 494, Type E)	Reduce water (minimum 5%) and accelerate set	See Water reducer, Type A (Accelerator is added)
Water reducer and retarder (ASTM C 494, Type D)	Reduce water (minimum 5%) and retard	See Water reducer, Type A
Water reducer — high range (ASTM C 494, Type F)	Reduce water demand (miniumum 12%)	See Superplasticizers
Water reducer — high range — and retarder (ASTM C 494, Type G)	Reduce water demand (miniumum 12%) and retard set	See Superplasticizers and also Water reducers
Workability agents	Improve workability	Air-entraining admixtures Finely divided admixtures, except silica fume Water reducers

[a] Superplasticizers are also referred to as high-range water reducers or plasticizers. These admixtures often meet both ASTM C 494 and C 1017 specifications simultaneously.

Source: From *Design and Control of Concrete Mixtures*, EB001, Portland Cement Association, Skokie, IL, 1992. With permission.

the presence of deicing chemicals. A typical air content for concrete would range from 5 to 8%. Reference 1 provides step-by-step procedures for proportioning concrete. Refer to Tables 12.5.6, 12.5.7, and 12.5.8.

Mixing, Transporting, and Placing Concrete

All concrete should be mixed thoroughly until it is uniform in appearance with all ingredients evenly distributed. If concrete has been adequately mixed, samples taken from different portions of a batch will have essentially the same unit weight, air content, slump, and strength. Concrete is sometimes mixed at a job site at a stationary mixer or paving mixer, and other times it is mixed in central mixers at ready-mix plants (ASTM C 94). Once concrete is transported to a job site it is then conveyed by a variety of methods including belt conveyors, buckets, shoots, cranes, pumps, wheelbarrows, and other equipment.

TABLE 12.5.5 Relationships Between Water Cement Ratio and Compressive Strength of Concrete

	Water-Portland Cement Ratio, by Mass	
Compressive Strength at 28 days, MPa (psi)	**Non-Air-Entrained Concrete**	**Air-Entrained Concrete**
40 (5800)	0.42	—
35 (5100)	0.47	0.39
30 (4400)	0.54	0.45
25 (3600)	0.61	0.52
20 (2900)	0.69	0.60
15 (2200)	0.79	0.70

Note: Strength is based on 150 × 300-mm cylinders moist cured 28 days at 23 ± 2°C. Relationship assumes maximum size of aggregate about 25 mm.

Adapted from *Design and Control of Concrete Mixtures,* EBDD1, Portland Cement Association, Skokie, IL, 1992. With permission.

Concrete should be conveyed in a manner in which the concrete is not allowed to dry out, be delayed, or allowed to segregate before it is placed.

Curing

All concrete must be properly cured. Curing is the maintenance of a satisfactory moisture content and temperature in concrete during some definite time period immediately following placing and finishing so that the desired properties of strength and durability may develop. Concrete should be moist cured for 7 days at a temperature between 10 and 27°C (50 and 80°F). Common methods of curing include ponding, spraying, or fogging; use of wet covers, impervious paper, plastic sheets, and membrane-forming curing compounds; or a combination of these.

Durability

Freeze-Thaw and Deicer Scaling Resistance

As water freezes in wet concrete, it expands 9%, producing hydraulic pressures in the cement paste and aggregate. Accumulated effects of successive freeze-thaw cycles and disruption of the paste and aggregate eventually cause significant expansion and extensive deterioration of the concrete. The deterioration is visible in the form of cracking, scaling, and crumbling.

The resistance of hardened concrete to freezing and thawing in a moist condition, with or without the presence of deicers, is significantly improved by the use of entrained air. Air entrainment prevents frost damage and scaling and is required for all concretes exposed to freezing and thawing or deicer chemicals. An air content of between 5 and 8% should be specified. Air-entrained concrete should be composed of durable materials and have a low water/cement ratio (maximum 0.45), a minimum cement content of 335 kg/m^3 (564 lb/yd^3) or move, proper finishing after bleed water has evaporated from the surface, adequate drainage, a minimum of 7-days moist curing at or above 10°C (50°F), a minimum compressive strength of 28 MPa (4000 psi), and a minimum 30-day drying period after moist curing. Sealers may also be applied to provide additional protection against the effects of freezing and thawing and deicers. However, a sealer should not be necessary for properly proportioned and placed concrete.

Sulfate-Resistant Concrete

Excessive amounts of sulfates in soil or water can, over 5 to 30 years, attack and destroy concrete that is not properly designed. Sulfates attack concrete by reacting with hydrated compounds in the hardened cement paste. Due to crystallization growth, these expansive reactions can induce sufficient pressure to

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TABLE 12.5.6a (Metric Units) Example Trial Mixtures for Air-Entrained Concrete of Medium Consistency, 80 to 100 mm Slump

					With Fine Sand, Fineness Modulus = 2.50			With Coarse Sand, Fineness Modulus = 2.90		
Water/ Cement Ratio, kg/kg	Nominal Maximum Size of Aggregate, mm	Air Content, %	Water, kg/m³ of Concrete	Cement kg/m³ of Concrete	Fine Aggregate % of Total Aggregate	Fine Aggregate, kg/m³ of Concrete	Coarse Aggregate, kg/m³ of Concrete	Fine Aggregate % of Total Aggregate	Fine Aggregate, kg/m³ of Concrete	Coarse Aggregate, kg/m³ of Concrete
0.40	10	7.5	202	505	50	744	750	54	809	684
	14	7.5	194	485	41	630	904	46	702	833
	20	6	178	446	35	577	1071	39	648	1000
	40	5	158	395	29	518	1255	33	589	1184
0.45	10	7.5	202	450	51	791	750	56	858	684
	14	7.5	194	428	43	678	904	47	750	833
	20	6	178	395	37	619	1071	41	690	1000
	40	5	158	351	31	553	1255	35	625	1184
0.50	10	7.5	202	406	53	833	750	57	898	684
	14	7.5	194	387	44	714	904	49	785	833
	20	6	178	357	38	654	1071	42	726	1000
	40	5	158	315	32	583	1225	36	654	1184
0.55	10	7.5	202	369	54	862	750	58	928	684
	14	7.5	194	351	45	744	904	49	815	833
	20	6	178	324	39	678	1071	43	750	1000
	40	5	158	286	33	613	1225	37	684	1184
0.60	10	7.5	202	336	54	886	750	58	952	684
	14	7.5	194	321	46	768	904	50	839	833
	20	6	178	298	40	702	1071	44	773	1000
	40	5	158	262	33	631	1225	37	702	1184
0.65	10	7.5	202	312	55	910	750	59	976	684
	14	7.5	194	298	47	791	904	51	863	823
	20	6	178	274	40	720	1071	44	791	1000
	40	5	158	244	34	649	1225	38	720	1184
0.70	10	7.5	202	288	55	928	750	59	994	684
	14	7.5	194	277	47	809	904	51	880	833
	20	6	178	256	41	738	1071	45	809	1000
	40	5	158	226	34	660	1225	38	732	1184

From *Design and Control of Concrete Mixtures,* EB001, Portland Cement Association, Skokie, IL, 1992. With permission.

TABLE 12.5.6b (English Units) Example Trial Mixtures for Air-Entrained Concrete of Medium Consistency, 3- to 4-in. Slump

					With Fine Sand, Fineness Modulus = 2.50			With Coarse Sand, Fineness Modulus = 2.90		
Water/ Cement Ratio, lb per lb	Maximum Size of Aggregate, in,	Air Content, %	Water, lb per cu yd of Concrete	Cement lb per cu yd of Concrete	Fine Aggregate % of Total Aggregate	Fine Aggregate, lb per cu yd of Concrete	Coarse Aggregate, lb per cu yd of Concrete	Fine Aggregate % of Total Aggregate	Fine Aggregate, lb per cu yd of Concrete	Coarse Aggregate, lb per cu yd of Concrete
0.40	$^{3}/_{8}$	7.5	340	850	50	1250	1260	54	1360	1150
	$^{1}/_{2}$	7.5	325	815	41	1060	1520	46	1180	1400
	$^{3}/_{4}$	6	300	750	35	970	1800	39	1090	1680
	1	6	285	715	32	900	1940	38	1010	1830
	$1^{1}/_{2}$	5	265	665	29	870	2110	33	990	1990
0.45	$^{3}/_{8}$	7.5	340	755	51	1330	1260	56	1440	1150
	$^{1}/_{2}$	7.5	325	720	43	1140	1520	47	1260	1400
	$^{3}/_{4}$	6	300	665	37	1040	1800	41	1160	1680
	1	6	285	635	33	970	1940	37	1080	1830
	$1^{1}/_{2}$	5	265	590	31	930	2110	35	1050	1990
0.50	$^{3}/_{8}$	7.5	340	680	53	1400	1260	57	1510	1150
	$^{1}/_{2}$	7.5	325	650	44	1200	1520	49	1320	1400
	$^{3}/_{4}$	6	300	600	38	1100	1800	42	1220	1680
	1	6	285	570	34	1020	1940	38	1130	1830
	$1^{1}/_{2}$	5	265	530	32	980	2110	36	1100	1990
0.55	$^{3}/_{8}$	7.5	340	620	54	1450	1260	58	1550	1150
	$^{1}/_{2}$	7.5	325	590	45	1250	1520	49	1370	1400
	$^{3}/_{4}$	6	300	545	39	1140	1800	43	1260	1680
	1	6	285	520	35	1060	1940	39	1170	1830
	$1^{1}/_{2}$	5	265	480	33	1030	2110	37	1150	1990
0.60	$^{3}/_{8}$	7.5	340	565	54	1490	1260	58	1600	1150
	$^{1}/_{2}$	7.5	325	540	46	1290	1520	50	1410	1400
	$^{3}/_{4}$	6	300	500	40	1180	1800	44	1300	1680
	1	6	285	475	36	1100	1940	40	1210	1830
	$1^{1}/_{2}$	5	265	440	33	1060	2110	37	1180	1990
0.65	$^{3}/_{8}$	7.5	340	525	55	1530	1260	59	1640	1150
	$^{1}/_{2}$	7.5	325	500	47	1330	1520	51	1450	1400
	$^{3}/_{4}$	6	300	460	40	1210	1800	44	1330	1680
	1	6	285	440	37	1130	1940	40	1240	1830
	$1^{1}/_{2}$	5	265	410	34	1090	2110	38	1210	1990

TABLE 12.5.6b (English Units) Example Trial Mixtures for Air-Entrained Concrete of Medium Consistency, 3- to 4-in. Slump (continued)

					With Fine Sand, Fineness Modulus = 2.50			With Coarse Sand, Fineness Modulus = 2.90		
Water/ Cement Ratio, lb per lb	Maximum Size of Aggregate, in,	Air Content, %	Water, lb per cu yd of Concrete	Cement lb per cu yd of Concrete	Fine Aggregate % of Total Aggregate	Fine Aggregate, lb per cu yd of Concrete	Coarse Aggregate, lb per cu yd of Concrete	Fine Aggregate % of Total Aggregate	Fine Aggregate, lb per cu yd of Concrete	Coarse Aggregate, lb per cu yd of Concrete
0.70	$^{3}/_{8}$	7.5	340	485	55	1560	1260	59	1670	1150
	$^{1}/_{2}$	7.5	325	465	47	1360	1520	51	1480	1400
	$^{3}/_{4}$	6	300	430	41	1240	1800	45	1360	1680
	1	6	285	405	37	1160	1940	41	1270	1830
	$1^{1}/_{2}$	5	265	380	34	1110	2110	38	1230	1990

TABLE 12.5.7 Proportions by Mass to Make $^1/_{10}$ m^3 of Concrete for Small Jobs

	Air-Entrained Concrete				**Non-Air-Entrained Concrete**			
Maximum-Size Coarse Aggregate, mm	**Cement, kg**	**Wet Fine Aggregate, kg**	**Wet Coarse Aggregate, kg**	**Water, kg**	**Cement, kg**	**Wet Fine Aggregate, kg**	**Wet Coarse Aggregate, kg**[a]	**Water, kg**
10	46	85	74	16	46	94	74	18
14	43	74	88	16	43	85	88	18
20	40	67	104	16	40	75	104	16
40	37	61	120	14	37	69	120	14

[a] If crushed stone is used, decrease coarse aggregate by 5 kg and increase fine aggregate by 5 kg.

Source: From *Design and Control of Concrete Mixtures*, EB001, Portland Cement Associate, Skokie, IL, 1992. With permission.

TABLE 12.5.8 Proportions by Volume[a] of Concrete for Small Jobs

	Air-Entrained Concrete				**Non-Air-Entrained Concrete**			
Maximum-Size Coarse Aggregate, mm	**Cement**	**Wet Fine Aggregate**	**Wet Coarse Aggregate**	**Water**	**Cement**	**Wet Fine Aggregate**	**Wet Coarse Aggregate**	**Water**
10	1	$2^1/_4$	$1^1/_2$	$^1/_2$	1	$2^1/_2$	$1^1/_2$	$^1/_2$
14	1	$2^1/_4$	2	$^1/_2$	1	$2^1/_2$	2	$^1/_2$
20	1	$2^1/_4$	$2^1/_2$	$^1/_2$	1	$2^1/_2$	$2^1/_2$	$^1/_2$
40	1	$2^1/_4$	3	$^1/_2$	1	$2^1/_2$	3	$^1/_2$

[a] The combined volume is approximately $^2/_3$ of the sum of the original bulk volumes.

Source: From *Design and Control of Concrete Mixtures*, EB001, Portland Cement Associate, Skokie, IL, 1992. With permission.

disrupt the cement paste, resulting in cracking and disintegration of the concrete. The first defense against sulfate attack is to use a low water/cement ratio (0.45 or preferably less), and to select a Type II or V cement (see the section on cement).

Corrosion Protection

Concrete protects embedded steel from corrosion through its highly alkaline nature. The high-pH environment (usually greater than 12.5) causes a passive and noncorroding protective oxide film to form on steel. However, carbonation or the presence of chloride ions from deicers or seawater can destroy or penetrate the film, causing rusting of the reinforcing steel. In addition to using a water/cement ratio of 0.40 or less, the following protective strategies can be used individually or in combination to reduce the risk of corrosion:

1. Cover thickness of 90 mm (3.5 in.) or more of concrete over top, reinforcing steel of compression zones. [*Note:* Excessive cover in tension zones exacerbates surface crack width.]
2. Low-slump dense concrete overlay
3. Latex-modified concrete overlay
4. Interlayer membrane/asphaltic concrete systems
5. Epoxy-coated reinforcing steel
6. Corrosion-inhibiting admixtures in concrete
7. Sealers with or without overlay
8. Silica-fume or other pozzolans that significantly reduce concrete permeability
9. Low water/cement ratio (<0.35) superplasticized concrete
10. Cathodic protection
11. Polymer concrete overlay

12. Galvanized reinforcing steel
13. Polymer impregnation
14. Lateral and longitudinal prestressing for crack control
15. Blended cements containing silica fume or other pozzolans to reduce permeability

Alkali–Silica Reaction

Most aggregates are chemically stable in hydraulic cement concrete, without deleterious interaction with other concrete ingredients. However, this is not the case for aggregates containing certain siliceous substances that react with soluble alkalis in concrete. Alkali–silica reactivity (ASR) is an expansive reaction between reactive forms of silica in aggregate and alkali hydroxides in concrete. Very reactive aggregates can induce cracks within a year, whereas slowly reactive aggregates can take over 20 years to induce noticeable cracks. ASR is best controlled through the use of fly ash, slag, silica fume, natural pozzolans, or blended hydraulic cement. With proper care in analyzing aggregates and selecting appropriate concrete ingredients, ASR can be effectively minimized using available materials. Reference 2 provides guidance on ASR.

Related Standards and Specifications

American Society for Testing and Materials (ASTM)

C 33	Specification for Concrete Aggregates
C 150	Specification for Portland Cement
C 595	Specification for Blended Hydraulic Cements
C 618	Specification for Fly Ash and Raw and Calcined Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete
C 989	Specification for Ground Granulated Blast-Furnace Slag for Use in Concrete and Mortars
C 1157	Performance Specification for Blended Hydraulic Cement
C 1240	Specification for Silica Fume for Use in Hydraulic-Cement Concrete and Mortar

References

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3. *Specifications for Structural Concrete for Buildings*, ACI 301, American Concrete Institute, Farmington Hills, MI, 1996, 43 pages.
4. *Guide to Durable Concrete*, ACI 201.2R-92, American Concrete Institute, Farmington Hills, MI, 1992, 39 pages.
5. Wood, S.L., Evaluation of the Long-Term Properties of Concrete. Research and Development Bulletin RD102T, Portland Cement Association, Skokie, IL, 1992.

12.6 Composites

Introduction

Victor A. Greenhut

A composite material is a macroscopic, physical combination of two or more materials in which one material usually provides reinforcement. Composites have been developed where no single, quasi-continuous material will provide the required properties. In most composites one phase (material) is continuous and is termed the *matrix*, while the second, usually discontinuous phase, is termed the *reinforcement*, in some cases *filler* is applied when the reinforcement is not a quasi-continuous fiber. Matrix-filler nomenclature is one method of categorization. This yields the categories *metal matrix* (MMC), *polymer (plastic) matrix* (PMC), and *ceramic matrix* (CMC) composites — the major subdivisions of this section. Other categories are given the shape and configuration of the reinforcing phase. The reinforcement is usually a ceramic and/or glass. If it is similar in all dimensions, it is a *particulate-reinforced* composite; if needle-shaped single crystals, it is *whisker-reinforced*; if cut continuous filament, *chopped fiber-reinforced*; and if continuous fiber, *fiber composite*. For fiber composites configuration gives a further category. If fibers are aligned in one direction, it is a *uniaxial fiber composite*; if arranged in layers, it is a *laminar composite*; if a three-dimensional arrangement, it is a *3D weave composite*. Laminates and 3D weaves can be further divided by the weave used for the fiber.

Composites are not new materials. Perhaps the first important engineering structural composite was the Biblical straw-reinforced, sun-dried mud brick — adobe. Laminated structures such as bows have been used since prehistoric times. In the early 1900s doped fabric was employed in early aircraft surfaces. Reinforced phenolics were developed in the 1930s and glass-reinforced plastics in the 1940s. More recently, emphasis turned to reinforcements, with graphitic and boron-based fibers developed in the 1960s. High-performance aramids, such as Kevlar™, were developed in the 1970s. This and the previous decade have seen new developments in both fiber and matrix with lightweight aerospace MMCs and high-temperature CMCs showing major advances.

This section will concentrate on advanced composites in which major structural performance is achieved, but it should be noted that the largest tonnage and dollar value of composites is driven by the cost of materials. Polymers are reinforced with glass particulate or chipped fiber because it lowers the price per pound of a plastic, hence the term *filler* for reinforcement material. The structural properties are also improved, as PMCs show increased stiffness (resistance to bending) and strength (resistance to failure). These and other properties will receive the emphasis in this section. In MMCs high hardness, maintenance of hardness at elevated temperature, and precise tolerance are often lead properties, although stiffness and strength are important. The metal matrix confers some ductility so that the catastrophic failure of a solely ceramic material is avoided. In CMCs the reinforcement is chiefly incorporated to prevent catastrophic failure to introduce a more predictable failure stress (increased reliability), and to a lesser extent to increase strength. Particulate-reinforced plastics and fiberglass (glass fiber–reinforced plastic) have become commonplace engineering materials, as have ceramic-reinforced metal matrices (cemented carbides and cermets). Reinforcement with graphite and other advanced technology fibers has emerged for aerospace applications, biomedical use, and high-performance/high-cost consumer products such as sporting goods. Fiber-reinforced MMCs and ceramic–ceramic composites have developed greatly, but are still quite limited in application to very advanced technologies which can bear relatively high costs.

An important consideration for composite production is the bond between the matrix and the reinforcement. For MMCs and PMCs load must be transferred (Figure 12.6.1) to the relatively high-strength, high-elastic-modulus ceramic or glass in order to maximize the mechanical performance. For best transfer there must be no relative sliding or interface failure, so the strain at the matrix-to-reinforcement area can be maximum and equal ($\varepsilon_{\text{matrix}} = \varepsilon_{\text{reinforcement}} = \varepsilon_{m,c}$). This means that the reinforcement bears the major portion of the load, σ_c, while the weaker matrix bears a lower load, σ_m, because it has lower modulus.

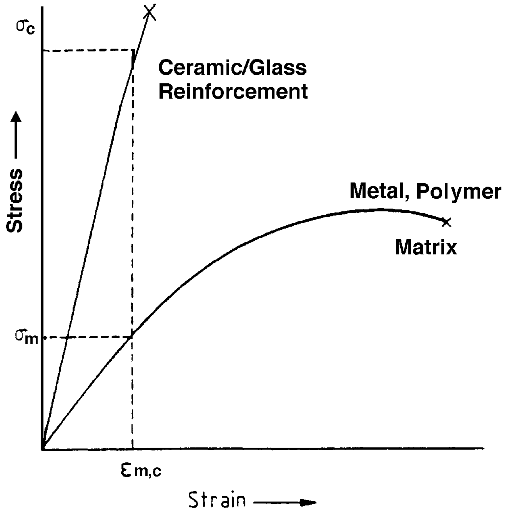

FIGURE 12.6.1 In a composite with good bonding between high-modulus ceramic and low-modulus metal or polymer matrix the interfacial strain must be the same. Thus, the high-strength ceramic fiber bears most of the load (stress).

To accomplish load transfer the bond interface must be engineered because metal and polymers do not show intrinsic bonding to ceramic reinforcement. A *coupling agent*, often a xylene, is applied to the ceramic or glass to promote bonding to a polymer. For metals, a metal matrix often has to be selected because it will wet and bond to the selected ceramic when molten or sintering during fabrication. Commonly, a controlled “forming gas” atmosphere must be used to produce MMCs composites so that a strong metal-to-ceramic bond is made.

The situation is somewhat different for ceramic–ceramic composites. These materials usually bond strongly to each other during fabrication. However, unlike the PMCs and MMc a less perfect bond is required. This is because local failure is required between matrix and reinforcement to introduce toughness or noncatastrophic fracture. This will be discussed further in the section on CMCs.

Polymer Matrix Composites

Weiping Wang, R. Allan Ridilla, and Mathew B. Buczek

Introduction

PMCs are used extensively as commodity and specialty engineering materials and constitute the largest class of composite materials on a dollar basis. The enormous success of PMCs arises from the wide range of properties which can be obtained and the low cost of low-end materials, such as fiberglass-reinforced polyester. Furthermore, the combination of high-strength/high-stiffness fibers in commodity polymer matrices offers an outstanding example of the composite principle — taking the best properties of both materials. The result is a strong, tough, stiff material which, depending on the matrix and reinforcement type, provides value in applications as diverse as consumer products, construction, and aerospace.

A distinction must be made between reinforced plastics and advanced composites. The term *reinforced plastics* generally refers to plastic materials fabricated with a relatively low percentage of discontinuous, randomly oriented fibers, with rather moderate properties, and used in commodity applications. *Advanced composites,* on the other hand, refers to a class of materials where a high percentage of continuous, highly oriented fibers are combined with a suitable polymeric matrix to produce articles of high specific strength and specific stiffness. At present, composites are widely used in the aerospace and sporting

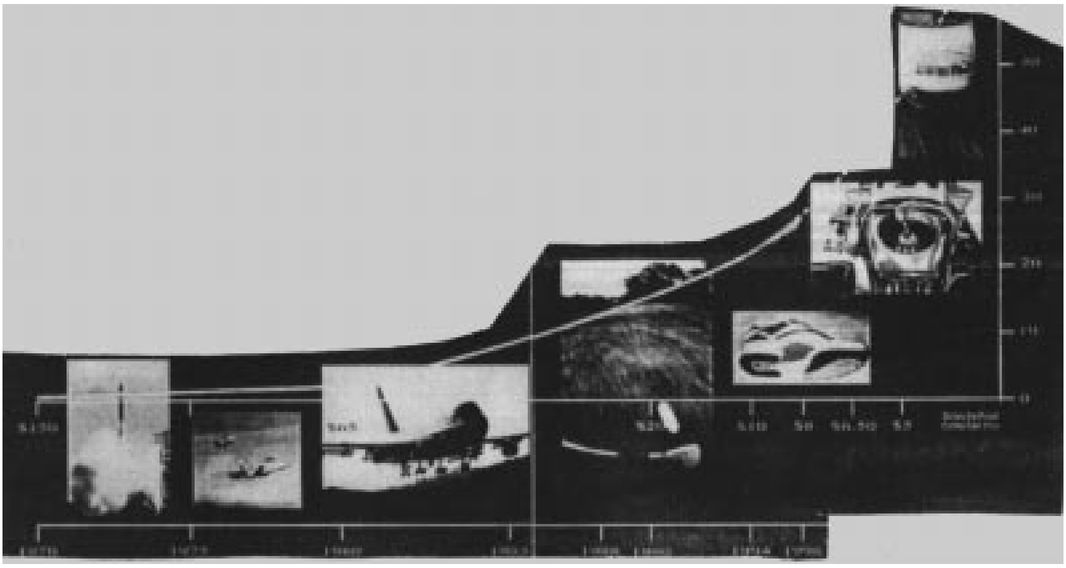

FIGURE 12.6.2 The evolution of carbon fiber composite applications since 1970 with fiber price and industry volume illustrated. (Source: Zoltek Co. Inc.)

goods industries for their superior performance. Figure 12.6.2 illustrates the evolution of applications for carbon fibers.

Polymers are also often “filled” with particulate reinforcements to increase certain properties, such as deflection temperature under load (DTUL). Although these materials are formally composites, they are usually regarded as filled polymers and not composites and thus will not be discussed explicitly in this section. Refer to the polymer section of this chapter.

Architecture

Each of the constituent materials in advanced composites must act synergistically to provide aggregate properties that are superior to the materials individually. The functional effectiveness of composites is principally due to the anisotropy of the materials and the laminate concept, where materials are bonded together in multiple layers. This allows the properties to be tailored to the applied load so that the structure can be theoretically more efficient than if isotropic materials were used. The reinforcements come in a variety of forms. Unidirectional tapes with all fibers along a common axis, woven fabrics constructed with fibers along both axes in the x–y plane, and 3-D architectures with reinforcements in more than two axial directions are just a few of the building blocks of composite structures.

The concept of laminate is illustrated in Figure 12.6.3. On the left is the unidirectional composite where all reinforcements are aligned in one direction. This construction provides excellent properties in the fiber direction but is limited to the properties of the resin in the transverse directions. The cross-plied construction on the right creates a structure that has common properties in the x- and y-direction but is limited to the characteristics of the resin in the z-direction. A large number of variations exist, allowing the designer to tailor the properties of the structure by varying the type of fibers and fiber orientations. Shown in Figure 12.6.4 are typical values of specific tensile strength (strength-to-density ratio) and specific tensile modulus (modulus-to-density ratio) for 65% volume fraction, cross-plied quasi-isotropic composites. Also included in the plot for comparison are properties of mild steel, titanium (Ti-6A1-4V), and aluminum (2024-T6). The actual properties of a composite will vary significantly due to flaws created during processing.

In selecting polymer composite materials for design, one should consider both the potential advantages and concerns typical to composites as illustrated in Table 12.6.1. Clearly, the advantages of materials should be put into use to achieve higher levels of performance in many kinds of products. On the other

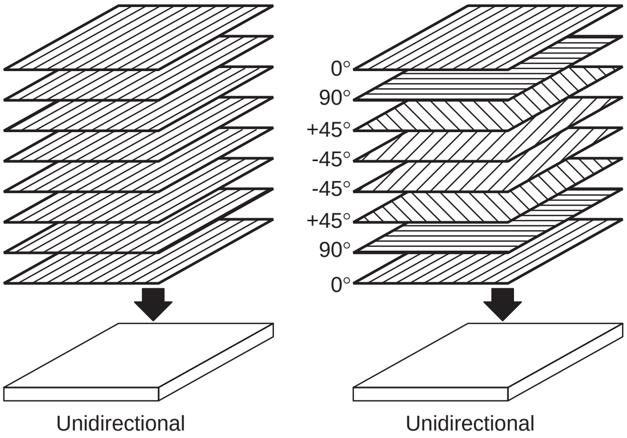

FIGURE 12.6.3 The basic concept of composite laminate.

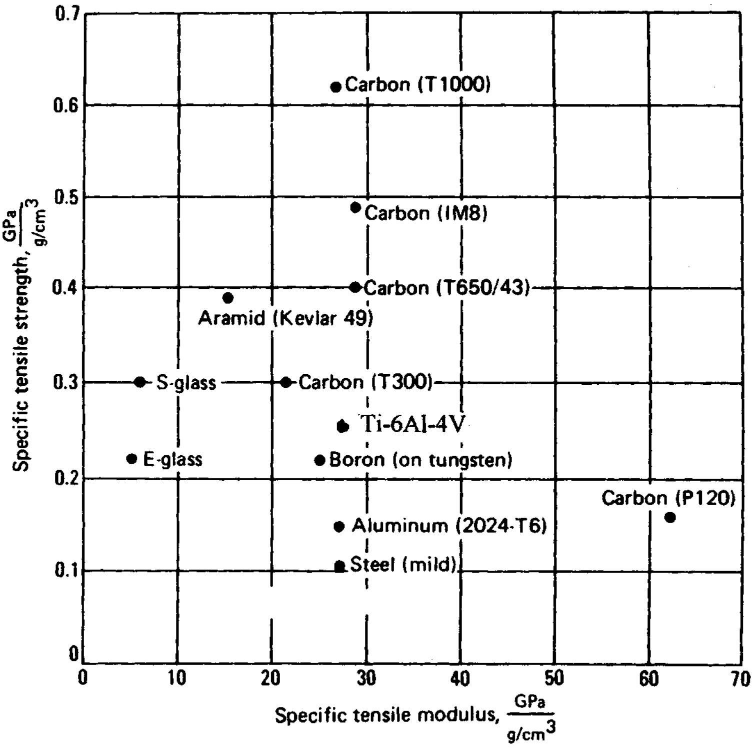

FIGURE 12.6.4 A comparative plot of specific tensile strength (strength-to-density) and specific tensile modulus (modulus-to-density) of composite material.

hand, potential issues in higher raw material cost and lower production volume and yield should also be weighed.

Fiber

Introduction. The most common reinforcement in polymer composites are fibers. Fibrous reinforcements come from compounds of light elements, (e.g., B, C, Si, O). These compounds typically contain

TABLE 12.6.1 Advantages and Limitations of Polymer Matrix Composites

Potential Advantages	Potential Limitations
High strength-to-density ratio	Low–volume production methods
High stiffness-to-density ratio	High raw material cost
Excellent corrosion resistance	Poor impact resistance
Good fatigue resistance	Poor high-temperature performance
Low thermal expansion	Delamination/out-of-plane loading

stable covalent bonds which impart greater strength and stiffness compared with metallic or ionic bonds. The compounds are processed to the final unable form of a fiber or filament with a highly aligned and directional microstructure so that the strength and stiffness properties are optimized along the fiber axis. Glass, graphite/carbon, aramid, and boron are among most notable fibers currently used in polymer composites.

Glass Fiber. Glass fiber reinforcements represent the largest volume used in the composites industry. These fibers are characterized by their low cost, clear to white color, good mechanical and electrical properties, high moisture and chemical resistance, and excellent dimensional stability with operational service to 550°C. Manufacturing of the fibers begins with molten glass which is drawn through a furnace into a fibrous form of final diameter of about 10 μm and then quenched to secure the final amorphous microstructure prior to applying final coatings or sizing. Common types of commercially available glass fiber are E-glass and S-glass, both of which are low alkali boro-alumino-silicate glasses. E-glass fiber, the workhorse of glass fiber applications, is the lower-cost fiber and is used in both structural and electrical applications. S-glass provides higher tensile properties and increased temperature resistance needed for aerospace and aircraft applications with a price premium. Representative properties for the glass fibers are shown in Table 12.6.2.

TABLE 12.6.2 Fibers Used in Polymer Composites — Mechanical Properties

	E-Glass	S-Glass	AS4 PAN-Based Carbon	IM7 PAN-Based Carbon	P120 Pitch-Based Graphite	Kevlar-49	Boron
Tensile strength (ksi)	510	670	578	710	325	530	525
Tensile modulus (MSI)	10.5	12.8	35.5	46	120	18	58
Elongation (%)	4.9	5.5	1.6	1.7	0.27	2.5	1
Density (lb/in^3)	0.095	0.09	0.065	0.063	0.079	0.052	0.093
Axial coefficient of expansion (10^{-6} in./in. F)	2.8	3.1	0 to –0.4	0 to –0.6	0 to –0.7	–1.1	2.5

Carbon Fiber. Graphite/carbon fibers are the reinforcement of industrial choice for advanced composite applications where stiffness and performance are critical. Typical attributes of these fibers are excellent tensile strength and elastic modulus, ease of handling, black color, and a wide range of properties and cost. Graphite fibers are initially formed as from polymer precursor compounds such as polyacrylonitrile (PAN) or rayon and pitch, an amorphous, aromatic by-product of petroleum distillation. PAN-based graphite fiber, the predominant commercial fiber, starts with the liquid PAN polymer, which is spun into a fiber and stretched to align the microstructure. It is then stabilized and the microstructure is aligned at 400 to 500°F in an oxidizing atmosphere under tension. Next, carbonization occurs in an inert atmosphere at 1800 to 2300°F to remove most noncarbon elements. Finally, the graphitization step is performed on the carbon fiber by applying tension to the fiber in an inert atmosphere at 3600 to 6500°F. The result is a highly aligned, highly graphitic fiber with preferred graphite orientation along the fiber axis. The temperature and tension fabrication parameters of the graphitization step, along with the purity of the initial PAN polymer, are the variables which are modified to differentiate “low-end” (low strength, modulus, cost) from the “high-end” fiber (high strength, modulus, cost) and all of the grades in between. Typical properties of several commercial grades of carbon/graphite fiber are listed in Table 12.6.2.

Aramid Fibers. The aramid fiber derives its properties from long, rodlike aromatic polyamides. These fibers are characterized by low density, white yellow color, extremely high tensile properties, poor compressive strength, and high toughness, and they are difficult to cut mechanically. The manufacturing process for these fibers involves complex polymerization steps as the liquid polymer in acid is extruded or spun into a fiber form, water washed, dried, and finally heat treated under tension. The result is a highly aligned radial system of axially pleated lamellae in the microstructure. Aramid fibers have proved extremely useful in tension-critical application where the intrinsic compressive weaknesses of the fiber cannot be exploited. Commercially known as Kevlar, the most notable applications for aramid fibers are bulletproof vests (without matrix), and various high-pressure composite vessels. Typical properties for Kevlar 49 are listed in Table 12.6.2.

Boron Fibers. Boron reinforcements are referred to as filaments rather than fibers since they are made by the chemical vapor deposition of boron onto a fine tungsten wire. This fabrication process produces a large-diameter, stiff, and expensive reinforcement that is somewhat difficult to handle and produce into subsequent product forms such as fabrics and contoured structures. Although boron filaments possess the combination of high strength and high specific modulus that glass could not achieve, its use has been reduced to a minuscule level. Carbon/graphite fiber varieties have supplanted boron where high specific modulus is a requirement. A small volume of boron filaments still remain in a handful of military aircraft as well as in some recreational products such as golf club shafts. Typical properties of boron filaments are shown in Table 12.6.2.

Polymer Matrix Materials

Introduction. While fibers provide much of the strength and stiffness in advanced composites, equally important is the matrix resin. The matrix holds the fiber network together, to protect the structure from environmental attack and to support the fibers so that loads can be transferred throughout the structure through a shear mechanism. Polymeric matrices can either be thermoset or thermoplastic resins.

Thermosets cannot be reformed or thermally reworked after polymerization (curing). They are subdivided into categories based on their chemical reactions. The first are addition-type polymers, generally considered easier to process, where two (or more) reactants combine to form the final cured product. The second is the condensation type, in which the reactants combine to form products in addition to water and other volatile constituents. These systems are more difficult to process due to the required management of the volatile to minimize process defects such as porosity.

Thermoplastic materials, on the other hand, are polymers which can be softened and melted with the application of heat. Although they can be recycled, thermoplastic matrices have found more-limited applications in the advanced composite applications since they are particularly susceptible to attack by fluids and to creep at high stresses, and are relatively difficult to handle in laminate or structural form prior to final consolidation. The remainder of this discussion will focus on thermoset matrices which account for more than 90% of present-day advanced composite applications. Three principal organic matrix materials will be discussed: polyesters, epoxies, and polyimides.

Polyester Matrix. Low-cost polyester resins constitute the highest volume usage for the general composite industry. There are many resins, formulations, curatives, and other additive constituents that provide a wide array of properties and performance characteristics, such as mechanical strength, toughness, and heat resistance. The vast majority of applications utilize glass since its interfacial adhesion to these resins has been optimized by the development of silane surface treatments. These resins when combined with glass have found wide application in the chemical processing construction, and marine industries where cured properties and low cost are tailor-made for design requirements. Applications with carbon/graphite and aramid fibers are far less frequent since adhesion to these fibers is generally poor and cure shrinkage on these resins is quite high. Additionally, structures requiring the high performance of carbon/graphite can often justify the use of more-expensive epoxy resins.

Epoxy Matrix. Epoxy resins are the prevalent polymer used with advanced composites. Their extensive use is primarily due to their superior mechanical properties, excellent adhesion, good processibility utilizing addition-type reactions, low cure shrinkage and low cost. When choosing epoxy resins two elements are crucial: the base resin and the curing agent or hardener. Since there are many base resins and curing agents, the following general relationships are given to provide a practical framework when utilizing epoxy compounds:

- *Chemistry*: Aromatic compounds are more thermally stable, stronger, and more resistant to fluids than are aliphatics.
- *Cross-link density*: Higher-temperature cures and longer cure times will increase cross-link density and therefore strength/modulus, service temperature, and chemical resistance.
- *Curing agents*: Amine-cured systems have better chemical resistance and superior thermal stability, but are more brittle than anhydride-cured systems.

Epoxies are categorized by the cure temperature. The “250 F epoxies” are those that cure at 250°F and are suitable for service up to 250°F. The “350 F epoxies” are those with higher processing and service temperatures. One of the design concerns with epoxies is moisture absorption. The effects of moisture often require design stresses to be reduced in applications where moisture is a concern. Modern epoxy formulations include lower cost, higher toughness, and other properties which continue to make epoxies attractive to the end user.

Polyimide resins span the temperature spectrum from 350 to 600°F. There are three general types of polyimides:

1. *Addition-reaction* polyimides such as bismaleimides (BMI)
2. *Condensation-reaction* polyimides such as commercial Monsanto Skybond resin
3. *Combination* condensation/addition-reaction polyimides such as PMR-15

BMIs are similar to epoxies in that they undergo addition reactions, are easy to process, and share many of the handling characteristics that make epoxies desirable. These materials are the composite resins of choice for temperatures in the range of 350 to 450°F to bridge the temperature gap between epoxies and other polyimides. They are more expensive and tend to be more brittle than epoxies. Condensation polyimides are used for composite applications from 450 to 520°F. These materials are difficult to process and tend to be quire brittle so their application is limited to adhesive bonding with some structural composite hardware. Combination-reaction polyimides have the highest thermal and oxidative stability and are used at service temperatures to 600°F. These resins are considerably more complicated because of their reaction mechanisms and the handling difficulties of the chemicals. Their application is principally restricted to aerospace composite structures where the performance needs to justify the difficult processing and high cost.

Processing

Continuous-fiber composites are manufactured in two steps, preform fabrication and consolidation/curing. The material comes in either the dry-fiber (without resin) form or with resin included called *prepreg*. Dry fibers are used in filament winding, pultrusion, weaving, braiding. In the case of filament winding and pultrusion, resin is introduced at the same time fibers are during the time of winding and pultrusion. Resin can also be introduced to the fiber later by resin-transfer molding (RTM). Prepreg, at a higher material cost, eliminates the step of resin addition and provides the adhesion to hold the material together. Layup of prepreg, a time-consuming process, is a common method used in the aerospace industry where complex contoured surfaces are present.

Consolidation and curing consist of compacting the material to remove entrapped air, volatile, and excess resins while developing the structural properties by increasing the polymer chain length and

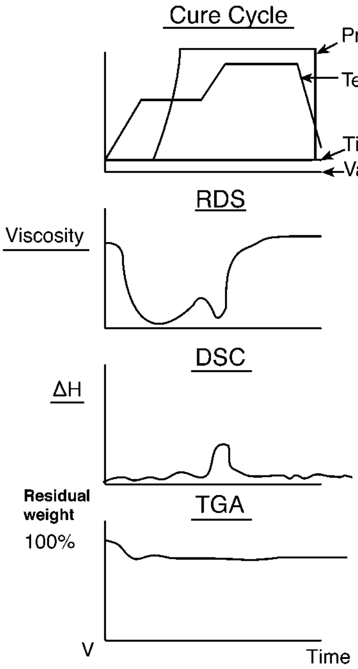

FIGURE 12.6.5 A typical curing cycle of epoxy composite with corresponding Rheometric Dynamic Spectroscopy (RDS), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA) curves.

cross-linking. Thermosetting polymer matrices must be cured *in situ* with the fibers to form composites. The goals of a successful cure are good consolidation with low porosity and high conversion of initial monomeric constituents to polymer (degree of cure).

The cure cycle of an epoxy resin composite is shown in Figure 12.6.5. At the start of the cure cycle, the material is normally under vacuum to remove residual volatile. The temperature is then ramped to the point where the polymer is melted. The ramp rates on heating must be slow enough as not to cause unnecessary thermal gradients and to avoid dangerous exotherm (runaway reactions) but not so slow as to cause excessive process time or premature cross-linking. Normal ramp rates are generally in the 1 to 5°F/min range. An isothermal hold of about 30 to 60 min is performed at the point where the resin reaches its minimum in viscosity, during which pressure is applied and the polymer allowed to flow, thus consolidating the laminate. Following consolidation, the temperature is increased to the point where cross-linking occurs (350°F for this example). An additional hold of about 30 to 90 min is performed at this temperature to allow for the material to complete cross-linking. This event is shown as the end of the exothermic peak in the DSC curve as well as the asymptotic high-viscosity region.

Epoxies cure via addition reactions where no volatile is generated during the cross-linking process. However, many other matrix materials (e.g., phenolics and many polyimides) cure via condensation reactions.

Mechanical Properties

Mechanical properties of polymer composites depend substantially on the processing and fabrication methods used, as well as on the fiber orientation. Thus, standard materials do not exist and it is difficult to generalize regarding properties. The three most significant factors in determining properties are the type of fiber, the volume fraction fiber, and the orientation of the fiber. High-strength high-modulus graphitic carbon fibers will, of course, produce stronger, stiffer composites than those produced from fiberglass. Similarly, 60 vol % fiber composites will be stronger and stiffer than 30 vol %, and uniaxially aligned fiber composites will have maximum properties along the alignment axis, but will be highly anisotropic and will have poor properties in off-axis orientations. Cross-ply and laminated structures are standard approaches to reducing anisotropy.

Composite stiffness, E_c, can be approximated for polymer composites by application of the rule of mixtures:

$$E_c = E_f V_f + E_m \left(1 - V_f\right)$$

where E is the modulus of elasticity and V is the volume fraction fibers. Subscripts c, f, and m refer to composite, fiber, and matrix, respectively. Similar expressions approximate other properties. Properties of commonly used commodity composite materials are given in Tables 12.6.3 to 12.6.5. Advanced engineering polymer composites have specialized properties which depend on the parameters discussed previously. Expected properties of such advanced polymer composites can only be approximated once the component and material variables are determined during the design stage. The recommended approach is to work with a composite fabricator during the design phase to establish the expected mechanical properties.

TABLE 12.6.3 Typical Properties of Glass Fiber–Reinforced Polymers

	Base Resin				
Property	**Polyester**	**Phenolic**	**Epoxy**	**Melamine**	**Polyurethane**
Molding quality	Excellent	Good	Excellent	Good	Good
Compression molding					
Temperature, °F	170–320	280–350	300–330	280–340	300–400
Pressure, psi	250–2000	2000–4000	300–5000	2000–8000	100–5000
Mold shrinkage, in./in.	0.0–0.002	0.0001–0.001	0.001–0.002	0.001–0.004	0.009–0.03
Specific gravity	1.35–2.3	1.75–1.95	1.8–2.0	1.8–2.0	1.11–1.25
Tensile strength, 1000 psi	25–30	5–10	14–30	5–10	4.5–8
Elongation, %	0.5–5.0	0.02	4	—	10–650
Modulus of elasticity, 10^{-5} psi	8–20	33	30.4	24	—
Compression strength, 1000 psi	15–30	17–26	30–38	20–35	20
Flexural strength, 1000 psi	10–40	10–60	20–26	15–23	7–9
Impact. Izod, ft-lb/in. or notch	2–10	10–50	8–15	4–6	No break
Hardness, Rockwell	M70–M120	M95–M100	M100–M108	—	M28–R60
Thermal expansion, per °C	$2–5 \times 10^{-5}$	1.6×10^{-5}	$1.1–3.0 \times 10^{-5}$	1.5×10^{-5}	$10–20 \times 10^{-5}$
Volume resistivity at 50% RH, 23°C, Ω-cm	1×10^{14}	7×10^{12}	3.8×10^{15}	2×10^{11}	$2 \times 10^{11}–10^{14}$
Dielectric strength $^1/_8$ in. thickness, v/mil	350–500	140–370	360	170–300	330–900
Dielectric constant					
At 60 Hz	3.8–6.0	7.1	5.5	9.7–11.1	5.4–7.6
At 1 kHz	4.0–6.0	6.9	—	—	5.6–7.6
Dissipation factor					
At 60 Hz	0.01–0.04	0.05	0.087	0.14–0.23	0.015–0.048
At 1 kHz	0.01–0.05	0.02	—	—	0.043–0.060
Water absorption, %	0.01–1.0	0.1–1.2	0.05–0.095	0.09–0.21	0.7–0.9
Sunlight (change)	Slight	Darkens	Slight	Slight	None to slight
Chemical resistance	Fair[a]	Fair[a]	Excellent	Very good[b]	Fair
Machining qualities	Good	—	Good	Good	Good

Note: Filament-wound components with high glass content, highly oriented, have higher strengths. The decreasing order of tensile strength is: roving, glass cloth, continuous mat, and chopped-strand mat.

[a] Attacked by strong acids or alkalies.

[b] Attacked by strong acids.

From Spang, C.A. and Davis, G.J., *Machine Design,* 40(29); 32, Dec. 12, 1968. With permission.

TABLE 12.6.4 Properties of Reinforced Nylon Polymer

Property	Type 6/6	Type 6	Type 6/10	Type 11	Glass-Reinforced Type 6/6, 40%	MoS$_2$-filled, $2\frac{1}{2}$%	Direct Polymerized, Castable
Mechanical							
Tensile strength, psi	11,800	11,800	8200	8500	30,000	10,000–14,000	11,000–14,000
Elongation, %	60	200	240	120	1.9	5–150	10–50
Tensile yield stress, psi	11,800	11,800	8500	—	30,000	—	—
Flexural modulus, psi	410,000	395,000	280,000	151,000	1,800,000	450,000	—
Tensile modulus, psi	420,000	380,000	280,000	178,000	—	450,000–600,000	350,000–450,000
Hardness, Rockwell	118R	119R	111R	55A	75E–80E	110R–125R	112R–120R
Impact strength, tensile, ft-lb/sq in.	76	—	160	—	—	50–180	80–100
Impact strength, Izod. ft-lb/in. of notch	0.9	1.0	1.2	3.3	3.7[a]	0.6	0.9
Deformation under load, 2000 psi, 122°F, %	1.4	1.8	4.2	2.02[b]	0.4[c]	0.5–2.5	0.5–1
Thermal							
Heat deflection temp, °F							
At 66 psi	360	365	300	154	509	400–490	400–425
At 264 psi	150	152	135	118	502	200–470	300–425
Coefficient of thermal expansion per °F	4.5×10^{-5}	4.6×10^{-5}	5×10^{-5}	10×10^{-5}	0.9×10^{-5}	3.5×10^{-5}	5.0×10^{-5}
Coefficient of thermal conductivity, Btu in./hr ft^3 °F	1.7	1.7	1.5	—	—	—	—
Specific heat	0.3–0.5	0.4	0.3–0.5	0.58	—	—	—
Brittleness temp, °F	–112	—	–166	—	—	—	—
Electrical							
Dielectric strength, short time, v/mil	385	420	470	425	480	300–400	500–600[d]
Dielectric constant							
At 60 Hz	4.0	3.8	3.9	—	4.45	—	3.7
At 10^3 Hz	3.9	3.7	3.6	3.3	4.40	—	3.7
At 10^6 Hz	3.6	3.4	3.5	—	4.10	—	3.7
Power factor							
At 60 Hz	0.014	0.010	0.04	0.03	0.009	—	0.02
At 10^3 Hz	0.02	0.016	0.04	0.03	0.011	—	0.02
At 10^6 Hz	0.04	0.020	0.03	0.02	0.018	—	0.02
Volume resistivity, Ω-cm	10^{14}–10^{15}	3×10^{15}	10^{14}–10^{15}	2×10^{13}	2.6×10^{15}	2.5×10^{13}	—
General							
Water absorption, 24 hr, %	1.5	1.6	0.4	0.4	0.6	0.5–1.4	0.9

TABLE 12.6.4 Properties of Reinforced Nylon Polymer (continued)

Property	Type 6/6	Type 6	Type 6/10	Type 11	Glass-Reinforced Type 6/6, 40%	MoS_2-filled, $2^1/_2$%	Direct Polymerized, Castable
Specific gravity	1.13–1.15	1.13	1.07–1.09	1.04	1.52	1.14–1.18	1.15–1.17
Melting point, °F	482–500	420–435	405–430	367	480–490	496 ± 9	430 ± 10
Flammability	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing	Self-extinguishing
Chemical resistance to							
Strong acids	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Strong bases	Good	Good	Good	Fair	Good	Good	Good
Hydrocarbons	Excellent	Excellent	Excellent	Good	Excellent	Excellent	Excellent
Chlorinated hydrocarbons	Good	Good	Good	Fair	Good	Good	Good
Aromatic alcohols	Good	Good	Good	Good	Good	Good	Good
Aliphatic alcohols	Good	Good	Good	Fair	Good	Good	Good

Notes: Most nylon resins listed in this table are used for injection molding, and test values are determined from standard injection-molded specimens. In these cases a single typical value is listed. Exceptions are MoS_2-filled nylon and direct-polymerized (castable) nylon, which are sold principally in semifinished stock shapes. Ranges of values listed are based on tests on various forms and sizes produced under varying processing conditions.

Because single values apply only to standard molded specimens, and properties vary in finished parts of different sizes and forms produced by various processes, these values should be used for comparison and preliminary design considerations only. For final design purposes the manufacturer should be consulted for test experience with the form being considered. Listed values should not be used for specification purposes.

[a] $^1/_2 \times ^1/_4$-in. bar.

[b] 2000 psi, 73°F.

[c] 4000 psi, 122°F.

[d] 0.040-in. thick.

From Carswell, D.D., *Machine Design,* 40(29), 62, Dec. 12. 1968. With permission.

TABLE 12.6.5 Comparative Properties of Reinforced Plastics

	Polyamide		Polystyrene[a]		Polycarbonate		Styrene Acrylonitrile[b]		Polypropylene		Acetal		Linear Polyethylene	
Property	**U**	**R**	**U**	**R**	**U**	**R**	**U**	**R**	**U**	**R**	**U**	**R**	**U**	**R**
Tensile strength, 1000 psi	11.8	30.0	8.5	14.0	9.0	20.0	11.0	18.0	5.0	6.6	10.0	12.5	3.3	11.0
Impact strength, notched, ft-lb/in.														
At 73°F	0.9	3.8	0.3	2.5	2.0[c]	4.0[c]	0.45	3.0	1.3–2.1	2.4	60.0	3.0	—	4.5
At –40°F	0.6	4.2	0.2	3.2	1.5[c]	4.08[c]	—	4.0	—	2.2	—	3.0	—	5.0
Tensile modulus, 10^5 psi	4.0	—	4.0	12.1	3.2	17.0	5.2	15.0	2.0	4.5	4.0	8.1	1.2	9.0
Shear strength, 1000 psi	9.6	14.0	—	9.0	9.2	12.0	—	12.5	4.6	4.7	9.5	9.1	—	5.5
Flexural strength, 1000 psi	11.5	37.0	11.0	20.0	12.0	26.0	17.0	26.0	6–8	7.0	14.0	16.0	—	12.0
Compressive strength, 1000 psi	4.9[d]	24.0	14.0	17.0	11.0	19	17.0	22.0	8.5	6.0	5.2	13.0	2.7–3.6	6.0
Deformation, 4000-psi load, %	2.5	0.4	1.6	0.6	0.3	0.1	—	0.3	—	6.0	—	1.0	—	0.4[e]
Elongation, %	60.0	2.2	2.0	1.1	60–100	1.7	3.2	1.4	>200	3.6	9–15	1.5	60.0	3.5
Water absorption, in 24 hr, %	1.5	0.6	0.03	0.07	0.3	0.09	0.2	1.15	0.01	0.05	0.20	1.1	0.01	0.04
Hardness, Rockwell	M79	E75–80	M70	E53	M70	E57	M83	E65	R101	M50	M94	M90	R64	R60
Specific gravity	1.14	1.52	1.05	1.28	1.2	1.52	1.07	1.36	0.90	1.05	1.43	1.7	0.96	1.30
Heat distortion temperature, at 264 psi, °F	150	502	190	220	280	300	200	225	155	280	212	335	126	260
Coefficient of thermal expansion, per F × 10^{-5}	5.5	0.9	4.0	2.2	3.9	0.9	4.0	1.9	4.7	2.7	4.5	1.9	9.0	1.7
Dielectric strength, short time, v/mil	385	480	500	396	400	482	450	515	750	—	500	—	—	600
Volume resistivity Ω-cm × 10^{15}	450	2.6	10.0	36.0	20.0	1.4	10^{16}	43.5	17.0	15.0	0.6	38.0	10^{15}	29.0
Dielectric constant, at 60 Hz	4.1	4.5	2.6	3.1	3.1	3.8	3.0	3.6	2.3	—	—	—	2.3	2.9
Power factor, at 60 Hz	0.0140	0.009	0.0030	0.0048	0.0009	0.0030	0.0085	0.005	—	—	—	—	—	0.001
Approximate cost, ¢/in.^{3}	3.0	8.0	0.5	2.5	3.6	6.5	0.9	3.5	0.6	2.1	3.3	7.8	0.7	3.1

Note: U = reinforced; R = reinforced. Multiply tabular values in psi by 6895 to obtain N/m^2.

[a] Medium-flow, general-purpose grade.

[b] Heat-resistant grade.

[c] Impact values for polycarbonates are a function of thickness.

[d] At 1% deformation.

[e] 1000-psi load.

From Lachowecki, W., *Machine Design*, 40(29), 34, Dec. 12, 1968. With permission.

Metal Matrix Composites

Introduction

The term *metal matrix composites* is usually reserved for fiber-reinforced materials, although technically it applies to particulate-reinforced systems also. The general term for particulate-, whisker-, and chopped-fiber-reinforced systems is *cermet*. A majority of commonly used systems are based upon particulate reinforcements.

Cermets and Cemented Carbides — Particulate-Reinforced MMCs

The term *cemented carbide* is applied to particulate composites based upon tungsten carbide in a cobalt matrix. This distinction is largely historical, not technical. The tungsten carbide–cobalt-based materials were first developed in Germany, while development of other cermets (including noncarbide-, oxide-, and nitride-based systems) occurred in the United States during and immediately after World War II. Thus, a distinguishing nomenclature was developed both because “carbide” was no longer completely appropriate with oxide systems available and for geopolitical reasons. This nomenclature confusion between the most common cermets, the cemented carbides, and other materials still survives. The structure consists of a continuous metal alloy functioning as cement which holds together particles of carbide, oxide, or nitride ceramic. These materials provide strength, high hardness, wear (abrasion) resistance, low sliding friction, and precise tolerance even at quite high temperatures. Cermets and cemented carbides derive their usefulness when the compressive strength, hardness, and thermal resistance of the ceramic reinforcement is coupled with the ductility, toughness, adhesion, and lubricity provided by the metal. Common applications include metal and rock cutting and grinding tools, high-temperature containers, and pouring spouts, rocket nozzles, turbine parts, flame nozzles, friction and glide parts, seals, magnetron tube cathodes, flame nozzles, and ballpoint pen tips.

A cermet is usually fabricated by mixing the ceramic and metal powders together with a binder incorporated. This often requires high-energy mixing because of density differences with tooling made of the same cermet to avoid contamination. Subsequently, the part is formed, commonly by unidirectional or isostatic pressing, to final shape (accounting for shrinkage) with a wear-resistant die and with the formed object then liquid phase sintered in a controlled-atmosphere furnace. The chemistry is often quite complex in order to control the structure and the interfacial bond between metal and ceramic. Molybdenum promotes wetting of titanium carbide by molten nickel. Tantalum and titanium carbides are usually added to tungsten carbide–cobalt cemented carbides. Some cermets are prepared by slip casting, liquid metal infiltration, hot pressing, or solid-state sintering of parts. In some cases the material is “deficient” in metal to provide porosity for the passage of ink (pen tips) or incorporation of lubricant.

As indicated in the introduction to this section, a good bond between ceramic grain and metal “cement” is required for proper load transfer and to provide a homogeneous structure for good load bearing and uniform deformation. This normally requires a good wetting between liquid metal and ceramic grains. This is affected by minor alloying additions to the metal and the firing atmosphere.

The distribution, stability, and composition of phases have profound effects on properties. The production of WC–6 $^{w}/_{o}$ Co is a good example of the need for strict compositional control. The tertiary-phase diagram shows that the composition range from 6.00 to 6.12 $^{w}/_{o}$ must be adhered to in order to prevent formation of phases other than WC and Co — a composition range of less than 0.12 $^{w}/_{o}$! Embrittlement by graphite occurs at higher carbon content and by eta phase (η–WC_{1-x}) at lower carbon levels. Precise formulation and furnace atmosphere control is required, usually assisted by using a graphite-lined furnace. About 0.1% outside the acceptable composition range there is a drop of about 25% from the optimum strength.

It is important to engineer the microstructure of cermets in order to optimize properties. A uniform dispersion of round oxide, carbide, or nitride grains in the matrix of metal binder is desired. Inhomogeneity and sharp grain corners can act as failure origins. Round grains result from powder preparation and/or partial dissolution of sharp contours in the molten metal. As the amount of binder increases (Figure 12.6.6), the indentation hardness of the composite decreases, because metal, compared with

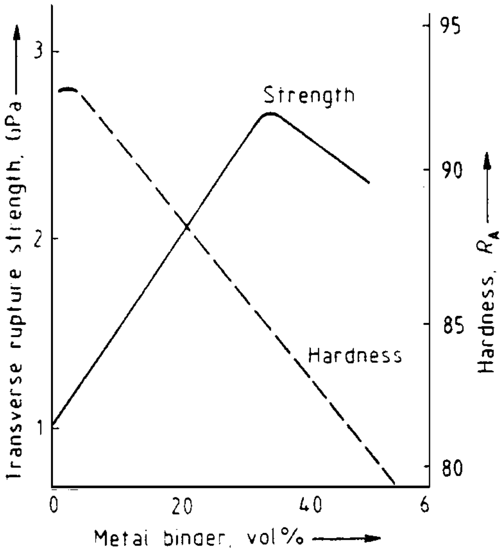

FIGURE 12.6.6 Effect of increased binder on strength and hardness of a TiC-Ni-Mo cermet with a 1 μm average carbide particle size.

ceramic, has a lower elastic modulus and will deform more easily. Fracture strength increases with binder because the metal phase confers fracture toughness. Generally, as ceramic grain size decreases, hardness and resistance to deformation increase for a fixed relative amount of ceramic. However, if the surface area increases sufficiently because of small grain size, there may not be sufficient metal to wet all the grain.

With these diverse factors a simplified way of looking at microstructural features and adjusting them for optimum performance is the mean free path, the average distance between neighboring ceramic grains (the average thickness of the binder phase). The mean free path depends on the size and shape of the grains and the amount of metal matrix available. Hardness, elevated-temperature hardness, strength, and toughness depend on the mean free path because it is the zone for absorption of crack energy and the medium for load transfer from grain-to-grain. Figure 12.6.7 shows that hardness varies with mean free path for a variety of cobalt contents and tungsten carbide grain sizes in cemented carbide. The curve does not continue below 0.1 μm because the metal binder becomes discontinuous.

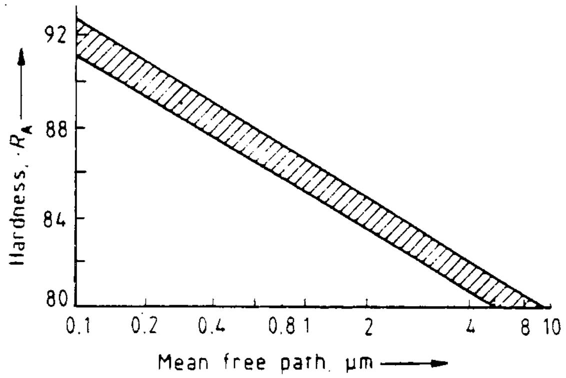

FIGURE 12.6.7 Effect of mean free path on hardness for a cemented carbide.

TABLE 12.6.6 Particle-Reinforced Metals

A. Metals Strengthened by Dispersed Powders

	Strengthener		**Stress, kpsi**	
Matrix Metals	**Component**	**% vol**	**Matrix Only, No Reinforcement**	**Composite Material**
Pure iron	Al_2O_3	4	2.2[a]	10[a]
Pure iron	Al_2O_3	10	2.2[a]	21[a]
Pure copper	Al_2O_3	10	2.2[b]	20[b]
Platinum	ThO_2	12.5	0.6[c]	6.1[c]
Uranium	Al_2O_3	3.5	6[d]	14[d]
Uranium	Al_2O_3	7.5	6[d]	20[d]
Copper	W (powder)	60	(E = 18)[e]	(E = 34)[e]

[a] Stress for 100-hr rupture life, 650°C.
[b] Stress for 100-hr rupture life, 450°C.
[c] Stress for 100-hr rupture life, 1100°C.
[d] Stress for 10^{-4} in./in./hr creep rate.
[e] Modulus of elasticity, E = stress/strain.

B. Strength Ratios at High Temperatures

	Dispersed Particles		**Strength by Test**	
Matrix Metal	**Material**	**% by Volume (Range)**	**Range of Test Temperatures, °F**	**Strength Ratio, (Referred to Matrix at Same Temperature)**
Aluminum	Al_2O_3	10–15	400–800	2–4[a]
Copper	Al_2O_3	3–10	800–1100	5–10
Iron	Al_2O_3	8–10	1100–1300	5–10
Nickel	ThO_2	3	1600–2100	Strength higher than that of many super alloys
Platinum	ThO_2	12	2000–2400	8–11
Uranium	Al_2O_3	4–7	900–1100	2–3

[a] The tensile strength of the final product is two to four times the strength of the aluminum.

Table 12.6.6 presents data for selected metal matrix systems with particulate reinforcement, including strength values at elevated temperatures. A section of Table 12.6.7 provides stiffness values for cobalt and nickel strengthened with sintered carbides.

Fiber-Reinforced MMCs

Fiber-reinforced MMCs may still be classed as an emerging materials area. A number of applications have been practiced driven by the need for a lightweight, high-stiffness material and/or for elevated-temperature resistance in structures. These applications are typically for aerospace and similar advanced applications which can use a premium material. The limited scope of current practical application and the limitations placed on technology disclosure by the Export Control Act and International Traffic-in-Arms Regulations make this section brief.

High-strength/high-elastic-modulus fibers such as boron, silicon carbide, graphite, aluminum oxide, and tungsten metal are typically incorporated in light metal matrices such as aluminum, magnesium, and titanium. The specific modulus (elastic modulus divided by density) has been shown to be two to four times that of high-strength structural metals. The specific strength may be substantially higher than the metal. These properties are maintained to many hundreds of degrees above ambient, while those of many advanced structural metals deteriorate both in immediate heating and long-term creep. Some systems have been shown to have considerable fatigue resistance, showing several times the stress for equivalent cycle lifetimes. These properties are important for structural shapes in which light weight and elevated-temperature resistance can afford a premium. Some applications have been struts and tubes

TABLE 12.6.7 Fiber- and Particle-Reinforced Metals — Test Results on Composite Metals

	Strengthener		Stress, kpsi	
Matrix Metals	Components	% Vol	Matrix Only, No Reinforcement	Composite Material
Metals Strengthened by Fibers				
Copper	W fibers	60	20	200[a]
Silver	Al_2O_3 whiskers	35	10[b]	75[b]
Aluminum	Glass fibers	50	(23%)[c]	(94%)[c]
Aluminum	Al_2O_3	35	25[d]	161[d]
Aluminum	Steel	25	25[d]	173[d]
Nickel	B	8	70[d]	384[d]
Iron	Al_2O_3	36	40[d]	237[d]
Titanium	Mo	20	80[d]	96[d]
Metals Strengthened by Sintered Carbides				
Cobalt	WC	90	(E = 30)[e]	(E = 85)[e]
Nickel	TiC	75	(E = 31)[f]	(E = 55)[f]

[a] Tensile strength with continuous fibers.

[b] Tensile strength at 350°C; modulus of elasticity: Cu = 17, composite 42 (millions of psi).

[c] Percentage of tensile strength at room temperature retained when tested at 300°C.

[d] Tensile strength, room temperature.

[e] Modulus of elasticity, E, measured in compression; hardness, 90 R-A; compressive strength, about 600,000 psi.

[f] Modulus of elasticity, E measured in compression; hardness about 85 R-A.

Compiled from various sources.

for space structures, bicycle frames, turbine parts, propellers, and engine components. The fiber may be incorporated unidirectionally, as a woven 2D laminate or a 3D structure. Fabrication methods include diffusion bonding, pultrusion (hot isostatic drawing), hot rolling, molten metal infiltration, and casting.

Table 12.6.7 gives metal matrix strengthening values for fiber reinforcements added in volume percentages from 8 to 60%.

Ceramic Matrix Composites

Richard L. Lehman and Daniel J. Strange

CMCs are ceramic matrix materials, either oxide, carbide, nitride, boride, or similar material, reinforced with particulates, whiskers, or continuous fibers. The reinforcing phase may be of any material, but most interest is directed toward ceramic reinforcement media. The following sections address fiber- and whisker-reinforced ceramic composites, the materials which offer the greatest potential for ameliorating the brittleness of ceramics and for developing exceptional mechanical and structural properties.

Ceramic Matrix Fiber Composites

Introduction. Ceramic matrix fiber composites (CMFCs) are the focus of substantial research but of limited commercial application as of this writing. The research enthusiasm is stimulated by the potential of high strength and toughness, mechanical and chemical durability, hardness, and oxidation resistance, all at elevated temperatures in the range 1000 to 1400°C. The limited commercialization, which is principally in military and aerospace applications, stems from the substantial cost of the fabricated materials, often in the range of thousands of dollars per kilogram. Fiber and matrix materials and properties used in CMFCs are presented in Table 12.6.8.

TABLE 12.6.8 Ceramic Matrix Composites: Fiber and Matrix Properties

Material	*E*	*a*	*R*	UTS	*e**	*g*(*Kc*)	*T*	*r*
Nicalon	180–200	3.1–4.0	7.5	2.5–3.0	1.4	(2.3)	1300	2.55
HM-carbon	345–414	–8–0.8	4	1.7–2.8	0.7	—	400, 3500	1.91
SCS-6 (SiC)	350–415	3.6	70	3.45	0.83	—	1300	3.3
FP-Al2O3	380	5.7	10	1.4	0.37	—	1316	3.9
Nextel 440	180	3.5	6	2.7	1.2	—	1426	3.1
Tyranno	193	3.1	5	2.76	1.5	—	1300	2.5
Ca-aluminosilicate	88–89	4.5–5.0	—	0.08–0.17	0.15	25 (2.2)	1350	2.8
Borosilicate glass	63–68	3.2–3.5	—	0.1	0.16	4.7, 40	600	2.2
Li aluminosilicate	74–88	0.9–1.5	—	0.17	0.21	10–40	1000–1200	2.1–2.4
Mg aluminosilicate	110	2.6	—	0.14	0.13	—	1200	2.6–2.8
Ba Mg aluminosilicate	106	2.7	—	—	—	40	1250	2.6
AS-1723	70–88	5.2	—	—	—	7–9, 40	700	—
7761	63	2.6	—	—	—	—	—	—
9741	50	4.9	—	—	—	—	—	—
7052	57	5.2	—	—	—	—	—	—
Reaction-bonded Si_3N_4	110	3.6	—	0.084	0.08	—	1900	3.2
SiC	340–380	4.3	—	0.35–0.92	0.1	(1.5–4.2)	1500	3.2
SiO_2	70–80	1.0	—	—	—	7–9	1150	—
ZrO_2	195	4.2	—	0.216	0.11	(2.5)	1500	6.0
Mullite	145	5.7	—	0.185	—	(2.2)	—	2.8

Note: *E* = Young's modulus (GPa), *a* = coefficient of thermal expansion ($\times 10^6$/°C), *R* = fiber radius (μm), UTS = ultimate tensile strength (GPa), *e** = failure strain (%), *g* = surface energy (J/m^2), *Kc* = fracture toughness (MPa $m^{1/2}$), *T* = maximum-use temperature (°C), *r* = density (g/cm^3).

Source: Karandikar, P.G. and Chou, T.-W., in *Handbook on Continuous Fiber-Reinforced Ceramic Matrix Composites,* Lehman, R.L. et al., Eds., Purdue Research Foundation, 1995, West Lafayette, IN. With permission.

Mechanical Behavior. The primary goal of reinforcing a ceramic material with ceramic fibers is to increase the fracture toughness of otherwise brittle ceramic materials. In a monolithic ceramic, a flaw will propagate through the material under tension due to stress concentration at the crack tip. CMCs are designed with $E_f/E_m > 1$ so that the reinforcing fiber absorbs stresses which tend to open and propagate cracks. Thus, the stress at the crack tip is reduced. Fiber debonding at the crack front, sliding, crack deflection, and other mechanisms also contribute to toughness. Often this is referred to as "rising R-curve" behavior, indicating that the strength of the ceramic at a crack tip increases with increasing crack length, stopping or slowing further crack growth. The most significant feature of CMFCs is the extensive fiber pullout, which occurs during failure. The fiber pullout results from low interfacial shear strengths, τ, which is designed into the composite by modifying interfacial properties and by using fibers with a *low* Weibull modulus. Loading is characterized by an initial elastic region followed by progressive failure of the matrix. The behavior is illustrated in Figure 12.6.8. During this matrix failure region, monotonically increasing loads are supported by the fibers. Ultimately, the fibers begin to fail according to bundle theory and the remaining load support is provided by the frictional resistance to fiber pullout, a highly significant effect which absorbs large amount of energy and contributes a high strain-to-failure performance previously unknown in ceramics. This "graceful" failure allows for a less catastrophic failure than normally encountered in ceramics and is of great significance in the design of such materials as turbine blades where the consequences of catastrophic failure are severe.

Continuous and Chopped Fiber Composites. The use of a continuous fiber reinforcement can have several advantages over the use of chopped fibers. There is a larger strain to pullout due to the increased fiber length, and the continuous fibers do not have stress-concentrating "flaws" as do the exposed ends of chopped fibers. Also, the prearrangement of the fibers allows very careful control of the properties in each direction, and the properties parallel to the fiber orientation will more closely mirror those of the fibers themselves than of the matrix. However, this type of composite is much more difficult to fabricate because of the problems of fiber weaving and forming, resistance to matrix infiltration, and

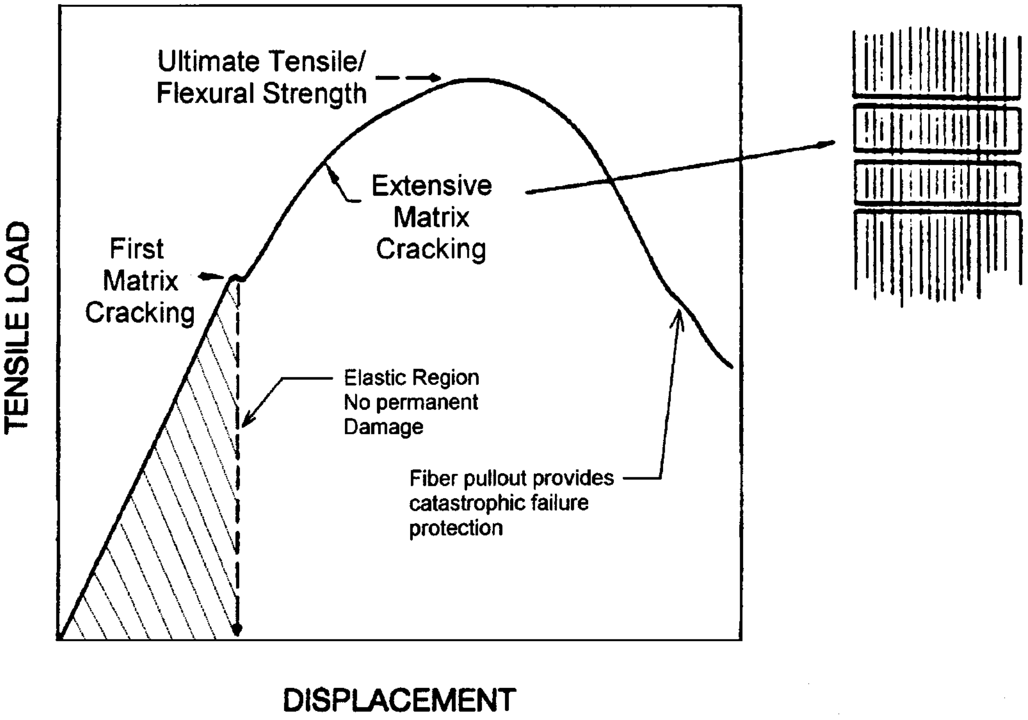

FIGURE 12.6.8 Load deflection behavior of CMFCs illustrating regions of fracture behavior.

resistance to densification, which necessitates expensive densification techniques, such as hot pressing, chemical vapor infiltration, polymer pyrolysis, directed metal oxidation, or sol–gel infiltration.

Glass Matrix CMFCs. A broad class of CMFCs has been developed and commercialized based on glassy matrix materials. The incentive for using a glassy matrix is the ease with which the matrix can be densified at low temperatures by vitreous sintering as opposed to the high-temperature solid-state sintering required for crystalline matrices. The low-temperature processing, in addition to being lower cost, preserves the high-strength properties of the fibers, which can easily be degraded at high temperatures. Unfortunately, the useful temperature of a glass-based CMC is limited to the T_g of the matrix, or slightly above, which prohibits traditional glass matrix CMCs from being used in extreme temperature applications (above approximately 1000°C). Newer glass and glass–ceramic compositions in the CaO-Al_2O_3-SiO_2 system are pushing this limit to the region of 1300°C. Two commercial glass matrix composites are Compglas™ and Blackglas™, both glass and glass/ceramic matrix materials reinforced with SiC fibers.

Polycrystalline matrix CMCs achieve higher temperature stability than the glass matrix composites, allow a wider choice of matrix materials, and generally have fewer problems with matrix reactivity. Typical crystalline matrix materials are the SiC, Si_3N_4, Al_2O_3, ZrO_2, and mixed silicates. Unfortunately, it is extremely difficult to sinter a CMC with a polycrystalline matrix to full density because of the interference of the fibers. This is particularly true with the nonoxide matrix materials. Pressureless sintering is ineffective for these materials, which necessitates the use of hot pressing or other exotic forming processes which raise material costs considerably.

Ceramic Matrix Whisker Composites (CMWCs)

Whisker reinforcement of ceramic matrices, while not as exotic, can dramatically increase toughness while preserving relatively inexpensive forming techniques. Figure 12.6.9 illustrates the “rising R-curve” behavior of alumina with the addition of SiC whiskers, while Figure 12.6.10 shows the increase in fracture strength. The composites can generally be fully densified with hot pressing or hot isostatic pressing (HIP). Unfortunately, the toughness values achieved to date with whisker reinforcement are not as high as those for continuous-fiber reinforcement, although the lower cost of whisker composites has stimulated industrial applications. Cutting tool inserts, which must withstand high stresses at elevated temperatures (1200°C), are fabricated commercially from SiC-whisker-reinforced Al_2O_3 (SiC/Al_2O_3). These composite inserts have been a commercial product for a decade and are an excellent example of cost-effective CMCs, i.e., high-value-added material applied to a small part exposed to extreme conditions. Health concerns regarding highly durable ceramic whiskers produced from SiC or Si_3N_4 have severely limited development and commercialization of these composites in the United States and Europe.

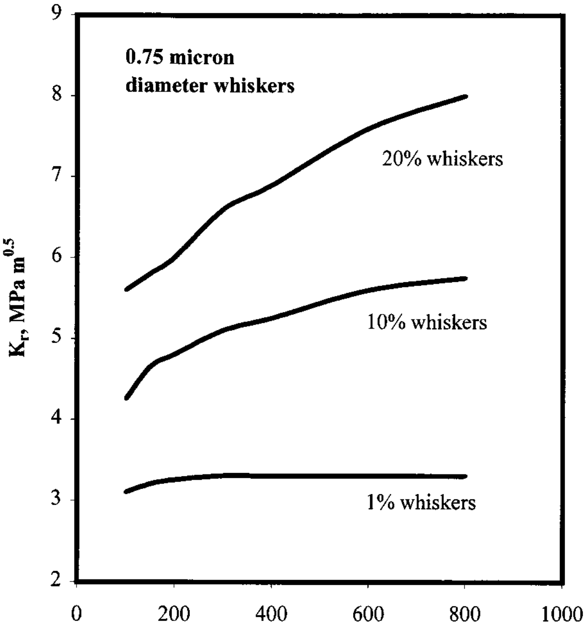

FIGURE 12.6.9 Fracture toughness and R-curve behavior of ceramic matrix whisker composites.

Carbon–Carbon Composites

Introduction

Carbon–carbon composites were originally developed for rocket nose cones in the 1960s because of their high specific strength, fracture toughness, thermal shock, and erosion resistance. Today, carbon–carbon composites are used in a broader range of applications, including brake components, fasteners, heaters, crucibles, and other assorted high-strength/high-temperature products.

High-Temperature Oxidation

Perhaps the greatest obstacle to the use of carbon–carbon composites as an engineering material, aside from high cost, is low oxidation resistance above 500°C. Although carbon–carbon maintains its mechanical properties to very high temperatures (>2000°C), it must be protected from oxidizing atmospheres at these temperatures or it will quickly degrade. Generally this is accomplished with SiC coatings with varying degrees of success. For most high-temperature oxidizing applications, carbon–carbon composite components are simply replaced when erosion reaches specified limits.

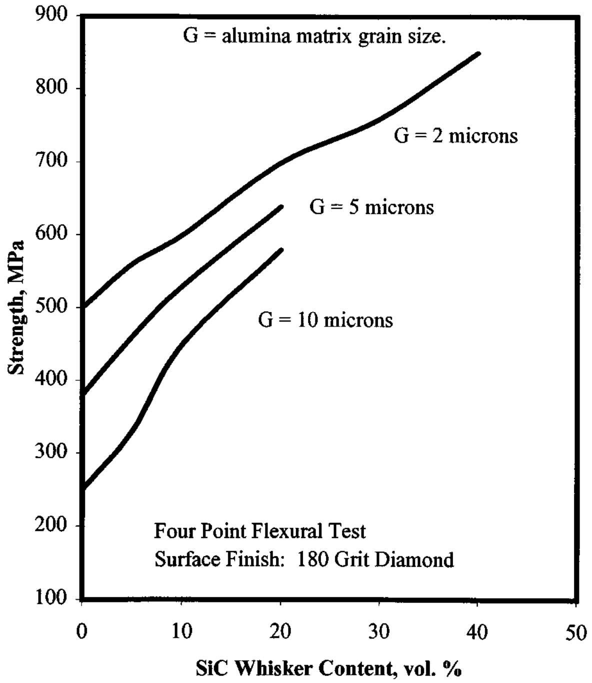

FIGURE 12.6.10 Strength behavior of SiC whisker-reinforced alumina matrix ceramic composite.

Fabrication

Most carbon–carbon composites are fabricated by polymer pyrolysis, the process of soaking carbon fiber yarns in a solution of a suitable polymer, then winding or laminating the fibers into the desired shape. Coal tar–based pitches, phenolics, and polyimides are also used as precursors.

The resulting green composite is then pressed, cured, and heated to 800 to 1200°C in an inert atmosphere, carbonizing the precursor. Some structures are heated to 2500°C to graphitize the matrix. The matrix after carbonization will contain a high porosity, typically 30%. This porosity is reduced by infiltrating the matrix with the precursor again and repeating the carbonization cycle. The densification cycle is repeated until the desired density is reached.

Carbon–carbon composites can be formed in random, unidirectional, 2D, 2.5D, and 3D weaves. Unidirectional weaves provide the highest strength along the fiber axis, but much lower strength in other directions. Unidirectional weaves are generally only used in laboratory investigations, as they have little technical value. 2D weaves (fabrics) are by far the most common due to the relative ease of manufacture and good mechanical properties in the plane of the fabric. 2.5D and 3D weaves allow the weaving of very complex structures with good properties in any desired direction, yet the weaving costs can be prohibitive and unnecessary for most industrial applications.

Mechanical Properties

Properties of some carbon–carbon composite materials are given in Table 12.6.9. The properties can vary considerably, however, depending upon factors such as the weave, tow diameter, precursor, pressing pressure, heat-treatment temperature, and number of densification cycles.

Under cyclical loading, carbon–carbon withstands 70 to 80% of its ultimate tensile strength. Carbon–carbon composites also have large strains to failure, exhibiting pseudoplastic behavior. This is unusual for a high-temperature ceramic material and is one of its prime attractions. The responsibility for this behavior lies with the low fiber–matrix interfacial bond strength and matrix microcracking. Unlike most high-temperature materials, the mechanical properties of carbon–carbon do not degrade at

TABLE 12.6.9 Properties of Selected Carbon–Carbon Composites

		Structural Grade[a]			**Fastener Grade**[b]		
Property	**Units**	**Warp Direction**	**Fill Direction**	**Across Ply**	**Warp Direction**	**Fill Direction**	**Across Ply**
Tensile strength	MPa	112	115	N/A	139	128	N/A
Tensile modulus	Gpa	89.6	91	N/A	71	717	N/A
Tensile strain to fail	%	0.126	0.126	N/A	0.271	0.242	N/A
Compressive strength	MPa	57	67	122 (min)	68	60	122 (min)
Flexural strength	MPa	86.2	N/A	N/A	106	106	N/A
Interlaminar shear	MPa	3.92	N/A	N/A	8.62	N/A	N/A
Thermal conductivity	J m^{-1} s^{-1} °C^{-1}	5.82	4.22	1.44	6.73	10.1	3.43
Coefficient of thermal expansion	10^{-7}°C^{-1} at 371°C	–0.94	–0.94	23.4	–1.2	–1.0	20.4
Density	g/cc		1.52			1.7	
Izod impact value	J cm^{-1}		3.52			5.95	
Hardness (Shore) “D” method			69.8			79.8	
Porosity	%			<20			<8.5
Resistivity, in plane, room-temperature	Ω-cm			24×10^{-4}			21×10^{-4}
Resistivity, in plane, 1750°C	Ω-cm			24×10^{-4}			—

[a] Fiber materials C^3 16 PC — 2 × 2 twill, 1780 denier continuous PAN fibers.

[b] Fiber materials C^3 40 PS — 8 harness satin, 600 denier, staple PAN fibers.

Source: Fiber Materials Incorporated, Biddeford, Maine.

high temperatures. In fact, in inert atmospheres the strength of carbon–carbon composites increases by 40 to 50% up to a temperature of 1600°C.

Thermal conduction, electrical conduction, and thermal expansion are all much greater along the direction of the weave than perpendicular to it. Interestingly, thermal expansion is negative in 2D weaves perpendicular to the fibers. It is therefore possible to use the fiber architecture to achieve near zero thermal expansion in some directions.

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12.7 Ceramics and Glass

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Traditional Ceramics

Traditional ceramics encompass many materials, not simply pottery, dinnerware, tile, and sanitaryware, but also technical whitewares, structural clay products, refractories, glazes, and enamels. The product and processing technology of these materials has advanced substantially in recent years which has improved products, reduced costs, and expanded application. Refer to Table 12.7.1 for properties of selected ceramics in this group.

TABLE 12.7.1 (Part I) Physical Properties of Selected Ceramics

Material	Porcelain	Cordierite Refractory	Alumina, Alumina Silicate Refractories	Magnesium Silicate
Specific gravity	2.2–2.4	1.6–2.1	2.2–2.4	2.3–2.8
Coefficient of linear thermal expansion, ppm/°C, 20–700°	5.0–6.5 × 10^6	2.5–3.0 × 10^6	5.0–7.0 × 10^6	11.5 × 10^6
Safe operating temperature, °C	~400	1,250	1,300–1,700	1,200
Thermal conductivity (cal/cm^2/cm/sec/°C)	0.004–0.005	0.003–0.004	0.004–0.005	0.003–0.005
Tensile strength (psi)	1,500–2,500	1,000–3,500	700–3,000	2,500
Compressive strength (psi)	25,000–50,000	20,000–45,000	13,000–60,000	20,000–30,000
Flexural strength (psi)	3,500–6,000	1,500–7,000	1,500–6,000	7,000–9,000
Impact strength (ft-lb; $^1/_2$″ rod)	0.2–0.3	0.2–0.25	0.17–0.25	0.2–0.3
Modulus of elasticity (psi)	7–10 × 10^6	2–5 × 10^6	2–5 × 10^6	4–5 × 10^6
Thermal shock resistance	Moderate	Excellent	Excellent	Good
Dielectric strength, (V/mil; 0.25″ specimen)	40–100	40–100	40–100	80–100
Resistivity (Ω/cm^2, 22°C)	10^2–10^4	10^2–10^4	10^2–10^4	10^2–10^5
Power factor at 10^6 Hz	0.010–0.020	0.004–0.010	0.002–0.010	0.008–0.010
Dielectric constant	6.0–7.0	4.5–5.5	4.5–6.5	5.0–6.0

Whitewares

Whitewares are principally comprised of traditional ceramic bodies that are white, cream, ivory, or light gray in appearance. Most whiteware materials are formulated from clay, flint, and feldspar (triaxial compositions) although other additives may be incorporated. The engineering properties of whitewares are strongly affected by porosity, a characteristic that reduces frost resistance and cleanability but is essential for certain aesthetic effects.

Vitreous. Vitreous whiteware bodies are translucent and have no open porosity, while earthenware and wall tile, for example, have substantial porosity, and semivitreous bodies bridge the gap in both porosity and translucency. The firing temperature is largely responsible for the differences in properties of the bodies by affecting the degree of vitrification. The general categories of products within the whiteware group are given in Table 12.7.2.

Earthenware. Earthenware materials are defined as a nonvitreous clay-based ceramic ware of medium porosity (4 to 20%). They can be glazed or unglazed in their finished form. There are four primary subclasses of earthenware, natural clay, fine, semivitreous, and talc earthenware. Natural clay earthenware is derived from a single, unbeneficiated clay, whereas fine earthenware possesses beneficiated clays, as well as nonplastic materials, to comprise a triaxial body. Semivitreous earthenware is also a triaxial body, but it is fired to a higher temperature to form a more glassy phase, thereby creating a body with

TABLE 12.7.1 (Part II) Physical Properties of Selected Ceramics

Material	High-Voltage Porcelain	Alumina Porcelain	Steatite	Forsterite	Zirconia Porcelain	Lithia Porcelain	Titania/Titanate Ceramics
Specific gravity	2.3–2.5	3.1–3.9	2.5–2.7	2.7–2.9	3.5–3.8	2.34	3.5–5.5
Coefficient of linear thermal expansion, ppm/°C, 20–700°	5.0–6.8 $\times 10^6$	5.5–8.1 $\times 10^6$	8.6–10.5 $\times 10^6$	11 $\times 10^6$	3.5–5.5 $\times 10^6$	1 $\times 10^6$	7.0–10.0 $\times 10^6$
Safe operating temperature, °C	1,000	1,350–1,500	1,000–1,100	1,000–1,100	1,000–1,200	1,000	—
Thermal conductivity (cal/cm^2/cm/sec/°C)	0.002–0.005	0.007–0.05	0.005–0.006	0.005–0.010	0.010–0.015	—	0.008–0.01
Tensile strength (psi)	3,000–8,000	8,000–30,000	8,000–10,000	8,000–10,000	10,000–15,000	—	4,000–10,000
Compressive strength (psi)	25,000–50,000	80,000–25,000	65,000–130,000	60,000–100,000	80,000–150,000	60,000	40,000–120,000
Flexural strength (psi)	9,000–15,000	20,000–45,000	16,000–24,000	18,000–20,000	20,000–35,000	8,000	10,000–22,000
Impact strength (ft-lb; $^1/_2$″ rod)	0.2–0.3	0.5–0.7	0.3–0.4	0.3–0.4	0.4–0.5	0.3	0.3–0.5
Modulus of elasticity (psi)	7–14 $\times 10^6$	15–52 $\times 10^6$	13–15 $\times 10^6$	13–15 $\times 10^6$	20–30 $\times 10^6$	—	0.3–0.5 $\times 10^6$
Thermal shock resistance	Moderate–good	Good	Moderate	Poor	Good	Excellent	Poor
Dielectric strength, (V/mil; 0.25″ specimen)	250–400	250–400	200–350	200–300	250–350	200–300	50–300
Resistivity (Ω/cm^2, 22°C)	10^{12}–10^{14}	10^{14}–10^{15}	10^{13}–10^{15}	10^{13}–10^{15}	10^{13}–10^{15}	—	10^{8}–10^{15}
Power factor at 10^6 Hz	0.006–0.010	0.001–0.002	0.008–0.035	0.0003	0.0006–0.0020	0.05	0.0002–0.050
Dielectric constant	6.0–7.0	8–9	5.5–7.5	6.2	8.0–9.0	5.6	15–10,000

TABLE 12.7.2 Whiteware Materials

Class and Subclass	Percent Water Absorption	Example Product Type
Earthenware		
Natural clay	>15	Artware and tableware
Fine earthenware	10–15	Tableware, kitchenware, and artware
Semivitreous Earthenware	4–9	Tableware and artware
Talc earthenware	10–20	Ovenware and artware
Stoneware		
Natural stoneware	<5	Kitchware, artware, and drainage pipes
Fine stoneware	<5	Cookware, tableware and artware
Jasper stoneware	<1	Artware
Basalt stoneware	<1	Artware
Technical vitreous stoneware	<0.2	Chemicalware
China		
Vitreous china	0.1–0.3	Sanitaryware
Hotel china	0.1–0.3	Tableware
Cookware	1–5	Ovenware and stoveware
Technical china	<0.5	Chemicalware and ball mill jars and media
Fine china	<0.5	Tableware and artware
Porcelains		
Technical porcelains	<0.2	Chemicalware
Triaxial electrical porcelains	<0.2	Low-frequency insulators
High-strength electrical porcelains	<0.2	Low-frequency insulators
Dental porcelains	<0.1	Dental fixtures

the lowest porosity of the earthenware group, usually between 4 and 9%. The final earthenware body is talc earthenware, produced principally from raw talc, with porosity ranging up to 20%. Earthenware bodies range in color from white for the talc and triaxial bodies, to tan and brown for many artware bodies, to a rusty red for terra-cotta.

Stoneware. Stoneware bodies can be either vitreous or semivitreous. They are primarily composed of nonrefractory fireclays or a combination of triaxial materials that matches the forming, firing, and finished properties of a natural stoneware body, bodies made from a single, naturally occurring, largely unbeneficiated clay-bearing material. Fine stonewares incorporate beneficiated clays, as well as nonplastics. Jasper stonewares are composed primarily from barium-containing compounds, while basalt stonewares contain large amounts of iron oxide.

Vitreous stoneware bodies are made from blends of a variety of beneficiated materials that are fired to higher temperatures to achieve low porosity levels (0 to 5%) necessary for many applications. Stoneware bodies are usually quite durable and resistant to chipping. However, translucency is less than that of china and the colors are not as white because of the presence of iron and other impurities.

China and Porcelain. China and porcelain are nearly synonymous terms which refer to fully vitreous (no porosity) clay, flint, feldspar compositions which are typically glazed, fired to high temperatures, and exhibit strength, hardness, and chemical durability. The term *china* is used to describe exceptionally fine materials prepared from low-impurity raw materials and used in artware and dinnerware. In modern times there has been a trend toward highly vitreous and highly translucent china compositions. Porcelain is used to describe mostly technical ceramics of the triaxial composition which are used as electrical insulators, sanitaryware, and chemical ware.

Subclassifications of china exist, such as vitreous china, hotel china, cookware, technical ceramics, fine chinas, and porcelains. Body formulations are usually based on the triaxial body, clays, flint/silica and fluxing agents, most usually feldspathic materials. However, there are a large number of bodies that are composed of a large fraction of other materials. Inclusive of these are alumina, bone ash, cordierite, other fluxes, and/or lithium compounds. Vitreous china is a category of traditional ceramics referring to the various sanitaryware plumbing fixtures and accompaniments. Hotel chinas, as the name implies, are generally used in commercial food establishments. Both bodies are glazed in a single firing operation in which both the body and glaze mature at the same time.

Technical whitewares account for a wide variety of vitreous ceramics used in the chemical, dental, refractory, mechanical, electrical, and structural areas. The compositions of most of these materials are similar to that used in the hotel chinas, with the possible substitution of alumina and zircon for some or all of the silica. These materials can be either glazed or unglazed with water absorption less than 0.5%.

Fine china bodies, including bone china, are highly vitrified and translucent materials that are usually fired in two or more separate operations. The first, higher-temperature firing matures the body and a second, lower-temperature firing matures the newly applied glaze. The separate firing conditions allow for the use of high-gloss glazes. Subsequent firings are used to apply decals and metallic decorations.

Porcelain ceramics are mostly used in technical applications. The typical body is triaxial (Table 12.7.2), although some or all of the silica can be replaced with alumina to increase the mechanical properties. Aside from triaxial porcelains, compositions in the $MgO \cdot Al_2O_3 \cdot SiO_2$ composition range are popular for electronic applications due to the absence of mobile alkali ions.

Refractories

Introduction. Refractory ceramic materials are by nature inert, high-melting-point compounds that are resistant to corrosion throughout the temperature range of use. Refractories must also withstand thermal cycling, thermal shock, mechanical fatigue, and a range of chemical attack from the elevated-temperature environments typical of most applications. Refractory materials are used in the processing of metals (75% of all refractories), glass, cement, and in the processing of nearly all ceramics.

Temperature Tolerance. A quality refractory must be stable at the intended use temperature. Refractoriness is a measure of the highest use temperature the material can withstand and is limited by the softening or melting point of the constituent oxides. Most refractories are a mixture of phases, and, as such, do not display a distinct melting point, but have a range of temperatures where the material starts to soften or melt. Most frequently, a refractory is categorized by an upper use temperature, but sometimes the refractoriness is quantified by the PCE or pyrometric cone equivalent. The PCE is a measure of the heat content that the refractory can withstand before beginning to soften, which is determined by the slumping of pyrometric cones during thermal cycle testing. This value may correspond to different temperatures under different environments or atmospheres and is thus a good indicator of maximum-use conditions. Refractory suppliers can provide PCEs for specific products. Another measure of a refractory quality is the failure under load temperature. The temperature where a refractory sags or deforms is part of all refractory specifications and is related to the amount and composition of the glassy phase within the material.

Dimensional Stability and Spalling. Dimensional stability and resistance to spalling are important performance criteria for most refractories. Spalling is the cracking or flaking of the refractory which usually results from thermal cycling, thermal gradients within the refractory, or compression effects due to differing thermal expansion of the different system materials. Spalling reduces the effectiveness and lifetime of the refractory. The dimensional stability of the refractory is also important. Since the refractory is subjected to both heating and cooling cycles, as well as thermal gradients in use, the expansion of the material is very important when choosing a refractory. Large changes in the size of a refractory set up stresses that can reduce the effectiveness of the refractory and may result in its failure.

Porosity. Refractory porosity is closely controlled in manufacturing since it leads to a reduction in the mechanical strength of the material and allows for the penetration and chemical attack of liquids or gases to the internal surface of the refractory. However, on the positive side, the presence of internal pores reduces the thermal conductivity of the material and increases fracture toughness, K_{IC}.

Fireclay Refractories. Fireclay refractories are composed of hydrated aluminosilicates with silica content of up to 75% or more with alumina and other minor contents of less than 40%, although alumina-fortified fireclay refractories are made with considerably higher alumina contents. Properties vary greatly over this wide range of compositions — generally, the higher the alumina content, the higher the performance. Fireclay refractories based on kaolin have a high refractoriness and high load resistance. Resistance to chemical attack and thermal conductivity decrease with increasing porosity, whereas spalling resistance increases. Increased alumina content raises the resistance of the material to attack in molten environments. Fireclay refractories are the most widely used refractory and find application in many industries.

Alumina Refractories. High-alumina refractories contain 80 to 99% or more aluminum oxide. As with fireclay materials, the higher the alumina content, the higher the refractoriness and the higher the load-bearing capacity. The chemical resistance of alumina refractories is greater than that of the fireclay refractories. Alumina brick is used to replace fireclay brick in more severe applications in the steel industry. Alumina bricks with phosphate bonding are used in the production of aluminum because of their refractoriness and the resistance of the phosphate bonding to chemical attack by the molten aluminum. Mullite ($3Al_2O_3 \cdot 2SiO_2$) refractories are similar to alumuna refractories in performance, but are cheaper and more resistant to thermal shock at the expense of some temperature capability.

Silica. Silica brick refractories, used in the glassmaking industry, range in composition from almost pure silica to mixtures containing lime, iron oxide, and alumina, depending on the degree of beneficiation of the raw materials. These refractories show a high degree of volume stability below 650°C (1200°F) and a lower degree of spalling than the fireclay bricks, largely because of the low thermal expansion of the silica.

Basic Refractories. Basic refractories are constituted from magnesite (MgO), calcia (CaO), and chrome (Cr_2O_3) and are used widely in metallurgical industries where basic slags predominate. They are not suitable in acid, or high-silica, environments. Refractories in this group, such as pure magnesite, dolomite (CaO-MgO), and chrome magnesite materials, have high refractoriness, volume stability, and are very resistant to chemical attack. Magnesite refractories have between 80 and 95% MgO content, a level at which the refractoriness and resistance to chemical attack is extremely high. Chromite refractories also have excellent chemical resistance in basic environments, with moderate resistance in acidic environments. The chrome content in these refractories ranges between 30 and 45%. Chrome–magnesite refractories are composed of over 60% MgO. Compositions and properties of selected basic and high-duty refractories are given in Table 12.7.3.

Glazes and Enamels

A glaze is a continuous glassy layer that is bonded to the surface of a ceramic. The glaze is typically hard, impervious to moisture, and easily cleaned. An enamel is similar in properties to a glaze, but the substrate is metallic. The surface finish of either can be altered from glossy to matte by varying the composition or the firing conditions. A glaze is usually composed of an aqueous suspension of ceramic particles that is applied to the surface of a material, dried, and fired. During firing, the materials within the glaze react and melt, forming a thin glassy layer on the surface of the ceramic material. Some materials are prefired and then the glaze is applied, or, as is becoming more common, the glaze can be fired along with the body. The maturing temperature of most glazes is on the order of 500 to 1500°C, or 930 to 2730°F. Glazes can be either clear, transparent, or opaque. Some glazes are formulated to form crystals within the glaze for a variety of optical effects, such as opalescence.

There are three main types of glazes used. The first of these are the raw glazes. Raw glazes can be further broken down into leaded, leadless, zinc-containing, slip, and porcelain glazes. Lead promotes the processing of the glaze via low viscosity and surface tension and imparts a high refractive index to the finished glaze. However, due to the health hazards associated with free lead, there has been a movement toward lead-free glazes in certain applications. Lead-free glazes require an increase in the

TABLE 12.7.3 Compositions and Properties of Selected Basic and High-Duty Refractories

Refractory	Composition	Maximum Use Temperature in O_2		Thermal Conductivity		
		(°C)	(°F)	100°C/212°F	500°C/930°F	100°C/1830°F
Basic Refractories						
Silica	93–96% SiO_2	1700	3090	0.8–1.0	1.2–1.4	1.5–1.7
Fireclay	55–80% SiO_2 and 15–45% Al_2O_3	1300–1450	1370–2640	0.8–0.9	0.9–1.1	2.4–2.6
Magnesite	80–95% MgO Fe_2O_3 Al_2O_3	1800	3270	3.8–9.7	2.7–4.7	2.2–2.6
Chromite	30–45% Cr_2O_3, 14–19% MgO, 10–17% Fe_2O_3, 15–33% Al_2O_3	1700	3090	1.3	1.5	1.7
Chromite–magnesite	60+% Fe_2O_3 Al_2O_3	1800	3270	1.9–3.5	1.2–2.3	1.6
High-Duty Refractory						
Alumina	100% Al_2O_3	1950	3540	26	9.4	5.3
Magnesia	100% MgO	2400	4350	31	12	6
Silica	100% SiO_2	1200	2190	0.8	1.4	1.8
Mullite	72% Al_2O_3, 28% SiO_2	1850	3360	5.3	3.8	3.4

firing temperature of approximately 150°C, from 1030 to around 1190°C. Porcelain glazes mature at temperatures in the same regime as the underlying body from which they get their name. Zinc-containing glazes are similar to porcelain glazes except that they mature at lower temperatures. Slip glazes are used in artware glazing and high-tension electrical insulators. Fritted glazes are in the form of prereacted glass which has been ground to form a powder. Special glazes offer special optical properties in the finished surface. Salt glazes are formed by injecting salts into the firing kiln, with the resulting glaze having a complex pattern of crystalline and glassy phases. Crystalline glazes are often zinc based and produce crystals within the glaze, again for artistic value. Luster glazes form a metallic coating on the glaze.

Structural Clay Products

Ceramic materials are used in a wide variety of applications in the construction industry, ranging from concrete and cement for buildings and highways, to structural clay materials for use in piping and roofing. For a discussion of concrete materials refer to Section 12.5.

Structural clay products have been used for millennia. Original uses included tile and clay brick for building construction, as well as pipes in water supply and sewer applications. These materials are still used today because of their high compressive strength and imperviousness to water. Structural ceramics are coarse-grained materials with the one exception of ceramic tile. Typical raw material compositions for these bodies are 35 to 55% clay, 25 to 45% filler, usually silica, and 25 to 55% fluxing material. Colors range from white for the kaolinitic clay products, to a buff for the fireclay materials, to red for the illitic materials. Properties vary widely between the different materials. Most concern is placed on the water absorption, which relates to freeze/thaw durability and compressive strength.

Advanced Ceramics

Classes of Advanced Ceramics

Advanced ceramic materials are materials which have been engineered to possess exceptional levels of mechanical, optical, thermal, or other property. Most often the materials possess high strength, high stiffness, or are chemically inert. Typical materials contain oxides, nitrides, or carbides which may be monolithic structures or reinforced with various particulate and/or fibrous materials. Refer to Section

12.6 for a detailed discussion of composites. The reinforcement phase usually, but not necessarily, differs from the matrix material. Phases used in designing engineered ceramics are listed in Table 12.7.4 with specific property characteristics as indicated. Advanced ceramic materials are currently much more varied and less standardized than metals, and materials from different manufacturers, or even from different production lots, will have varied properties.

TABLE 12.7.4 Selected Properties of Crystalline Phases Used in Engineered Ceramics

Crystalline Phases	Formula	Melting Temperature (C)	Thermal Expansion α (ppm/°C)	Dielectric Constant κ
Magnesia	MgO	2852	14	5.5
Magnesia spinel	$MgO \cdot Al_2O_3$	2135	8	8.0
Alumina	Al_2O_3	2072	9	10.0
Mullite	$3Al_2O_3 \cdot 2SiO_2$	1920	5.5	4.5
Silica	SiO_2	1723	—	3.8
Protoenstatite	$MgO \cdot SiO_2$	1557	8.0	6.0
Forsterite	$2MgO \cdot SiO_2$	1910	12.0	6.0
Cordierite	$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$	1450	2.0	5.0
Carbon	C	3652	4.4	—
Silicon carbide	SiC	2700	4.4	—
Silicon nitride	Si_3N_4	1900	—	—
Zirconium oxide	ZrO_2	5000	—	—
Zircon	$ZrO_2 \cdot SiO_2$	2550	4.5	6.5
Wollastonite	$CaO \cdot SiO_2$	1540	5.5	6.0
Titania	TiO_2	1830	—	90
Calcium titanate	$CaO \cdot TiO_2$	1975	—	180
Strontium titanate	$SrO \cdot TiO_2$	—	—	360
Magnesium titanate	$MgO \cdot TiO_2$	—	—	14
Barium titanate	$BaO \cdot TiO_2$	—	—	2000
Magnesium ferrite	$MgO \cdot Fe_2O_3$	—	—	—
Zinc ferrite	$ZnO \cdot Fe_2O_3$	—	—	—

Structural Ceramics

Required Properties. Structural applications involve the use of ceramic materials in load-bearing situations. Material properties required for these conditions include strength over a wide temperature range, often as high as 1400°C, stiffness, creep resistance, resistance to corrosion and oxidation, and, ideally, damage tolerance or toughness. The major difficulty in the use of ceramics for structural applications is their low fracture toughness compared with metals. Conversely, ceramics excel at high-temperature behavior, have low density/weight ratios, high stiffness, and chemical inertness. At the present level of technology, there is a trade-off between high strength and high toughness. To get a high-strength material usually requires a fine-grain-sized ceramic, while a tough ceramic material often has elongated grains or reinforcement phases that are usually quite large.

Applications. Existing and potential applications include automotive, biomedical, power generation, heat exchangers, wear materials, aerospace and military applications, cutting tools, and various other technologies. Table 12.7.5 provides the mechanical properties of selected advanced ceramics. The property values listed are guidelines; exact properties are difficult to specify since the exact properties depend largely on processing. Material selection is governed by the environmental conditions of each application.

Electronic and Magnetic Ceramics

Electronic and magnetic ceramic materials have a variety of useful functions. Alumina, alumina titanate, and aluminum nitride are used as substrate materials, zirconia is used in oxygen sensors, lead zirconate

TABLE 12.7.5 Mechanical Properties of Selected Advanced Ceramic Materials

Material	Composition	Density (g/cc)	Elastic Modulus (GPa)	Fracture Strength (MPa)	Fracture Toughness K_{IC} (MPa · $m^{0.5}$)	Hardness (Vickers)
Alumina	Al_2O_3	3.9	380	Up to 400	4–9	2000
Beryllia	BeO	2.8–2.9	340	125	5	1100–1400
Chromic oxide	Cr_2O_3	4.2–4.4	—	—	4–9	—
Magnesia	MgO	3.5	300	—	3–5	500–600
Spinel	$MgAl_2O_4$	3.2	260	50–100	2–5	1200–1500
Zircon	ZrO_2 SiO_2	4.25	160	50–100	2–4	—
Zirconia	ZrO_2 stabilized with CaO	5.5	200	500	Up to 13	1200–1500
Zirconia	ZrO_2 stabilized with MgO	5.5	200	500	Up to 13	1200–1500
Zirconia	ZrO_2 stabilized with Y_2O_3	5.6	200	500–600	Up to 13	1200–1500
Zirconia (tetragonal)	ZrO_2	6.0	200	750	Up to 13	—
Zirconia (monoclinic)	ZrO_2	5.5	200	450	Up to 10	—
Reaction-bonded silicon nitride (RBSN)	Si_3N_4	1.9–2.8	150–250	300–400	Up to 12	750
Silicon nitride (hot pressed)	Si_3N_4	3.1–3.2	310	400–700	5–9	1600–2800
Silicon carbide (sintered)	SiC	3.0–3.2	400	400–500	6–9	2400–2800
Silicon carbide (hot pressed)	SiC	3.0–3.2	440	550–650	7–9	2500
Silicon carbide (RBSC)	SiC	3.0–3.15	350–400	300–400	4–8	2000
Boron carbide	B_4C	2.3–2.5	450	400–600	—	2800–3200
Boron nitride	BN	2.0–2.1	20–100[a]	—	—	Soft anisotropic
Graphite	C	1.9	3–15[a]	<50	—	Soft
Tungsten carbide	WC	15	600	450–750	Up to 20[b]	1300–1600
Titanium nitride	TiN	4.9	—	—	—	—
Titanium carbide	TiC	4.9	—	—	—	2800–3700

[a] Anisotropic.

[b] With Co additions.

titanate (PZT) and lead magnesium niobate are common actuator and transducer materials, and barium titanate and related materials are used in capacitors. Ceramic materials are used not only in military and aerospace applications, but also in consumer electronics, computers, automotive and transportation systems, and power generation systems. Electronic/magnetic ceramics are useful as a result of a variety of properties. Refer to Table 12.7.1 for dielectric property data of selected compositions.

Optical Ceramics

Zirconia and transparent alumina, or sapphire, are often used as high-temperature windows, due to their high melting points, chemical inertness, and high transparency. They are also used as watch crystals, due to their high scratch resistance. Mirrors made from silicon carbide are being evaluated because of the higher strength-to-weight ratio compared with glass materials and the relatively low coefficient of thermal expansion of SiC. Laser crystals are a group of materials which are often based on doped crystals — yttrium aluminum garnet (YAG) is representative, Infrared (IR) transparent windows and shields are used principally in military and aerospace applications to protect IR sensors from damage. Missile nose cones, or randomes, must possess high mechanical strength and be resistant to mechanical erosion and thermal shock. Typical materials include aluminum oxynitride, spinel, zinc sulfide, calcium fluoride, yttria, and sapphire. Refer to Table 12.7.6 for IR absorption ranges of important ceramic materials.

Effect of Finishing and Machining on Properties

Final finishing of many advanced ceramics is required to obtain the optimum mechanical properties or to meet design tolerances. Since sharp corners act as stress concentrators and are not associated with good design, they are usually machined to a several-millimeter radius if they occur in the as-manufactured product. Other operations include surface grinding, polishing, or lapping operations. Ceramics are very hard materials, which makes final matching machining extremely time-consuming and expensive. Every effort should be made to fabricate components to close to net shape tolerances, or to machine the piece as much as possible prior to final firing.

Traditional Glasses

Definition and Introduction

Traditionally, glass is defined as an inorganic product of fusion which has cooled to a rigid state without crystallizing. This broad definition says nothing about the chemistry of the glass but rather refers to the traditional concept of cooling liquid melts below the melting point to form substances which are rigid elastic mechanical solids but which have not crystallized. The historical model for this process is the melting of soda–lime silicate glass by fusing the raw materials at high temperature and cooling quickly to form the well-known window and container glass still in wide use today. Although this definition is still generally valid, processes exist today in which glass is made without fusion. Chemical and physical vapor deposition, and sol–gel processes are examples. Many organic and metallic materials form glasses and are in commercial use today, thus rendering the “inorganic” part of the historical definition inappropriate.

A more applicable definition of glass is an X-ray diffraction amorphous material which exhibits a glass transition. A glass transition is the temperature point at which the amorphous solid exhibits a continuous change in thermodynamic quantities such as heat capacity and expansion coefficient. Because the structure of the glass is frozen before it reaches equilibrium, a glass is metastable with respect to its corresponding crystalline phase. Unlike the crystalline phase, the glass can have a range of physical properties depending upon the rate of cooling (thermal history) and these properties are universally isotropic.

Although glass can be made from an enormous range of polymers, oxides, metals, and inorganic and organic salts, the principle glasses of interest to a mechanical engineer will be glasses with oxide network formers such as SiO_2, B_2O_3, P_2O_5. These oxides, among others, are known as glass formers. They are capable of forming the three-dimensional network essential to the existence of the glassy state. Other

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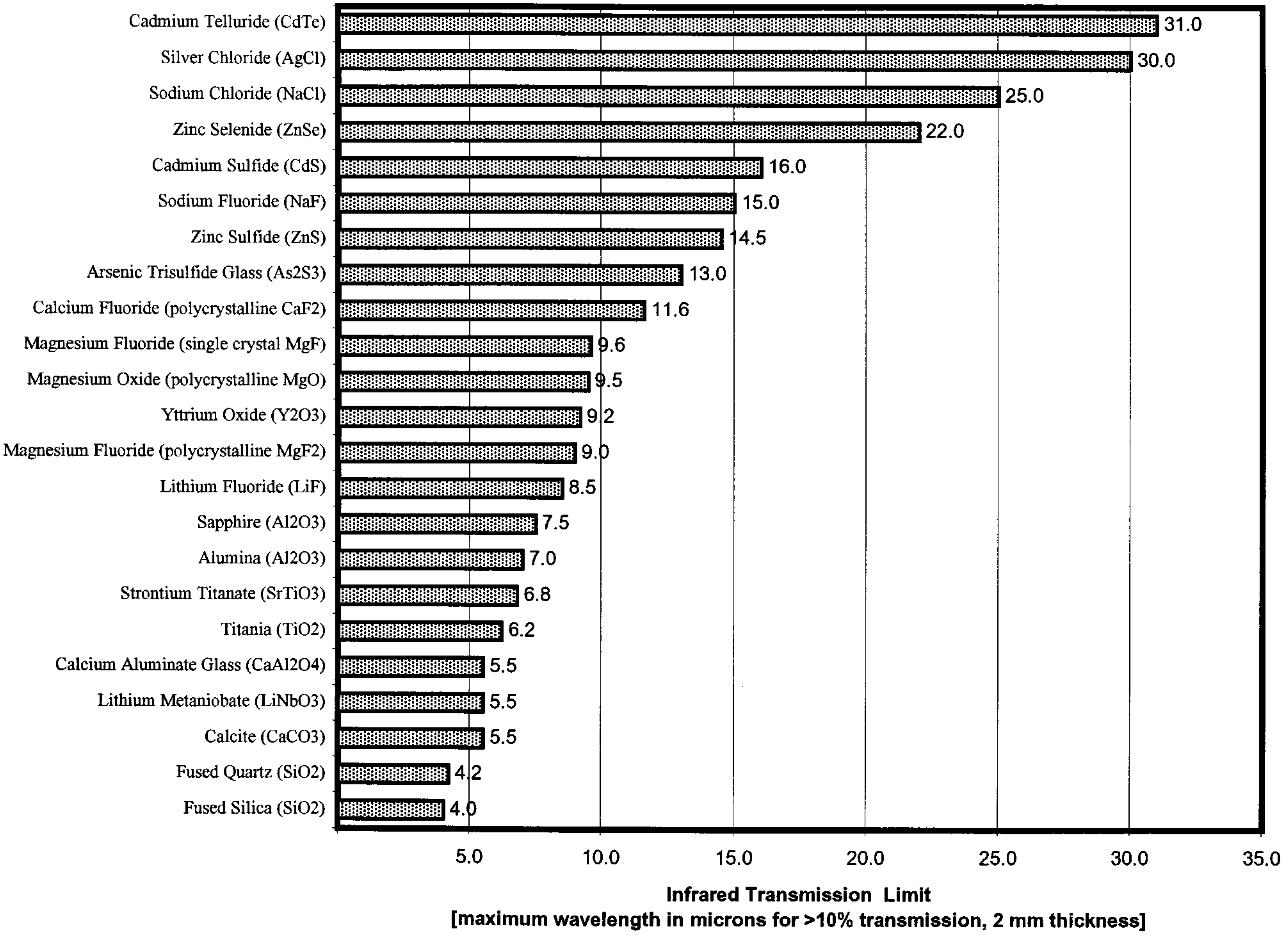
TABLE 12.7.6 IR Transmission Limits for Selected Materials



oxides, such as alkalis, alkaline earths, and various transition elements simply serve to modify the basic network to produce varying properties.

The most common glass in use today is the very old soda–lime–silicate glass composition based on the weight composition: 74% SiO_2, 16% Na_2O, and 10% CaO. In this composition the silica is the network former, the sodium breaks up the silicate network to permit melting and fabrication at reasonable temperatures, and the calcia provides ionic bonding within the network to provide chemical durability. This composition is used today, with minor variations, for early all container, window, and tableware glass articles.

Composition/Properties

Traditional glasses are silicate glasses, i.e., glass which contain SiO_2 as the principal network-forming oxide. Table 12.7.7 give compositions for a representative range of commercial glasses, and Table 12.7.8 lists properties for flat glass. All glasses in Table 12.7.7 contain at least 50% SiO_2 and many are quite close to the traditional 74/16/10 composition mentioned above. The types and amount of modifier oxides are determined by the properties required in use. A more specific list of technical glass compositions from Corning, Inc., and identified by Corning glass codes, is given in Table 12.7.9. Principal glass types are discussed in the following sections.

Pure Silica Glass. Pure silica glass (fused silica) has excellent thermal, mechanical, chemical, and optical properties. Thermal expansion is 5.5×10^{-7}°C^{-1}, use temperature is above 1000°C, and it has excellent visible and ultraviolet (UV) transmission. However, the melting point is greater than 2000°C, which makes manufacture extremely difficult and expensive. Therefore, fused silica is used primarily for such demanding applications as optical fibers, semiconductor process equipment, UV lamps, optics, and space shuttle windows. If 7 wt% titanium dioxide (TiO_2) is added, the thermal expansion coefficient is reduced to zero in normal temperature ranges. This glass (ULE, or ultra low expansion) is used in applications which require exceptional dimensional stability. Telescope mirrors are an example.

High-Silica Glass. The high melting temperatures needed to produce pure SiO_2 glass can be avoided by first melting a special sodium borosilicate glass which can be formed into the desired shape. This glass (Vycor®) phase separates and after acid leaching results in a high (>96%) silica glass with nearly the same properties as pure vitreous silica.

Soda Silica. In order to lower the melting point, a flux is added. The most common flux is sodium oxide (Na_2O), which makes a low-melting glass that is soluble in water and is called water glass. Dissolved glass is used to seal or bond materials such as low-speed grinding wheels.

Soda–Lime–Silica. This is the most common glass and accounts for more than 90% of all the glasses made today. In this glass, lime (CaO) has been added to improve the durability of simple soda–silica glass. Small amounts of other oxides such as alumina (Al_2O_3), magnesium oxide (MgO), and potassium oxide (K_2O) are also added to further enhance the desired properties. The lime is usually obtained from limestone, and the sodium monoxide is obtained from any number of sodium compounds, notably sodium bicarbonate or common baking soda.

Aluminosilicate Glass. Aluminosilicate glass is produced by adding up to 20% Al_2O_3 to soda–lime glass. Aluminosilicate glasses are resistant to thermal shock and high temperatures, and they are not as difficult to produce as silica glass. They find wide use in electronics and in high-temperature laboratory equipment.

Borosilicate Glass. In borosilicate glass much of the soda and lime of ordinary glass is replaced by boric oxide. The result is a glass that has a low thermal expansion and is thus resistant to heat and to sudden changes in temperature. The first borosilicate glass was developed by the Corning Glass Works under the trade name Pyrex. Borosilicate glasses are used in laboratory glassware, as well as in home ovenware. Because of their low thermal expansion they are suitable for applications requiring dimensional stability.

TABLE 12.7.7 Commercial Glass Compositions by Application (Wt% oxide)

Oxide	(Optical) Vitreous silica	(High silica) Vycor	Plate	Window	Con-tainer	Light bulb	Tubing	Lime table-ware	Low-expansion boro-silicate	Thermo-meter	Boro-silicate Crown	Lead table-ware	Halogen lamp	(Textile fiber) E glass	S glass	Optical flint
SiO_2	100.0	94.0	72.7	72.0	74.0	73.6	72.1	74.0	81.0	72.9	69.6	67.0	60.0	52.9	65.0	49.8
Al_2O_3			0.5	0.6	1.0	1.0	1.6	0.5	2.0	6.2		0.4	14.3	14.5	25.0	0.1
B_2O_3		5.0							12.0	10.4	9.9			9.2		
SO_3			0.5	0.7	tr	5.2							0.3			
CaO			13.0	10.0	5.4	3.6	5.6	7.5		0.4			6.5	17.4		
MgO				2.5	3.7		3.4			0.2				4.4	10.0	
BaO					tr						2.5		18.3			13.4
PbO												17.0				18.7
Na_2O		1.0	13.2	14.2	15.3	16.0	16.3	18.0	4.5	9.8	8.4	6.0	0.01			1.2
K_2O					0.6	0.6	1.0			0.1	8.4	9.6	tr	1.0		8.2
ZnO																8.0
As_2O_3			tr	tr	tr	tr		tr		tr	0.3	tr				0.4

Source: Varshneya, A.K., *Fundamentals of Inorganic Glasses,* Academic Press, New York, 1994. With permission.

TABLE 12.7.8 Properties of Clear and Tinted Flat Glass (Applicable Federal Specification Standard DD-G-451c)

Property	Value
Specific gravity	2.5
Specific heat	0.21
Hardness (Moh's)	5–6
Softening point, °C	729
Refractive index, sodium D-line	1.52
Modulus of elasticity, GPa	70
Tensile strength, MPa	45
Poisson's ratio	0.23
Coefficient of linear expansion, ppm/°C	8.8
Dielectric constant, 1 Mhz	7.1

Lead Silicates. Lead silicate glass has a higher index of refraction and also a higher dispersion than soda–lime–silicate glass and thus finds use in optical applications. The high gloss resulting from high Fresnel reflection makes lead glasses of 24 to 35% PbO popular for consumer products in the form of artware and lead crystal glass. Lead glasses of different compositions are used widely in electronic applications since low-melting sealing glasses can be formed with little or no alkali, a constituent which promotes high electrical loss.

Strength of Glass

Theoretical Strength. Glass below the glass transition temperature (T_g) is a brittle solid, with failure originating at flaws (scratches, defects, minute compositional differences) which act as stress concentrators. Without flaws of any kind the strength of glass approaches theoretical levels of about 17 GPa (2.5×10^6 psi). Unfortunately, unless glass is processed under the utmost pristine conditions and then immediately coated to prevent surface abrasion by dust or other environmental agents, the glass will contain flaws which decrease the strength by several orders of magnitude from theoretical levels. Synthetic silica glass optical fibers, prepared under meticulous conditions and tested at 77 K, are among the few glass materials which exhibit nearly theoretical strength.

Nominal and Design Strength. The exact failure stress for a specific piece of glass will depend upon the configuration and size of the defect at the crack origin. Since these defects vary in size over a wide range, the standard deviation in the strength of glass will also be large. The glass design engineer must allow large safety factors, often 20 to 50%, to account for the statistical variation. For most types of glass a nominal strength of 70 MPa and a design stress of 7 MPa are typical. Table 12.7.10 summarizes strength and variability in the strength of glasses.

Strengthening and Tempering. Glass can be substantially strengthened, or tempered, either by rapid cooling or by ion-exchange of the surface to develop compressive stresses. Fast, uniform cooling of glass plates heated to the softening point will introduce surface compressive stresses on the glass (with corresponding tensile stress in the center) which become permanently frozen into place upon cooling to room temperature. These compressive stresses, typically 70 to 200 MPa, will resist externally applied tensile stresses and help to prevent crack propagation. Tempering will increase the strength of glass by as much as three to six times. Tempered glass will shatter violently when it fails as a result of the sudden release of stored elastic energy, although the broken pieces will not be sharp. Generally, only simple shapes can safely be thermally tempered.

Ion-exchange tempering also improves the strength of the glass by introducing surface compression. In the ion-exchange process large ions are "stuffed" into the interstices in the glass structure previously occupied by smaller ions. This is done by immersing the glass in a molten bath of the alkali salt (typically KNO_3 for a sodium-containing glass) at an elevated temperature. The larger ions will introduce a compressive strain as they force their way into the glass network. The strains obtainable are much higher

TABLE 12.7.9 Compositions of Silicate Glasses — Corning Glass Types by Number (approximate wt%)

Glass No.[a]	SiO_2, Silica	Na_2O, Soda	K_2O, Potash	PbO, Lead	CaO, Lime	B_2O_3, Boric Oxide	Al_2O_3, Aluminum Oxide	Other
0010	63	7	7	22	—	—	1	—
0080	73	17	—	—	5	—	1	4% MgO
0120	56	4	9	29	—	—	2	—
1720	62	1	—	—	8	5	17	7% MgO
1723	57	—	—	—	10	5	15	6% BaO, 7 MgO
1990	41	5	12	40	—	—	—	2% Li_2O
2405	70	5	—	—	—	12	1	11% ZnO + CdS, Se
2475	67	10	7	—	—	—	—	12% ZnO, 2% CdO + F^-
3320	76	4	2	—	—	14	3	1% U_3O_8
6720	60	9	2	—	5	1	10	9% ZnO + 4% F^-
6750	61	15	—	—	—	1	11	9% BaO + 3% F^-
6810	56	7	1	3	4	1	10	12% ZnO + 6% F^-
7040	67	4	3	—	—	23	3	—
7050	67	7	—	—	—	24	2	—
7052	65	2	3	—	—	18	7	3% BaO + F^-, 1% Li_2O
7056	70	1	8	—	—	17	3	1% Li_2O
7070	71	0.5	1	—	—	26	1	0.5% Li_2O
7250	78	5	—	—	—	15	2	—
7570	3	—	—	75	—	11	11	—
7720	73	4	—	6	—	15	2	—
7740	81	4	—	—	—	13	2	—
7760	79	2	2	—	—	15	2	—
7900	96	—	—	—	—	3	0.3	—
7913	96.5	—	—	—	—	3	0.5	—
7940	99.9	—	—	—	—	—	—	0.1% H_2O
8160	56	3	10	23	1	—	2	5% BaO + F^-
8161	40	—	5	51	—	—	—	2% BaO + 2% Rb_2O
8363	5	—	—	82	—	10	3	—
8871	42	2	6	49	—	—	—	1% Li_2O
9010	67	7	7	2	—	—	4	12% BaO + Co_3O_4 + NiO + F^-, 1% Li_2O
9606	56	—	—	—	—	—	20	9% TiO_2, 15% MgO
9700	80	5	—	—	—	13	2	—
9741	66	2	—	—	—	24	6	1% F^-, 1% Li_2O

[a] See Table C.12 in Appendix.

Source: Hutchins, J.R., III and Harrington, R.V., *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 10, p. 542. Copyright © 1966 by John Wiley & Sons, Inc. Reprinted by permission.

than those from thermal tempering, generating stresses as high as 700 MPa, although the surface compressive layer is quite shallow and subject to penetration. Ion-exchanged glasses can be more than 10 to 20 times as strong as normal glass and are used, for example, in aircraft windshields to resist bird impacts.

Behavior at Elevated Temperatures

Glasses do not have a clearly defined melting temperature. Instead, there is a temperature range where the viscosity of the glass changes smoothly from solid (greater than 10^{14} Pa · sec) to liquid (less than 10 Pa · sec). It is useful to define some points on the viscosity–temperature curve to create a clearer

TABLE 12.7.10 Ideal and Practical Strengths of Glass, Glass Fibers, and Glass–Ceramics

Type of Glass	Tensile Strength, psi	Strength/Weight Ratio, psi/lb per cu. in.
Untreated Glass		
Theoretical strength	1,000,000–4,000,000	45,000,000
Fibers, protected in vacuum	Up to 2,000,000	—
Fibers, in air, commercially available	250,000 average	6,000,000 average
Fibers, effective strength in plastic	150,000 average	1,800,000–4,500,000
Bulk glass, protected in vacuum	Up to 500,000	—
Blown ware, unabraded	Up to 100,000	90,000
Pressed ware, unabraded	8,000 average	55,000
Bulk glass, abraded	4,000–8,000 average	30,000
Bulk glass, abraded, 1000-hr stress	2,000 minimum	—
Bulk glass, abraded, design strength	500–1,500	—
Tempered Glass		
Bulk glass, abraded	15,000–35,000	—
Normal design strength	1,500–6,000	—
Chemically Strengthened Glass		
Bulk glass, abraded	100,000 and more	—
Glass–Ceramics		
Bulk material, unabraded	20,000–35,000	27,000
Bulk material, abraded	10,000–24,000	—
Design strength	3,000–6,000	—
Chemically Strengthened Glass–Ceramics		
Bulk material, abraded	200,000 and more	—

Compiled from several sources.

picture of the viscosity behavior of a glass. The strain point is defined as the temperature at which a glass will release 95% of its stresses within a period of 6 hr. This occurs at a viscosity of approximately $10^{13.5}$ Pa · sec. The annealing point occurs at 10^{12} Pa · sec a viscosity at which 95% of stresses will be released in 15 min. At $10^{6.6}$ Pa · sec, the softening point, the glass will deform under its own weight. The working point is defined as 10^3 Pa · sec, and is a typical minimum viscosity for machine working during forming. Refer to Table C.12 in the Appendix, Properties of Silicate Glasses. Many properties of glasses are presented in this comprehensive table, including maximum application temperatures (upper working temperature) and viscosity data for most common glasses. Generally, the extreme upper working temperature corresponds to the strain point of the glass. Normal service conditions are typically 50 to 60% of the strain point on the Kelvin temperature scale. Under normal service conditions glass is a brittle, mechanical solid, it possesses no mechanical characteristics of a liquid, and it will not flow. Specific heat and thermal conductivity data are presented in Table 12.7.11. Below the glass transition, glass is not a supercooled liquid, it is a glass. Old windows are not thicker at the bottom because of viscous flow.

Chemical Durability

Although glass is often considered an extraordinarily inert material, even the most durable glasses undergo some environmental degradation and many glasses are rapidly attacked by strong acid or basic solutions. Corrosive aqueous environments can cause the ions in the glass to be extracted by a leaching process. Chemical durability behavior is difficult to generalize and trial-and-error testing is usually required for each application. The most severe attack is experienced at extreme high and low pH values; neutral pH solutions rarely attack glass at significant rates. Glasses high in SiO_2, Al_2O_3, and CaO are generally most durable. Glasses high in alkali, such as Na_2O or K_2O, are less durable. B_2O_3 and PbO are intermediate.

A notable form of chemical degradation which occurs under simple, apparently benign, conditions is weathering. Standard soda–lime–silicate window glass can be permanently damaged in a short time (~30 days) if held under high humidity with a means to retain adsorbed moisture on the surface. Such a means

TABLE 12.7.11 Thermal Properties of Several Glass Types

	Specific Heat			Thermal Conductivity, cal/cm sec°C × 10^4[a]			
Material	**25°C**	**500°C**	**1000°C**	**–100°C**	**0°C**	**100°C**	**400°C**
Fused silica	0.173	0.268	0.292	25.0	31.5	35.4	—
7900	0.18	0.24	0.29	24	30	34	—
7740	0.17	0.28	—	21	26	30	—
1723	0.18	0.26	—	—	29	33	—
0311 (chemically strengthened)	0.21	0.28	—	—	27	29	35
Soda–lime window glass	0.190	0.300	0.333	19	24	27	—
Heavy flint, 80% PbO, 20% SiO_2	—	—	—	10	12	14	—
Foamglass insulation	0.20	—	—	(0.97)	1.3	1.73	(2.81)
Fibrous glass	—	—	—	—	(0.8)	—	—
9606 glass–ceramic	0.185	0.267	0.311	—	90	86	75
9608 low-expansion glass–ceramic	0.195	0.286	—	—	48	51	55

Notes: Parentheses indicate extrapolated values. Specific heat increases with temperature and approaches zero at 0° K. There are no critical temperatures or phase changes. Thermal conductivity increases with temperature and is very high for glass ceramics.

[a] To convert to SI units, 1 cal/cm sec °C = 418.6 w/mk.

Source: Hutchins, J.R. III and Harrington, R.V., *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 10, p. 598. Copyright © 1966 by John Wiley & Sons, Inc. Reprinted by permission.

can be a dirt film or perhaps a sheet of newspaper. The moisture ion-exchanges with sodium ions in the glass, which form a high-pH surface film which accelerates the attack on the glass. Pitting and adherent surface deposits can quickly form, making the glass unusable.

For container applications requiring extremely high purity, it is common to use a durable glass such as a borosilicate or to increase the chemical resistance of the glass using surface treatments of SO_2, SnO_2, or TiO_2.

Optical Properties

Traditional glasses are principally used because they are transparent in the visible region of the spectrum; windows, containers, and precision optics are examples. Although pure silica is highly transmissive overt the entire visible spectrum, impurities impart coloration which detract from the performance of some glasses but which can also be used to produce beautiful and useful colored glasses. Table 12.7.12 lists impurity ions and their resulting colors. Iron is the most common impurity, imparting a blue-green-yellow tint depending on the oxidation state. It is possible to neutralize but not bleach impurity colors by “decolorization,” the addition of complementary coloring oxides to produce an overall neutral gray absorption. Traditional glasses do not transmit well in the UV or IR range, with the exception of certain specialty glasses. Pure silica is the best example, enabling high transmission levels (>10%, 2 mm thickness) from 160 nm to 4 µm.

The refractive index of common silicate glasses are in the range of 1.5 to 1.7 and specific values are given in Table C.12 in the Appendix, *Properties of Silicate Glasses*.

Specialty Glasses

Non-Silica-Oxide Glasses

Glasses made from B_2O_3 and P_2O_3 glass formers rather than SiO_2 possess some special thermal, optical, and chemical properties which make them of interest in certain narrow engineering fields. Borate glasses, often in combination with PbO, are useful solder and sealing glasses for electronic applications; phosphate glasses have special optical properties and are also used as water-soluble chemicals in industry. Tellurite glasses have high refractive indexes and, hence, are used in some demanding refractive optic applications. Glasses based on Bi_2O_3, Sb_2O_3, TeO_2, or V_2O_5 have very low melting points, suggesting their use as low-temperature electrical seals. Boro-aluminates have very high electrical resistivities. Alkaline earth aluminates have excellent IR transmitting properties and make excellent high-temperature

TABLE 12.7.12 Coloring Additives to Glass

Color	Additive
Red	Colloidal Au or Cu, Cd-Se (S, Te)
Pink	$MnO_2 \cdot CeO_2$, Se^{2-}
Orange	CdS (Se)
Amber	FeS_x, $Fe_2O_3 \cdot TiO_2$
Yellow	UO_2, $CeO_2 \cdot TiO_2$, CdS
Green	Cr_2O_3, Fe_2O_3, CuO, U_2O_3
Blue	CoO, FeO, CuO
Violet	NiO, Mn_2O_3
Gray	$Co_3O_4 \cdot NiO$
Black	$Mn_2O_3 \cdot Cr_2O_3$, PbS, FeS, $CoSe_x$
UV absorption	CeO_2, TiO_2, Fe_2O_3, V_2O_5, CrO_3
IR absorption	FeO, CuO
Decolorization, i.e., mask Fe_2O_3 color	MnO, Se^{2-}, NiO, Co_3O_4
Opacification, i.e., white opals	CaF_2, NaF, ZnS, $Ca_2(PO_4)_3$
Solarization	Cerium, arsenic

lamp seals. Despite their unique properties, non-silica-oxide glasses are costly and make up only a very small percentage of the glass produced annually.

Chalcogenide Glasses

A class of excellent IR-transmitting glasses, the chalcogenides, are obtained by combining group VI elements with group V and IV elements. Glasses in this group also exhibit photoconductivity and semiconductivity. Applications for these glasses consist of IR-transmitting optical waveguides (to 20 μm), high-performance IR optical applications, and specialty applications which utilize their photoconductivity properties. Most notable of these applications is the photosensitive coating applied to photocopy drums. Purity issues have limited applications in optical fibers as of this writing.

Heavy Metal Fluoride Glasses

Heavy metal fluoride glasses (HMFG) are an important new (1975) composition group because of their extremely low theoretical optical attenuation (10^{-3} dB/km at 3.5 μm), which makes them candidates for repeaterless transoceanic communication links. Unfortunately, this magnitude of transmission has not been obtained in practice because of problems with high oxygen impurities and crystallization. Furthermore, HMFGs are readily attacked by water, and current development efforts are aimed at improving chemical durability. At present, HMFGs are limited to short transmission distance IR optical applications.

Amorphous Metals

Certain metal compositions can be fabricated as glasses by subjecting streams of the molten metal to extremely rapid quenching rates (10^5 to 10^8°C/sec). The resulting glasses possess intriguing properties. Strengths approach theoretical limits, and electrical resistivities are greater than their crystalline counterparts yet decrease with temperature. Most importantly, they have extremely low B–H hysteresis curves. For this reason they are used commercially as power transformer core laminations.

Amorphous Semiconductors

Many elements and compounds which exhibit semiconducting properties in the crystalline state are also semiconductors in the amorphous state. Si, Ge, P, As, $CdGe_xAs_2$ ($x = 0$ to 1.2), $Si_{l\text{-}x}H_x$ ($x = 0.1$ to 0.2) are important examples. These materials are use in fabrication of inexpensive vapor deposition fabrication of photovoltaic cells.

Glass Ceramics

A useful group of materials is made by batching, melting, and forming a product as a glass followed by heat treatment to nucleate and grow crystalline phases from the glass to produce a ceramic with up to 99% crystalline phase content. The microstructure contains crystals of about 1 μm size, a glassy matrix, and no porosity. The processing route is a principal advantage since high-speed glass-forming methods can be used, no porosity exists, the formed shape can be inspected as a transparent glass, and rejects at the forming stage can be recycled.

Glass ceramics are typically stronger than most ceramics as a result of zero porosity, and they are tougher than glass because of the deflection of crack fronts around the crystals. High-temperature properties are generally not good due to the glassy phase and the nature of the process, thus limiting most glass ceramics to low- and intermediate-temperature applications (<1000°C). A wide range of products has been made from glass ceramics, from home cookware to industrial bearings and aerospace radomes.

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