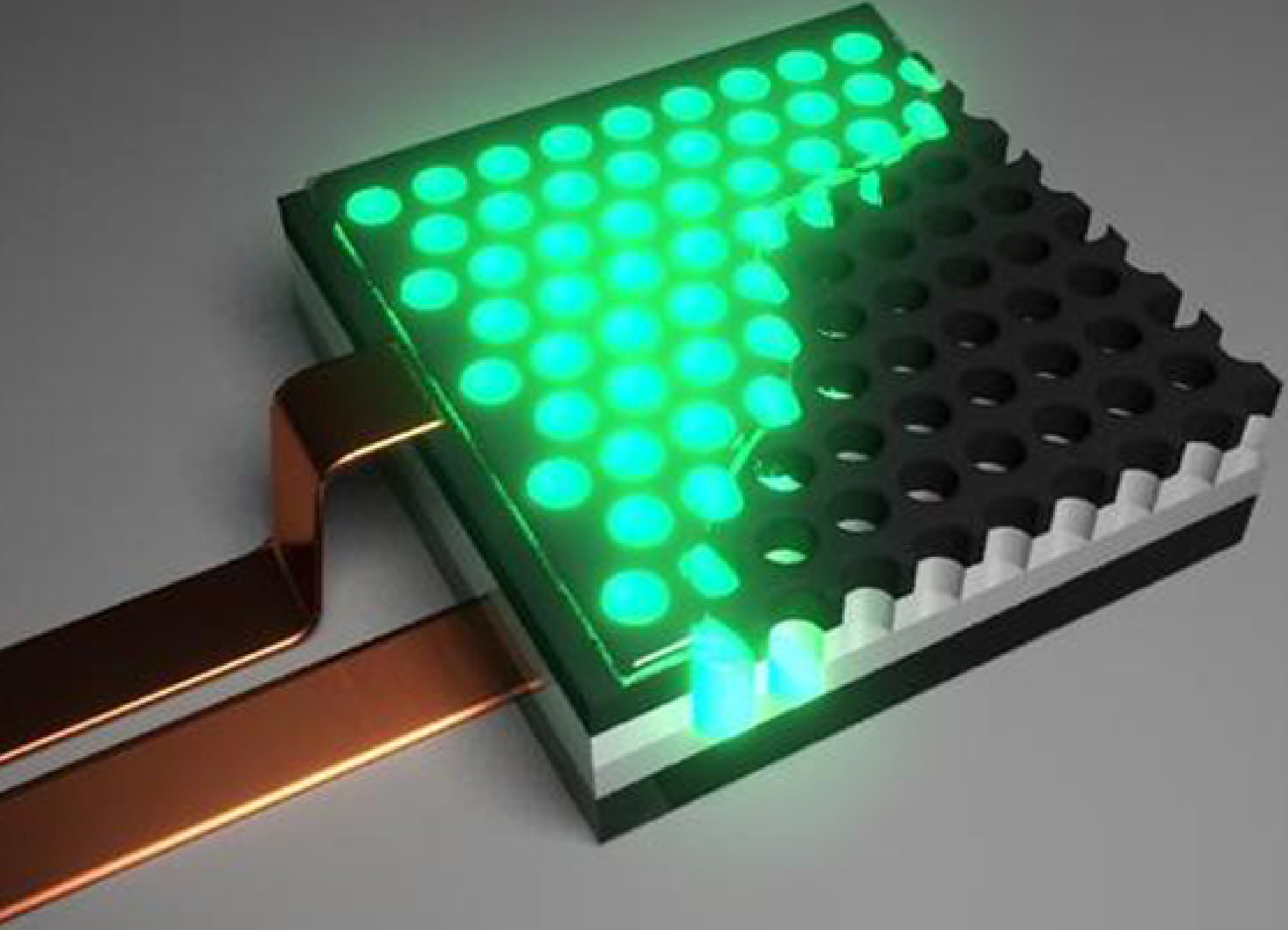

Types of Solid Materials and Their Scientific Applications

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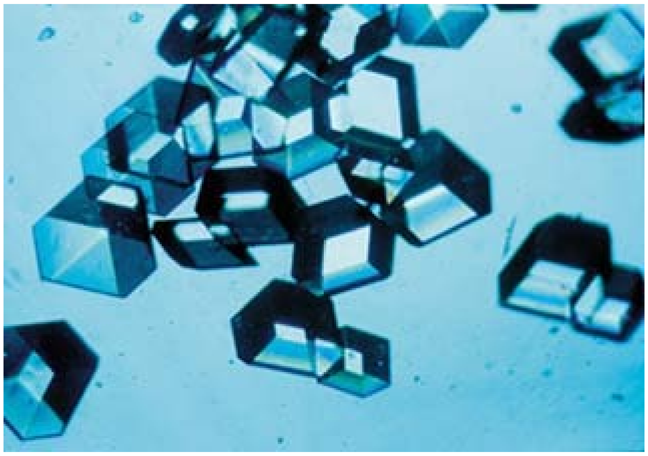
Solid



Single crystalline form of solid Insulin

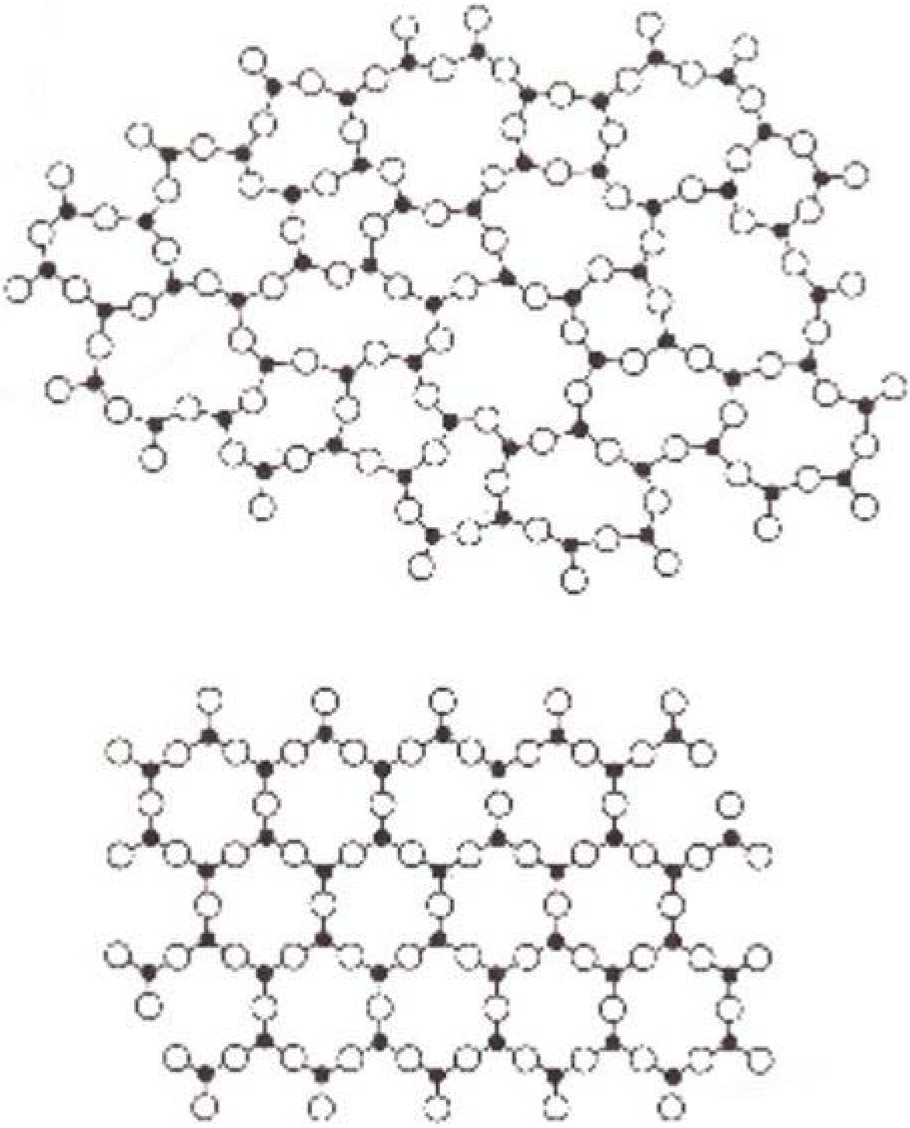
Solid is one of the major states of matter. It is characterized by structural rigidity and resistance to changes of shape or volume. Unlike a liquid, a solid object does not flow to take on the shape of its container, nor does it expand to fill the entire volume available to it like a gas does. The atoms in a solid are tightly bound to each other, either in a regular geometric lattice (crystalline solids, which include metals and ordinary water ice) or irregularly (an amorphous solid such as common window glass).

The branch of physics that deals with solids is called solid-state physics, and is the main branch of condensed matter physics (which also includes liquids). Materials science is primarily concerned with the physical and chemical properties of solids. Solid-state chemistry is especially concerned with the synthesis of novel materials, as well as the science of identification and chemical composition.

Metamorphic banded gneiss

Microscopic description

Model of closely packed atoms within a crystalline solid



Schematic representation of a random-network glassy form (top) and ordered crystalline lattice (bottom) of identical chemical composition.

The atoms, molecules or ions which make up a solid may be arranged in an orderly repeating pattern, or irregularly. Materials whose constituents are arranged in a regular pattern are known as crystals. In some cases, the regular ordering can continue unbroken over a large scale, for example diamonds, where each diamond is a single crystal. Solid objects that are large enough to see and handle are rarely composed of a single crystal, but instead are made of a large number of single crystals, known as crystallites, whose size can vary from a few nanometers to several meters. Such materials are called polycrystalline. Almost all common metals, and many ceramics, are polycrystalline.

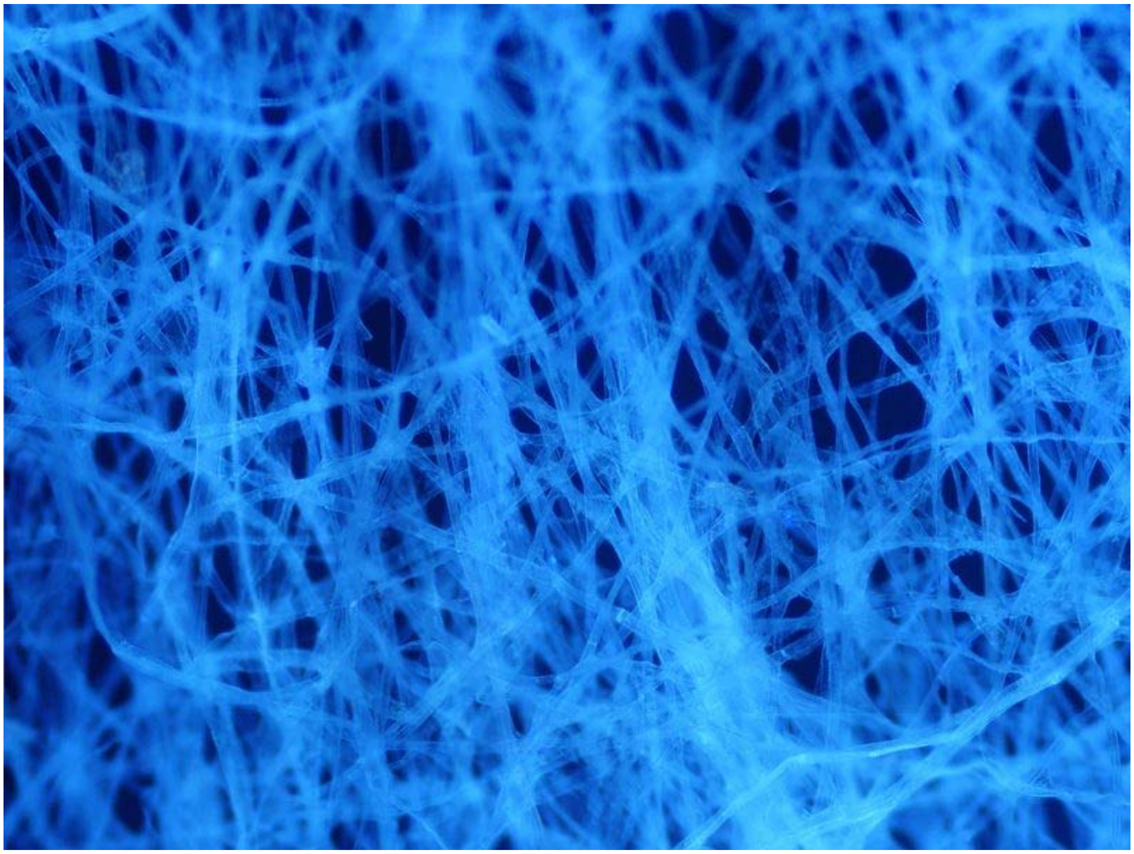
In other materials, there is no long-range order in the position of the atoms. These solids are known as amorphous solids; examples include polystyrene and glass.

Whether a solid is crystalline or amorphous depends on the material involved, and the conditions in which it was formed. Solids which are formed by slow cooling will tend to be crystalline, while solids which are frozen rapidly are more likely to be amorphous. Likewise, the specific crystal structure adopted by a crystalline solid depends on the material involved and on how it was formed.

While many common objects, such as an ice cube or a coin, are chemically identical throughout, many other common materials comprise a number of different substances packed together. For example, a typical rock is an aggregate of several different minerals and mineraloids, with no specific chemical composition. Wood is a natural organic material consisting primarily of cellulose fibers embedded in a matrix of organic lignin. In materials science, composites of more than one constituent material can be designed to have desired properties.

The forces between the atoms in a solid can take a variety of forms. For example, a crystal of sodium chloride (common salt) is made up of ionic sodium and chlorine, which are held together by ionic bonds. In diamond or silicon, the atoms share electrons and form covalent bonds. In metals, electrons are shared in metallic bonding. Some solids, particularly most organic compounds, are held together with van der Waals forces resulting from the polarization of the electronic charge cloud on each molecule. The dissimilarities between the types of solid result from the differences between their bonding.

Organic solids



The individual wood pulp fibers in this sample are around 10 µm in diameter

Organic chemistry studies the structure, properties, composition, reactions, and preparation by synthesis (or other means) of chemical compounds of carbon and hydrogen, which may contain any number of other elements such as nitrogen, oxygen and the halogens: fluorine, chlorine, bromine and iodine. Some organic compounds may also contain the elements phosphorus or sulfur. Examples of organic solids include wood, paraffin wax, naphthalene and a wide variety of polymers and plastics.

Nanomaterials

Bulk silicon (left) and silicon nanopowder (right)

Many traditional solids exhibit different properties when they shrink to nanometer sizes. For example, nanoparticles of usually yellow gold and gray silicon are red in color; gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C); and metallic nanowires are much stronger than the corresponding bulk metals. The high surface area of nanoparticles makes them extremely attractive for certain applications in the field of energy. For example, platinum metals may be provide improvements as automotive fuel catalysts, as well as proton exchange membrane (PEM) fuel cells. Also, ceramic oxides (or cermets) of lanthanum, cerium, manganese and nickel are now being developed as solid oxide fuel cells (SOFC). Lithium, lithium titanate and tantalum nanoparticles are being applied in lithium ion batteries. Silicon nanoparticles have been shown to dramatically expand the storage capacity of lithium ion batteries during the expansion/contraction cycle. Silicon nanowires cycle without significant degradation and present the potential for use in batteries with greatly expanded storage times. Silicon nanoparticles are also being used in new forms of solar energy cells. Thin film deposition of silicon quantum dots on the polycrystalline silicon substrate of a photovoltaic (solar) cell increases voltage output as much as 60% by fluorescing the incoming light prior to capture. Here again, surface area of the nanoparticles (and thin films) plays a critical role in maximizing the amount of absorbed radiation.

Physical Properties

Physical properties of elements and compounds which provide conclusive evidence of chemical composition include odor, color, volume, density (mass per unit volume), melting point, boiling point, heat capacity, physical form and shape at room temperature (solid, liquid or gas; cubic, trigonal crystals, etc.), hardness, porosity, index of refraction and many others.

Mechanical

Granite rock formation in the Chilean Patagonia. Like most inorganic minerals formed by oxidation in the Earth's atmosphere, granite consists primarily of crystalline silica SiO_2 and alumina Al_2O_3.

The mechanical properties of materials describe characteristics such as their strength and resistance to deformation. For example, steel beams are used in construction because of their high strength, meaning that they neither break nor bend significantly under the applied load.

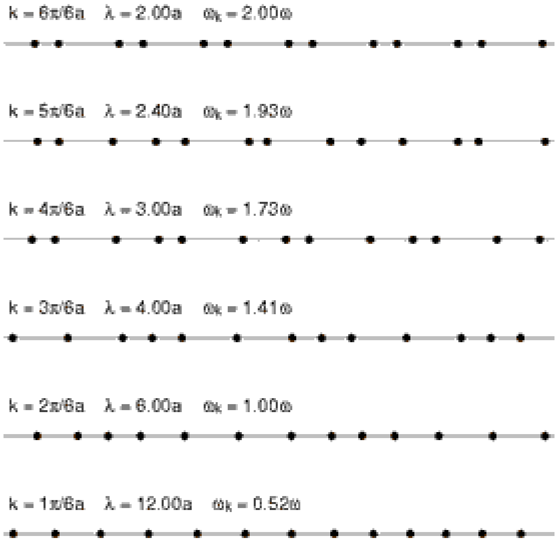
Mechanical properties include elasticity and plasticity, tensile strength, compressive strength, shear strength, fracture toughness, ductility (low in brittle materials), and indentation hardness. Solid mechanics is the study of the behavior of solid matter under external actions such as external forces and temperature changes.

A solid does not exhibit macroscopic flow, as fluids do. Any degree of departure from its original shape is called deformation. The proportion of deformation to original size is called strain. If the applied stress is sufficiently low, almost all solid materials behave in such a way that the strain is directly proportional to the stress (Hooke's law). The coefficient of the proportion is called the modulus of elasticity or Young's modulus. This region of deformation is known as the linearly elastic region. Three models can describe how a solid responds to an applied stress:

- Elasticity – When an applied stress is removed, the material returns to its undeformed state.
- Viscoelasticity – These are materials that behave elastically, but also have damping. When the applied stress is removed, work has to be done against the damping effects and is converted to heat within the material. This results in a hysteresis loop in the stress–strain curve. This implies that the mechanical response has a time-dependence.
- Plasticity – Materials that behave elastically generally do so when the applied stress is less than a yield value. When the stress is greater than the yield stress, the material behaves plastically and does not return to its previous state. That is, irreversible plastic deformation (or viscous flow) occurs after yield which is permanent.

Many materials become weaker at high temperatures. Materials which retain their strength at high temperatures, called refractory materials, are useful for many purposes. For example, glass-ceramics have become extremely useful for countertop cooking, as they exhibit excellent mechanical properties and can sustain repeated and quick temperature changes up to 1000 °C. In the aerospace industry, high performance materials used in the design of aircraft and/or spacecraft exteriors must have a high resistance to thermal shock. Thus, synthetic fibers spun out of organic polymers and polymer/ceramic/metal composite materials and fiber-reinforced polymers are now being designed with this purpose in mind.

Thermal



Normal modes of atomic vibration in a crystalline solid

Because solids have thermal energy, their atoms vibrate about fixed mean positions within the ordered (or disordered) lattice. The spectrum of lattice vibrations in a crystalline or glassy network provides the foundation for the kinetic theory of solids. This motion occurs at the atomic level, and thus cannot be observed or detected without highly specialized equipment, such as that used in spectroscopy.

Thermal properties of solids include thermal conductivity, which is the property of a material that indicates its ability to conduct heat. Solids also have a specific heat capacity, which is the capacity of a material to store energy in the form of heat (or thermal lattice vibrations).

Electrical

Image of superconducting levitation of YBCO

Electrical properties include conductivity, resistance, impedance and capacitance. Electrical conductors such as metals and alloys are contrasted with electrical insulators such as glasses and ceramics. Semiconductors behave somewhere in between. Whereas conductivity in metals is caused by electrons, both electrons and holes contribute to current in semiconductors. Alternatively, ions support electric current in ionic conductors.

Many materials also exhibit superconductivity at low temperatures; they include metallic elements such as tin and aluminium, various metallic alloys, some heavily doped semiconductors, and certain ceramics. The electrical resistivity of most electrical (metallic) conductors generally decreases gradually as the temperature is lowered, but remains finite. In a superconductor however, the resistance drops abruptly to zero when the material is cooled below its critical temperature. An electric current flowing in a loop of superconducting wire can persist indefinitely with no power source.

A dielectric, or electrical insulator, is a substance that is highly resistant to the flow of electric current. A dielectric, such as plastic, tends to concentrate an applied electric field within itself which property is used in capacitors. A capacitor is an electrical device that can store energy in the electric field between a pair of closely spaced conductors (called 'plates'). When voltage is applied to the capacitor, electric charges of equal magnitude, but opposite polarity, build up on each plate. Capacitors are used in electrical circuits as energy-storage devices, as well as in electronic filters to differentiate between high-frequency and low-frequency signals.

Electro-mechanical

Piezoelectricity is the ability of crystals to generate a voltage in response to an applied mechanical stress. The piezoelectric effect is reversible in that piezoelectric crystals, when subjected to an externally applied voltage, can change shape by a small amount. Polymer materials like rubber, wool, hair, wood fiber, and silk often behave as electrets. For example, the polymer polyvinylidene fluoride (PVDF) exhibits a piezoelectric response several times larger than the traditional piezoelectric material quartz (crystalline SiO_2). The deformation (~0.1%) lends itself to useful technical applications such as high-voltage sources, loudspeakers, lasers, as well as chemical, biological, and acousto-optic sensors and/or transducers.

Optical

Materials can transmit (e.g. glass) or reflect (e.g. metals) visible light.

Many materials will transmit some wavelengths while blocking others. For example, window glass is transparent to visible light, but much less so to most of the frequencies of ultraviolet light that cause sunburn. This property is used for frequency-selective optical filters, which can alter the color of incident light.

For some purposes, both the optical and mechanical properties of a material can be of interest. For example, the sensors on an infrared homing ("heat-seeking") missile must be protected by a cover which is transparent to infrared radiation. The current material of choice for high-speed infrared-guided missile domes is single-crystal sapphire. The optical transmission of sapphire does not actually extend to cover the entire mid-infrared range (3–5 µm), but starts to drop off at wavelengths greater than approximately 4.5 µm at room temperature. While the strength of sapphire is better than that of other available mid-range infrared dome materials at room temperature, it weakens above 600 °C. A long standing trade-off exists between optical bandpass and mechanical durability; new materials such as transparent ceramics or optical nanocomposites may provide improved performance.

Guided lightwave transmission involves the field of fiber optics and the ability of certain glasses to transmit, simultaneously and with low loss of intensity, a range of frequencies (multi-mode optical waveguides) with little interference between them. Optical waveguides are used as components in integrated optical circuits or as the transmission medium in optical communication systems.

Chapter- 2

Metal

The pinnacle of New York's Chrysler Building, the world's tallest steel-supported brick building, is clad with stainless steel.

A **metal** is a chemical element that is a good conductor of both electricity and heat and forms cations and ionic bonds with non-metals. In chemistry, a **metal** (from Greek "μέταλλον" - *métallon*, "mine") is an element, compound, or alloy characterized by high electrical conductivity. In a metal, atoms readily lose electrons to form positive ions (cations). Those ions are surrounded by delocalized electrons, which are responsible for the conductivity. The solid thus produced is held by electrostatic interactions between the ions and the electron cloud, which are called metallic bonds.

Usage in astronomy is quite different.

Definition

Metals are sometimes described as an arrangement of positive ions surrounded by a sea of delocalized electrons. They are one of the three groups of elements as distinguished by their ionization and bonding properties, along with the metalloids and non-metals.

Metals occupy the bulk of the periodic table, while non-metallic elements can only be found on the right-hand-side of the Periodic Table of the Elements. A diagonal line, drawn from boron (B) to polonium (Po), separates the metals from the nonmetals. Most elements on this line are metalloids, sometimes called semiconductors. This is because these elements exhibit electrical properties common to both conductors and insulators. Elements to the lower left of this division line are called metals, while elements to the upper right of the division line are called non-metals.

An alternative definition of metal refers to the band theory. If one fills the energy bands of a material with available electrons and ends up with a top band partly filled then the material is a metal. This definition opens up the category for metallic polymers and other organic metals, which have been made by researchers and employed in high-tech devices. These synthetic materials often have the characteristic silvery gray reflectiveness (luster) of elemental metals.

Astronomy

In the specialized usage of astronomy and astrophysics, the term "metal" is often used to refer collectively to all elements other than hydrogen or helium, including substances as chemically non-metallic as neon, fluorine, and oxygen. Nearly all the hydrogen and helium in the Universe was created in Big Bang nucleosynthesis, whereas all the "metals" were produced by nucleosynthesis in stars or supernovae. The Sun and the Milky Way Galaxy are composed of roughly 74% hydrogen, 24% helium, and 2% "metals" (the rest of the elements; atomic numbers 3-118) by mass.

The concept of a metal in the usual chemical sense is irrelevant in stars, as the chemical bonds that give elements their properties cannot exist at stellar temperatures.

Properties

Chemical

Metals are usually inclined to form cations through electron loss, reacting with oxygen in the air to form oxides over changing timescales (iron rusts over years, while potassium burns in seconds). Examples:

$4\ Na + O_2 \rightarrow 2\ Na_2O$ (sodium oxide)
$2\ Ca + O_2 \rightarrow 2\ CaO$ (calcium oxide)
$4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$ (aluminium oxide)

The transition metals (such as iron, copper, zinc, and nickel) take much longer to oxidize. Others, like palladium, platinum and gold, do not react with the atmosphere at all. Some metals form a barrier layer of oxide on their surface which cannot be penetrated by further oxygen molecules and thus retain their shiny appearance and good conductivity for many decades (like aluminium, magnesium, some steels, and titanium). The oxides of metals are generally basic, as opposed to those of nonmetals, which are acidic.

Painting, anodizing or plating metals are good ways to prevent their corrosion. However, a more reactive metal in the electrochemical series must be chosen for coating, especially when chipping of the coating is expected. Water and the two metals form an electrochemical cell, and if the coating is less reactive than the coatee, the coating actually *promotes* corrosion.

Physical

Gallium crystals

Metals in general have high electrical conductivity, thermal conductivity, luster and density, and the ability to be deformed under stress without cleaving. While there are several metals that have low density, hardness, and melting points, these (the alkali and alkaline earth metals) are extremely reactive, and are rarely encountered in their elemental, metallic form. Optically speaking, metals are opaque, shiny and lustrous. This is because visible lightwaves are not readily transmitted through the bulk of their microstructure. The large number of free electrons in any typical metallic solid (element or alloy) is responsible for the fact that they can never be categorized as transparent materials.

The majority of metals have higher densities than the majority of nonmetals. Nonetheless, there is wide variation in the densities of metals; lithium is the least dense solid element and osmium is the densest. The metals of groups I A and II A are referred to as the light metals because they are exceptions to this generalization. The high density of most metals is due to the tightly packed crystal lattice of the metallic structure. The strength of metallic bonds for different metals reaches a maximum around the center of the transition series, as those elements have large amounts of delocalized electrons in a metallic bond. However, other factors (such as atomic radius, nuclear charge, number of bonding orbitals, overlap of orbital energies, and crystal form) are involved as well.

Electrical

The electrical and thermal conductivity of metals originate from the fact that in the metallic bond, the outer electrons of the metal atoms form a gas of nearly free electrons, moving as an electron gas in a background of positive charge formed by the ion cores. Good mathematical predictions for electrical conductivity, as well as the electrons' contribution to the heat capacity and heat conductivity of metals can be calculated from the free electron model, which does not take the detailed structure of the ion lattice into account.

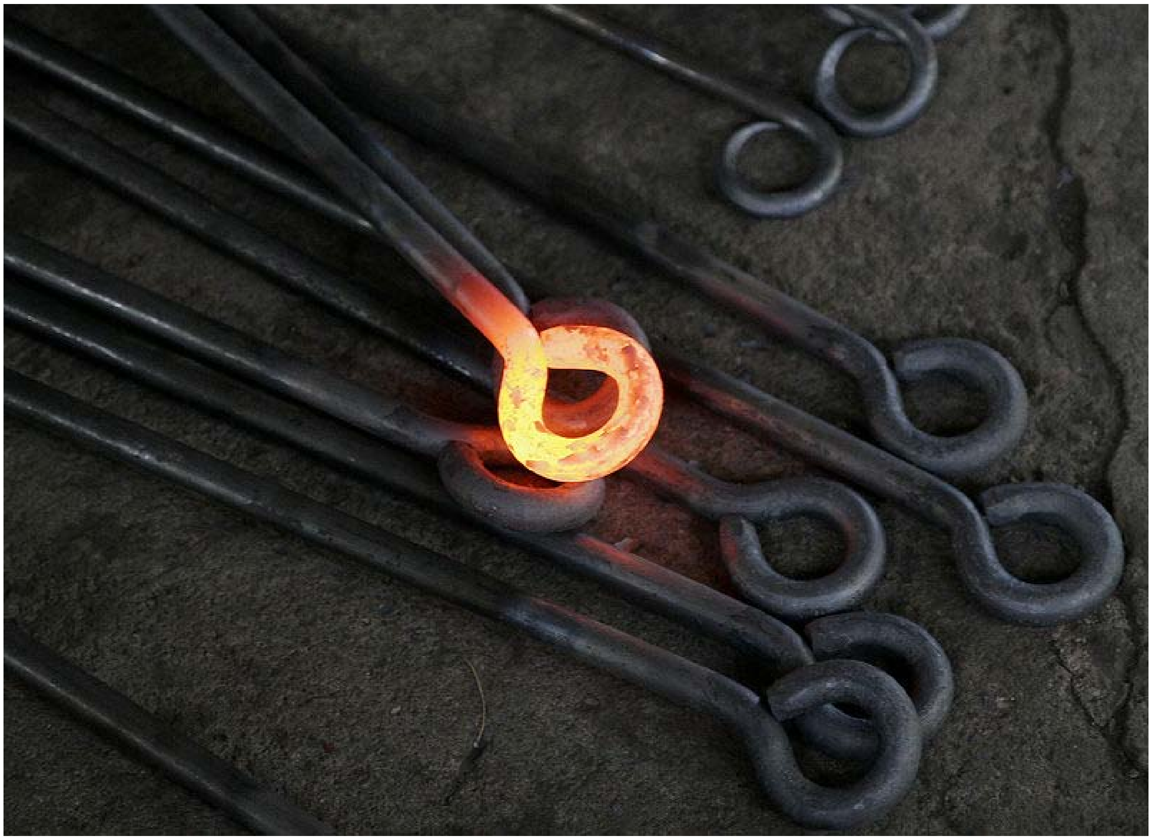
When considering the exact band structure and binding energy of a metal, it is necessary to take into account the positive potential caused by the specific arrangement of the ion cores - which is periodic in crystals. The most important consequence of the periodic potential is the formation of a small band gap at the boundary of the Brillouin zone. Mathematically, the potential of the ion cores can be treated by various models, the simplest being the nearly free electron model.

Mechanical

Mechanical properties of metals include ductility, which is largely due to their inherent capacity for plastic deformation. Reversible elasticity in metals can be described by Hooke's Law for restoring forces, where the stress is linearly proportional to the strain. Forces larger than the elastic limit, or heat, may cause a permanent (irreversible) deformation of the object, known as plastic deformation or plasticity. This irreversible change in atomic arrangement may occur as a result of:

- The action of an applied force (or work). An applied force may be tensile (pulling) force, compressive (pushing) force, shear, bending or torsion (twisting) forces.

- A change in temperature (or heat). A temperature change may affect the mobility of the structural defects such as grain boundaries, point vacancies, line and screw dislocations, stacking faults and twins in both crystalline and non-crystalline solids. The movement or displacement of such mobile defects is thermally activated, and thus limited by the rate of atomic diffusion.



Hot metal work from a blacksmith

Viscous flow near grain boundaries, for example, can give rise to internal slip, creep and fatigue in metals. It can also contribute to significant changes in the microstructure like grain growth and localized densification due to the elimination of intergranular porosity. Screw dislocations may slip in the direction of any lattice plane containing the dislocation, while the principal driving force for "dislocation climb" is the movement or diffusion of vacancies through a crystal lattice.

In addition, the nondirectional nature of metallic bonding is also thought to contribute significantly to the ductility of most metallic solids. When the planes of an ionic bond slide past one another, the resultant change in location shifts ions of the same charge into close proximity, resulting in the cleavage of the crystal; such shift is not observed in covalently bonded crystals where fracture and crystal fragmentation occurs.

Alloys

Steel is a metal alloy whose major component is iron, with carbon content between 0.02% and 2.14% by mass.

An **alloy** is a partial or complete solid solution of one or more elements in a metallic matrix. Complete solid solution alloys give single solid phase microstructure, while partial solutions give two or more phases that may be homogeneous in distribution depending on thermal (heat treatment) history. Alloys usually have different properties from those of the component elements.

Alloys' constituents are usually measured by mass.

Theory

Alloying one metal with other metal(s) or non-metal(s) often enhances its properties. For example, steel is stronger than iron, its primary element. The physical properties, such as density, reactivity, Young's modulus, and electrical and thermal conductivity, of an alloy may not differ greatly from those of its elements, but engineering properties such as tensile strength and shear strength may be substantially different from those of the constituent materials. This is sometimes due to the sizes of the atoms in the alloy, since larger atoms exert a compressive force on neighboring atoms, and smaller atoms exert a tensile force on their neighbors, helping the alloy resist deformation. Sometimes alloys may exhibit marked differences in behavior even when small amounts of one element occur. For example, impurities in semi-conducting ferromagnetic alloys lead to different properties, as first predicted by White, Hogan, Suhl, Tian Abrie and Nakamura. Some alloys are made by melting and mixing two or more metals. Bronze, an alloy of copper and tin, was the first alloy discovered, during the prehistoric period now known as the bronze age; it was harder than pure copper and originally used to make tools and weapons, but was later superseded by metals and alloys with better properties. In later times bronze has been used for ornaments, bells, statues, and bearings. Brass is an alloy made from copper and zinc.

Unlike pure metals, most alloys do not have a single melting point, but a melting range in which the material is a mixture of solid and liquid phases. The temperature at which melting begins is called the solidus, and the temperature when melting is just complete is called the liquidus. However, for most alloys there is a particular proportion of constituents (in rare cases two)—the eutectic mixture—which gives the alloy a unique melting point.

Terminology

In practice, some alloys are used so predominantly with respect to their base metals that the name of the primary constituent is also used as the name of the alloy. For example, 14 karat gold is an alloy of gold with other elements. Similarly, the silver used in jewelry and the aluminium used as a structural building material are also alloys.

The term "alloy" is sometimes used in everyday speech as a synonym for a particular alloy. For example, automobile wheels made of an aluminium alloy are commonly referred to as simply "alloy wheels", although in point of fact steels and most other metals in practical use are also alloys.

History

A meteorite is shown below a hatchet that was forged from meteoric iron

Bronze axe 1100 BC

The use of alloys by humans started with the use of meteoric iron, a naturally occurring alloy of nickel and iron. As no metallurgic processes were used to separate iron from nickel, the alloy was used as it was. Meteoric iron could be forged from a red heat to make objects such as tools, weapons, and nails. In many cultures it was shaped by cold hammering into knives and arrowheads. They were often used as anvils. Meteoric iron was very rare and valuable, and difficult for ancient people to work.

Iron is usually found as iron ore on Earth, except for one deposit of native iron in Greenland, which was used by the Inuit people. Native copper, however, was found worldwide, along with silver, gold and platinum, which were also used to make tools, jewelry, and other objects since Neolithic times. Copper was the hardest of these metals, and the most widely distributed. It became one of the most important metals to the ancients. Eventually, humans learned to smelt metals such as copper and tin from ore, and, around 2500 BC, began alloying the two metals to form bronze, which is much harder than its ingredients. Tin was rare, however, being found mostly in Great Britain. In the Middle East, people began alloying copper with zinc to form brass. Ancient civilizations made use of the information contained in modern alloy constitution diagrams, taking into account the mixture and the various properties it produced, such as hardness, toughness and melting point, under various conditions of temperature and work hardening.

The first known smelting of iron began in Anatolia, around 1800 BC Called the bloomery process, it produced very soft but ductile wrought iron and, by 800 BC, the technology had spread to Europe. Pig iron, a very hard but brittle alloy of iron and carbon, was being produced in China as early as 1200 BC, but did not arrive in Europe until the Middle Ages. These metals found little practical use until the introduction of crucible steel around 300 BC. These steels were of poor quality, and the introduction of pattern welding, around the 1st century AD, sought to balance the extreme properties of the alloys by laminating them, to create a tougher metal.

Mercury had been smelted from cinnabar for thousands of years. Mercury dissolves many metals, such as gold, silver, and tin, to form amalgams, (an alloy in a soft, paste, or liquid form at ambient temperature). Amalgams have been used since 200 BC in China for plating objects with precious metals, called gilding, such as armor and mirrors. The ancient Romans often used mercury-tin amalgams for gilding their armor. The amalgam was applied as a paste and then heated until the mercury vaporized, leaving the gold, silver, or tin behind. Mercury was often used in mining, to extract precious metals like gold and silver from their ores.

Many ancient civilizations alloyed metals for purely aesthetic purposes. In ancient Egypt and Mycenae, gold was often alloyed with copper to produce red-gold, or iron to produce a bright burgundy-gold. Silver was often found alloyed with gold. These metals were also used to strengthen each other, for more practical purposes. Quite often, precious metals were alloyed with less valuable substances as a means to deceive buyers. Around 250 BC, Archimedes was commissioned by the king to find a way to check the purity of the gold in a crown, leading to the famous bath-house shouting of "Eureka!" upon the discovery of Archimedes principle.

While the use of iron started to become more widespread around 1200 BC, mainly due to interruptions in the trade routes for tin, the metal is much softer than bronze. However, very small amounts of steel, (an alloy of iron and around 1% carbon), was always a byproduct of the bloomery process. The ability to modify the hardness of steel by heat treatment had been known since 1100 BC, and the rare material was valued for use in tool and weapon making. Since the ancients could not produce temperatures high enough to fully melt iron, the production of steel in decent quantities did not occur until the introduction of blister steel during the Middle Ages. This method introduced carbon by heating wrought iron in charcoal for long periods of time, but the penetration of carbon was not very deep, so the alloy was not very homogenous. In 1740, Benjamin Huntsman began melting blister steel in a crucible to even out the carbon content, creating the first process for the mass production of tool steel. Huntsman's process was used for manufacturing tool steel until the early 1900s.

With the introduction of the blast furnace to Europe in the Middle Ages, pig iron was able to be produced in much higher volumes than wrought iron. Since pig iron could be melted, people began to develop processes of reducing the carbon in the liquid pig iron in order to create steel. Puddling was introduced during the 1700s, where molten pig iron was stirred while exposed to the air, to remove the carbon by oxidation. In 1858, Sir Henry Bessemer developed a process of steel making by blowing hot air through liquid pig iron to reduce the carbon content. The Bessemer process was able to produce the first large scale manufacture of steel. Once the Bessemer process began to gain widespread use, other alloys of steel began to follow, such as mangalloy, an alloy of steel and manganese, which exhibits extreme hardness and toughness.

Categories

Base metal

In chemistry, the term *base metal* is used informally to refer to a metal that oxidizes or corrodes relatively easily, and reacts variably with dilute hydrochloric acid (HCl) to form hydrogen. Examples include iron, nickel, lead and zinc. Copper is considered a base metal as it oxidizes relatively easily, although it does not react with HCl. It is commonly used in opposition to noble metal.

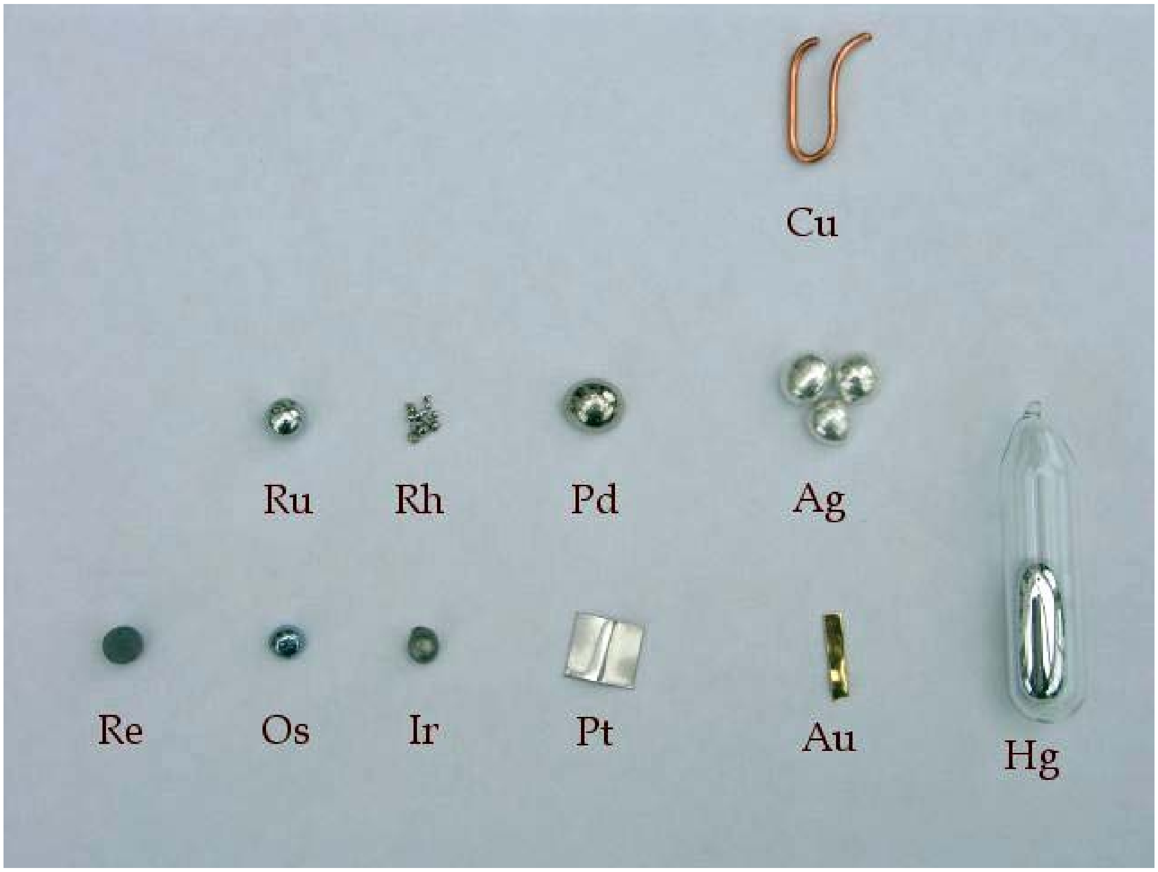
In alchemy, a *base metal* was a common and inexpensive metal, as opposed to precious metals, mainly gold and silver. A longtime goal of the alchemists was the transmutation of base metals into precious metals.

In numismatics, coins used to derive their value primarily from the precious metal content. Most modern currencies are fiat currency, allowing the coins to be made of *base metal*.

Ferrous metal

The term "ferrous" is derived from the Latin word meaning "containing iron". This can include pure iron, such as wrought iron, or an alloy such as steel. Ferrous metals are often magnetic, but not exclusively.

Noble metal



The noble metals including mercury and rhenium together with the non-noble metal copper ordered according their position in the periodic table of the elements

Noble metals are metals that are resistant to corrosion and oxidation in moist air, unlike most base metals. They tend to be precious, often due to their rarity in the Earth's crust. The noble metals are considered to be (in order of increasing atomic number) ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold.

Other sources include mercury or even rhenium as a noble metal. On the other hand, neither titanium nor niobium nor tantalum are called noble metals despite the fact that they are very resistant to corrosion.

Noble metals should not be confused with precious metals (although many noble metals are precious).

Introduction

Palladium, osmium, platinum, gold and mercury can be dissolved in aqua regia, a highly concentrated mixture of hydrochloric acid and nitric acid, but iridium and silver cannot. (Silver can dissolve in nitric acid though.) Ruthenium can be dissolved in aqua regia only when in the presence of oxygen, while rhodium must be in a fine pulverized form. Niobium and tantalum are resistant to acids, including aqua regia.

This term can also be used in a relative sense, considering "noble" as an adjective for the word "metal". A "galvanic series" is a hierarchy of metals (or other electrically conductive materials, including composites and semimetals) that runs from *noble* to *active*, and allows designers to see at a glance how materials will interact in the environment used to generate the series. In this sense of the word, graphite is more noble than silver and the relative nobility of many materials is highly dependent upon context, as for aluminium and stainless steel in conditions of varying pH.

In physics, the definition of a noble metal is even more strict. It is required that the d-bands of the electronic structure are filled. Taking this into account, only copper, silver and gold are noble metals, as all d-like band are filled and don't cross the Fermi level. For platinum two d-bands cross the Fermi level, changing its chemical behaviour; it is used as a catalyst. The different reactivity can easily be seen while preparing clean metal surfaces in ultra high vacuum; surfaces of "physical defined" noble metals (e.g., gold) are easy to clean and stay clean for a long time, while those of platinum or palladium, for example, are covered by carbon monoxide very quickly.

Electrochemistry

Metallic elements, including several non-noble metals, sorted by their chemical "nobility" (noble metals bolded):

element	group	reaction	potential
Gold	Ib/6	$Au \rightarrow Au^{3+} + 3\ e^{-}$	1.498 V
Platinum	VIIIb/6	$Pt \rightarrow Pt^{2+} + 2\ e^{-}$	1.18 V
Iridium	VIIIb/6	$Ir \rightarrow Ir^{3+} + 3\ e^{-}$	1.156 V
Palladium	VIIIb/5	$Pd \rightarrow Pd^{2+} + 2\ e^{-}$	0.987 V
Osmium	VIIIb/6	$Os + 4\ H_2O \rightarrow OsO_4 + 8\ H^{+} + 8\ e^{-}$	0.838 V
Silver	Ib/5	$Ag \rightarrow Ag^{+} + e^{-}$	0.7996 V
Mercury	IIb/6	$2\ Hg \rightarrow Hg_2^{2+} + 2\ e^{-}$	0.7973 V
Polonium	VIa/6	$Po \rightarrow Po^{2+} + 2\ e^{-}$	0.65 V
Rhodium	VIIIb/5	$Rh \rightarrow Rh^{2+} + 2\ e^{-}$	0.600 V
Ruthenium	VIIIb/5	$Ru \rightarrow Ru^{2+} + 2\ e^{-}$	0.455 V
Copper	Ib/4	$Cu \rightarrow Cu^{2+} + 2\ e^{-}$	0.337 V

Bismuth	Va/6	$Bi \rightarrow Bi^{3+} + 3\ e^{-}$	0.308 V
Technetium	VIIb/5	$Tc + 2\ H_2O \rightarrow TcO_2 + 4\ H^{+} + 4\ e^{-}$	0.272 V
Rhenium	VIIb/6	$Re + 2\ H_2O \rightarrow ReO_2 + 4\ H^{+} + 4\ e^{-}$	0.259 V
Antimony	Va/5	$2\ Sb + 3\ H_2O \rightarrow Sb_2O_3 + 6\ H^{+} + 6\ e^{-}$	0.152 V

The column *group* denotes its position in the periodic table, hence electronic configuration. The simplified *reaction*s, listed in the next column, can also be read in detail from the Pourbaix diagrams of the considered element in water. Finally the column *potential* indicates the electric potential of the element measured against a H-electrode in aqueous, pH 7 solution. All missing elements in this table are either not metals or have a negative standard potential.

Antimony and polonium are considered metalloids and thus can not be noble metals. Also chemists and metallurgists consider copper and bismuth not noble metals because they easily oxidize due to the reaction $O_2 + 2H_2O + 4e^{-} \rightleftarrows 4OH^{-}(aq)$ +0.40 V which is possible in moist air.

Silver and copper film over and oxidize easily and readily, thus the copper sheets with a patina of oxidation used in architectural designs and the resultant market for a myriad of silver polishing compounds. The film over of Silver is due to its high sensibility to hydrogen sulfide. Chemically patina is caused by an attack of oxygen in wet air and by CO_2 afterward. On the other hand, rhenium coated mirrors are said to be very durable, despite the fact that rhenium and technetium are said to tarnish slowly in moist atmosphere.

Precious metal

A gold nugget

A **precious metal** is a rare, naturally occurring metallic chemical element of high economic value, which is not radioactive (excluding natural polonium, radium, actinium and protactinium). Chemically, the precious metals are less reactive than most elements, have high lustre, are softer or more ductile, and have higher melting points than other metals. Historically, precious metals were important as currency, but are now regarded mainly as investment and industrial commodities. Gold, silver, platinum, and palladium each have an ISO 4217 currency code.

The best-known precious metals are the coinage metals gold and silver. While both have industrial uses, they are better known for their uses in art, jewellery and coinage. Other precious metals include the platinum group metals: ruthenium, rhodium, palladium, osmium, iridium, and platinum, of which platinum is the most widely traded.

The demand for precious metals is driven not only by their practical use, but also by their role as investments and a store of value. Historically, precious metals have commanded much higher prices than common industrial metals. In December 2009, gold reached a price of over \$1200.00/troy ounce and silver was about \$15.00/troy ounce, compared to copper at \$0.11/troy ounce and nickel at \$0.36/troy ounce.

Bullion

A 500 gram silver bullion bar produced by Johnson Matthey

American Platinum Eagle bullion coin

A metal is deemed to be *precious* if it is rare. The discovery of new sources of ore or improvements in mining or refining processes may cause the value of a precious metal to diminish. The status of a "precious" metal can also be determined by high demand or market value. Precious metals in bulk form are known as *bullion*, and are traded on commodity markets. Bullion metals may be cast into ingots, or minted into coins. The defining attribute of bullion is that it is valued by its mass and purity rather than by a face value as money.

Many nations mint bullion coins. Although nominally issued as legal tender, these coins' face value as currency is far below that of their value as bullion. For instance, Canada mints a gold bullion coin (the Gold Maple Leaf) at a face value of $50 containing one troy ounce (31.1035 g) of gold—as of July 2009, this coin is worth about $1,075 CAD as bullion. Bullion coins' minting by national governments gives them some numismatic value in addition to their bullion value, as well as certifying their purity.

Silver 1000oz bar

The level of purity varies from issue to issue. 99.9% purity is common. The purest mass-produced bullion coins are in the Canadian Gold Maple Leaf series, which go up to 99.999% purity. Note that a 100% pure bullion is not possible, as absolute purity in extracted and refined metals can only be asymptotically approached. Many bullion coins contain a stated quantity (such as one troy ounce) of the marginally-impure alloy. In contrast, the Krugerrand is one of many historic and modern bullion coins of 22 Kt Crown gold, with a stated content (usually one troy ounce) of "fine gold", with the other component(s) of the alloy making the coin heavier than one ounce in total. Still more bullion coins (for example: British Sovereign) state neither the purity nor the fine-gold weight on the coin, but are recognized and consistent in their composition, and many historically stated a denomination in currency (example: American Double Eagle).

One of the largest bullion coins in the world is the 10,000 dollar Australian Gold Nugget coin minted in Australia which consists of a full kilogram of 99.9% pure gold. There have been a small number of larger bullion coins, but they are impractical to handle and not produced in mass quantities. China has produced coins in very limited quantities (less than 20 pieces minted) that exceed 260 troy ounces (8 kg) of gold. Austria has minted a coin containing 31 kg of gold (the Vienna Philharmonic Coin minted in 2004 with a face value of 100,000 euro). As a stunt to publicise the 99.999% pure one-ounce Canadian Gold Maple Leaf series, in 2007 the Royal Canadian Mint made a 100 kg 99.999% gold coin, with a face value of $1 million, and now manufactures them to order, but at a substantial premium over the market value of the gold.

Gold and silver are often seen as hedges against both inflation and economic downturn. Silver coins have become popular with collectors due to their relative affordability, and unlike most gold and platinum issues which are valued based upon the markets, silver issues are more often valued as collectables, far higher than their actual bullion value.

Aluminium

A precious metal that became common is aluminium. Although aluminium is one of the most commonly occurring elements in the Earth's crust, it was at one time found to be exceedingly difficult to extract from its various ores. This made the little available pure aluminium, which had been refined at great expense, more valuable than gold. Bars of aluminium were exhibited alongside the French crown jewels at the Exposition Universelle of 1855, and Napoleon III's most important guests were given aluminium cutlery, while those less worthy dined with mere silver. Additionally, the pyramidal top to the Washington Monument is made of 100 ounces of pure aluminium. At the time of the monument's construction, aluminium was as expensive as silver. Over time, however, the price of the metal has dropped; the invention of the Hall-Héroult process in 1886 caused the high price of aluminium to permanently collapse.

Bismuth and tellurium

Bismuth and tellurium are the only two metals which have abundances less than 10^{-8} by mass part (g/g) in the Earth's crust, but which are currently not of high economic value.

Extraction

Metals are often extracted from the Earth by means of mining, resulting in ores that are relatively rich sources of the requisite elements. Ore is located by prospecting techniques, followed by the exploration and examination of deposits. Mineral sources are generally divided into surface mines, which are mined by excavation using heavy equipment, and subsurface mines.

Once the ore is mined, the metals must be extracted, usually by chemical or electrolytic reduction. Pyrometallurgy uses high temperatures to convert ore into raw metals, while hydrometallurgy employs aqueous chemistry for the same purpose. The methods used depend on the metal and their contaminants.

When a metal ore is an ionic compound of that metal and a non-metal, the ore must usually be smelted — heated with a reducing agent — to extract the pure metal. Many common metals, such as iron, are smelted using carbon as a reducing agent. Some metals, such as aluminium and sodium, have no commercially practical reducing agent, and are extracted using electrolysis instead.

Sulfide ores are not reduced directly to the metal but are roasted in air to convert them to oxides.

Metallurgy

Metallurgy is a domain of materials science that studies the physical and chemical behavior of metallic elements, their intermetallic compounds, and their mixtures, which are called alloys.

Applications

Some metals and metal alloys possess high structural strength per unit mass, making them useful materials for carrying large loads or resisting impact damage. Metal alloys can be engineered to have high resistance to shear, torque and deformation. However the same metal can also be vulnerable to fatigue damage through repeated use or from sudden stress failure when a load capacity is exceeded. The strength and resilience of metals has led to their frequent use in high-rise building and bridge construction, as well as most vehicles, many appliances, tools, pipes, non-illuminated signs and railroad tracks.

The two most commonly used structural metals, iron and aluminium, are also the most abundant metals in the Earth's crust.

Metals are good conductors, making them valuable in electrical appliances and for carrying an electric current over a distance with little energy lost. Electrical power grids rely on metal cables to distribute electricity. Home electrical systems, for the most part, are wired with copper wire for its good conducting properties.

The thermal conductivity of metal is useful for containers to heat materials over a flame. Metal is also used for heat sinks to protect sensitive equipment from overheating.

The high reflectivity of some metals is important in the construction of mirrors, including precision astronomical instruments. This last property can also make metallic jewelry aesthetically appealing.

Some metals have specialized uses; radioactive metals such as uranium and plutonium are used in nuclear power plants to produce energy via nuclear fission. Mercury is a liquid at room temperature and is used in switches to complete a circuit when it flows over the switch contacts. Shape memory alloy is used for applications such as pipes, fasteners and vascular stents.

Chapter- 3

Minerals

An assortment of minerals

A **mineral** is a naturally occurring solid chemical substance that is formed through geological processes and that has a characteristic chemical composition, a highly ordered atomic structure, and specific physical properties. By comparison, a rock is an aggregate of minerals and/or mineraloids and does not have a specific chemical composition. Minerals range in composition from pure elements and simple salts to very complex silicates with thousands of known forms. The study of minerals is called mineralogy.

Mineral definition and classification

To be classified as a true mineral, a substance must be a solid and have a crystalline structure. It must also be a naturally occurring, homogeneous substance with a defined chemical composition. Traditional definitions excluded *organically derived* material. However, the International Mineralogical Association in 1995 adopted a new definition:

a mineral is an element or chemical compound that is normally crystalline and that has been formed as a result of geological processes.

The modern classifications include an *organic class* – in both the new Dana and the Strunz classification schemes.

The chemical composition may vary between end members of a mineral system. For example the plagioclase feldspars comprise a continuous series from sodium and silicon-rich albite ($NaAlSi_3O_8$) to calcium and aluminium-rich anorthite ($CaAl_2Si_2O_8$) with four recognized intermediate compositions between. Mineral-like substances that don't strictly meet the definition are sometimes classified as mineraloids. Other natural-occurring substances are nonminerals. Industrial minerals is a market term and refers to commercially valuable mined materials.

A *crystal structure* is the orderly geometric spatial arrangement of atoms in the internal structure of a mineral. There are 14 basic crystal lattice arrangements of atoms in three dimensions, and these are referred to as the 14 "Bravais lattices". Each of these lattices can be classified into one of the seven crystal systems, and all crystal structures currently recognized fit in one Bravais lattice and one crystal system. This crystal structure is based on regular internal atomic or ionic arrangement that is often expressed in the geometric form that the crystal takes. Even when the mineral grains are too small to see or are irregularly shaped, the underlying crystal structure is always periodic and can be determined by X-ray diffraction. Chemistry and crystal structure together define a mineral. In fact, two or more minerals may have the same chemical composition, but differ in crystal structure (these are known as *polymorphs*). For example, pyrite and marcasite are both iron sulfide, but their arrangement of atoms differs. Similarly, some minerals have different chemical compositions, but the same crystal structure: for example, halite (made from sodium and chlorine), galena (made from lead and sulfur) and periclase (made from magnesium and oxygen) all share the same cubic crystal structure.

Crystal structure greatly influences a mineral's physical properties. For example, though diamond and graphite have the same composition (both are pure carbon), graphite is very soft, while diamond is the hardest of all known minerals. This happens because the carbon atoms in graphite are arranged into sheets which can slide easily past each other, while the carbon atoms in diamond form a strong, interlocking three-dimensional network.

There are currently more than 4,000 known minerals, according to the International Mineralogical Association, which is responsible for the approval of and naming of new mineral species found in nature. Of these, perhaps 100 can be called "common", 50 are "occasional", and the rest are "rare" to "extremely rare".

Differences between minerals and rocks

A mineral is a naturally occurring solid with a definite chemical composition and a specific crystalline structure. A rock is an aggregate of one or more minerals. (A rock may also include organic remains and mineraloids.) Some rocks are predominantly composed of just one mineral. For example, limestone is a sedimentary rock composed almost entirely of the mineral calcite. Other rocks contain many minerals, and the specific minerals in a rock can vary widely. Some minerals, like quartz, mica or feldspar are common, while others have been found in only four or five locations worldwide. The vast majority of the rocks of the Earth's crust consist of quartz, feldspar, mica, chlorite, kaolin, calcite, epidote, olivine, augite, hornblende, magnetite, hematite, limonite and a few other minerals. Over half of the mineral species known are so rare that they have only been found in a handful of samples, and many are known from only one or two small grains.

Commercially valuable minerals and rocks are referred to as industrial minerals. Rocks from which minerals are mined for economic purposes are referred to as ores (the rocks and minerals that remain, after the desired mineral has been separated from the ore, are referred to as tailings).

Mineral composition of rocks

A main determining factor in the formation of minerals in a rock mass is the chemical composition of the mass, for a certain mineral can be formed only when the necessary elements are present in the rock. Calcite is most common in limestones, as these consist essentially of calcium carbonate; quartz is common in sandstones and in certain igneous rocks which contain a high percentage of silica.

Other factors are of equal importance in determining the natural association or paragenesis of rock-forming minerals, principally the mode of origin of the rock and the stages through which it has passed in attaining its present condition. Two rock masses may have very much the same bulk composition and yet consist of entirely different assemblages of minerals. The tendency is always for those compounds to be formed which are stable under the conditions under which the rock mass originated. A granite arises by the consolidation of a molten magma at high temperatures and great pressures and its component minerals are those stable under such conditions. Exposed to moisture, carbonic acid and other subaerial agents at the ordinary temperatures of the Earth's surface, some of these original minerals, such as quartz and white mica are relatively stable and remain unaffected; others weather or decay and are replaced by new combinations. The feldspar passes into kaolinite, muscovite and quartz, and any mafic minerals such as pyroxenes, amphiboles or biotite have been present they are often altered to chlorite, epidote, rutile and other substances. These changes are accompanied by disintegration, and the rock falls into a loose, incoherent, earthy mass which may be regarded as a sand or soil. The materials thus formed may be washed away and deposited as sandstone or siltstone. The structure of the original rock is now replaced by a new one; the mineralogical constitution is profoundly altered; but the bulk chemical composition may not be very different. The sedimentary rock may again undergo metamorphism. If penetrated by igneous rocks it may be recrystallized or, if subjected to enormous pressures with heat and movement during mountain building, it may be converted into a gneiss not very different in mineralogical composition though radically different in structure to the granite which was its original state.

Physical properties of minerals

Classifying minerals can range from simple to very difficult. A mineral can be identified by several physical properties, some of them being sufficient for full identification without equivocation. In other cases, minerals can only be classified by more complex chemical or X-ray diffraction analysis; these methods, however, can be costly and time-consuming.

Physical properties commonly used are:

- *Crystal structure and habit*: A mineral may show good crystal habit or form, or it may be massive, granular or compact with only microscopically visible crystals.

Talc

Rough diamond

- *Hardness*: the physical hardness of a mineral is usually measured according to the Mohs scale. This scale is relative and goes from 1 to 10. Minerals with a given Mohs hardness can scratch the surface of any mineral that has a lower hardness than itself.
    - Mohs hardness scale:

1. Talc $Mg_3Si_4O_{10}(OH)_2$
2. Gypsum $CaSO_4·2H_2O$
3. Calcite $CaCO_3$
4. Fluorite CaF_2
5. Apatite $Ca_5(PO_4)_3(OH,Cl,F)$
6. Orthoclase $KAlSi_3O_8$
7. Quartz SiO_2
8. Topaz $Al_2SiO_4(OH,F)_2$
9. Corundum Al_2O_3
10. Diamond C (pure carbon)

- *Luster* indicates the way a mineral's surface interacts with light and can range from dull to glassy (vitreous).
    - Metallic – high reflectivity like metal: galena and pyrite
    - Sub-metallic – slightly less than metallic reflectivity: magnetite
    - Non-metallic lusters:
        - *Adamantine* – brilliant, the luster of diamond also cerussite and anglesite
        - *Vitreous* – the luster of a broken glass: quartz
        - *Pearly* – iridescent and pearl-like: talc and apophyllite
        - *Resinous* – the luster of resin: sphalerite and sulfur
        - *Silky* – a soft light shown by fibrous materials: gypsum and chrysotile

    - Dull/earthy – shown by finely crystallized minerals: the kidney ore variety of hematite

- *Color* indicates the appearance of the mineral in reflected light or transmitted light for translucent minerals (i.e. what it looks like to the naked eye).
    - *Iridescence* – the *play of colors* due to surface or internal interference. Labradorite exhibits internal iridescence whereas hematite and sphalerite often show the surface effect.
- *Streak* refers to the color of the powder a mineral leaves after rubbing it on an unglazed porcelain *streak plate*. Note that this is not always the same color as the original mineral.
- *Cleavage* describes the way a mineral may split apart along various planes. In thin sections, cleavage is visible as thin parallel lines across a mineral.
- *Fracture* describes how a mineral breaks when broken contrary to its natural cleavage planes.
    - *Chonchoidal fracture* is a smooth curved fracture with concentric ridges of the type shown by glass.
    - *Hackley* is jagged fracture with sharp edges.
    - *Fibrous*
    - *Irregular*
- *Specific gravity* relates the mineral mass to the mass of an equal volume of water, namely the density of the material. While most minerals, including all the common rock-forming minerals, have a specific gravity of 2.5–3.5, a few are noticeably more or less dense, e.g. several sulfide minerals have high specific gravity compared to the common rock-forming minerals.
- Other properties: fluorescence (response to ultraviolet light), magnetism, radioactivity, tenacity (response to mechanical induced changes of shape or form), piezoelectricity and reactivity to dilute acids.

Types and Chemical properties of minerals

Types of Minerals

1. Silicate Mineral

The **silicate minerals** make up the largest and most important class of rock-forming minerals, constituting approximately 90 percent of the crust of the Earth. They are classified based on the structure of their silicate group. Silicate minerals all contain silicon and oxygen.

Nesosilicates or orthosilicates

Nesosilicates (from Greek νησος nēsos, island), or orthosilicates, have isolated (insular) $[SiO_4]^{4-}$ tetrahedra that are connected only by interstitial cations.

- Phenacite group
  - Phenacite - Be_2SiO_4
  - Willemite - Zn_2SiO_4
- Olivine group
  - Forsterite - Mg_2SiO_4
  - Fayalite - Fe_2SiO_4
- Garnet group
  - Pyrope - $Mg_3Al_2(SiO_4)_3$
  - Almandine - $Fe_3Al_2(SiO_4)_3$
  - Spessartine - $Mn_3Al_2(SiO_4)_3$
  - Grossular - $Ca_3Al_2(SiO_4)_3$
  - Andradite - $Ca_3Fe_2(SiO_4)_3$
  - Uvarovite - $Ca_3Cr_2(SiO_4)_3$
  - Hydrogrossular - $Ca_3Al_2Si_2O_8(SiO_4)_{3-m}(OH)_{4m}$
- Zircon group
  - Zircon - $ZrSiO_4$
  - Thorite - $(Th,U)SiO_4$

Kyanite crystals (unknown scale)

- Al_2SiO_5 group
  - Andalusite - Al_2SiO_5

    - Kyanite - Al_2SiO_5
    - Sillimanite - Al_2SiO_5
    - Dumortierite - $Al_{6.5\text{-}7}BO_3(SiO_4)_3(O,OH)_3$
    - Topaz - $Al_2SiO_4(F,OH)_2$
    - Staurolite - $Fe_2Al_9(SiO_4)_4(O,OH)_2$
- Humite group - $(Mg,Fe)_7(SiO_4)_3(F,OH)_2$
    - Norbergite - $Mg_3(SiO_4)(F,OH)_2$
    - Chondrodite - $Mg_5(SiO_4)(F,OH)_2$
    - Humite - $Mg_7(SiO_4)(F,OH)_2$
    - Clinohumite - $Mg_9(SiO_4)(F,OH)_2$
- Datolite - $CaBSiO_4(OH)$
- Titanite - $CaTiSiO_5$
- Chloritoid - $(Fe,Mg,Mn)_2Al_4Si_2O_{10}(OH)_4$

Sorosilicates

Sorosilicates have isolated double tetrahedra groups with $(Si_2O_7)^{6-}$ or a ratio of 2:7.

- Hemimorphite (calamine) - $Zn_4(Si_2O_7)(OH)_2{\cdot}H_2O$
- Lawsonite - $CaAl_2(Si_2O_7)(OH)_2{\cdot}H_2O$
- Ilvaite - $CaFe^{2+}{}_2Fe^{3+}O(Si_2O_7)(OH)$
- Epidote group (has both $(SiO_4)^{4-}$ and $(Si_2O_7)^{6-}$ groups)
    - Epidote - $Ca_2(Al,Fe)_3O(SiO_4)(Si_2O_7)(OH)$
    - Zoisite - $Ca_2Al_3O(SiO_4)(Si_2O_7)(OH)$
    - Clinozoisite - $Ca_2Al_3O(SiO_4)(Si_2O_7)(OH)$
    - Tanzanite - $Ca_2Al_3O(SiO_4)(Si_2O_7)(OH)$
    - Allanite - $Ca(Ce,La,Y,Ca)Al_2(Fe^{2+},Fe^{3+})O(SiO_4)(Si_2O_7)(OH)$
    - Dollaseite-(Ce) - $CaCeMg_2AlSi_3O_{11}F(OH)$
- Vesuvianite (idocrase) - $Ca_{10}(Mg,Fe)_2Al_4(SiO_4)_5(Si_2O_7)_2(OH)_4$

Cyclosilicates

Cyclosilicates, or ring silicates, have linked tetrahedra with $(Si_xO_{3x})^{2x-}$ or a ratio of 1:3. These exist as 3-member $(Si_3O_9)^{6-}$, 4-member $(Si_4O_{12})^{8-}$ and 6-member $(Si_6O_{18})^{12-}$ rings.

- 3-member ring
    - Benitoite - $BaTi(Si_3O_9)$
- 4-member ring
    - Axinite - $(Ca,Fe,Mn)_3Al_2(BO_3)(Si_4O_{12})(OH)$
- 6-member ring
    - Beryl/Emerald - $Be_3Al_2(Si_6O_{18})$
    - Cordierite - $(Mg,Fe)_2Al_3(Si_5AlO_{18})$
    - Tourmaline - $(Na,Ca)(Al,Li,Mg)_{3-}(Al,Fe,Mn)_6(Si_6O_{18})(BO_3)_3(OH)_4$

Inosilicates

Inosilicates (from Greek ις [genitive: ινος *inos*], fibre), or chain silicates, have interlocking chains of silicate tetrahedra with either SiO_3, 1:3 ratio, for single chains or Si_4O_{11}, 4:11 ratio, for double chains.

Single chain inosilicates

- Pyroxene group
  - Enstatite - orthoferrosilite series
    - Enstatite - $MgSiO_3$
    - Ferrosilite - $FeSiO_3$
  - Pigeonite - $Ca_{0.25}(Mg,Fe)_{1.75}Si_2O_6$
  - Diopside - hedenbergite series
    - Diopside - $CaMgSi_2O_6$
    - Hedenbergite - $CaFeSi_2O_6$
    - Augite - $(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$
  - Sodium pyroxene series
    - Jadeite - $NaAlSi_2O_6$
    - Aegirine (Acmite) - $NaFe^{3+}Si_2O_6$
  - Spodumene - $LiAlSi_2O_6$
- Pyroxenoid group
  - Wollastonite - $CaSiO_3$
  - Rhodonite - $MnSiO_3$
  - Pectolite - $NaCa_2(Si_3O_8)(OH)$

Double chain inosilicates

- Amphibole group
  - Anthophyllite - $(Mg,Fe)_7Si_8O_{22}(OH)_2$
  - Cumingtonite series
    - Cummingtonite - $Fe_2Mg_5Si_8O_{22}(OH)_2$
    - Grunerite - $Fe_7Si_8O_{22}(OH)_2$
  - Tremolite series
    - Tremolite - $Ca_2Mg_5Si_8O_{22}(OH)_2$
    - Actinolite - $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
  - Hornblende - $(Ca,Na)_{2-3}(Mg,Fe,Al)_5Si_6(Al,Si)_2O_{22}(OH)_2$
  - Sodium amphibole group
    - Glaucophane - $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$
    - Riebeckite (asbestos) - $Na_2Fe^{2+}{}_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$
    - Arfvedsonite - $Na_3(Fe,Mg)_4FeSi_8O_{22}(OH)_2$

Phyllosilicates

Phyllosilicates (from Greek φύλλον *phyllon*, leaf), or sheet silicates, form parallel sheets of silicate tetrahedra with Si_2O_5 or a 2:5 ratio.

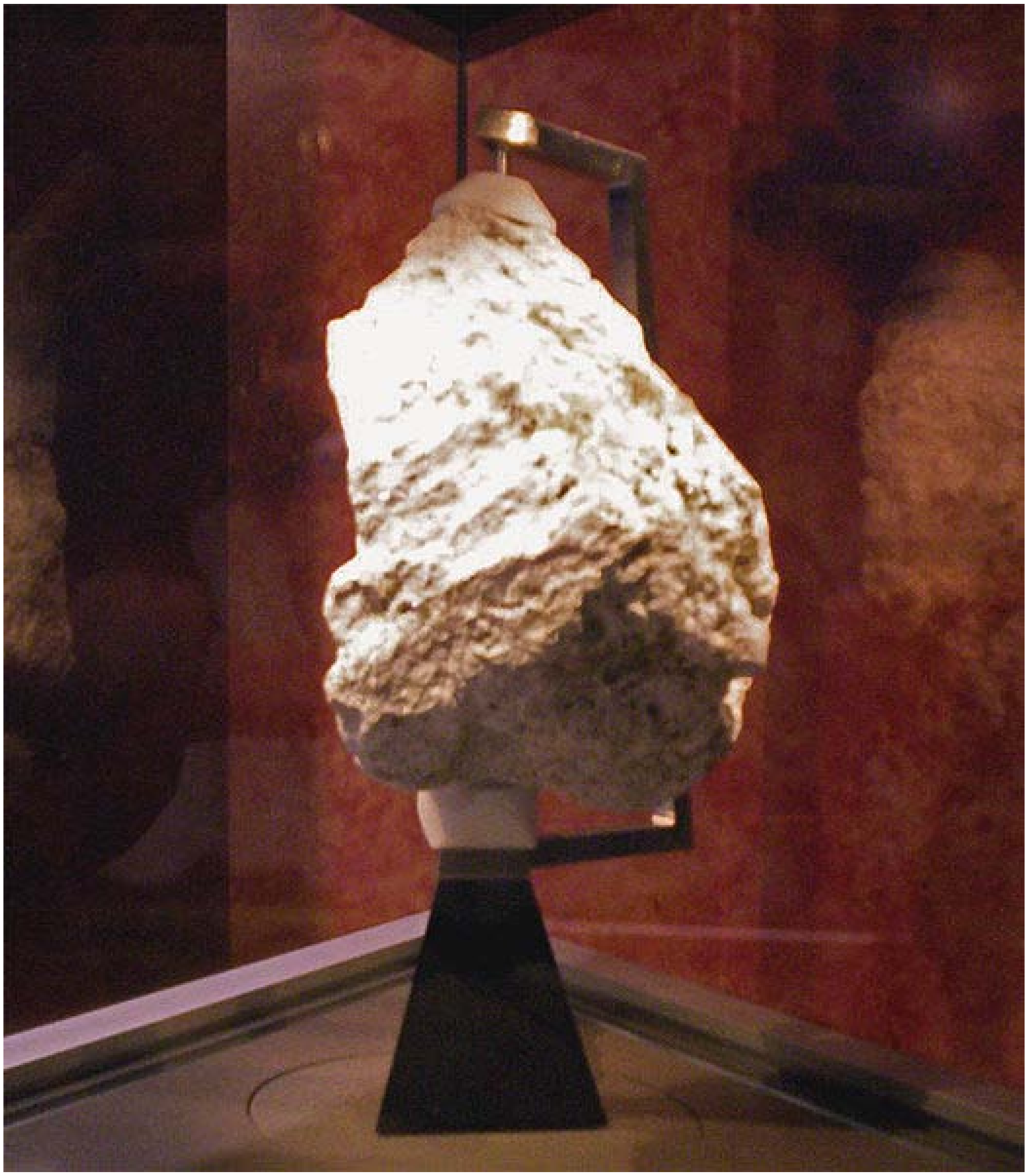
Kaolin

- Serpentine group
    - Antigorite - $Mg_3Si_2O_5(OH)_4$
    - Chrysotile - $Mg_3Si_2O_5(OH)_4$
    - Lizardite - $Mg_3Si_2O_5(OH)_4$
- Clay mineral group
    - Halloysite - $Al_2Si_2O_5(OH)_4$
    - Kaolinite - $Al_2Si_2O_5(OH)_4$
    - Illite - $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
    - Montmorillonite - $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$
    - Vermiculite - $(MgFe,Al)_3(Al,Si)_4O_{10}(OH)_2\cdot 4H_2O$
    - Talc - $Mg_3Si_4O_{10}(OH)_2$
    - Palygorskite - $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$
    - Pyrophyllite - $Al_2Si_4O_{10}(OH)_2$
- Mica group
    - Biotite - $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$
    - Muscovite - $KAl_2(AlSi_3O_{10})(OH)_2$
    - Phlogopite - $KMg_3Si_4O_{10}(OH)_2$
    - Lepidolite - $K(Li,Al)_{2\text{-}3}(AlSi_3O_{10})(OH)_2$
    - Margarite - $CaAl_2(Al_2Si_2O_{10})(OH)_2$
    - Glauconite - $(K,Na)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$
- Chlorite group
    - Chlorite - $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2\bullet(Mg,Fe)_3(OH)_6$

Tectosilicates

Tectosilicates, or "framework silicates," have a three-dimensional framework of silicate tetrahedra with SiO_2 or a 1:2 ratio. This group comprises nearly 75% of the crust of the Earth. Tectosilicates, with the exception of the quartz group, are aluminosilicates.

Quartz



Lunar Ferroan Anorthosite #60025 (Plagioclase Feldspar). Collected by Apollo 16 from the Lunar Highlands near Descartes Crater.

- Quartz group
    - Quartz - SiO_2
    - Tridymite - SiO_2
    - Cristobalite - SiO_2
- Feldspar group
    - Alkali-feldspars
        - Potassium-feldspars
            - Microcline - $KAlSi_3O_8$
            - Orthoclase - $KAlSi_3O_8$
            - Sanidine - $KAlSi_3O_8$

        - Anorthoclase - $(Na,K)AlSi_3O_8$
    - Plagioclase feldspars
        - Albite - $NaAlSi_3O_8$
        - Oligoclase - $(Na,Ca)(Si,Al)_4O_8$ (Na:Ca 4:1)
        - Andesine - $(Na,Ca)(Si,Al)_4O_8$ (Na:Ca 3:2)
        - Labradorite - $(Na,Ca)(Si,Al)_4O_8$ (Na:Ca 2:3)
        - Bytownite - $(Na,Ca)(Si,Al)_4O_8$ (Na:Ca 1:4)
        - Anorthite - $CaAl_2Si_2O_8$
- Feldspathoid group
    - Nosean - $Na_8Al_6Si_6O_{24}(SO_4)$
    - Cancrinite - $Na_6Ca_2(CO_3,Al_6Si_6O_{24}).2H_2O$
    - Leucite - $KAlSi_2O_6$
    - Nepheline - $(Na,K)AlSiO_4$
    - Sodalite - $Na_8(AlSiO_4)_6Cl_2$
        - Hauyne - $(Na,Ca)_{4-8}Al_6Si_6(O,S)24(SO_4,Cl)_{1-2}$
    - Lazurite - $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$
- Petalite - $LiAlSi_4O_{10}$
- Scapolite group
    - Marialite - $Na_4(AlSi_3O_8)_3(Cl_2,CO_3,SO_4)$
    - Meionite - $Ca_4(Al_2Si_2O_8)_3(Cl_2CO_3,SO_4)$
- Analcime - $NaAlSi_2O_6{\bullet}H_2O$
- Zeolite group
    - Natrolite - $Na_2Al_2Si_3O_{10}{\bullet}2H_2O$
    - Chabazite - $CaAl_2Si_4O_{12}{\bullet}6H_2O$
    - Heulandite - $CaAl_2Si_7O_{18}{\bullet}6H_2O$
    - Stilbite - $NaCa_2Al_5Si_{13}O_{36}{\bullet}17H_2O$

2. Carbonate Mineral

Calcite crystals from the Sweetwater Mine, Viburnum Trend District, Reynolds County, Missouri - 6.2 x 6 x 3.3 cm

Carbonate minerals are those minerals containing the carbonate ion: CO_3^{2-}.

Carbonate classes

Anhydrous carbonates

Rhodochrosite, Sweet Home Mine, Alma, Colorado - 5.2 x 4.2 x 2.3 cm

Smithsonite, Silver Bill Mine, Dragoon Mts, Cochise County, Arizona - 4.8 x 4.1 x 2.4 cm

- Calcite group: Trigonal
  - Calcite $CaCO_3$
  - Gaspeite $(Ni,Mg,Fe^{2+})CO_3$
  - Magnesite $MgCO_3$
  - Otavite $CdCO_3$
  - Rhodochrosite $MnCO_3$
  - Siderite $FeCO_3$
  - Smithsonite $ZnCO_3$
  - Sphaerocobaltite $CoCO_3$
- Aragonite group: Orthorhombic
  - Aragonite $CaCO_3$
  - Cerussite $PbCO_3$
  - Strontianite $SrCO_3$
  - Witherite $BaCO_3$
  - Rutherfordine UO_2CO_3
  - Natrite Na_2CO_3

Anhydrous carbonates with compound formulas

Dolomite with calcite and chalcopyrite from the Picher Field, Tri-State district, Cherokee County, Kansas; 12.0 x 9.7 x 4.3 cm

- Dolomite group: Trigonal
  - Ankerite $CaFe(CO_3)_2$
  - Dolomite $CaMg(CO_3)_2$
  - Minrecordite $CaZn(CO_3)_2$
  - Barytocite $BaCa(CO_3)_2$

Carbonates with hydroxyl or halogen

Azurite and malachite, Beaver Dam Mts, Washington County, Utah - 5.1 x 3.9 x 2.4 cm

- Carbonate with hydroxide: Monoclinic
    - Azurite $Cu_3(CO_3)_2(OH)_2$
    - Hydrocerussite $Pb_3(CO_3)_2(OH)_2$
    - Malachite $Cu_2CO_3(OH)_2$
    - Rosasite $(Cu,Zn)_2CO_3(OH)_2$
    - Phosgenite $Pb_2(CO_3)Cl_2$
    - Hydrozincite $Zn_5(CO_3)_2(OH)_6$
    - Aurichalcite $(Zn,Cu)_5(CO_3)_2(OH)_6$

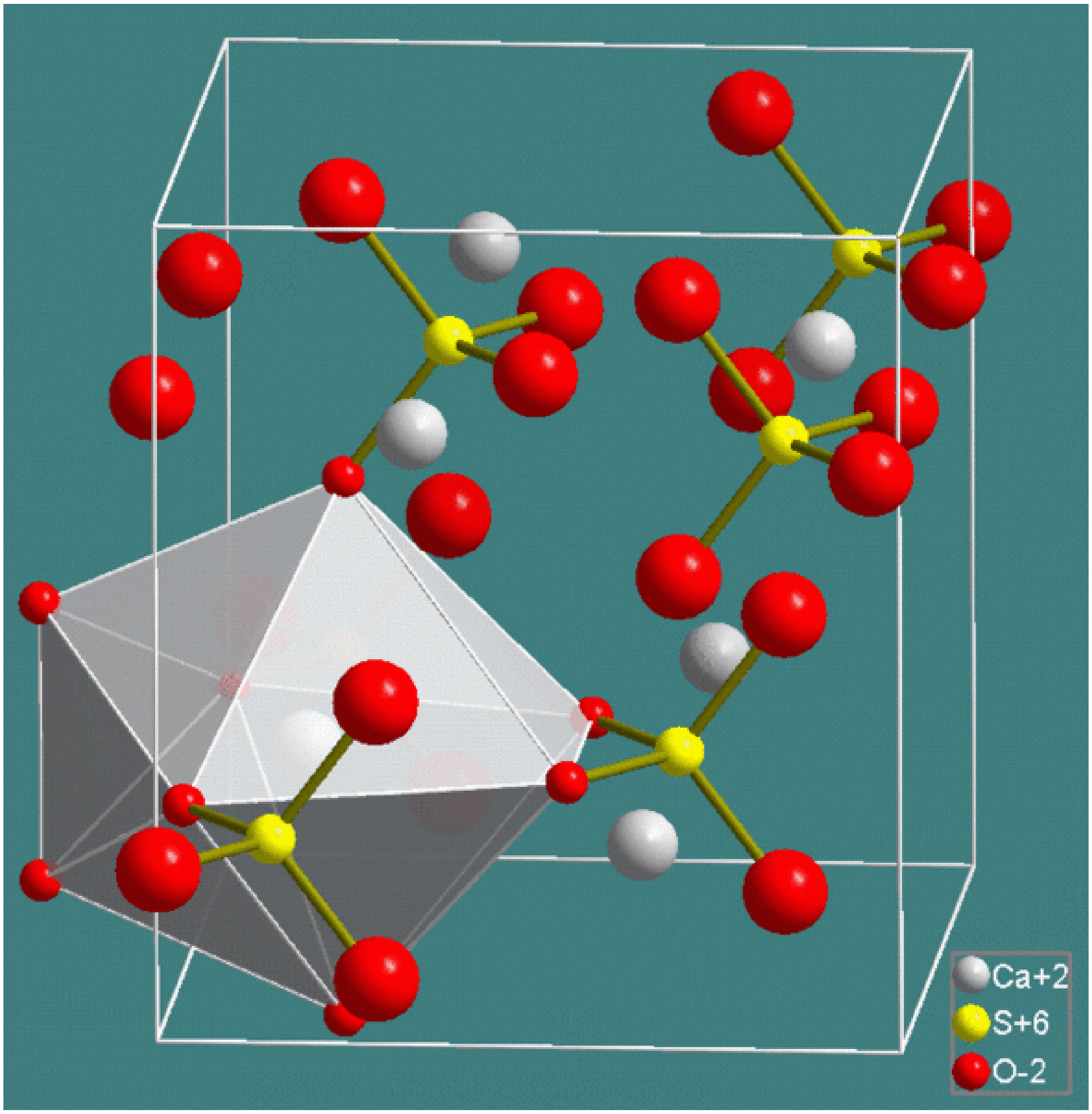
Hydrated carbonates

- Ikaite $CaCO_3.6(H_2O)$
- Lansfordite $MgCO_3 \cdot 5(H_2O)$
- Monohydrocalcite $CaCO_3.H_2O$
- Natron $Na_2CO_3 \cdot 10(H_2O)$
- Zellerite $Ca(UO_2)(CO_3)_2 \cdot 5(H_2O)$

The carbonate class in both the Dana and the Strunz classification systems includes the nitrates, the borates, and the iodates.

3. Sulfate Mineral

The **sulfate mineral** class are those minerals which include the sulfate ion (SO_4^{2-}) within their structure. The sulfate minerals occur commonly in primary evaporite depositional environments, as gangue minerals in hydrothermal veins and as secondary minerals in the oxidizing zone of sulfide mineral deposits. The chromate and manganate minerals have a similar structure and are often included with the sulfates in mineral classification systems.



Anhydrite crystal structure

Barite with cerussite

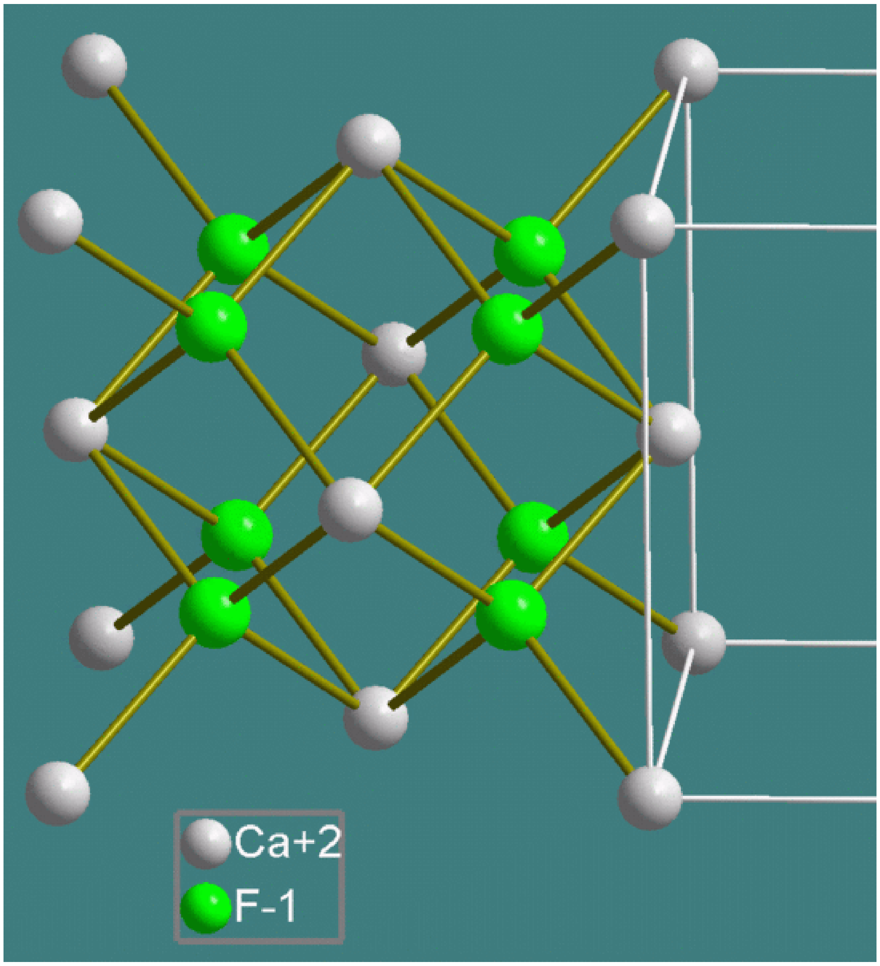
Sulfate minerals include:

- Anhydrous sulfates
    - Barite $BaSO_4$
    - Celestite $SrSO_4$
    - Anglesite $PbSO_4$
    - Anhydrite $CaSO_4$
- Hydroxide and hydrous sulfates
    - Gypsum $CaSO_4 \cdot 2H_2O$
    - Chalcanthite $CuSO_4 \cdot 5H_2O$
    - Kieserite $MgSO_4 \cdot H_2O$
    - Starkeyite $MgSO_4 \cdot 4H_2O$
    - Hexahydrite $MgSO_4 \cdot 6H_2O$
    - Epsomite $MgSO_4 \cdot 7H_2O$
    - Meridianiite $MgSO_4 \cdot 11H_2O$
    - Melanterite $FeSO_4 \cdot 7H_2O$
    - Antlerite $Cu_3SO_4(OH)_4$
    - Brochantite $Cu_6SO_4(OH)_6$
    - Alunite $KAl_3(SO_4)_2(OH)_6$
    - Jarosite $KFe_3(SO_4)_2(OH)_6$

4. Halide Mineral

The **halide mineral** class include those minerals with a dominant halide anion (F^-, Cl^-, Br^- and I^-). Complex halide minerals may also have polyatomic anions in addition to or that include halides.

Halite



Fluorite structure

Examples include the following:

- Halite $NaCl$
- Sylvite KCl
- Chlorargyrite $AgCl$ and bromargyrite $AgBr$
- Fluorite CaF_2
- Atacamite $Cu_2Cl(OH)_3$
- Bischofite ($MgCl_2 \cdot 6H_2O$)
- Carnallite $KMgCl_3 \cdot 6H_2O$
- Cryolite Na_3AlF_6
- Cryptohalite $(\alpha)(NH_4)_2SiF_6$
- Bararite $(\beta)(NH_4)_2SiF_6$

Commercially significant halide minerals

Two commercially important halide minerals are halite and fluorite. The former is a major source of sodium chloride, in parallel with sodium chloride extracted from sea water or brine wells. Fluorite is a major source of hydrogen fluoride, complementing the supply obtained as a byproduct of the production of fertilizer. Carnallite and bischofite are important sources of magnesium. Natural cryolite was historically required for the production of aluminium, however, currently most cryolite used is produced synthetically.

5. Oxide Mineral

The **oxide mineral** class includes those minerals in which the oxide anion (O^{2-}) is bonded to one or more metal ions. The hydroxide bearing minerals are typically included in the oxide class. The minerals with complex anion groups such as the silicates, sulfates, carbonates and phosphates are classed separately.

Simple oxides:

- X_2O and XO
    - Cuprite Cu_2O
    - Ice H_2O
    - Periclase group
        - Periclase MgO
        - Manganosite MnO
    - Zincite group
        - Zincite ZnO
        - Bromellite BeO
        - Tenorite CuO
        - Litharge PbO

- X_2O_3
    - Hematite group
        - Corundum Al_2O_3
        - Hematite Fe_2O_3
        - Ilmenite $FeTiO_3$
- XO_2
    - Rutile group
        - Rutile TiO_2
        - Pyrolusite MnO_2
        - Cassiterite SnO_2
    - Baddeleyite ZrO_2
    - Uraninite UO_2
    - Thorianite ThO_2
- XY_2O_4
    - Spinel group
        - Spinel $MgAl_2O_4$
        - Gahnite $ZnAl_2O_4$
        - Magnetite Fe_3O_4 ($Fe^{2+}Fe^{3+}{}_2O_4$)
        - Franklinite $(Zn,Fe,Mn)(Fe,Mn)_2O_4$
        - Chromite $FeCr_2O_4$
    - Chrysoberyl $BeAl_2O_4$
    - Columbite$(Fe,Mn)(Nb,Ta)_2O_6$

Hyroxide subgroup:

- Brucite $Mg(OH)_2$
- Manganite $MnO(OH)$
- Romanechite $BaMn^{2+}Mn^{4+}{}_8O_{16}(OH)_4$
- Goethite group
    - Diaspore $\alpha AlO(OH)$
    - Goethite $\alpha FeO(OH)$

6. Sulfide Mineral

A **sulfide mineral** is a mineral containing sulfide (S^{2-}) as the major anion. Sulfides are economically important as metal ores. The sulfide class also includes the selenides, the tellurides, the arsenides, the antimonides, the bismuthinides, the sulfarsenides and the sulfosalts.

Common or important examples include:

Sulfides:

- acanthite Ag_2S
- chalcocite Cu_2S
- bornite Cu_5FeS_4
- galena PbS
- sphalerite ZnS
- chalcopyrite $CuFeS_2$
- pyrrhotite $Fe_{1-x}S$
- millerite NiS
- pentlandite $(Fe,Ni)_9S_8$
- covellite CuS
- cinnabar HgS
- realgar AsS
- orpiment As_2S_3
- stibnite Sb_2S_3
- pyrite FeS_2
- marcasite FeS_2
- molybdenite MoS_2

Arsenides:

- nickeline $NiAs$
- skutterudite $(Co,Ni)As_3$

Antimonides:

- breithauptite $NiSb$

Tellurides:

- altaite $PbTe$
- calaverite $AuTe_2$
- sylvanite $(Au,Ag)Te_2$

Sulfarsenides:

- cobaltite $(Co,Fe)AsS$
- arsenopyrite $FeAsS$
- gersdorffite $NiAsS$

Sulfosalts:

- pyrargyrite Ag_3SbS_3
- proustite Ag_3AsS_3
- tetrahedrite $Cu_{12}Sb_4S_{13}$
- tennantite $Cu_{12}As_4S_{13}$
- enargite Cu_3AsS_4

- bournonite $PbCuSbS_3$
- jamesonite $Pb_4FeSb_6S_{14}$
- cylindrite $Pb_3Sn_4FeSb_2S_{14}$

7. Phosphate Mineral

Phosphate minerals are those minerals that contain the tetrahedrally coordinated phosphate (PO_4^{3-}) anion along with the freely substituting arsenate (AsO_4^{3-}) and vanadate (VO_4^{3-}). Chlorine (Cl^-), fluorine (F^-), and hydroxide (OH^-) anions also fit into the crystal structure.

The phosphate class of minerals is a large and diverse group, however, only a few species are relatively common.

Phosphate minerals include:

- triphylite $Li(Fe,Mn)PO_4$
- monazite $(Ce,La,Y,Th)PO_4$
- Apatite group $Ca_5(PO_4)_3(F,Cl,OH)$
    - hydroxylapatite $Ca_5(PO_4)_3OH$
    - fluorapatite $Ca_5(PO_4)_3F$
    - chlorapatite $Ca_5(PO_4)_3Cl$
    - bromapatite
- hinsdalite $PbAl_3(PO_4)(SO_4)(OH)_6$
- pyromorphite $Pb_5(PO_4)_3Cl$
- vanadinite $Pb_5(VO_4)_3Cl$
- erythrite $Co_3(AsO_4)_2{\bullet}8H_2O$
- amblygonite $LiAlPO_4F$
- lazulite $(Mg,Fe)Al_2(PO_4)_2(OH)_2$
- wavellite $Al_3(PO_4)_2(OH)_3{\bullet}5H_2O$
- turquoise $CuAl_6(PO_4)_4(OH)_8{\bullet}5H_2O$
- autunite $Ca(UO_2)_2(PO_4)_2{\cdot}10\text{-}12H_2O$
- carnotite $K_2(UO_2)_2(VO_4)_2{\bullet}3H_2O$
- phosphophyllite $Zn_2(Fe,Mn)(PO_4)_2{\bullet}4H_2O$
- struvite $(NH_4)MgPO_4{\cdot}6H_2O$

Applications

Phosphate rock is a general term that refers to rock with high concentration of phosphate minerals, most commonly of the apatite group. It is the major resource mined to produce phosphate fertilisers for the agriculture sector. Phosphate is also used in animal feed supplements, food preservatives, anti-corrosion agents, cosmetics, fungicides, ceramics, water treatment and metallurgy.

The largest use of minerals mined for their phosphate content is the production of fertilizer.

Phosphate minerals are often used for control of rust and prevention of corrosion on ferrous materials applied with electrochemical conversion coatings.

Chemical properties of minerals

Minerals may be classified according to chemical composition. They are here categorized by anion group. The list below is in approximate order of their abundance in the Earth's crust. The list follows the Dana classification system which closely parallels the Strunz classification.

Silicate class

Quartz

The largest group of minerals by far are the silicates (most rocks are ≥95% silicates), which are composed largely of silicon and oxygen, with the addition of ions such as aluminium, magnesium, iron, and calcium. Some important rock-forming silicates include the feldspars, quartz, olivines, pyroxenes, amphiboles, garnets, and micas.

Carbonate class

The carbonate minerals consist of those minerals containing the anion $(CO_3)^{2-}$ and include calcite and aragonite (both calcium carbonate), dolomite (magnesium/calcium carbonate) and siderite (iron carbonate). Carbonates are commonly deposited in marine settings when the shells of dead planktonic life settle and accumulate on the sea floor. Carbonates are also found in evaporitic settings (e.g. the Great Salt Lake, Utah) and also in karst regions, where the dissolution and reprecipitation of carbonates leads to the formation of caves, stalactites and stalagmites. The carbonate class also includes the nitrate and borate minerals.

Sulfate class

Sulfate minerals all contain the sulfate anion, SO_4^{2-}. Sulfates commonly form in evaporitic settings where highly saline waters slowly evaporate, allowing the formation of both sulfates and halides at the water-sediment interface. Sulfates also occur in hydrothermal vein systems as gangue minerals along with sulfide ore minerals. Another occurrence is as secondary oxidation products of original sulfide minerals. Common sulfates include anhydrite (calcium sulfate), celestine (strontium sulfate), barite (barium sulfate), and gypsum (hydrated calcium sulfate). The sulfate class also includes the chromate, molybdate, selenate, sulfite, tellurate, and tungstate minerals.

Halide class

Halite

The halide minerals are the group of minerals forming the natural salts and include fluorite (calcium fluoride), halite (sodium chloride), sylvite (potassium chloride), and sal ammoniac (ammonium chloride). Halides, like sulfates, are commonly found in evaporite settings such as salt lakes and landlocked seas such as the Dead Sea and Great Salt Lake. The halide class includes the fluoride, chloride, bromide and iodide minerals.

Oxide class

Oxide minerals are extremely important in mining as they form many of the ores from which valuable metals can be extracted. They also carry the best record of changes in the Earth's magnetic field. They commonly occur as precipitates close to the Earth's surface, oxidation products of other minerals in the near surface weathering zone, and as accessory minerals in igneous rocks of the crust and mantle. Common oxides include hematite (iron oxide), magnetite (iron oxide), chromite (iron chromium oxide), spinel (magnesium aluminium oxide – a common component of the mantle), ilmenite (iron titanium oxide), rutile (titanium dioxide), and ice (hydrogen oxide). The oxide class includes the oxide and the hydroxide minerals.

Sulfide class

Many sulfide minerals are economically important as metal ores. Common sulfides include pyrite (iron sulfide – commonly known as *fools' gold*), chalcopyrite (copper iron sulfide), pentlandite (nickel iron sulfide), and galena (lead sulfide). The sulfide class also includes the selenides, the tellurides, the arsenides, the antimonides, the bismuthinides, and the sulfosalts (sulfur and a second anion such as arsenic).

Phosphate class

The phosphate mineral group actually includes any mineral with a tetrahedral unit AO_4 where A can be phosphorus, antimony, arsenic or vanadium. By far the most common phosphate is apatite which is an important biological mineral found in teeth and bones of many animals. The phosphate class includes the phosphate, arsenate, vanadate, and antimonate minerals.

Element class

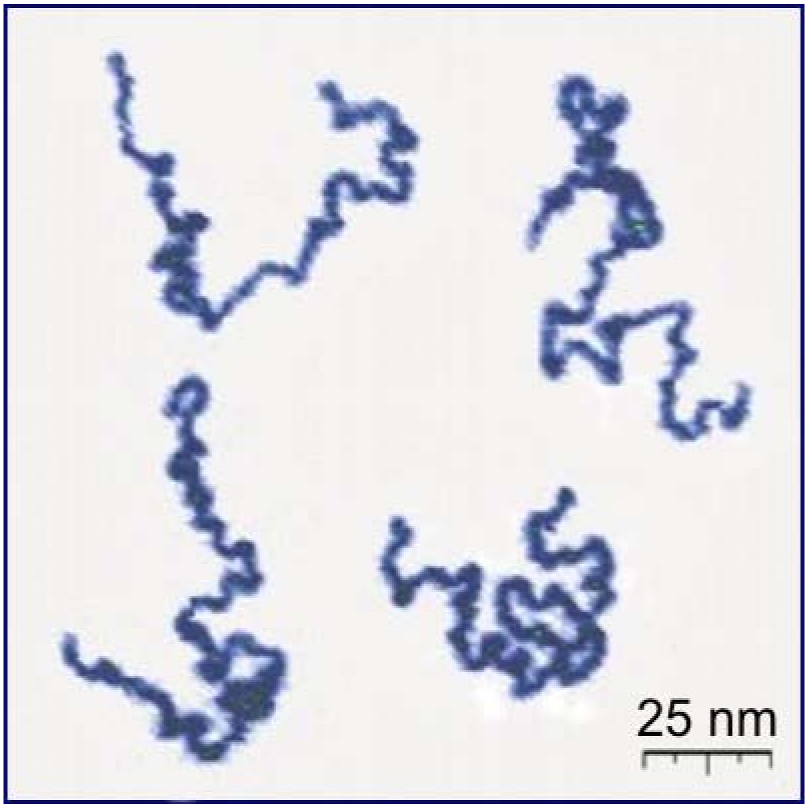
The elemental group includes native metals and intermetallic elements (gold, silver, copper), semi-metals and non-metals (antimony, bismuth, graphite, sulfur). This group also includes natural alloys, such as electrum (a natural alloy of gold and silver), phosphides, silicides, nitrides and carbides (which are usually only found naturally in a few rare meteorites).

Organic class

The organic mineral class includes biogenic substances in which geological processes have been a part of the genesis or origin of the existing compound. Minerals of the organic class include various oxalates, mellitates, citrates, cyanates, acetates, formates, hydrocarbons and other miscellaneous species. Examples include whewellite, moolooite, mellite, fichtelite, carpathite, evenkite and abelsonite.

Chapter- 4

Polymer



Appearance of real linear polymer chains as recorded using an atomic force microscope on surface under liquid medium. Chain contour length for this polymer is ~204 nm; thickness is ~0.4 nm.

A **polymer** is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. Whereas the term *polymer* is sometimes taken to refer to plastics, it actually encompasses a large class of natural and synthetic materials with a wide variety of properties.

Because of the extraordinary range of properties of polymeric materials, they play an essential and ubiquitous role in everyday life, ranging from familiar synthetic plastics and elastomers to natural biopolymers such as nucleic acids and proteins that are essential for life. Natural polymeric materials such as shellac, amber, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper. The list of synthetic polymers includes synthetic rubber, Bakelite, neoprene, nylon, PVC, polystyrene, polyethylene, polypropylene, polyacrylonitrile, PVB, silicone, and many more.

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene, whose repeating unit is based on ethylene monomer. However, other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being silly putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

Polymers are studied in the fields of polymer chemistry, polymer physics, and polymer science.

Etymology

The word ***polymer*** is derived from the Greek words *πολυ-* - *poly-* meaning "many"; and *μέρος* - *meros* meaning "part". The term was coined in 1833 by Jöns Jacob Berzelius, although his definition of a polymer was quite different from the modern definition.

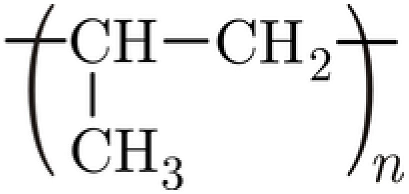
Historical development

Starting in 1811, Henri Braconnot did pioneering work in derivative cellulose compounds, perhaps the earliest important work in polymer science. The development of vulcanization later in the nineteenth century improved the durability of the natural polymer rubber, signifying the first popularized semi-synthetic polymer. In 1907, Leo Baekeland created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde at precisely controlled temperature and pressure. Bakelite was then publicly introduced in 1909.

Despite significant advances in synthesis and characterization of polymers, a correct understanding of polymer molecular structure did not emerge until the 1920s. Before then, scientists believed that polymers were clusters of small molecules (called colloids), without definite molecular weights, held together by an unknown force, a concept known as association theory. In 1922, Hermann Staudinger proposed that polymers consisted of long chains of atoms held together by covalent bonds, an idea which did not gain wide acceptance for over a decade and for which Staudinger was ultimately awarded the Nobel Prize. Work by Wallace Carothers in the 1920s also demonstrated that polymers could be synthesized rationally from their constituent monomers. An important contribution to synthetic polymer science was made by the Italian chemist Giulio Natta and the German chemist Karl Ziegler, who won the Nobel Prize in Chemistry in 1963 for the development of the Ziegler-Natta catalyst. Further recognition of the importance of polymers came with the award of the Nobel Prize in Chemistry in 1974 to Paul Flory, whose extensive work on polymers included the kinetics of step-growth polymerization and of addition polymerization, chain transfer, excluded volume, the Flory-Huggins solution theory, and the Flory convention.

Synthetic polymer materials such as nylon, polyethylene, Teflon, and silicone have formed the basis for a burgeoning polymer industry. These years have also shown significant developments in rational polymer synthesis. Most commercially important polymers today are entirely synthetic and produced in high volume on appropriately scaled organic synthetic techniques. Synthetic polymers today find application in nearly every industry and area of life. Polymers are widely used as adhesives and lubricants, as well as structural components for products ranging from children's toys to aircraft. They have been employed in a variety of biomedical applications ranging from implantable devices to controlled drug delivery. Polymers such as poly(methyl methacrylate) find application as photoresist materials used in semiconductor manufacturing and low-k dielectrics for use in high-performance microprocessors. Recently, polymers have also been employed as flexible substrates in the development of organic light-emitting diodes for electronic display.

Polymer synthesis



$$\left(-CH(CH_3)-CH_2- \right)_n$$

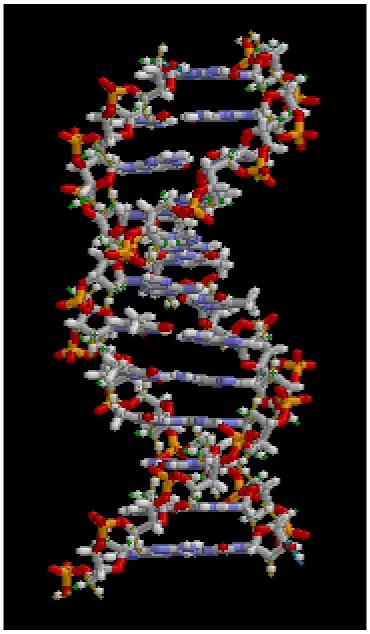
The repeating unit of the polymer polypropylene

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain. During the polymerization process, some chemical groups may be lost from each monomer. This is the case, for example, in the polymerization of PET polyester. The monomers are terephthalic acid ($HOOC-C_6H_4-COOH$) and ethylene glycol ($HO-CH_2-CH_2-OH$) but the repeating unit is $-OC-C_6H_4-COO-CH_2-CH_2-O-$, which corresponds to the combination of the two monomers with the loss of two water molecules. The distinct piece of each monomer that is incorporated into the polymer is known as a repeat unit or monomer residue.

Laboratory synthesis

Laboratory synthetic methods are generally divided into two categories, step-growth polymerization and chain-growth polymerization. The essential difference between the two is that in chain growth polymerization, monomers are added to the chain one at a time only, whereas in step-growth polymerization chains of monomers may combine with one another directly. However, some newer methods such as plasma polymerization do not fit neatly into either category. Synthetic polymerization reactions may be carried out with or without a catalyst. Laboratory synthesis of biopolymers, especially of proteins, is an area of intensive research.

Biological synthesis



Microstructure of part of a DNA double helix **biopolymer**

There are three main classes of biopolymers: polysaccharides, polypeptides, and polynucleotides. In living cells, they may be synthesized by enzyme-mediated processes, such as the formation of DNA catalyzed by DNA polymerase. The synthesis of proteins involves multiple enzyme-mediated processes to transcribe genetic information from the DNA to RNA and subsequently translate that information to synthesize the specified protein from amino acids. The protein may be modified further following translation in order to provide appropriate structure and functioning.

Modification of natural polymers

Many commercially important polymers are synthesized by chemical modification of naturally occurring polymers. Prominent examples include the reaction of nitric acid and cellulose to form nitrocellulose and the formation of vulcanized rubber by heating natural rubber in the presence of sulfur.

Polymer properties

Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents.

Monomers and repeat units

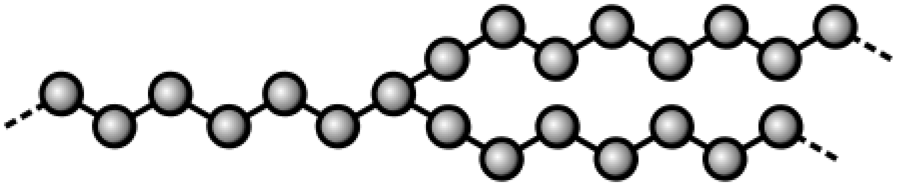
The identity of the monomer residues (repeat units) comprising a polymer is its first and most important attribute. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer. Polymers that contain only a single type of repeat unit are known as homopolymers, while polymers containing a mixture of repeat units are known as copolymers. Poly(styrene), for example, is composed only of styrene monomer residues, and is therefore classified as a homopolymer. Ethylene-vinyl acetate, on the other hand, contains more than one variety of repeat unit and is thus a copolymer. Some biological polymers are composed of a variety of different but structurally related monomer residues; for example, polynucleotides such as DNA are composed of a variety of nucleotide subunits.

A polymer molecule containing ionizable subunits is known as a polyelectrolyte or ionomer.

Microstructure

The microstructure of a polymer (sometimes called configuration) relates to the physical arrangement of monomer residues along the backbone of the chain. These are the elements of polymer structure that require the breaking of a covalent bond in order to change. Structure has a strong influence on the other properties of a polymer. For example, two samples of natural rubber may exhibit different durability, even though their molecules comprise the same monomers.

Polymer architecture

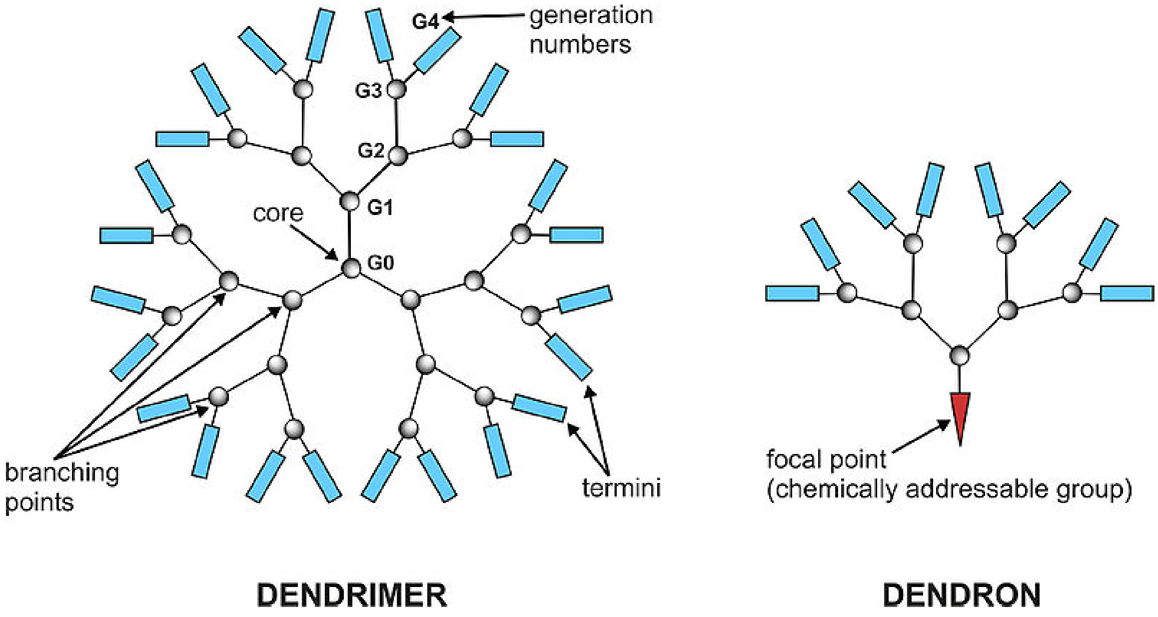


Branch point in a polymer

An important microstructural feature determining polymer properties is the polymer architecture. The simplest polymer architecture is a *linear* chain: a single backbone with no branches. A related unbranching architecture is a *ring* polymer. A branched polymer molecule is composed of a main chain with one or more substituent side chains or branches. Special types of branched polymers include star polymers, comb polymers, brush polymers, dendronized polymers, *ladders*, and dendrimers.

Branching of polymer chains affects the ability of chains to slide past one another by altering intermolecular forces, in turn affecting bulk physical polymer properties. Long chain branches may increase polymer strength, toughness, and the glass transition temperature (T_g) due to an increase in the number of entanglements per chain. The effect of such long-chain branches on the size of the polymer in solution is characterized by the branching index. Random length and atactic short chains, on the other hand, may reduce polymer strength due to disruption of organization and may likewise reduce the crystallinity of the polymer.

A good example of this effect is related to the range of physical attributes of polyethylene. High-density polyethylene (HDPE) has a very low degree of branching, is quite stiff, and is used in applications such as milk jugs. Low-density polyethylene (LDPE), on the other hand, has significant numbers of both long and short branches, is quite flexible, and is used in applications such as plastic films.



Dendrimer and dendron

Dendrimers are a special case of polymer where every monomer unit is branched. This tends to reduce intermolecular chain entanglement and crystallization. Alternatively, dendritic polymers are not perfectly branched but share similar properties to dendrimers due to their high degree of branching.

The architecture of the polymer is often physically determined by the **functionality** of the monomers from which it is formed. This property of a monomer is defined as the number of reaction sites at which may form chemical covalent bonds. The basic functionality required for forming even a linear chain is two bonding sites. Higher functionality yields branched or even crosslinked or networked polymer chains.

An effect related to branching is chemical crosslinking - the formation of covalent bonds between chains. Crosslinking tends to increase T_g and increase strength and toughness. Among other applications, this process is used to strengthen rubbers in a process known as vulcanization, which is based on crosslinking by sulfur. Car tires, for example, are highly crosslinked in order to reduce the leaking of air out of the tire and to toughen their durability. Eraser rubber, on the other hand, is not crosslinked to allow flaking of the rubber and prevent damage to the paper.

A cross-link suggests a branch point from which four or more distinct chains emanate. A polymer molecule with a high degree of crosslinking is referred to as a polymer network. Sufficiently high crosslink concentrations may lead to the formation of an infinite network, also known as a gel, in which networks of chains are of unlimited extent—essentially all chains have linked into one molecule.

Chain length

The physical properties of a polymer are strongly dependent on the size or length of the polymer chain.. For example, as chain length is increased, melting and boiling temperatures increase quickly. Impact resistance also tends to increase with chain length, as does the viscosity, or resistance to flow, of the polymer in its melt state. Chain length is related to melt viscosity roughly as $1:10^{3.2}$, so that a tenfold increase in polymer chain length results in a viscosity increase of over 1000 times. Increasing chain length furthermore tends to decrease chain mobility, increase strength and toughness, and increase the glass transition temperature (T_g). This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that come with increased chain length. These interactions tend to fix the individual chains more strongly in position and resist deformations and matrix breakup, both at higher stresses and higher temperatures.

A common means of expressing the length of a chain is the degree of polymerization, which quantifies the number of monomers incorporated into the chain. As with other molecules, a polymer's size may also be expressed in terms of molecular weight. Since synthetic polymerization techniques typically yield a polymer product including a range of molecular weights, the weight is often expressed statistically to describe the distribution of chain lengths present in the same. Common examples are the number average molecular weight and weight average molecular weight. The ratio of these two values is the polydispersity index, commonly used to express the "width" of the molecular weight distribution. A final measurement is contour length, which can be understood as the length of the chain backbone in its fully extended state.

The flexibility of an unbranched chain polymer is characterized by its persistence length.

Monomer arrangement in copolymers

Monomers within a copolymer may be organized along the backbone in a variety of ways.

- **Alternating copolymers** possess regularly alternating monomer residues: $[AB...]_n$ (2).
- **Periodic copolymers** have monomer residue types arranged in a repeating sequence: $[A_nB_m...]$ m being different from n .
- **Statistical copolymers** have monomer residues arranged according to a known statistical rule. A statistical copolymer in which the probability of finding a particular type of monomer residue at an particular point in the chain is independent of the types of surrounding monomer residue may be referred to as a truly **random copolymer** (3).
- **Block copolymers** have two or more homopolymer subunits linked by covalent bonds (4). Polymers with two or three blocks of two distinct chemical species (e.g., A and B) are called diblock copolymers and triblock copolymers, respectively. Polymers with three blocks, each of a different chemical species (e.g., A, B, and C) are termed triblock terpolymers.
- **Graft or grafted copolymers** contain side chains that have a different composition or configuration than the main chain.(5)

Tacticity

Tacticity describes the relative stereochemistry of chiral centers in neighboring structural units within a macromolecule. There are three types: isotactic (all substituents on the same side), atactic (random placement of substituents), and syndiotactic (alternating placement of substituents).

Polymer morphology

Polymer morphology generally describes the arrangement and microscale ordering of polymer chains in space.

Crystallinity

When applied to polymers, the term *crystalline* has a somewhat ambiguous usage. In some cases, the term *crystalline* finds identical usage to that used in conventional crystallography. For example, the structure of a crystalline protein or polynucleotide, such as a sample prepared for x-ray crystallography, may be defined in terms of a conventional unit cell composed of one or more polymer molecules with cell dimensions of hundreds of angstroms or more.

A synthetic polymer may be lightly described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline.

The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.

Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. Thus for many polymers, reduced crystallinity may also be associated with increased transparency.

Chain conformation

The space occupied by a polymer molecule is generally expressed in terms of radius of gyration, which is an average distance from the center of mass of the chain to the chain itself. Alternatively, it may be expressed in terms of pervaded volume, which is the volume of solution spanned by the polymer chain and scales with the cube of the radius of gyration.

Mechanical properties

A polyethylene sample necking under tension

The bulk properties of a polymer are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale.

Tensile strength

The tensile strength of a material quantifies how much stress the material will endure before suffering permanent deformation. This is very important in applications that rely upon a polymer's physical strength or durability. For example, a rubber band with a higher tensile strength will hold a greater weight before snapping. In general, tensile strength increases with polymer chain length and crosslinking of polymer chains.

Young's modulus of elasticity

Young's Modulus quantifies the elasticity of the polymer. It is defined, for small strains, as the ratio of rate of change of stress to strain. Like tensile strength, this is highly relevant in polymer applications involving the physical properties of polymers, such as rubber bands. The modulus is strongly dependent on temperature.

Transport properties

Transport properties such as diffusivity relate to how rapidly molecules move through the polymer matrix. These are very important in many applications of polymers for films and membranes.

Phase behavior

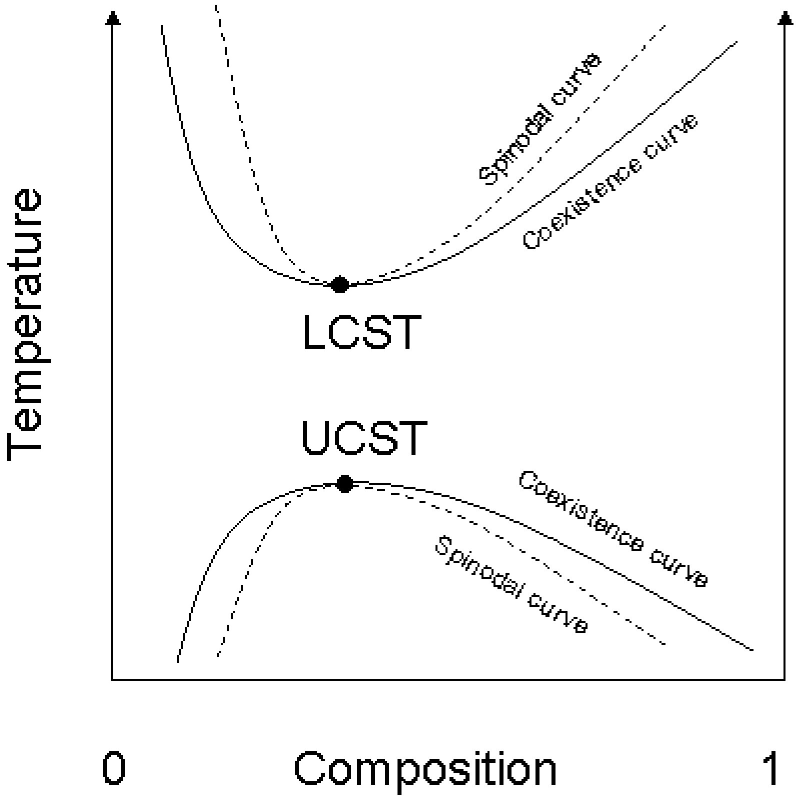
Melting point

The term *melting point*, when applied to polymers, suggests not a solid-liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase. Though abbreviated as simply T_m, the property in question is more properly called the crystalline melting temperature. Among synthetic polymers, crystalline melting is only discussed with regards to thermoplastics, as thermosetting polymers will decompose at high temperatures rather than melt.

Glass transition temperature

A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g), which describes the temperature at which amorphous polymers undergo a transition from a rubbery, viscous amorphous solid, to a brittle, glassy amorphous solid. The glass transition temperature may be engineered by altering the degree of branching or crosslinking in the polymer or by the addition of plasticizer.

Mixing behavior



Phase diagram of the typical mixing behavior of weakly interacting polymer solutions

In general, polymeric mixtures are far less miscible than mixtures of small molecule materials. This effect results from the fact that the driving force for mixing is usually entropy, not interaction energy. In other words, miscible materials usually form a solution not because their interaction with each other is more favorable than their self-interaction, but because of an increase in entropy and hence free energy associated with increasing the amount of volume available to each component. This increase in entropy scales with the number of particles (or moles) being mixed. Since polymeric molecules are much larger and hence generally have much higher specific volumes than small molecules, the number of molecules involved in a polymeric mixture is far smaller than the number in a small molecule mixture of equal volume. The energetics of mixing, on the other hand, is comparable on a per volume basis for polymeric and small molecule mixtures. This tends to increase the free energy of mixing for polymer solutions and thus make solvation less favorable. Thus, concentrated solutions of polymers are far rarer than those of small molecules.

Furthermore, the phase behavior of polymer solutions and mixtures is more complex than that of small molecule mixtures. Whereas most small molecule solutions exhibit only an upper critical solution temperature phase transition, at which phase separation occurs with cooling, polymer mixtures commonly exhibit a lower critical solution temperature phase transition, at which phase separation occurs with heating.

In dilute solution, the properties of the polymer are characterized by the interaction between the solvent and the polymer. In a good solvent, the polymer appears swollen and occupies a large volume. In this scenario, intermolecular forces between the solvent and monomer subunits dominate over intramolecular interactions. In a bad solvent or poor solvent, intramolecular forces dominate and the chain contracts. In the theta solvent, or the state of the polymer solution where the value of the second virial coefficient becomes 0, the intermolecular polymer-solvent repulsion balances exactly the intramolecular monomer-monomer attraction. Under the theta condition (also called the Flory condition), the polymer behaves like an ideal random coil. The transition between the states is known as a coil-globule transition.

Inclusion of plasticizers

Inclusion of plasticizers tends to lower T_g and increase polymer flexibility. Plasticizers are generally small molecules that are chemically similar to the polymer and create gaps between polymer chains for greater mobility and reduced interchain interactions. A good example of the action of plasticizers is related to polyvinylchlorides or PVCs. A uPVC, or unplasticized polyvinylchloride, is used for things such as pipes. A pipe has no plasticizers in it, because it needs to remain strong and heat-resistant. Plasticized PVC is used for clothing for a flexible quality. Plasticizers are also put in some types of cling film to make the polymer more flexible.

Chemical properties

The attractive forces between polymer chains play a large part in determining a polymer's properties. Because polymer chains are so long, these interchain forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymer can lend the polymer to ionic bonding or hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength and higher crystalline melting points.

The intermolecular forces in polymers can be affected by dipoles in the monomer units. Polymers containing amide or carbonyl groups can form hydrogen bonds between adjacent chains; the partially positively charged hydrogen atoms in N-H groups of one chain are strongly attracted to the partially negatively charged oxygen atoms in C=O groups on another. These strong hydrogen bonds, for example, result in the high tensile strength and melting point of polymers containing urethane or urea linkages. Polyesters have dipole-dipole bonding between the oxygen atoms in C=O groups and the hydrogen atoms in H-C groups. Dipole bonding is not as strong as hydrogen bonding, so a polyester's melting point and strength are lower than Kevlar's (Twaron), but polyesters have greater flexibility.

Ethene, however, has no permanent dipole. The attractive forces between polyethylene chains arise from weak van der Waals forces. Molecules can be thought of as being surrounded by a cloud of negative electrons. As two polymer chains approach, their electron clouds repel one another. This has the effect of lowering the electron density on one side of a polymer chain, creating a slight positive dipole on this side. This charge is enough to attract the second polymer chain. Van der Waals forces are quite weak, however, so polyethylene can have a lower melting temperature compared to other polymers.

Standardized polymer nomenclature

There are multiple conventions for naming polymer substances. Many commonly used polymers, such as those found in consumer products, are referred to by a common or trivial name. The trivial name is assigned based on historical precedent or popular usage rather than a standardized naming convention. Both the American Chemical Society and IUPAC have proposed standardized naming conventions; the ACS and IUPAC conventions are similar but not identical. Examples of the differences between the various naming conventions are given in the table below:

Common name	ACS name	IUPAC name
Poly(ethylene oxide) or PEO	Poly(oxyethylene)	Poly(oxyethene)
Poly(ethylene terephthalate) or PET	Poly(oxy-1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl)	Poly(oxyetheneoxyterephthaloyl)
Nylon 6	Poly[amino(1-oxo-1,6-hexanediyl)]	Poly[amino(1-oxohexan-1,6-diyl)]

In both standardized conventions, the polymers' names are intended to reflect the monomer(s) from which they are synthesized rather than the precise nature of the repeating subunit. For example, the polymer synthesized from the simple alkene ethene is called polyethylene, retaining the *-ene* suffix even though the double bond is removed during the polymerization process:

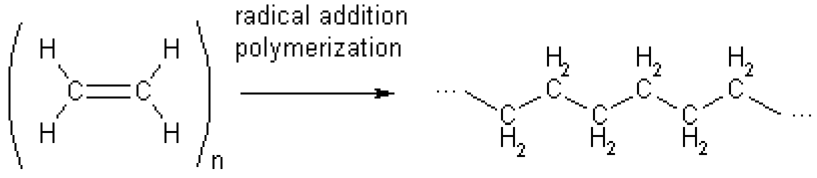
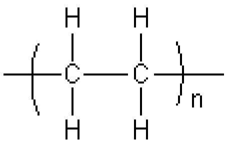


Fig 1: The polymerisation of ethene in to poly(ethene)

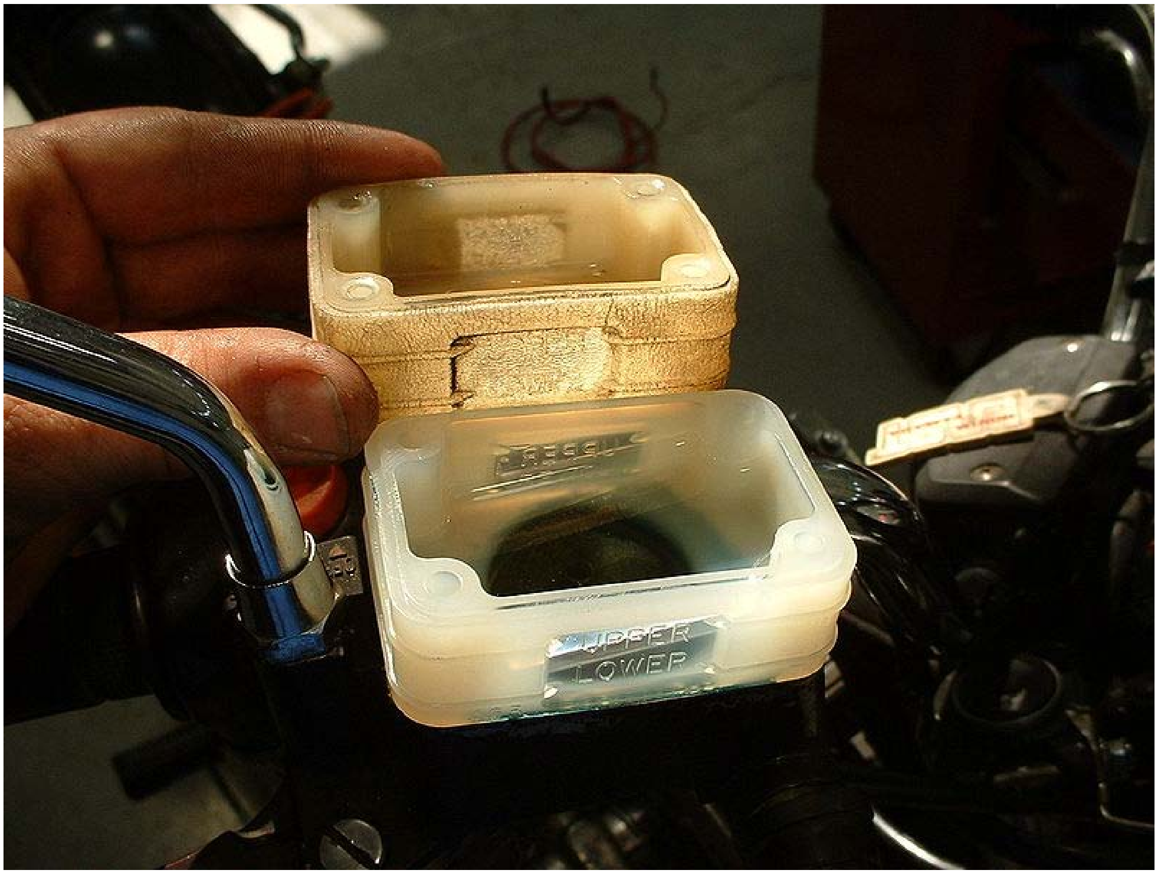


Polymer characterization

The characterization of a polymer requires several parameters which need to be specified. This is because a polymer actually consists of a statistical distribution of chains of varying lengths, and each chain consists of monomer residues which affect its properties.

A variety of lab techniques are used to determine the properties of polymers. Techniques such as wide angle X-ray scattering, small angle X-ray scattering, and small angle neutron scattering are used to determine the crystalline structure of polymers. Gel permeation chromatography is used to determine the number average molecular weight, weight average molecular weight, and polydispersity. FTIR, Raman and NMR can be used to determine composition. Thermal properties such as the glass transition temperature and melting point can be determined by differential scanning calorimetry and dynamic mechanical analysis. Pyrolysis followed by analysis of the fragments is one more technique for determining the possible structure of the polymer. Thermogravimetry is a useful technique to evaluate the thermal stability of the polymer. Detailed analyses of TG curves also allow us to know a bit of the phase segregation in polymers. Rheological properties are also commonly used to help determine molecular architecture (molecular weight, molecular weight distribution and branching)as well as to understand how the polymer will process, through measurements of the polymer in the melt phase. Another Polymer characterization technique is Automatic Continuous Online Monitoring of Polymerization Reactions (ACOMP) which provides real-time characterization of polymerization reactions. It can be used as an analytical method in R&D, as a tool for reaction optimization at the bench and pilot plant level and, eventually, for feedback control of full-scale reactors. ACOMP measures in a model-independent fashion the evolution of average molar mass and intrinsic viscosity, monomer conversion kinetics and, in the case of copolymers, also the average composition drift and distribution. It is applicable in the areas of free radical and controlled radical homo- and copolymerization, polyelectrolyte synthesis, heterogeneous phase reactions, including emulsion polymerization, adaptation to batch and continuous reactors, and modifications of polymers.

Polymer degradation



A plastic item with thirty years of exposure to heat and cold, brake fluid, and sunlight. Notice the discoloration, swollen dimensions, and tiny splits running through the material

Polymer degradation is a change in the properties—tensile strength, color, shape, molecular weight, etc.—of a polymer or polymer-based product under the influence of one or more environmental factors, such as heat, light, chemicals and, in some cases, galvanic action. It is often due to the scission of polymer chain bonds via hydrolysis, leading to a decrease in the molecular mass of the polymer.

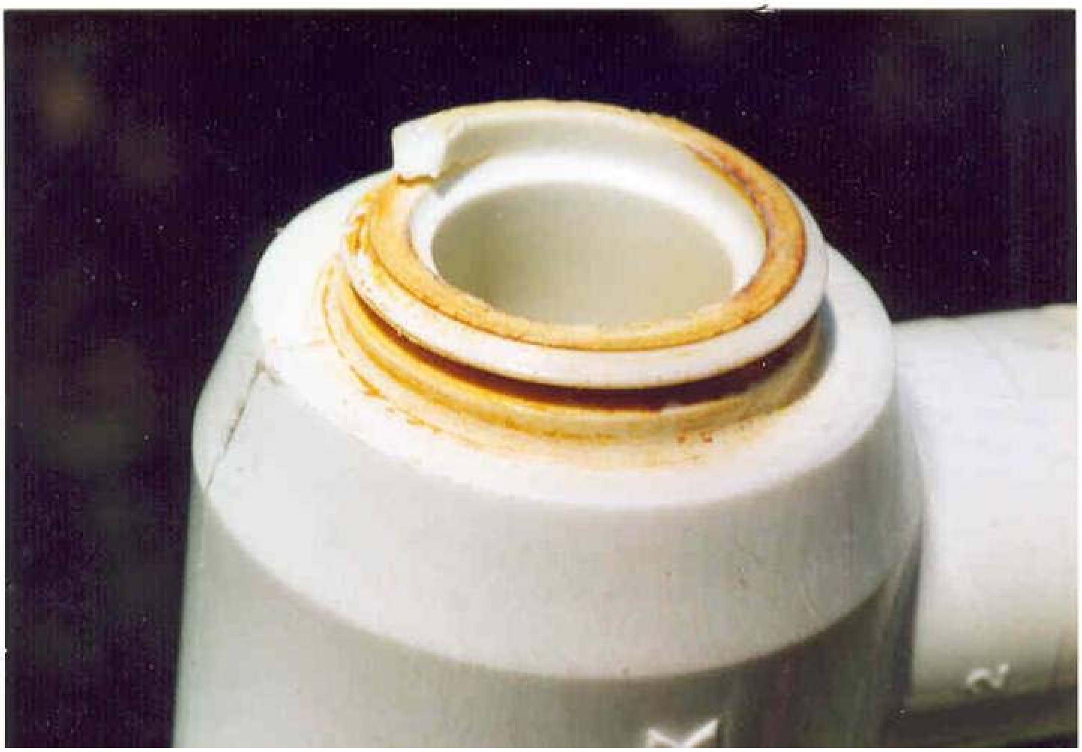
Although such changes are frequently undesirable, in some cases, such as biodegradation and recycling, they may be intended to prevent environmental pollution. Degradation can also be useful in biomedical settings. For example, a copolymer of Polylactic acid and polyglycolic acid is employed in hydrolysable stitches that slowly degrade after they are applied to a wound.

The susceptibility of a polymer to degradation depends on its structure. Epoxies and chains containing aromatic functionality are especially susceptible to UV degradation while polyesters are susceptible to degradation by hydrolysis, and some other polymers are especially susceptible to Ozone cracking. Carbon based polymers are more susceptible to thermal degradation than inorganically bound polymers such as Polydimethylsiloxane and are therefore not ideal for most high temperature applications.

The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. The degradation of polyethylene occurs by random scission—a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When heated above 450 °C it degrades to form a mixture of hydrocarbons. Other polymers—like polyalphamethylstyrene—undergo specific chain scission with breakage occurring only at the ends. They literally unzip or depolymerize to become the constituent monomer.

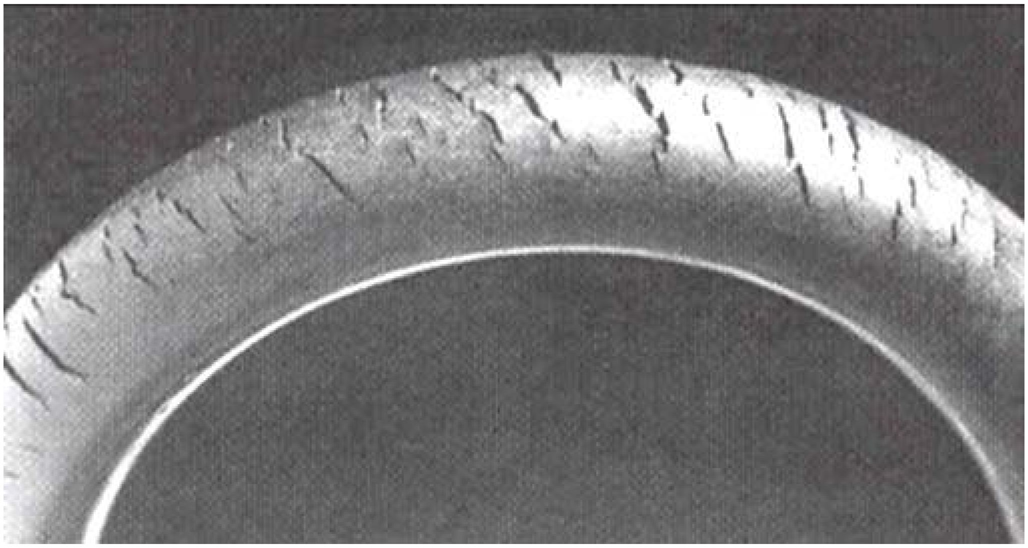
The sorting of polymer waste for recycling purposes may be facilitated by the use of the Resin identification codes developed by the Society of the Plastics Industry to identify the type of plastic.

Product failure



Chlorine attack of acetal resin plumbing joint

In a finished product, such a change is to be prevented or delayed. Failure of safety-critical polymer components can cause serious accidents, such as fire in the case of cracked and degraded polymer fuel lines. Chlorine-induced cracking of acetal resin plumbing joints and polybutylene pipes has caused many serious floods in domestic properties, especially in the USA in the 1990s. Traces of chlorine in the water supply attacked vulnerable polymers in the plastic plumbing, a problem which occurs faster if any of the parts have been poorly extruded or injection molded. Attack of the acetal joint occurred because of faulty molding, leading to cracking along the threads of the fitting which is a serious stress concentration.



Ozone-induced cracking in natural rubber tubing

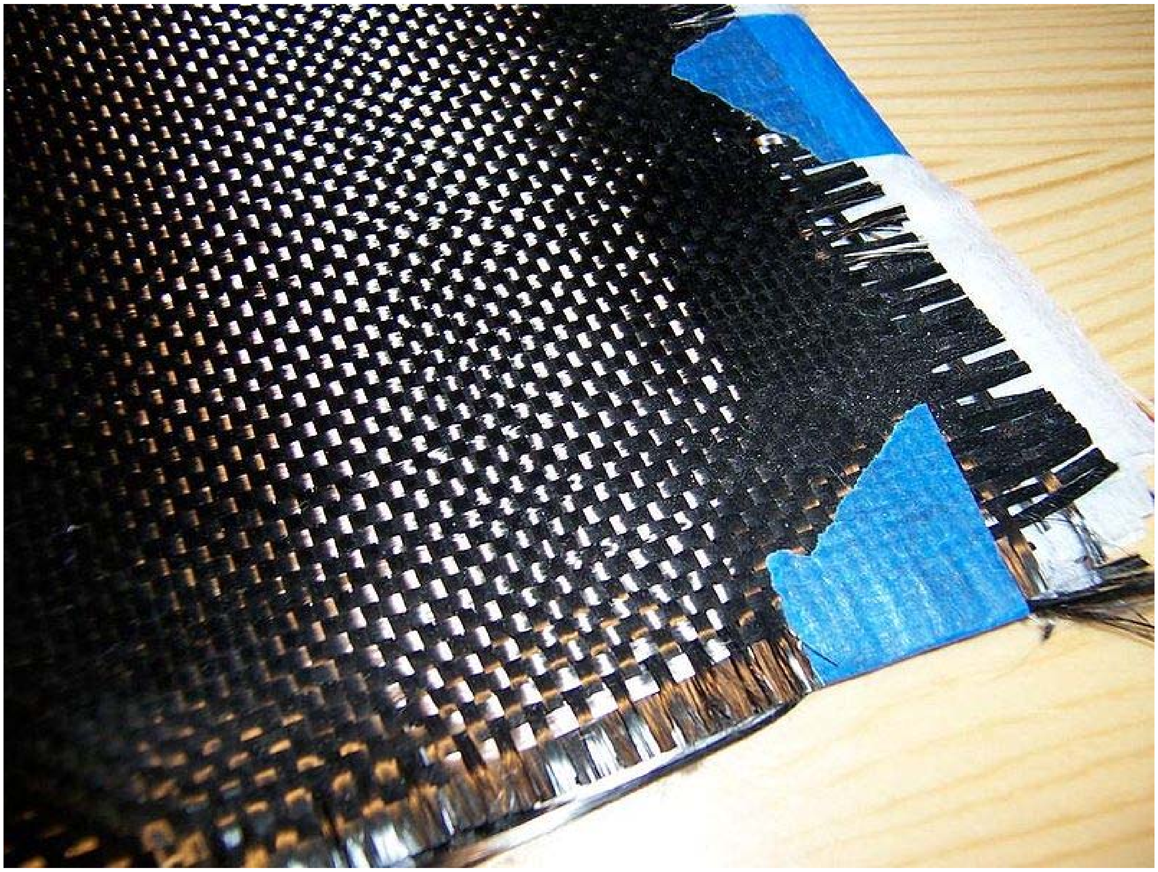
Polymer oxidation has caused accidents involving medical devices. One of the oldest known failure modes is ozone cracking caused by chain scission when ozone gas attacks susceptible elastomers such as natural rubber and nitrile rubber. They possess double bonds in their repeat units which are cleaved during ozonolysis. Cracks in fuel lines can penetrate the bore of the tube and cause fuel leakage. If cracking occurs in the engine compartment, electric sparks can ignite the gasoline and can cause a serious fire.

Fuel lines can also be attacked by another form of degradation: hydrolysis. Nylon 6,6 is susceptible to acid hydrolysis, and in one accident, a fractured fuel line led to a spillage of diesel into the road. If diesel fuel leaks onto the road, accidents to following cars can be caused by the slippery nature of the deposit, which is like black ice.

Chapter- 5

Composite Materials and Biomaterials

Composite Materials

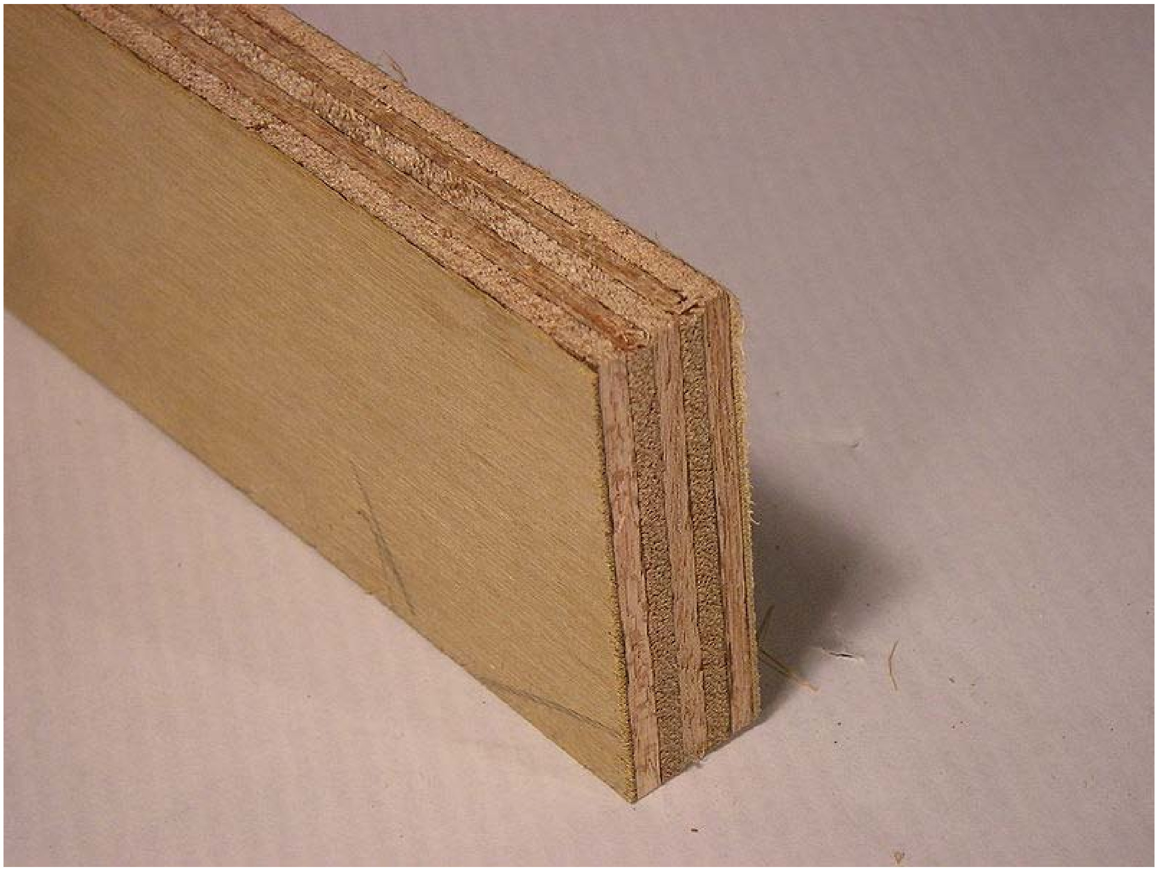


A cloth of woven carbon fiber filaments, a common element in composite materials

Composite materials, often shortened to **composites**, are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure.

The most visible applications is pavement in roadways in the form of either steel and aggregate reinforced Portland cement or asphalt concrete. Those composites closest to our personal hygiene form our shower stalls and bathtubs made of fibreglass. Imitation granite and cultured marble sinks and countertops are widely used. The most advanced examples perform routinely on spacecraft in demanding environments.

Composition



Plywood is a commonly encountered composite material

Wood is a natural composite of Cellulose fibers in a matrix of lignin. The earliest man-made composite materials were straw and mud combined to form bricks for building construction. The ancient brick-making process can still be seen on Egyptian tomb paintings in the Metropolitan Museum of Art.

Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials: matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination.

Engineered composite materials must be formed to shape. The matrix material can be introduced to the reinforcement before or after the reinforcement material is placed into the mould cavity or onto the mould surface. The matrix material experiences a melding event, after which the part shape is essentially set. Depending upon the nature of the matrix material, this melding event can occur in various ways such as chemical polymerization or solidification from the melted state.

A variety of moulding methods can be used according to the end-item design requirements. The principal factors impacting the methodology are the natures of the chosen matrix and reinforcement materials. Another important factor is the gross quantity of material to be produced. Large quantities can be used to justify high capital expenditures for rapid and automated manufacturing technology. Small production quantities are accommodated with lower capital expenditures but higher labour and tooling costs at a correspondingly slower rate.

Most commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, PEEK, and others. The reinforcement materials are often fibres but also commonly ground minerals. The various methods described below have been developed to reduce the resin content of the final product, or the fibre content is increased. As a rule of thumb, lay up results in a product containing 60% resin and 40% fibre, whereas vacuum infusion gives a final product with 40% resin and 60% fibre content. The strength of the product is greatly dependent on this ratio.

Moulding methods

In general, the reinforcing and matrix materials are combined, compacted and processed to undergo a melding event. After the melding event, the part shape is essentially set, although it can deform under certain process conditions. For a thermoset polymeric matrix material, the melding event is a curing reaction that is initiated by the application of additional heat or chemical reactivity such as an organic peroxide. For a thermoplastic polymeric matrix material, the melding event is a solidification from the melted state. For a metal matrix material such as titanium foil, the melding event is a fusing at high pressure and a temperature near the melt point.

For many moulding methods, it is convenient to refer to one mould piece as a "lower" mould and another mould piece as an "upper" mould. Lower and upper refer to the different faces of the moulded panel, not the mould's configuration in space. In this convention, there is always a lower mould, and sometimes an upper mould. Part construction begins by applying materials to the lower mould. Lower mould and upper mould are more generalized descriptors than more common and specific terms such as male side, female side, a-side, b-side, tool side, bowl, hat, mandrel, etc. Continuous manufacturing processes use a different nomenclature.

The moulded product is often referred to as a panel. For certain geometries and material combinations, it can be referred to as a casting. For certain continuous processes, it can be referred to as a profile. Applied with a pressure roller, a spray device or manually. This process is generally done at ambient temperature and atmospheric pressure. Two variations of open moulding are Hand Layup and Spray-up.

Vacuum bag moulding

A process using a two-sided mould set that shapes both surfaces of the panel. On the lower side is a rigid mould and on the upper side is a flexible membrane or vacuum bag. The flexible membrane can be a reusable silicone material or an extruded polymer film. Then, vacuum is applied to the mould cavity. This process can be performed at either ambient or elevated temperature with ambient atmospheric pressure acting upon the vacuum bag. Most economical way is using a venturi vacuum and air compressor or a vacuum pump.

A vacuum bag is a bag made of strong rubber-coated fabric or a polymer film used to bond or laminate materials. In some applications the bag encloses the entire material, or in other applications a mold is used to form one face of the laminate with the bag being single sided to seal the outer face of the laminate to the mold. The open end is sealed and the air is drawn out of the bag through a nipple using a vacuum pump. As a result, uniform pressure approaching one atmosphere is applied to the surfaces of the object inside the bag, holding parts together while the adhesive cures. The entire bag may be placed in a temperature-controlled oven, oil bath or water bath and gently heated to accelerate curing.

In commercial woodworking facilities vacuum bags are used to laminate curved and irregular shaped workpieces.

Vacuum bagging is widely used in the composites industry as well. Carbon fiber fabric and fiberglass, along with resins and epoxies are common materials laminated together with a vacuum bag operation.

Typically, polyurethane or vinyl materials are used to make the bag, which is commonly open at both ends. This gives access to the piece, or pieces to be glued. A plastic rod is laid onto the bag, which is then folded over the rod. A plastic sleeve with an opening in it, is then snapped over the rod. This procedure forms a seal at both ends of the bag, when the vacuum is ready to be drawn.

A "platen" is used inside the bag for the piece being glued to lay on. The platen has a series of small slots cut into it, to allow the air under it to be evacuated. The platen must have rounded edges and corners to prevent the vacuum from tearing the bag.

When a curved part is to be glued in a vacuum bag, it is important that the pieces being glued be placed over a solidly built form, or have an air bladder placed under the form. This air bladder has access to "free air" outside the bag. It is used to create an equal pressure under the form, preventing it from being crushed.

Pressure bag moulding

This process is related to vacuum bag moulding in exactly the same way as it sounds. A solid female mould is used along with a flexible male mould. The reinforcement is placed inside the female mould with just enough resin to allow the fabric to stick in place (wet lay up). A measured amount of resin is then liberally brushed indiscriminately into the mould and the mould is then clamped to a machine that contains the male flexible mould. The flexible male membrane is then inflated with heated compressed air or possibly steam. The female mould can also be heated. Excess resin is forced out along with trapped air. This process is extensively used in the production of composite helmets due to the lower cost of unskilled labor. Cycle times for a helmet bag moulding machine vary from 20 to 45 minutes, but the finished shells require no further curing if the moulds are heated.

Autoclave moulding

A process using a two-sided mould set that forms both surfaces of the panel. On the lower side is a rigid mould and on the upper side is a flexible membrane made from silicone or an extruded polymer film such as nylon. Reinforcement materials can be placed manually or robotically. They include continuous fibre forms fashioned into textile constructions. Most often, they are pre-impregnated with the resin in the form of prepreg fabrics or unidirectional tapes. In some instances, a resin film is placed upon the lower mould and dry reinforcement is placed above. The upper mould is installed and vacuum is applied to the mould cavity. The assembly is placed into an autoclave. This process is generally performed at both elevated pressure and elevated temperature. The use of elevated pressure facilitates a high fibre volume fraction and low void content for maximum structural efficiency.

Resin transfer moulding (RTM)

A process using a two-sided mould set that forms both surfaces of the panel. The lower side is a rigid mould. The upper side can be a rigid or flexible mould. Flexible moulds can be made from composite materials, silicone or extruded polymer films such as nylon. The two sides fit together to produce a mould cavity. The distinguishing feature of resin transfer moulding is that the reinforcement materials are placed into this cavity and the mould set is closed prior to the introduction of matrix material. Resin transfer moulding includes numerous varieties which differ in the mechanics of how the resin is introduced to the reinforcement in the mould cavity. These variations include everything from vacuum infusion to vacuum assisted resin transfer moulding (VARTM). This process can be performed at either ambient or elevated temperature.

Other

Other types of moulding include press moulding, transfer moulding, pultrusion moulding, filament winding, casting, centrifugal casting and continuous casting. There are also forming capabilities including CNC filament winding, vacuum infusion, wet lay-up, compression moulding, and thermoplastic moulding, to name a few. The use of curing ovens and paint booths is also needed for some projects.

Tooling

Some types of tooling materials used in the manufacturing of composites structures include invar, steel, aluminium, reinforced silicone rubber, nickel, and carbon fibre. Selection of the tooling material is typically based on, but not limited to, the coefficient of thermal expansion, expected number of cycles, end item tolerance, desired or required surface condition, method of cure, glass transition temperature of the material being moulded, moulding method, matrix, cost and a variety of other considerations.

Properties

Mechanics

The physical properties of composite materials are generally not isotropic (independent of direction of applied force) in nature, but rather are typically orthotropic (different depending on the direction of the applied force or load). For instance, the stiffness of a composite panel will often depend upon the orientation of the applied forces and/or moments. Panel stiffness is also dependent on the design of the panel. For instance, the fibre reinforcement and matrix used, the method of panel build, thermoset versus thermoplastic, type of weave, and orientation of fibre axis to the primary force.

In contrast, isotropic materials (for example, aluminium or steel), in standard wrought forms, typically have the same stiffness regardless of the directional orientation of the applied forces and/or moments.

The relationship between forces/moments and strains/curvatures for an isotropic material can be described with the following material properties: Young's Modulus, the shear Modulus and the Poisson's ratio, in relatively simple mathematical relationships. For the anisotropic material, it requires the mathematics of a second order tensor and up to 21 material property constants. For the special case of orthogonal isotropy, there are three different material property constants for each of Young's Modulus, Shear Modulus and Poisson's ratio—a total of 9 constants to describe the relationship between forces/moments and strains/curvatures.

Techniques that take advantage of the anisotropic properties of the materials include mortise and tenon joints (in natural composites such as wood) and Pi Joints in synthetic composites.

Resins

Typically, most common composite materials, including fiberglass, carbon fiber, and Kevlar, include at least two parts, the substrate and the resin.

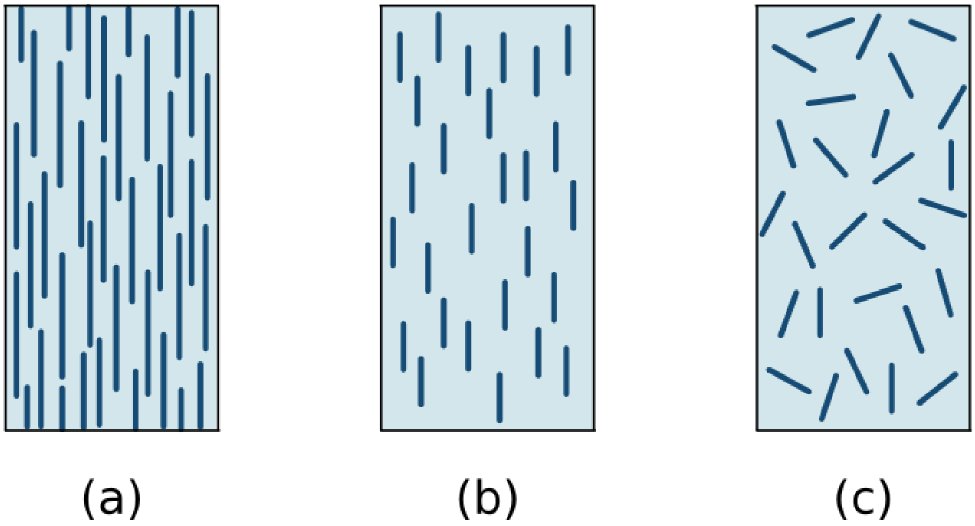
Polyester resin tends to have yellowish tint, and is suitable for most backyard projects. Its weaknesses are that it is UV sensitive and can tend to degrade over time, and thus generally is also coated to help preserve it. It is often used in the making of surfboards and for marine applications. Its hardener is a MEKP, and is mixed at 14 drops per oz. MEKP is composed of methyl ethyl ketone peroxide, a catalyst. When MEKP is mixed with the resin, the resulting chemical reaction causes heat to build up and cure or harden the resin.

Vinylester resin tends to have a purplish to bluish to greenish tint. This resin has lower viscosity than polyester resin, and is more transparent. This resin is often billed as being fuel resistant, but will melt in contact with gasoline. This resin tends to be more resistant over time to degradation than polyester resin, and is more flexible. It uses the same hardener as polyester resin (at the same mix ratio) and the cost is approximately the same.

Epoxy resin is almost totally transparent when cured. In the aerospace industry, epoxy is used as a structural matrix material or as a structural glue.

Shape memory polymer (SMP) resins have varying visual characteristics depending on their formulation. These resins may be epoxy-based, which can be used for auto body and outdoor equipment repairs; cyanate-ester-based, which are used in space applications; and acrylate-based, which can be used in very cold temperature applications, such as for sensors that indicate whether perishable goods have warmed above a certain maximum temperature. These resins are unique in that their shape can be repeatedly changed by heating above their glass transition temperature (T_g). When heated, they become flexible and elastic, allowing for easy configuration. Once they are cooled, they will maintain their new shape. The resins will return to their original shapes when they are reheated above their T_g. The advantage of shape memory polymer resins is that they can be shaped and reshaped repeatedly without losing their material properties, and these resins can be used in fabricating shape memory composites.

Categories of fiber-reinforced composite materials



Typologies of fibre-reinforced composite materials:
a) continuous fibre-reinforced
b) discontinuous aligned fibre-reinforced
c) discontinuous random-oriented fibre-reinforced.

Fiber-reinforced composite materials can be divided into two main categories normally referred to as short fiber-reinforced materials and continuous fiber-reinforced materials. Continuous reinforced materials will often constitute a layered or laminated structure. The woven and continuous fibre styles are typically available in a variety of forms, being pre-impregnated with the given matrix (resin), dry, uni-directional tapes of various widths, plain weave, harness satins, braided, and stitched.

The short and long fibers are typically employed in compression moulding and sheet moulding operations. These come in the form of flakes, chips, and random mate (which can also be made from a continuous fibre laid in random fashion until the desired thickness of the ply / laminate is achieved).

Failure

Shock, impact, or repeated cyclic stresses can cause the laminate to separate at the interface between two layers, a condition known as delamination. Individual fibres can separate from the matrix e.g. fibre pull-out.

Composites can fail on the microscopic or macroscopic scale. Compression failures can occur at both the macro scale or at each individual reinforcing fibre in compression buckling. Tension failures can be net section failures of the part or degradation of the composite at a microscopic scale where one or more of the layers in the composite fail in tension of the matrix or failure the bond between the matrix and fibres.

Some composites are brittle and have little reserve strength beyond the initial onset of failure while others may have large deformations and have reserve energy absorbing capacity past the onset of damage. The variations in fibres and matrices that are available and the mixtures that can be made with blends leave a very broad range of properties that can be designed into a composite structure. The best known failure of a brittle ceramic matrix composite occurred when the carbon-carbon composite tile on the leading edge of the wing of the Space Shuttle Columbia fractured when impacted during take-off. It led to catastrophic break-up of the vehicle when it re-entered the Earth's atmosphere on 1 February 2003.

Compared to metals, composites have relatively poor bearing strength.

Testing

To aid in predicting and preventing failures, composites are tested before and after construction. Pre-construction testing may use finite element analysis (FEA) for ply-by-ply analysis of curved surfaces and predicting wrinkling, crimping and dimpling of composites. Materials may be tested after construction through several nondestructive methods including ultrasonics, thermography, shearography and X-ray radiography

Examples

Materials

Fibre-reinforced polymers or FRPs include wood (comprising cellulose fibres in a lignin and hemicellulose matrix), carbon-fibre reinforced plastic or CFRP, and glass-reinforced plastic or GRP. If classified by matrix then there are thermoplastic composites, short fibre thermoplastics, long fibre thermoplastics or long fibre-reinforced thermoplastics. There are numerous thermoset composites, but advanced systems usually incorporate aramid fibre and carbon fibre in an epoxy resin matrix.

Shape memory polymer composites are high-performance composites, formulated using fibre or fabric reinforcement and shape memory polymer resin as the matrix. Since a shape memory polymer resin is used as the matrix, these composites have the ability to be easily manipulated into various configurations when they are heated above their activation temperatures and will exhibit high strength and stiffness at lower temperatures. They can also be reheated and reshaped repeatedly without losing their material properties. These composites are ideal for applications such as lightweight, rigid, deployable structures; rapid manufacturing; and dynamic reinforcement.

Composites can also use metal fibres reinforcing other metals, as in metal matrix composites or MMC. The benefit of magnesium is that it does not degrade in outer space.

Ceramic matrix composites include bone (hydroxyapatite reinforced with collagen fibres), Cermet (ceramic and metal) and concrete. Ceramic matrix composites are built primarily for toughness, not for strength. Organic matrix/ceramic aggregate composites include asphalt concrete, mastic asphalt, mastic roller hybrid, dental composite, syntactic foam and mother of pearl. Chobham armour is a special type of composite armour used in military applications.

Additionally, thermoplastic composite materials can be formulated with specific metal powders resulting in materials with a density range from 2 g/cm³ to 11 g/cm³ (same density as lead). The most common name for this type of material is High Gravity Compound (HGC), although Lead Replacement is also used. These materials can be used in place of traditional materials such as aluminium, stainless steel, brass, bronze, copper, lead, and even tungsten in weighting, balancing (for example, modifying the centre of gravity of a tennis racquet), vibration dampening, and radiation shielding applications. High density composites are an economically viable option when certain materials are deemed hazardous and are banned (such as lead) or when secondary operations costs (such as machining, finishing, or coating) are a factor.

Engineered wood includes a wide variety of different products such as plywood, oriented strand board, wood plastic composite (recycled wood fibre in polyethylene matrix), Pykrete (sawdust in ice matrix), Plastic-impregnated or laminated paper or textiles, Arborite, Formica (plastic) and Micarta. Other engineered laminate composites, such as Mallite, use a central core of end grain balsa wood, bonded to surface skins of light alloy or GRP. These generate low-weight, high rigidity materials.

Products

Composite materials have gained popularity (despite their generally high cost) in high-performance products that need to be lightweight, yet strong enough to take harsh loading conditions such as aerospace components (tails, wings, fuselages, propellers), boat and scull hulls, bicycle frames and racing car bodies. Other uses include fishing rods, storage tanks, and baseball bats. The new Boeing 787 structure including the wings and fuselage is composed largely of composites. Composite materials are also becoming more common in the realm of orthopedic surgery.

Carbon composite is a key material in today's launch vehicles and spacecraft. It is widely used in solar panel substrates, antenna reflectors and yokes of spacecraft. It is also used in payload adapters, inter-stage structures and heat shields of launch vehicles.

In 2007, an all-composite military High Mobility Multi-purpose Wheeled Vehicle (HMMWV or Hummvee) was introduced by TPI Composites Inc and Armor Holdings Inc, the first all-composite military vehicle. By using composites the vehicle is lighter, allowing higher payloads. In 2008, carbon fiber and DuPont Kevlar (five times stronger than steel) were combined with enhanced thermoset resins to make military transit cases by ECS Composites creating 30-percent lighter cases with high strength.

Recently, composite materials are designed such that the material will have more than one specific function therefore multi function structures emerge as a new technology.

Many composite layup designs also include a co-curing or post-curing of the prepreg with various other mediums, such as honeycomb or foam. This is commonly called a sandwich structure. This is a more common layup process for the manufacture of radomes, doors, cowlings, or non-structural parts.

The finishing of the composite parts is also critical in the final design. Many of these finishes will include rain-erosion coatings or polyurethane coatings.

Biomaterials

The development of **biomaterials**, as a science is about fifty years old. The study of biomaterials is called biomaterials science. It has experienced steady and strong growth over its history, with many companies investing large amounts of money into the development of new products. Biomaterials science encompasses elements of medicine, biology, chemistry, tissue engineering and materials science.

The iridescent nacre inside a Nautilus shell

Introduction

Biomaterials can generally be produced either in nature or synthesized in the laboratory using a variety of chemical approaches utilizing metallic components or ceramics. They are often used and/or adapted for a medical application, and thus comprises whole or part of a living structure or biomedical device which performs, augments, or replaces a natural function. Such functions may be benign, like being used for a heart valve, or may be bioactive with a more interactive functionality such as hydroxy-apatite coated hip implants. Biomaterials are also used every day in dental applications, surgery, and drug delivery. E.G. A construct with impregnated pharmaceutical products can be placed into the body, which permits the prolonged release of a drug over an extended period of time. A biomaterial may also be an autograft, allograft or xenograft used as a transplant material.

Materials scientists are currently paying more and more attention to the process inorganic crystallization within a largely organic matrix of naturally occurring compounds. This process typically generally occurs at ambient temperature and pressure. Interestingly, the vital organisms through which these crystalline minerals form are capable of consistently producing intricately complex structures. Understanding the processes in which living organisms are capable of regulating the growth of crystalline minerals such as silica could lead to significant scientific advances and novel synthesis techniques for nanoscale composite materials -- or nanocomposites.

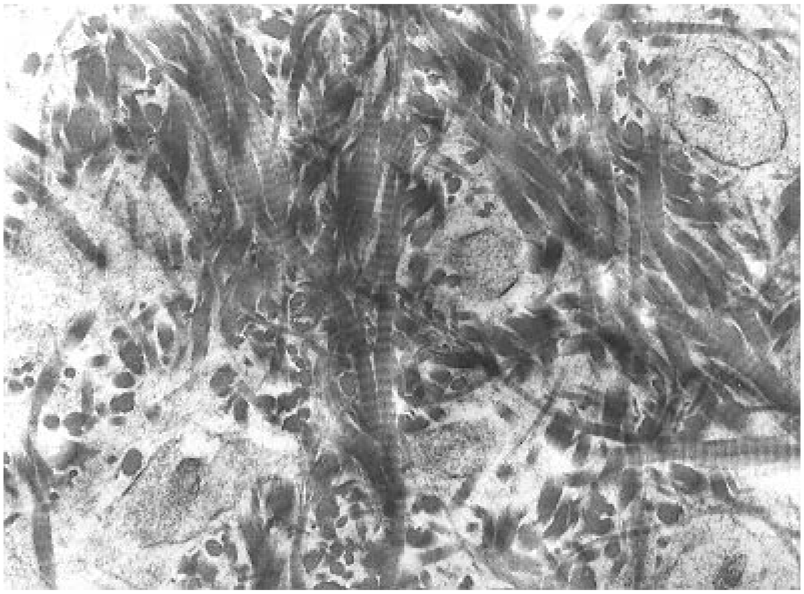
Biomineralization

Biomineralization (e.g. silicification) is quite common in the biological world and occurs in bacteria, single-celled organisms, plants (e.g. petrified wood), and animals (invertebrates and vertebrates). Crystalline minerals formed in this type of environment often show exceptional mechanical properties (e.g. strength, hardness, fracture toughness) and tend to form hierarchical structures that exhibit microstructural order over a range of length or spatial scales. The minerals are typically crystallized from an environment that is undersaturated with respect to certain metallic elements such as silicon, calcium and phosphorus, which are readily oxidized under conditions of neutral pH and low temperature (0 - 40 degrees C). Formation of the mineral may occur either within or outside of the cell wall of an organism, and specific biochemical reactions for mineral deposition exist that include lipids, proteins and carbohydrates. The significance of the cellular machinery cannot be overemphasized, and it is with advances in experimental techniques in cellular biology and the capacity to mimic the biological environment that significant progress is currently being reported.

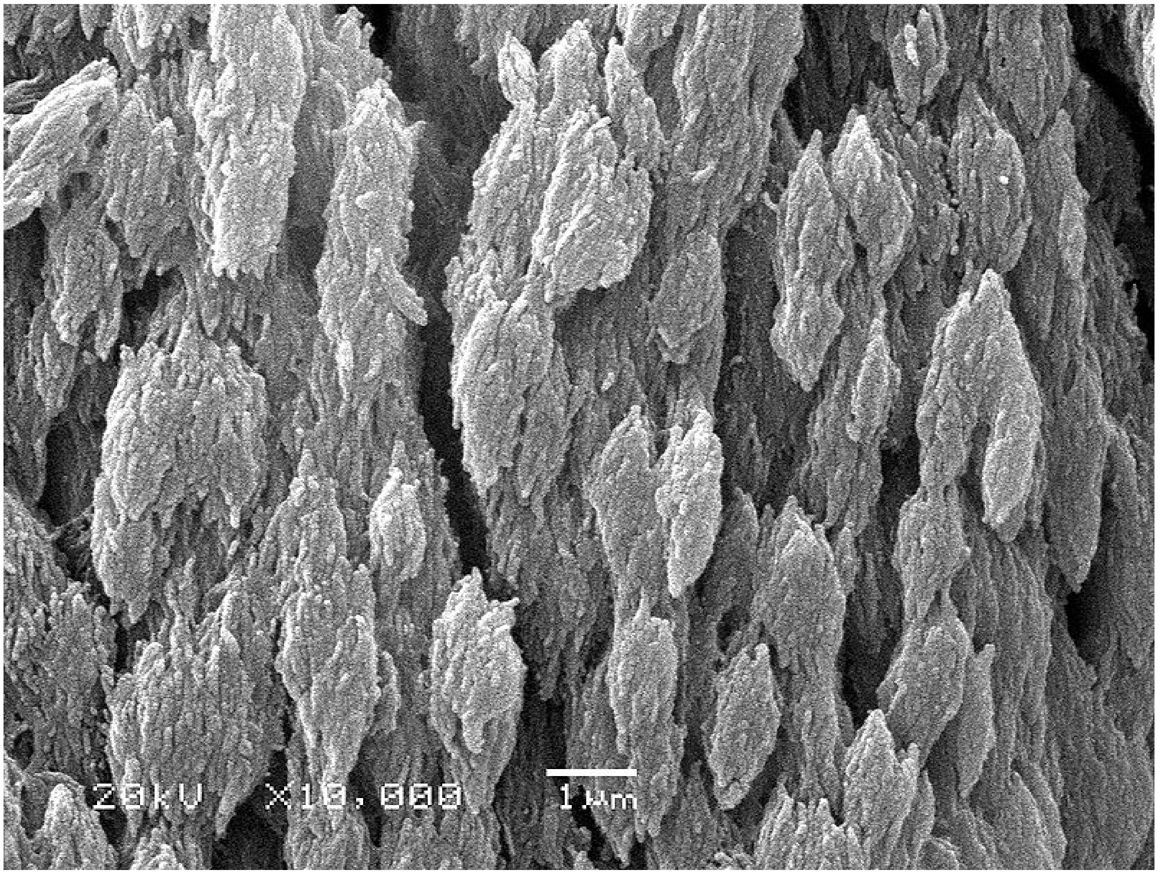
Sand from Pismo Beach, California including quartz, shell and rock fragments

Examples include silicates in algae and diatoms, carbonates in invertebrates, and calcium phosphates and carbonates in vertebrates. These minerals often form structural features such as sea shells and the bone mineral in mammals and birds. Organisms have been producing mineralized skeletons for nearly 600 million years. The most common biominerals are the phosphate and carbonate salts of calcium that are used in conjunction with organic polymers such as collagen and chitin to give mechanical strength to bones and shells. Other examples include copper, iron and gold deposits involving bacteria.

Thus, most natural (or biological) materials are complex composites whose mechanical properties are often outstanding, considering the weak constituents from which they are assembled. These complex structures, which have risen from hundreds of million years of evolution, are inspiring materials scientists interested primarily in the design of novel materials with exceptional physical properties for high performance in adverse conditions. Their defining characteristics such as hierarchy, multifunctionality, and the capacity for self-healing, are currently being investigated.



Collagen fibers of woven bone



SEM 10,000x magnification of crystalline bone mineral

The basic building blocks begin with the 20 amino acids and proceed to polypeptides and polysaccharides. These, in turn, compose the basic proteins, which are the primary constituents of the 'soft tissues' common to most biominerals. With well over 1000 proteins possible, current research emphasizes the use of collagen, chitin, keratin, and elastin. The 'hard' phases are often strengthened by crystalline minerals, which nucleate and grow in a biomediated environment that determines the size, shape and distribution of individual crystals. The most important silicate phases have been identified as hydroxyapatite, silica, and aragonite. Using the classification of Wegst and Ashby, the principal mechanical characteristics and structures of a number of biological ceramics, polymer composites, elastomers, and cellular materials have been recently characterized. Selected systems in each class are being investigated with emphasis on the relationship between their microstructure over a range of length scales and their mechanical response (esp. fracture toughness).

Thus, the crystallization of inorganic materials in nature generally occurs at ambient temperature and pressure. Yet the vital organisms through which these minerals form are capable of consistently producing extremely precise and complex structures. Understanding the processes in which living organisms control the growth of crystalline minerals such as silica could lead to significant advances in the field materials science, and open the door to novel synthesis techniques for nanoscale composite materials, or nanocomposites.

Abalone shell

Recently, the nacre from the nautilus shell of the abalone has become one of the more intensively studied biological structures in materials science community. The highly ordered microscale aragonite tiles separated by thin nanoscale organic sheets along with a macrostructure of larger periodic growth bands form a hierarchical composite. Early work showed that the overall composite consists of only 5 wt.% organic material—yet the work to fracture was increased by up to 3000 times over inorganic CaCO3 crystals as a result of the intricate hierarchy of structural organization. High-resolution SEM observations have since been performed on the microstructure of nacre. Clearly visible in these images are the neatly stacked (or ordered) mineral tiles separated by thin organic sheets along with a macrostructure of larger periodic growth bands which collectively form a hierarchical composite structure.

The process of mineral formation following periods of growth interruption (growth bands) has been described by several authors. Flat pearl implantation as well as a new trepanning method have been used to observe the transitory phases of calcium carbonate which nucleate and grow during this process. An initial random nucleation of the aragonite polymorph is observed. This nucleation and growth process is followed by a transition towards spherulitic growth. During this transition, the structural characteristics of the organism is determined by a combination of mechanical and chemical actions. About 6 weeks after implantation, a steady-state growth of aragonite tiles begins after shorter and more irregular tiles cover the outer surface of the spherulites. Finally, an organic scaffolding is observed during the steady-state growth of tiled aragonite.

In addition, observations of mineral growth following the deposition of these membranes confirm the presence of mineral bridges originating from subsurface tiles and extending through the organic matrix. Field emission scanning electron microscopy as well as TEM work on fractured deproteinated (deproteination) nacre have revealed the presence of mineral bridges existing between individual layers of tiles. These nanoscale bridges have been identified as the origins of the extreme fracture toughness of this biomaterial.

Recent joint collaboration at UC Santa Barbara and UC San Diego has produced striking results, including high resolution SEM images of the microstructure of the mother-of-pearl (or nacre) portion of the abalone shell, which exhibits the *highest mechanical strength and fracture toughness of any non-metallic substance known*.

Self-assembly

Self-assembly is the most common term in use in the modern scientific community to describe the spontaneous aggregation of particles (atoms, molecules, colloids, micelles, etc.) without the influence of any external forces. Large groups of such particles are known to assemble themselves into thermodynamically stable, structurally well-defined arrays, quite reminiscent of one of the 7 crystal systems found in metallurgy and mineralogy (e.g. face-centered cubic, body-centered cubic, etc.). The fundamental difference in equilibrium structure is in the spatial scale of the unit cell (or lattice parameter) in each particular case.

Molecular self-assembly is found widely in biological systems and provides the basis of a wide variety of complex biological structures. This includes an emerging class of mechanically superior biomaterials based on microstructural features and designs found in nature. Thus, self-assembly is also emerging as a new strategy in chemical synthesis and nanotechnology. Molecular crystals, liquid crystals, colloids, micelles, emulsions, phase-separated polymers, thin films and self-assembled monolayers all represent examples of the types of highly ordered structures which are obtained using these techniques. The distinguishing feature of these methods is self-organization.

Structural hierarchy

Nearly all materials could be seen as hierarchically structured, especially since the changes in spatial scale bring about different mechanisms of deformation and damage. However, in biological materials this hierarchical organization is inherent to the microstructure. One of the first examples of this, in the history of structural biology, is the early X-Ray scattering work on the hierarchical structure of hair and wool by Astbury and Woods. In bone, for example, collagen is the building block of the organic matrix—a triple helix with diameter of 1.5 nm. These tropocollagen molecules are intercalated with the mineral phase (hydroxyapatite, a calcium phosphate) forming fibrils that curl into helicoids of alternating directions. These "osteons" are the basic building blocks of bones, with the volume fraction distribution between organic and mineral phase being about 60/40. In another level of complexity, the hydroxyapatite crystals are platelets that have a diameter of approximately 70–100 nm and thickness of 1 nm. They originally nucleate at the gaps between collagen fibrils.

Similarly, the hierarchy of abalone shell begins at the nanolevel, with an organic layer having a thickness of 20–30 nm. This layer proceeds with single crystals of aragonite (a polymorph of CaCO3) consisting of "bricks" with dimensions of 0.5 and finishing with layers approximately 0.3 mm (mesostructure).

Crabs are arthropods whose carapace is made of a mineralized hard component (which exhibits brittle fracture) and a softer organic component composed primarily of chitin. The brittle component is arranged in a helical pattern. Each of these mineral ‘rods’ (1 µm diameter) contains chitin–protein fibrils with approximately 60 nm diameter. These fibrils are made of 3 nm diameter canals which link the interior and exterior of the shell.

Applications

Biomaterials are used in:

- Joint replacements
- Bone plates
- Bone cement
- Artificial ligaments and tendons
- Dental implants for tooth fixation
- Blood vessel prostheses
- Heart valves
- Skin repair devices (artificial tissue)
- Cochlear replacements
- Contact lenses
- Breast implants

Biomaterials must be compatible with the body, and there are often issues of biocompatibility which must be resolved before a product can be placed on the market and used in a clinical setting. Because of this, biomaterials are usually subjected to the same requirements of those undergone by new drug therapies. All manufacturing companies are also required to ensure traceability of all of their products so that if a defective product is discovered, others in the same batch may be traced.

Heart valves

In the United States, 45% of the 250,000 valve replacement procedures performed annually involve a mechanical valve implant. The most widely used valve is a bileaflet disc heart valve, or St. Jude valve. The mechanics involve two semicircular discs moving back and forth, with both allowing the flow of blood as well as the ability to form a seal against backflow. The valve is coated with pyrolytic carbon, and secured to the surrounding tissue with a mesh of woven fabric called Dacron^{TM} (du Pont's trade name for polyethylene terephthalate). The mesh allows for the body's tissue to grow while incorporating the valve.

Skin repair

Most of the time "artificial" tissue is grown from the patients own cells. However, when the damage is so extreme that it is impossible to use the patient's own cells, artificial tissue cells are grown. The difficulty is in finding a scaffold that the cells can grow and organize on. The characteristics of the scaffold must be that it is biocompatible, cells can adhere to the scaffold, mechanically strong and biodegradable. One successful scaffold is a copolymer of lactic acid and glycolic acid.

Compatibility

Biocompatibility is related to the behavior of biomaterials in various environments under various chemical and physical conditions. The term may refer to specific properties of a material without specifying where or how the material is to be used. For example, a material may elicit little or no immune response in a given organism, and may or may not able to integrate with a particular cell type or tissue). The ambiguity of the term reflects the ongoing development of insights into how biomaterials interact with the human body and eventually how those interactions determine the clinical success of a medical device (such as pacemaker or hip replacement. Modern medical devices and prostheses are often made of more than one material—so it might not always be sufficient to talk about the biocompatibility of a specific material.

Also, a material should not be toxic unless specifically engineered to be so—like "smart" drug delivery systems that target cancer cells and destroy them. Understanding of the anatomy and physiology of the action site is essential for a biomaterial to be effective. An additional factor is the dependence on specific anatomical sites of implantation. It is thus important, during design, to ensure that the implement will fit complementarily and have a beneficial effect with the specific anatomical area of action.

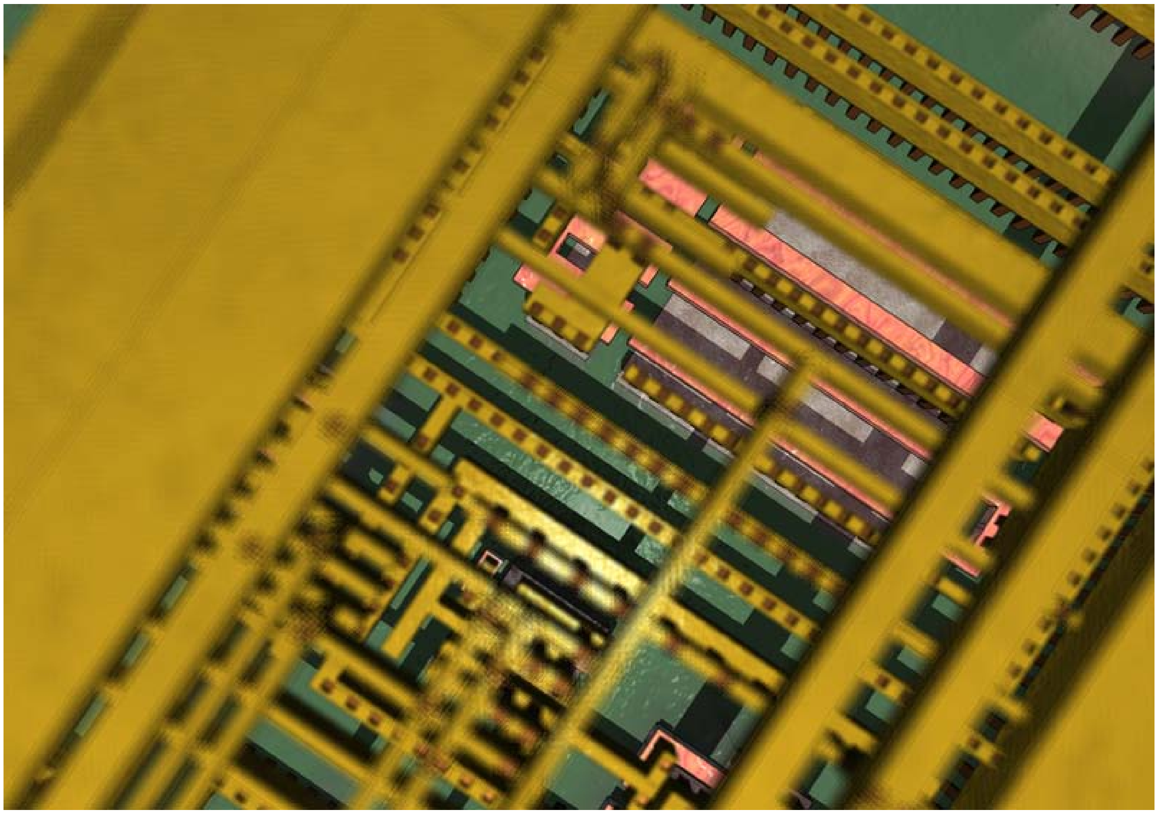
Biopolymers

Biopolymers are polymers produced by living organisms. Cellulose and starch, proteins and peptides, and DNA and RNA are all examples of biopolymers, in which the monomeric units, respectively, are sugars, amino acids, and nucleotides. Cellulose is both the most common biopolymer and the most common organic compound on Earth. About 33% of all plant matter is cellulose.

Some biopolymers are biodegradable. That is, they are broken down into CO_2 and water by microorganisms. In addition, some of these biodegradable biopolymers are compostable. That is, they can be put into an industrial composting process and will break down by 90% within 6 months. Biopolymers that do this can be marked with a 'compostable' symbol, under European Standard EN 13432 (2000). Packaging marked with this symbol can be put into industrial composting processes and will break down within 6 months (or less). An example of a compostable polymer is PLA film under 20 µm thick: films which are thicker than that do not qualify as compostable, even though they are biodegradable. A home composting logo may soon be established: this will enable consumers to dispose of packaging directly onto their own compost heap.

Chapter- 6

Semiconductor



Semiconductor chip on crystalline silicon substrate

A **semiconductor** is a material with electrical conductivity due to electron flow (as opposed to ionic conductivity) intermediate in magnitude between that of a conductor and an insulator. This means a conductivity roughly in the range of 10^3 to 10^{-8} siemens per centimeter. Semiconductor materials are the foundation of modern electronics, including radio, computers, telephones, and many other devices. Such devices include transistor, solar cells, many kinds of diodes including the light-emitting diode, the silicon controlled rectifier, and digital and analog integrated circuits. Similarly, semiconductor solar photovoltaic panels directly convert light energy into electrical energy. In a metallic conductor, current is carried by the flow of electrons. In semiconductors, current is often schematized as being carried either by the flow of electrons or by the flow of positively charged "holes" in the electron structure of the material. Actually, however, in both cases only electron movements are involved.

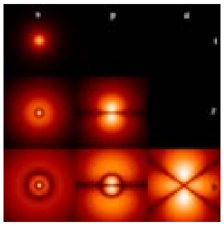
Common semiconducting materials are crystalline solids, but amorphous and liquid semiconductors are known. These include hydrogenated amorphous silicon and mixtures of arsenic, selenium and tellurium in a variety of proportions. Such compounds share with better known semiconductors intermediate conductivity and a rapid variation of conductivity with temperature, as well as occasional negative resistance. Such disordered materials lack the rigid crystalline structure of conventional semiconductors such as silicon and are generally used in thin film structures, which are less demanding for as concerns the electronic quality of the material and thus are relatively insensitive to impurities and radiation damage. Organic semiconductors, that is, organic materials with properties resembling conventional semiconductors, are also known.

Silicon is used to create most semiconductors commercially. Dozens of other materials are used, including germanium, gallium arsenide, and silicon carbide. A pure semiconductor is often called an “intrinsic” semiconductor. The electronic properties and the conductivity of a semiconductor can be changed in a controlled manner by adding very small quantities of other elements, called “dopants”, to the intrinsic material. In crystalline silicon typically this is achieved by adding impurities of boron or phosphorus to the melt and then allowing the melt to solidify into the crystal. This process is called "doping".

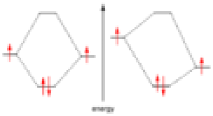
Explaining semiconductor energy bands

There are three popular ways to classify the electronic structure of a crystal.

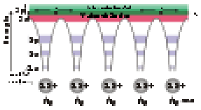
- Band structure



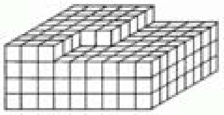
In a single H-atom an electron resides in well known orbitals. Note that the orbitals are called s,p,d in order of increasing circular current.



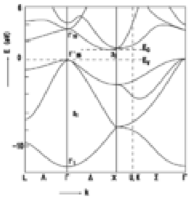
Putting two atoms together leads to delocalized orbitals across two atoms, yielding a covalent bond. Due to the Pauli exclusion principle, every state can contain



This can be continued with more atoms. Note: This picture shows a metal, not an actual semiconductor.



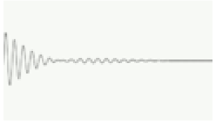
Continuing to add creates a crystal, which may then be cut into a tape and fused together at the ends to allow circular currents.



For this regular solid the band structure can be calculated or measured.

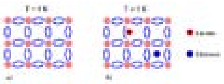
only one electron.

Integrating over the k axis gives the bands of a semiconductor showing a full valence band and an empty conduction band. Generally stopping at the vacuum level is undesirable, because some people want to calculate: photoemission, inverse photoemission



After the band structure is determined states can be combined to generate wave packets. As this is analogous to wave packages in free space, the results are similar.

An alternative description, which does not really appreciate the strong Coulomb interaction, shoots free electrons into the crystal and looks at the scattering.



A third alternative description uses strongly localized unpaired electrons in chemical bonds, which looks almost like a Mott insulator.

Energy bands and electrical conduction

In classic crystalline semiconductors, the electrons can have energies only within certain bands (i.e. ranges of levels of energy). Energetically, these bands are located between the energy of the ground state, corresponding to electrons tightly bound to the atomic nuclei of the material, and the free electron energy. The latter is the energy required for an electron to escape entirely from the material. The energy bands each correspond to a large number of discrete quantum states of the electrons, and most of the states with low energy (closer to the nucleus) are full, up to a particular band called the *valence band*. Semiconductors and insulators are distinguished from metals because the valence band in them is nearly filled with electrons under usual operating conditions, while very few (semiconductor) or virtually none (insulator) of them are available in the *conduction band*, the band immediately above the valence band.

The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the band gap between the bands. The size of this energy bandgap serves as an arbitrary dividing line (roughly 4 eV) between semiconductors and insulators.

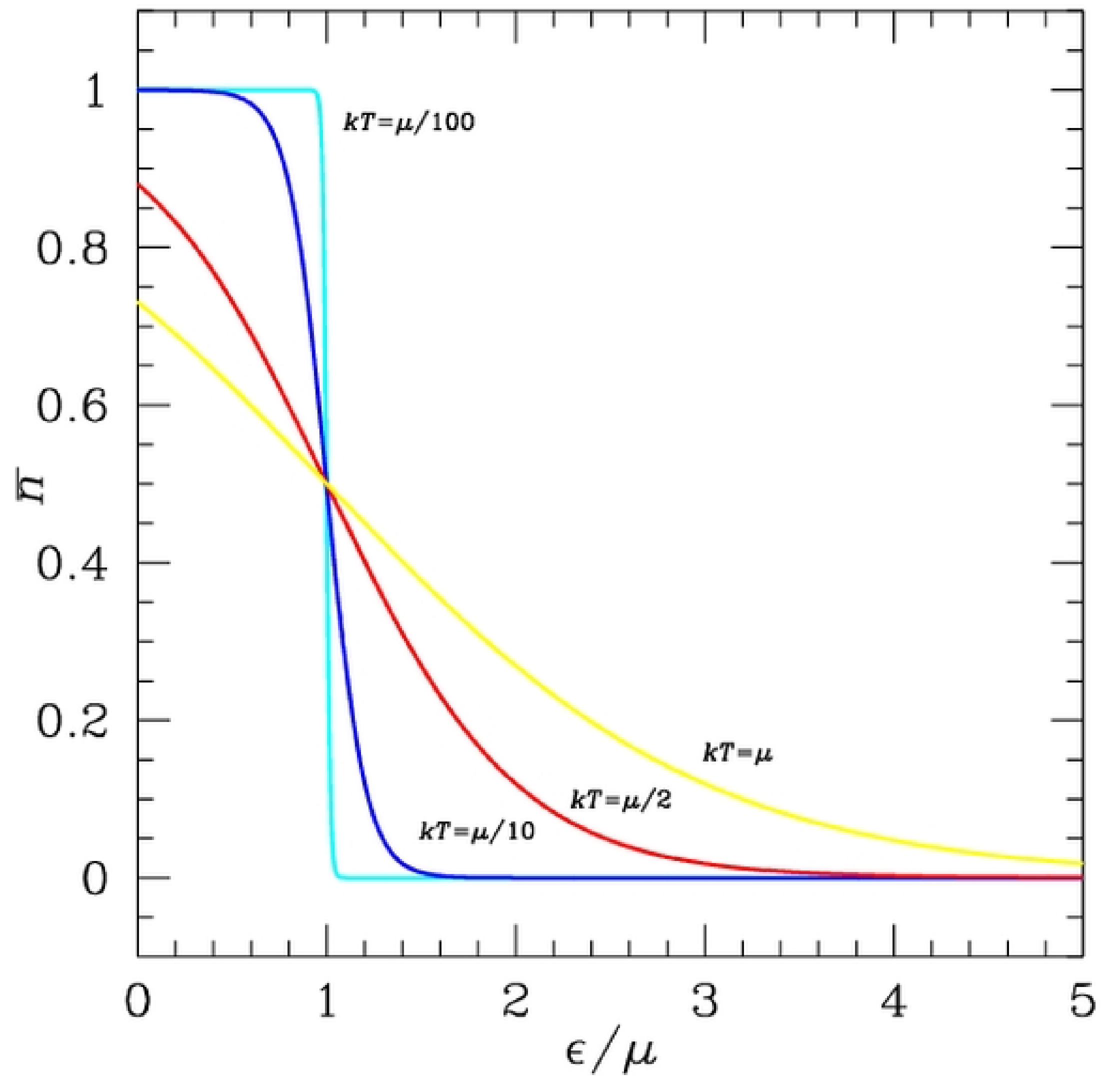
With covalent bonds, an electron moves by hopping to a neighboring bond. The Pauli exclusion principle requires the electron to be lifted into the higher anti-bonding state of that bond. For delocalized states, for example in one dimension – that is in a nanowire, for every energy there is a state with electrons flowing in one direction and another state with the electrons flowing in the other. For a net current to flow, more states for one direction than for the other direction must be occupied. For this to occur, energy is required, as in the semiconductor the next higher states lie above the band gap. Often this is stated as: full bands do not contribute to the electrical conductivity. However, as the temperature of a semiconductor rises above absolute zero, there is more energy in the semiconductor to spend on lattice vibration and — more importantly for us — on lifting some electrons into an energy states of the conduction band. The current-carrying electrons in the conduction band are known as "free electrons", although they are often simply called "electrons" if context allows this usage to be clear.

Electrons excited to the conduction band also leave behind electron holes, or unoccupied states in the valence band. Both the conduction band electrons and the valence band holes contribute to electrical conductivity. The holes themselves don't actually move, but a neighboring electron can move to fill the hole, leaving a hole at the place it has just come from, and in this way the holes appear to move, and the holes behave as if they were actual positively charged particles.

One covalent bond between neighboring atoms in the solid is ten times stronger than the binding of the single electron to the atom, so freeing the electron does not imply destruction of the crystal structure.

Holes: electron absence as a charge carrier

The concept of holes can also be applied to metals, where the Fermi level lies *within* the conduction band. With most metals the Hall effect indicates electrons are the charge carriers. However, some metals have a mostly filled conduction band. In these, the Hall effect reveals positive charge carriers, which are not the ion-cores, but holes. In the case of a metal, only a small amount of energy is needed for the electrons to find other unoccupied states to move into, and hence for current to flow. Sometimes even in this case it may be said that a hole was left behind, to explain why the electron does not fall back to lower energies: It cannot find a hole. In the end in both materials electron-phonon scattering and defects are the dominant causes for resistance.



Fermi-Dirac distribution. States with energy ε below the Fermi energy, here μ, have higher probability *n* to be occupied, and those above are less likely to be occupied. Smearing of the distribution increases with temperature.

The energy distribution of the electrons determines which of the states are filled and which are empty. This distribution is described by Fermi-Dirac statistics. The distribution is characterized by the temperature of the electrons, and the *Fermi energy* or *Fermi level*. Under absolute zero conditions the Fermi energy can be thought of as the energy up to which available electron states are occupied. At higher temperatures, the Fermi energy is the energy at which the probability of a state being occupied has fallen to 0.5.

The dependence of the electron energy distribution on temperature also explains why the conductivity of a semiconductor has a strong temperature dependency, as a semiconductor operating at lower temperatures will have fewer available free electrons and holes able to do the work.

Energy–momentum dispersion

In the preceding description an important fact is ignored for the sake of simplicity: the *dispersion* of the energy. The reason that the energies of the states are broadened into a band is that the energy depends on the value of the wave vector, or *k-vector*, of the electron. The k-vector, in quantum mechanics, is the representation of the momentum of a particle.

The dispersion relationship determines the effective mass, m^*, of electrons or holes in the semiconductor, according to the formula:

$$m^* = \hbar^2 \cdot \left[\frac{d^2E(k)}{dk^2}\right]^{-1} .$$

The effective mass is important as it affects many of the electrical properties of the semiconductor, such as the electron or hole mobility, which in turn influences the *diffusivity* of the charge carriers and the electrical conductivity of the semiconductor.

Typically the effective mass of electrons and holes are different. This affects the relative performance of *p-channel* and *n-channel* IGFETs.

The top of the valence band and the bottom of the conduction band might not occur at that same value of *k*. Materials with this situation, such as silicon and germanium, are known as *indirect bandgap* materials. Materials in which the band extrema are aligned in *k*, for example gallium arsenide, are called *direct bandgap* semiconductors. Direct gap semiconductors are particularly important in optoelectronics because they are much more efficient as light emitters than indirect gap materials.

Carrier generation and recombination

When ionizing radiation strikes a semiconductor, it may excite an electron out of its energy level and consequently leave a hole. This process is known as *electron–hole pair generation*. Electron-hole pairs are constantly generated from thermal energy as well, in the absence of any external energy source.

Electron-hole pairs are also apt to recombine. Conservation of energy demands that these recombination events, in which an electron loses an amount of energy larger than the band gap, be accompanied by the emission of thermal energy (in the form of phonons) or radiation (in the form of photons).

In some states, the generation and recombination of electron–hole pairs are in equipoise. The number of electron-hole pairs in the steady state at a given temperature is determined by quantum statistical mechanics. The precise quantum mechanical mechanisms of generation and recombination are governed by conservation of energy and conservation of momentum.

As the probability that electrons and holes meet together is proportional to the product of their amounts, the product is in steady state nearly constant at a given temperature, providing that there is no significant electric field (which might "flush" carriers of both types, or move them from neighbour regions containing more of them to meet together) or externally driven pair generation. The product is a function of the temperature, as the probability of getting enough thermal energy to produce a pair increases with temperature, being approximately $\exp(-E_G/kT)$, where k is Boltzmann's constant, T is absolute temperature and E_G is band gap.

The probability of meeting is increased by carrier traps—impurities or dislocations which can trap an electron or hole and hold it until a pair is completed. Such carrier traps are sometimes purposely added to reduce the time needed to reach the steady state.

Semi-insulators

Some materials are classified as **semi-insulators**. These have electrical conductivity nearer to that of electrical insulators. Semi-insulators find niche applications in micro-electronics, such as substrates for HEMT. An example of a common semi-insulator is gallium arsenide.

Doping

The property of semiconductors that makes them most useful for constructing electronic devices is that their conductivity may easily be modified by introducing impurities into their crystal lattice. The process of adding controlled impurities to a semiconductor is known as *doping*. The amount of impurity, or dopant, added to an *intrinsic* (pure) semiconductor varies its level of conductivity. Doped semiconductors are often referred to as *extrinsic*. By adding impurity to pure semiconductors, the electrical conductivity may be varied not only by the number of impurity atoms but also, by the type of impurity atom and the changes may be thousand folds and million folds. For example, 1 cm^3 of a metal or semiconductor specimen has a number of atoms on the order of 10^{22}. Since every atom in metal donates at least one free electron for conduction in metal, 1 cm^3 of metal contains free electrons on the order of 10^{22}. At the temperature close to 20 °C, 1 cm^3 of pure germanium contains about 4.2×10^{22} atoms and 2.5×10^{13} free electrons and 2.5×10^{13} holes (empty spaces in crystal lattice having positive charge) The addition of 0.001% of arsenic (an impurity) donates an extra 10^{17} free electrons in the same volume and the electrical conductivity increases about 10,000 times."

Dopants

The materials chosen as suitable dopants depend on the atomic properties of both the dopant and the material to be doped. In general, dopants that produce the desired controlled changes are classified as either electron acceptors or donors. A donor atom that activates (that is, becomes incorporated into the crystal lattice) donates weakly bound valence electrons to the material, creating excess negative charge carriers. These weakly bound electrons can move about in the crystal lattice relatively freely and can facilitate conduction in the presence of an electric field. (The donor atoms introduce some states under, but very close to the conduction band edge. Electrons at these states can be easily excited to the conduction band, becoming free electrons, at room temperature.) Conversely, an activated acceptor produces a hole. Semiconductors doped with *donor* impurities are called *n-type*, while those doped with *acceptor* impurities are known as *p-type*. The n and p type designations indicate which charge carrier acts as the material's majority carrier. The opposite carrier is called the minority carrier, which exists due to thermal excitation at a much lower concentration compared to the majority carrier.

For example, the pure semiconductor silicon has four valence electrons. In silicon, the most common dopants are IUPAC group 13 (commonly known as *group III*) and group 15 (commonly known as *group V*) elements. Group 13 elements all contain three valence electrons, causing them to function as acceptors when used to dope silicon. Group 15 elements have five valence electrons, which allows them to act as a donor. Therefore, a silicon crystal doped with boron creates a p-type semiconductor whereas one doped with phosphorus results in an n-type material.

Carrier concentration

The concentration of dopant introduced to an intrinsic semiconductor determines its concentration and indirectly affects many of its electrical properties. The most important factor that doping directly affects is the material's carrier concentration. In an intrinsic semiconductor under thermal equilibrium, the concentration of electrons and holes is equivalent. That is,

$$n = p = n_i.$$

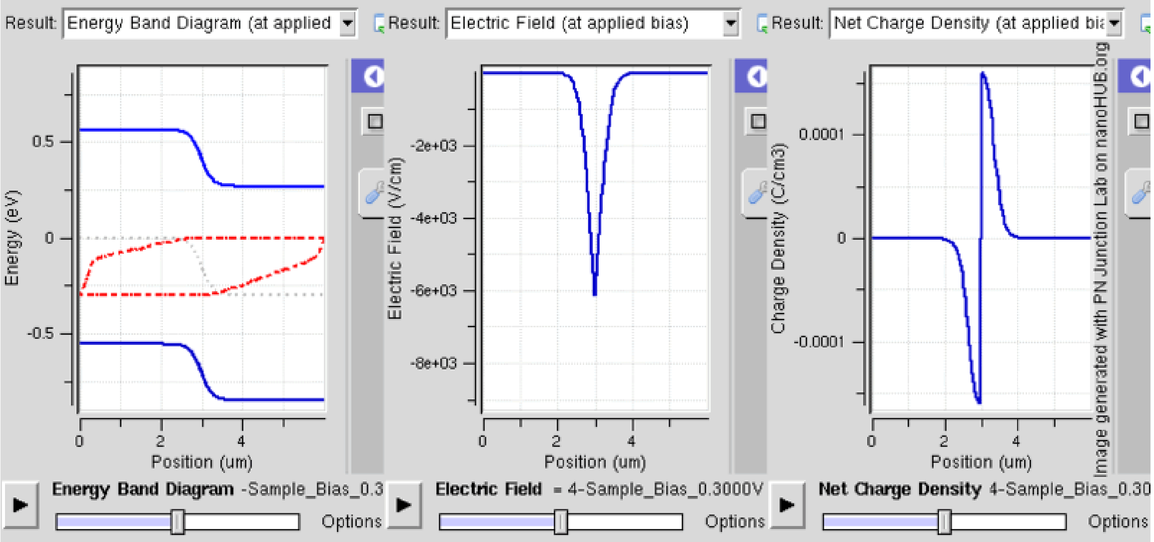
If we have a non-intrinsic semiconductor in thermal equilibrium the relation becomes:

$$n_0 \cdot p_0 = n_i^2$$

where n_0 is the concentration of conducting electrons, p_0 is the electron hole concentration, and n_i is the material's intrinsic carrier concentration. Intrinsic carrier concentration varies between materials and is dependent on temperature. Silicon's n_i, for example, is roughly 1.5×10^{10} cm^{-3} at 300 kelvins (room temperature).

In general, an increase in doping concentration affords an increase in conductivity due to the higher concentration of carriers available for conduction. Degenerately (very highly) doped semiconductors have conductivity levels comparable to metals and are often used in modern integrated circuits as a replacement for metal. Often superscript plus and minus symbols are used to denote relative doping concentration in semiconductors. For example, n^+ denotes an n-type semiconductor with a high, often degenerate, doping concentration. Similarly, p^- would indicate a very lightly doped p-type material. It is useful to note that even degenerate levels of doping imply low concentrations of impurities with respect to the base semiconductor. In crystalline intrinsic silicon, there are approximately 5×10^{22} atoms/cm³. Doping concentration for silicon semiconductors may range anywhere from 10^{13} cm^{-3} to 10^{18} cm^{-3}. Doping concentration above about 10^{18} cm^{-3} is considered degenerate at room temperature. Degenerately doped silicon contains a proportion of impurity to silicon on the order of parts per thousand. This proportion may be reduced to parts per billion in very lightly doped silicon. Typical concentration values fall somewhere in this range and are tailored to produce the desired properties in the device that the semiconductor is intended for.

Effect on band structure



Band diagram of PN junction operation in forward bias mode showing reducing depletion width. Both p and n junctions are doped at a 1e15/cm3 doping level, leading to built-in potential of ~0.59V. Reducing depletion width can be inferred from the shrinking charge profile, as fewer dopants are exposed with increasing forward bias .

Doping a semiconductor crystal introduces allowed energy states within the band gap but very close to the energy band that corresponds to the dopant type. In other words, donor impurities create states near the conduction band while acceptors create states near the valence band. The gap between these energy states and the nearest energy band is usually referred to as dopant-site bonding energy or E_B and is relatively small. For example, the E_B for boron in silicon bulk is 0.045 eV, compared with silicon's band gap of about 1.12 eV. Because E_B is so small, it takes little energy to ionize the dopant atoms and create free carriers in the conduction or valence bands. Usually the thermal energy available at room temperature is sufficient to ionize most of the dopant.

Dopants also have the important effect of shifting the material's Fermi level towards the energy band that corresponds with the dopant with the greatest concentration. Since the Fermi level must remain constant in a system in thermodynamic equilibrium, stacking layers of materials with different properties leads to many useful electrical properties. For example, the p-n junction's properties are due to the energy band bending that happens as a result of lining up the Fermi levels in contacting regions of p-type and n-type material.

This effect is shown in a *band diagram*. The band diagram typically indicates the variation in the valence band and conduction band edges versus some spatial dimension, often denoted x. The Fermi energy is also usually indicated in the diagram. Sometimes the *intrinsic Fermi energy*, E_i, which is the Fermi level in the absence of doping, is shown. These diagrams are useful in explaining the operation of many kinds of semiconductor devices.

Preparation of semiconductor materials

Semiconductors with predictable, reliable electronic properties are necessary for mass production. The level of chemical purity needed is extremely high because the presence of impurities even in very small proportions can have large effects on the properties of the material. A high degree of crystalline perfection is also required, since faults in crystal structure (such as dislocations, twins, and stacking faults) interfere with the semiconducting properties of the material. Crystalline faults are a major cause of defective semiconductor devices. The larger the crystal, the more difficult it is to achieve the necessary perfection. Current mass production processes use crystal ingots between 100 mm and 300 mm (4–12 inches) in diameter which are grown as cylinders and sliced into wafers.

Because of the required level of chemical purity and the perfection of the crystal structure which are needed to make semiconductor devices, special methods have been developed to produce the initial semiconductor material. A technique for achieving high purity includes growing the crystal using the Czochralski process. An additional step that can be used to further increase purity is known as zone refining. In zone refining, part of a solid crystal is melted. The impurities tend to concentrate in the melted region, while the desired material recrystalizes leaving the solid material more pure and with fewer crystalline faults.

In manufacturing semiconductor devices involving heterojunctions between different semiconductor materials, the lattice constant, which is the length of the repeating element of the crystal structure, is important for determining the compatibility of materials.