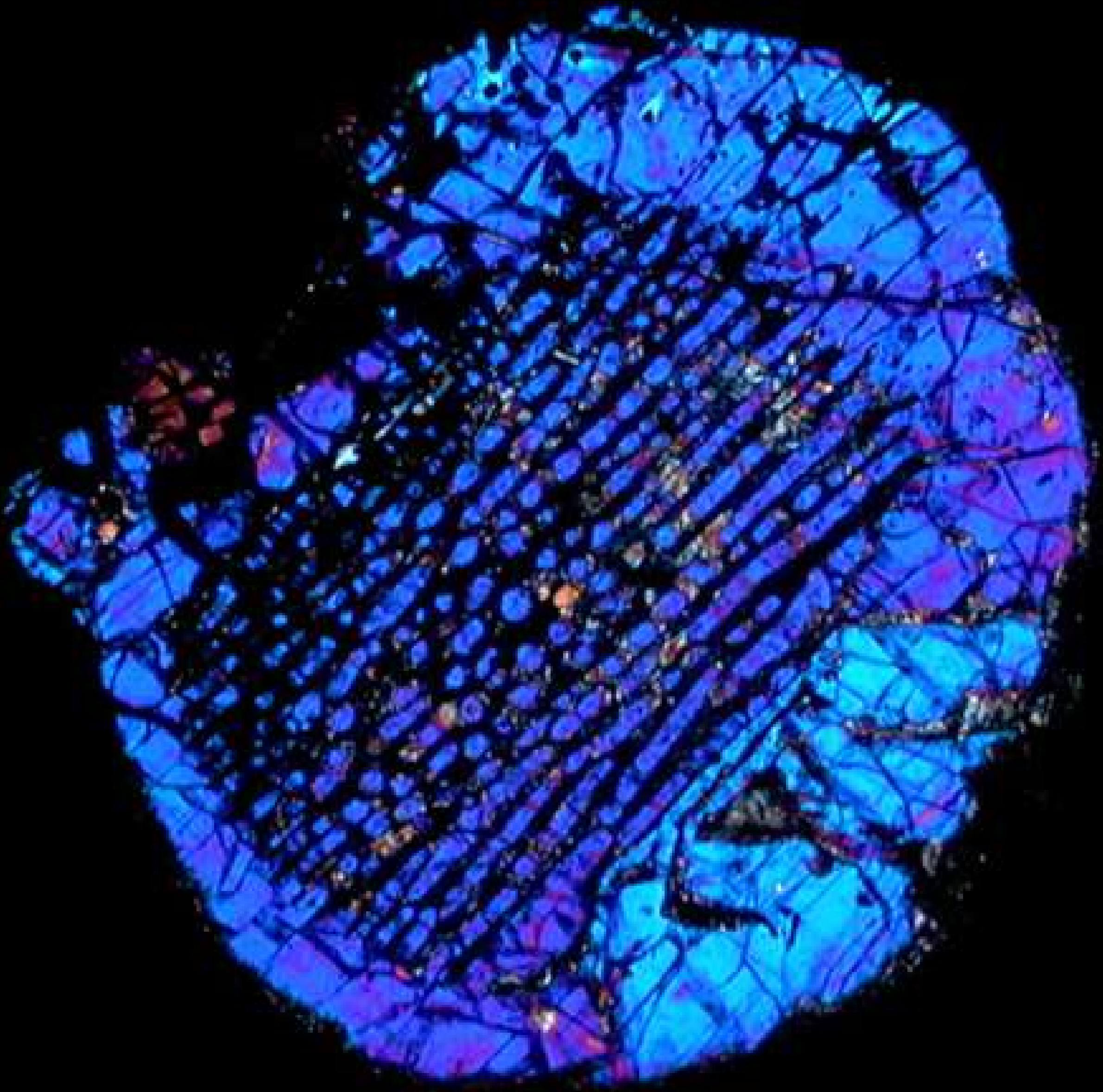
Materials Science



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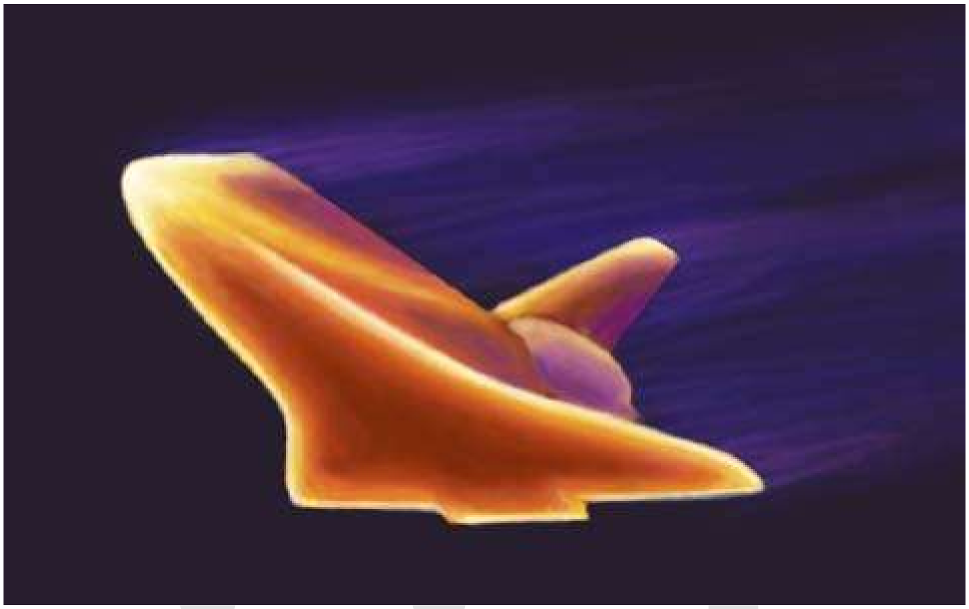


Simulation of the outside of the Space Shuttle as it heats up to over 1,500 °C (2,730 °F) during re-entry into the Earth's atmosphere

Materials science is an interdisciplinary field involving the properties of matter and its applications to various areas of science and engineering. This scientific field investigates the relationship between the structure of materials at atomic or molecular scales and their macroscopic properties. It incorporates elements of applied physics and chemistry. With significant media attention focused on nanoscience and nanotechnology in recent years, materials science has been propelled to the forefront at many universities. It is also an important part of forensic engineering and failure analysis. Materials science also deals with *fundamental properties* and *characteristics* of materials.

Fundamentals

In materials science, rather than haphazardly looking for and discovering materials and exploiting their properties, the aim is instead to understand materials so that new materials with the desired properties can be created.

The basis of materials science involves relating the desired properties and relative performance of a material in a certain application to the structure of the atoms and phases in that material through characterization. The major determinants of the structure of a material and thus of its properties are its constituent chemical elements and the way in which it has been processed into its final form. These characteristics, taken together and related through the laws of thermodynamics, govern a material's microstructure, and thus its properties.

The manufacture of a perfect crystal of a material is currently physically impossible. Instead materials scientists manipulate the defects in crystalline materials such as precipitates, grain boundaries (Hall-Petch relationship), interstitial atoms, vacancies or substitutional atoms, to create materials with the desired properties.

Not all materials have a regular crystal structure. Polymers display varying degrees of crystallinity, and many are completely non-crystalline. Glasses, some ceramics, and many natural materials are amorphous, not possessing any long-range order in their atomic arrangements. The study of polymers combines elements of chemical and statistical thermodynamics to give thermodynamic, as well as mechanical, descriptions of physical properties.

In addition to industrial interest, materials science has gradually developed into a field which provides tests for condensed matter or solid state theories. New physics emerge because of the diverse new material properties which need to be explained.

Materials in industry

Radical materials advances can drive the creation of new products or even new industries, but stable industries also employ materials scientists to make incremental improvements and troubleshoot issues with currently used materials. Industrial applications of materials science include materials design, cost-benefit tradeoffs in industrial production of materials, processing techniques (casting, rolling, welding, ion implantation, crystal growth, thin-film deposition, sintering, glassblowing, etc.), and analytical techniques (characterization techniques such as electron microscopy, x-ray diffraction, calorimetry, nuclear microscopy (HEFIB), Rutherford backscattering, neutron diffraction, small-angle X-ray scattering (SAXS), etc.

Besides material characterization, the material scientist/engineer also deals with the extraction of materials and their conversion into useful forms. Thus ingot casting, foundry techniques, blast furnace extraction, and electrolytic extraction are all part of the required knowledge of a metallurgist/engineer. Often the presence, absence or variation of minute quantities of secondary elements and compounds in a bulk material will have a great impact on the final properties of the materials produced, for instance, steels are classified based on 1/10th and 1/100 weight percentages of the carbon and other alloying elements they contain. Thus, the extraction and purification techniques employed in the extraction of iron in the blast furnace will have an impact of the quality of steel that may be produced.

The overlap between physics and materials science has led to the offshoot field of *materials physics*, which is concerned with the physical properties of materials. The approach is generally more macroscopic and applied than in condensed matter physics.

The study of metal alloys is a significant part of materials science. Of all the metallic alloys in use today, the alloys of iron (steel, stainless steel, cast iron, tool steel, alloy steels) make up the largest proportion both by quantity and commercial value. Iron alloyed with various proportions of carbon gives low, mid and high carbon steels. For the steels, the hardness and tensile strength of the steel is directly related to the amount of carbon present, with increasing carbon levels also leading to lower ductility and toughness. The addition of silicon and graphitization will produce cast irons (although some cast irons are made precisely with no graphitization). The addition of chromium, nickel and molybdenum to carbon steels (more than 10%) gives us stainless steels.

Other significant metallic alloys are those of aluminium, titanium, copper and magnesium. Copper alloys have been known for a long time (since the Bronze Age), while the alloys of the other three metals have been relatively recently developed. Due to the chemical reactivity of these metals, the electrolytic extraction processes required were only developed relatively recently. The alloys of aluminium, titanium and magnesium are also known and valued for their high strength-to-weight ratios and, in the case of magnesium, their ability to provide electromagnetic shielding. These materials are ideal for situations where high strength-to-weight ratios are more important than bulk cost, such as in the aerospace industry and certain automotive engineering applications.

Other than metals, polymers and ceramics are also an important part of materials science. Polymers are the raw materials (the resins) used to make what we commonly call plastics. Plastics are really the final product, created after one or more polymers or additives have been added to a resin during processing, which is then shaped into a final form. Polymers which have been around, and which are in current widespread use, include polyethylene, polypropylene, PVC, polystyrene, nylons, polyesters, acrylics, polyurethanes, and polycarbonates. Plastics are generally classified as "commodity", "specialty" and "engineering" plastics.

PVC (polyvinyl-chloride) is widely used, inexpensive, and annual production quantities are large. It lends itself to an incredible array of applications, from artificial leather to electrical insulation and cabling, packaging and containers. Its fabrication and processing are simple and well-established. The versatility of PVC is due to the wide range of plasticisers and other additives that it accepts. The term "additives" in polymer science refers to the chemicals and compounds added to the polymer base to modify its material properties.

Polycarbonate would be normally considered an engineering plastic (other examples include PEEK, ABS). Engineering plastics are valued for their superior strengths and other special material properties. They are usually not used for disposable applications, unlike commodity plastics.

Specialty plastics are materials with unique characteristics, such as ultra-high strength, electrical conductivity, electro-fluorescence, high thermal stability, etc.

The dividing line between the various types of plastics is not based on material but rather on their properties and applications. For instance, polyethylene (PE) is a cheap, low friction polymer commonly used to make disposable shopping bags and trash bags, and is considered a commodity plastic, whereas Medium-Density Polyethylene MDPE is used for underground gas and water pipes, and another variety called Ultra-high Molecular Weight Polyethylene UHMWPE is an engineering plastic which is used extensively as the glide rails for industrial equipment and the low-friction socket in implanted hip joints.

Another application of material science in industry is the making of composite materials. Composite materials are structured materials composed of two or more macroscopic phases. Applications range from structural elements such as steel-reinforced concrete, to the thermally insulative tiles which play a key and integral role in NASA's Space Shuttle thermal protection system which is used to protect the surface of the shuttle from the heat of re-entry into the Earth's atmosphere. One example is Reinforced Carbon-Carbon (RCC), The light gray material which withstands reentry temperatures up to 1510 °C (2750 °F) and protects the Space Shuttle's wing leading edges and nose cap. RCC is a laminated composite material made from graphite rayon cloth and impregnated with a phenolic resin. After curing at high temperature in an autoclave, the laminate is pyrolized to convert the resin to carbon, impregnated with furfural alcohol in a vacuum chamber, and cured/pyrolized to convert the furfural alcohol to carbon. In order to provide oxidation resistance for reuse capability, the outer layers of the RCC are converted to silicon carbide.

Other examples can be seen in the "plastic" casings of television sets, cell-phones and so on. These plastic casings are usually a composite material made up of a thermoplastic matrix such as acrylonitrile-butadiene-styrene (ABS) in which calcium carbonate chalk, talc, glass fibres or carbon fibres have been added for added strength, bulk, or electro-static dispersion. These additions may be referred to as reinforcing fibres, or dispersants, depending on their purpose.

Overview

- Nanotechnology – rigorously, the study of materials where the effects of quantum confinement, the Gibbs-Thomson effect, or any other effect only present at the nanoscale is the defining property of the material; but more commonly, it is the creation and study of materials whose defining structural properties are anywhere from less than a nanometer to one hundred nanometers in scale, such as molecularly engineered materials.
- Microtechnology - study of materials and processes and their interaction, allowing microfabrication of structures of micrometric dimensions, such as MicroElectroMechanical Systems (MEMS).

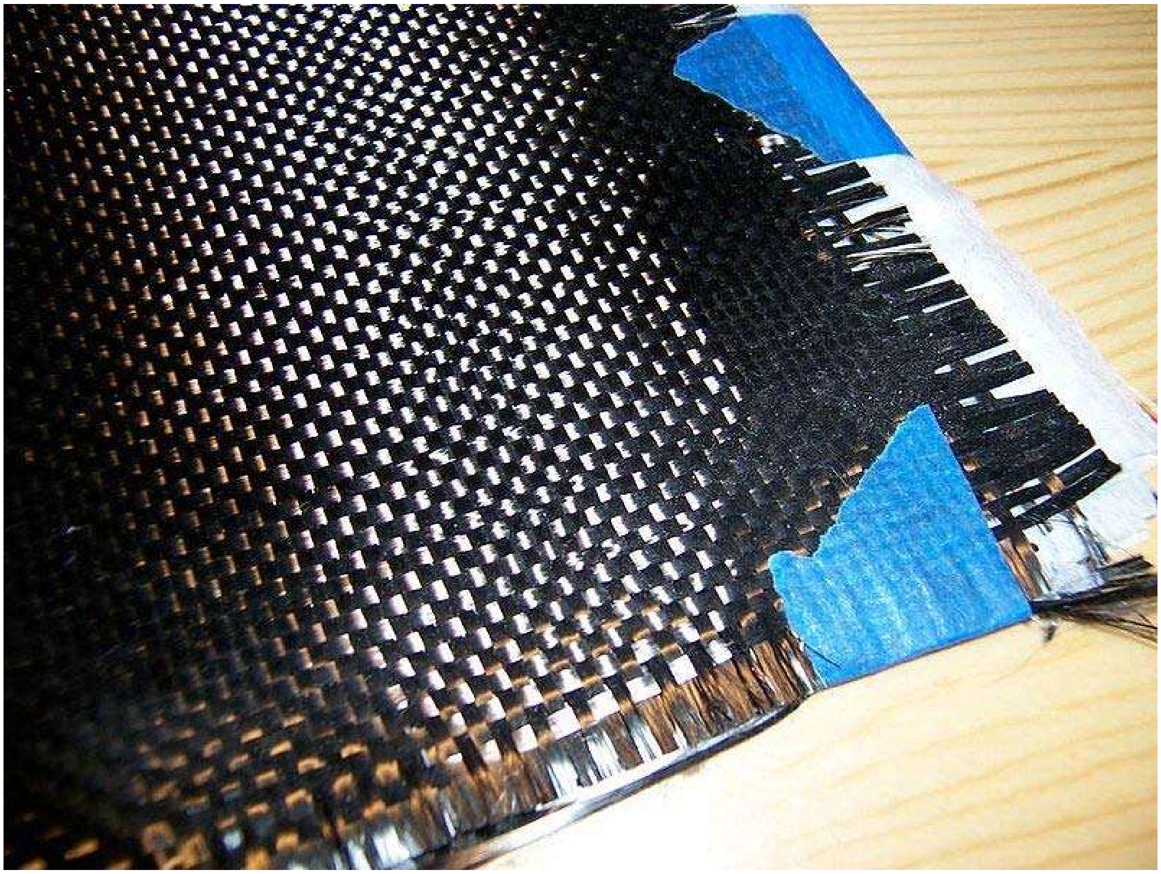
- Crystallography – the study of how atoms in a solid fill space, the defects associated with crystal structures such as grain boundaries and dislocations, and the characterization of these structures and their relation to physical properties.
- Materials Characterization – such as diffraction with x-rays, electrons, or neutrons, and various forms of spectroscopy and chemical analysis such as Raman spectroscopy, energy-dispersive spectroscopy (EDS), chromatography, thermal analysis, electron microscope analysis, etc., in order to understand and define the properties of materials.

Si_3N_4 ceramic bearing parts

- Metallurgy – the study of metals and their alloys, including their extraction, microstructure and processing.
- Biomaterials – materials that are derived from and/or used with biological systems.
- Electronic and magnetic materials – materials such as semiconductors used to create integrated circuits, storage media, sensors, and other devices.
- Tribology – the study of the wear of materials due to friction and other factors.
- Surface science/Catalysis – interactions and structures between solid-gas solid-liquid or solid-solid interfaces.

- Ceramography – the study of the microstructures of high-temperature materials and refractories, including structural ceramics such as RCC, polycrystalline silicon carbide and transformation toughened ceramics

Some practitioners often consider rheology a sub-field of materials science, because it can cover any material that flows. However, modern rheology typically deals with non-Newtonian fluid dynamics, so it is often considered a sub-field of continuum mechanics.



A cloth of woven carbon fiber filaments is commonly used for reinforcement in composite materials.

- Glass Science – any non-crystalline material including inorganic glasses, vitreous metals and non-oxide glasses.
- Forensic engineering – the study of how products fail, and the vital role of the materials of construction
- Forensic materials engineering – the study of material failure, and the light it sheds on how engineers specify materials in their product
- Textile Reinforced Materials - materials in the form of ceramic or concrete are reinforced with a primarily woven or non-woven textile structure to impose high strength with comparatively more flexibility to withstand vibrations and sudden jerks.

Primary topics

- Thermodynamics, statistical mechanics, and physical chemistry, for phase equilibrium conditions, phase diagrams of materials systems (multi-phase, multi-component, reacting and non-reacting systems)
- Phase transformation kinetics, for the kinetics of phase transformations (with particular emphasis on solid-solid phase transitions)
- Transport phenomena for the transport of heat, mass, and momentum in materials processing.
- Crystallography, quantum chemistry or quantum physics, for the structure (symmetry and defects) and bonding in materials (e.g., ionic, metallic, covalent, and van der Waals bonding)
- Mechanical behavior of materials, to understand the mechanical properties of materials, defects and their propagation, and their behavior under static, dynamic, and cyclic loads
- Electronic properties of materials, and solid-state physics, for the understanding of the electronic, thermal, magnetic, and optical properties of materials
- Diffraction and wave mechanics, for the science behind characterization systems, e.g., transmission electron microscopy (TEM)

Household items made of various kinds of plastic

- Polymer properties, synthesis, and characterization, for a specialized understanding of how polymers behave, how they are made, and how they are characterized; exciting applications of polymers include liquid crystal displays

(LCDs, the displays found in most cell-phones, cameras, and iPods), novel photovoltaic devices based on semiconductor polymers (which, unlike the traditional silicon solar panels, are flexible and cheap to manufacture, albeit with lower efficiency), and membranes for room-temperature fuel cells (as proton exchange membranes) and filtration systems in the environmental and biomedical fields

- Biomaterials, physiology, biomechanics, biochemistry, for a specialized understanding of how materials integrate into biological systems, e.g., through materiomics
- Semiconductor materials and semiconductor devices, for a specialized understanding of the advanced processes used in industry (e.g. crystal growth techniques, thin-film deposition, ion implantation, photolithography), their properties, and their integration in electronic devices
- Alloying, corrosion, and thermal or mechanical processing, for a specialized treatment of metallurgical materials—with applications ranging from aerospace and industrial equipment to the civil industries

Chapter- 2

History of Material Science

The **history of materials science** is the study of how different materials were used as influenced by the history of Earth and the culture of the peoples of the Earth.

Prehistory

Flint axe, about 31 cm long

The materials used by different cultures in most cases were the only records left for anthropologists to define the civilization. The progressive use of more sophisticated materials showed an innovative divide between peoples. This is partially due to the major material of use in that culture and its associated benefits and drawbacks. Stone Age cultures were limited by which stone could be found in the local area and what could be traded. The use of flint around 300,000 BCE is sometimes considered the beginning of the use of ceramics. The use of polished stone axes marks a significant advance because many more rocks could be used as tools.

A late Bronze Age sword or dagger blade

The innovation of smelting and casting metals in the Bronze Age started to change the way that cultures developed and interacted with each other. Native metals of copper and gold were reshaped without the use of fire for tools and weapons starting around 5500 BCE. Copper began to be heated and shaped with hammers around 5000 BCE. Melting and casting around 4000 BCE. Metallurgy had its dawn with the reduction of copper from its ore around 3500 BCE. And finally, the first alloy, bronze came into use around 3000 BCE.

In the 10th century BC, Glass production begins in ancient Near East. In the 3rd century BC, Wootz steel, the first crucible steel, is invented in ancient India. In the 1st century BC, Glassblowing techniques flourish in Phoenicia. In the 2nd century AD, steel-making becomes widespread used in Han Dynasty China. In the 4th century, the Iron pillar of Delhi is produced, and remains the oldest surviving example of corrosion-resistant steel.

Antiquity

The Pantheon in Rome

Wood, bone, stone, and earth are some of the materials which formed the structures of the Roman empire. Certain structures were made possible by the character of the land upon which these structures are built; a volcanic peninsula with stone aggregates and conglomerates containing crystalline material, will produce material which weathers differently from soft, sedimentary rock and silt. That is one of the reasons that the concrete Pantheon of Rome could last for 1850 years. And why the thatched farmhouses of Holland sketched by Rembrandt have long since decayed.

After the thighbone daggers of the early hunter-gatherers were superseded by wood and stone axes, and then by copper, bronze and iron implements of the Roman civilization, more precious materials could then be sought, and gathered together. Thus the medieval goldsmith Benvenuto Cellini could seek and defend the gold which he had to turn into objects of desire for dukes and popes. His *autobiography* contains one of the first descriptions of a metallurgical process.

Middle Ages

In the 8th century, porcelain is invented in Tang Dynasty China, the streets of Baghdad are the first to be paved with tar (derived from petroleum through destructive distillation), and the tin-glazing of ceramics is invented by Arabic chemists and potters in Basra, Iraq.

In the 9th century, stonepaste ceramics were invented in Iraq, and lustreware appeared in Mesopotamia.

In the 11th century, Damascus steel is developed in the Middle East. In the 15th century, Johann Gutenberg develops type metal alloy and Angelo Barovier invents cristallo, a clear soda-based glass.

Early modern period

In the 16th century, Vannoccio Biringuccio publishes first systematic book on metallurgy, Georg Agricola writes an influential book on metallurgy, and glass lens are developed in the Netherlands and used for the first time in microscopes and telescopes.

In the 17th century, Galileo's *Two New Sciences* (strength of materials and kinematics) includes the first quantitative statements in the science of materials. In the 18th century, William Champion patents a process for the production of metallic zinc by distillation from calamine and charcoal, Bry Higgins issued a patent for hydraulic cement (stucco) for use as an exterior plaster, and Alessandro Volta makes a copper/zinc acid battery.

In the 19th century, Thomas Johann Seebeck invents the thermocouple, Joseph Aspin invents Portland cement, Hans Christian Ørsted produces metallic aluminium, Charles Goodyear invents vulcanized rubber, Louis Daguerre and William Fox Talbot invent silver-based photographic processes, James Clerk Maxwell demonstrates color photography, and Charles Fritts makes the first solar cells using selenium waffles.

Modern materials science

In the early part of the 20th century, most engineering schools had a department of metallurgy and perhaps of ceramics as well. Much effort was expended on consideration of the austenite-martensite-cementite phases found in the iron-carbon phase diagram that underlies steel production. The fundamental understanding of other materials was not sufficiently advanced for them to be considered as academic subjects. In the post-WWII era, the systematic study of polymers advanced particularly rapidly. Rather than create new polymer science departments in engineering schools, administrators and scientists began to conceive of materials science as a new interdisciplinary field in its own right, one that considered all substances of engineering importance from a unified point of view. Northwestern University instituted the first materials science department in 1955.

The Materials Research Society (MRS) has been instrumental in creating an identity and cohesion for this young field. MRS was the brainchild of researchers at Penn State University and grew out of discussions initiated by Prof. Rustum Roy in 1970. The first meeting of MRS was held in 1973. As of 2006, MRS has grown into an international society that sponsors a large number of annual meetings and has over 13,000 members. MRS sponsors meetings that are subdivided into symposia on a large variety of topics as opposed to the more focused meetings typically sponsored by organizations like the

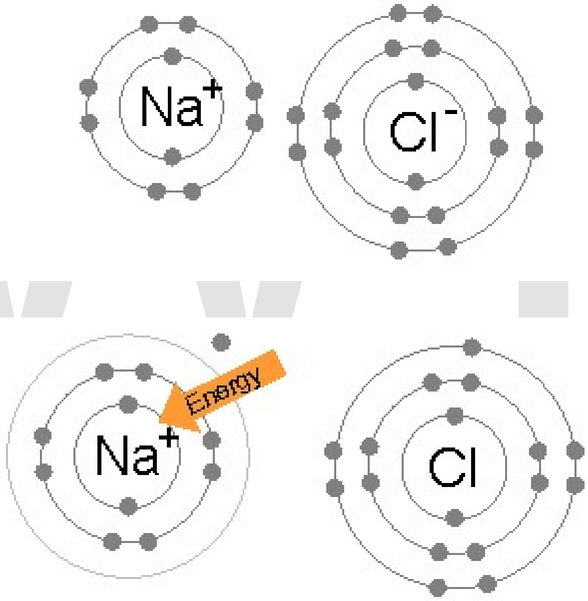
American Physical Society or the IEEE. The fundamentally interdisciplinary nature of MRS meetings has had a strong influence on the direction of science, particularly in the popularity of the study of soft materials, which are in the nexus of biology, chemistry, physics and mechanical and electrical engineering.

Chapter- 3

Class of Materials

Materials science encompasses various classes of materials, each of which may constitute a separate field. Materials are sometimes classified by the type of bonding present between the atoms:

1. Ionic Bond



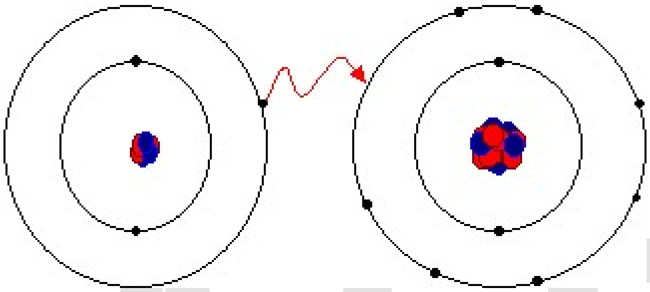
Sodium and chlorine bonding ionically to form sodium chloride. Sodium loses its outer electron to give it a stable electron configuration, and this electron enters the chlorine atom exothermically. The oppositely charged ions are then attracted to each other, and their bonding releases energy. The net transfer of energy is that energy leaves the atoms, so the reaction is able to take place.

An **ionic bond** is a type of chemical bond that involves a metal and a nonmetal ion (or polyatomic ions such as ammonium) through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions.

The metal donates one or more electrons, forming a positively charged ion or cation with a stable electron configuration. These electrons then enter the non metal, causing it to form a negatively charged ion or anion which also has a stable electron configuration. The electrostatic attraction between the oppositely charged ions causes them to come together and form a bond.

For example, common table salt is sodium chloride. When sodium (Na) and chlorine (Cl) are combined, the sodium atoms each lose an electron, forming cations (Na^+), and the chlorine atoms each gain an electron to form anions (Cl^-). These ions are then attracted to each other in a 1:1 ratio to form sodium chloride (NaCl).

$$Na + Cl \rightarrow Na^+ + Cl^- \rightarrow NaCl$$



Electron configurations of lithium and fluorine. Lithium has one electron in its outer shell, held rather loosely because the ionization energy is low. Fluorine carries 7 electrons in its outer shell. When one electron moves from lithium to fluorine, each ion acquires the noble gas configuration. The bonding energy from the electrostatic attraction of the two oppositely charged ions has a large enough negative value that the overall bonded state energy is lower than the unbonded state

The removal of electrons from the atoms is endothermic and causes the ions to have a higher energy. There may also be energy changes associated with breaking of existing bonds or the addition of more than one electron to form anions. However, the attraction of the ions to each other lowers their energy.

Ionic bonding will occur only if the overall energy change for the reaction is favourable – when the bonded atoms have a lower energy than the free ones. The larger the resulting energy change the stronger the bond. The low electronegativity of metals and high electronegativity of non-metals means that the energy change of the reaction is most favorable when metals lose electrons and non-metals gain electrons.

Pure ionic bonding is not known to exist. All ionic compounds have a degree of covalent bonding. The larger the difference in electronegativity between two atoms, the more ionic the bond. Ionic compounds conduct electricity when molten or in solution. They generally have a high melting point and tend to be soluble in water.

Ionic structure

Ionic compounds in the solid state form lattice structures. The two principal factors in determining the form of the lattice are the relative charges of the ions and their relative sizes. Some structures are adopted by a number of compounds; for example, the structure of the rock salt sodium chloride is also adopted by many alkali halides, and binary oxides such as MgO.

Strength of an ionic bond

For a solid crystalline ionic compound the enthalpy change in forming the solid from gaseous ions is termed the lattice energy. The experimental value for the lattice energy can be determined using the Born-Haber cycle. It can also be calculated using the Born-Landé equation as the sum of the electrostatic potential energy, calculated by summing interactions between cations and anions, and a short range repulsive potential energy term. The electrostatic potential can be expressed in terms of the inter-ionic separation and a constant (Madelung constant) that takes account of the geometry of the crystal. The Born-Landé equation gives a reasonable fit to the lattice energy of e.g. sodium chloride where the calculated value is −756 kJ/mol which compares to −787 kJ/mol using the Born-Haber cycle.

Polarization effects

Ions in crystal lattices of purely ionic compounds are spherical; however, if the positive ion is small and/or highly charged, it will distort the electron cloud of the negative ion, an effect summarised in Fajans' rules. This polarization of the negative ion leads to a build-up of extra charge density between the two nuclei, i.e., to partial covalency. Larger negative ions are more easily polarized, but the effect is usually only important when positive ions with charges of 3+ (e.g., Al^{3+}) are involved. However, 2+ ions (Be^{2+}) or even 1+ (Li^{+}) show some polarizing power because their sizes are so small (e.g., LiI is ionic but has some covalent bonding present). Note that this is not the ionic polarization effect which refers to displacement of ions in the lattice due to the application of an electric field.

Ionic versus covalent bonds

In an ionic bond, the atoms are bound by attraction of opposite ions, whereas, in a covalent bond, atoms are bound by sharing electrons. In covalent bonding, the molecular geometry around each atom is determined by VSEPR rules, whereas, in ionic materials, the geometry follows maximum packing rules.

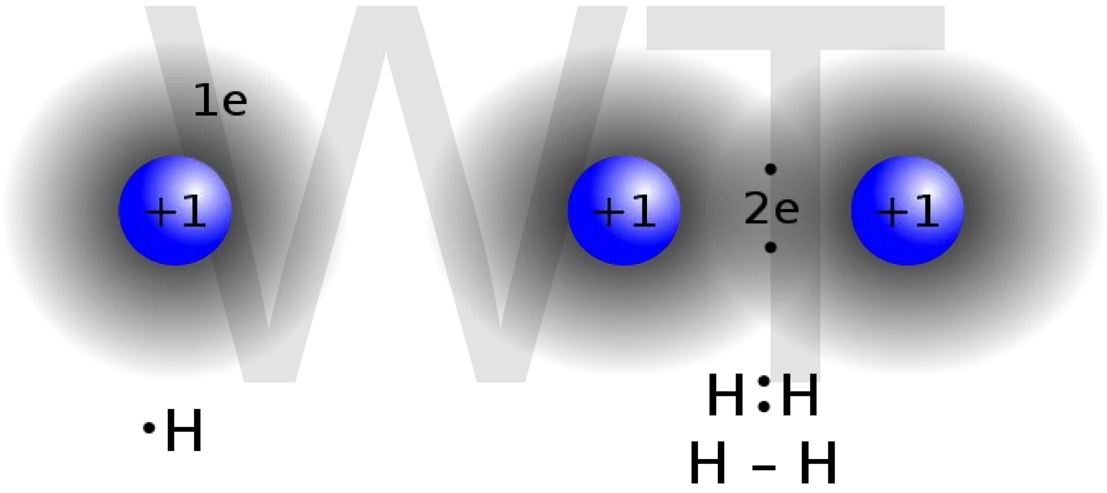
In reality, purely ionic bonds do not (and cannot) exist, as this would require an infinitely large electronegativity difference, and complete charge transfer is unfavorable from the viewpoint of raising the electronic kinetic energy. All ionic bonds have some covalent character. For example, Na–Cl and Mg–O bonds have a few percent covalency, while Si–O bonds are usually ~50% ionic and ~50% covalent. Predominantly covalent bonds with partial ionic character are called *polar covalent*.

Electrical conductivity

Ionic substances in solution conduct electricity because the ions are free to move and carry the electrical charge from the anode to the cathode.
Ionic substances conduct electricity when molten for the same reason i.e. that ions are free to move.

Some ionic compounds conduct electricity when solid. This is due to migration of ions under the influence of an electric field. These compounds are known as fast ion conductors.

2. Covalent Bond

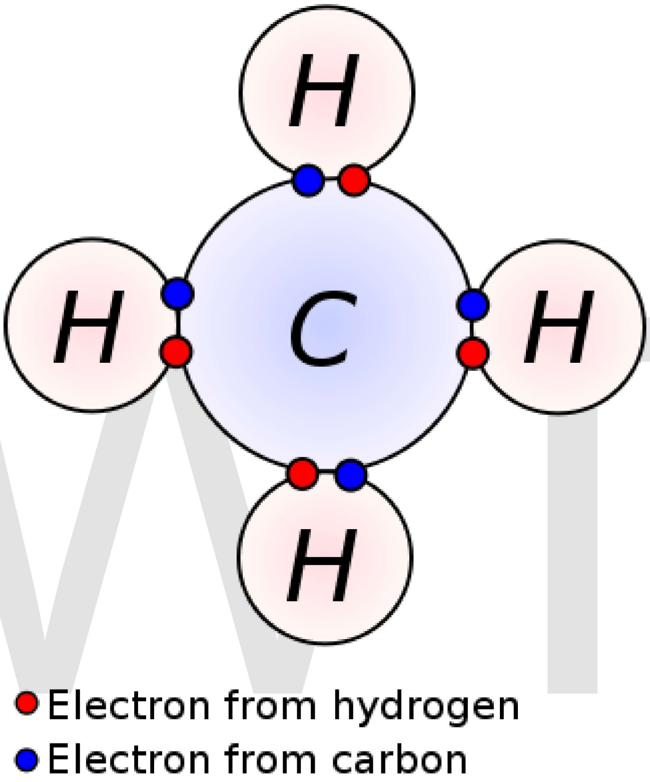


A covalent bond forming H_2 where two hydrogen atoms share the two electrons.\

A **covalent bond** is a form of chemical bonding that is characterized by the sharing of pairs of electrons between atoms, and other covalent bonds. In short, the stable balance of attractive and repulsive forces between atoms when they share electrons is known as covalent bonding.

Covalent bonding includes many kinds of interaction, including σ-bonding, π-bonding, metal to metal bonding, agostic interactions, and three-center two-electron bonds. The term *covalent bond* dates from 1939. The prefix *co-* means *jointly, associated in action, partnered to a lesser degree,* etc.; thus a "co-valent bond", essentially, means that the atoms share "valence", such as is discussed in valence bond theory. In the molecule H_2, the hydrogen atoms share the two electrons via covalent bonding. Covalency is greatest between atoms of similar electronegativities. Thus, covalent bonding does not necessarily require the two atoms be of the same elements, only that they be of comparable electronegativity. Although covalent bonding entails sharing of electrons, it is not necessarily delocalized. Furthermore, in contrast to electrostatic interactions ("ionic bonds") the strength of covalent bond depends on the angular relation between atoms in polyatomic molecules.

History



Early concepts in covalent bonding arose from this kind of image of the molecule of methane. Covalent bonding is implied in the Lewis structure that indicates sharing of electrons between atoms.

The term "covalence" in regard to bonding was first used in 1919 by Irving Langmuir in a *Journal of the American Chemical Society* article entitled "The Arrangement of Electrons in Atoms and Molecules". Langmuir wrote that "we shall denote by the term **covalence** the number of pairs of electrons which a given atom shares with its neighbors."

The idea of covalent bonding can be traced several years before 1919 to Gilbert N. Lewis, who in 1916 described the sharing of electron pairs between atoms. He introduced the so called *Lewis notation* or *electron dot notation or The Lewis Dot Structure* in which valence electrons (those in the outer shell) are represented as dots around the atomic symbols. Pairs of electrons located between atoms represent covalent bonds. Multiple pairs represent multiple bonds, such as double and triple bonds. Some examples of

Electron Dot Notation are shown in the following figure. An alternative form of representation, not shown here, has bond-forming electron pairs represented as solid lines. While the idea of shared electron pairs provides an effective qualitative picture of covalent bonding, quantum mechanics is needed to understand the nature of these bonds and predict the structures and properties of simple molecules. Walter Heitler and Fritz London are credited with the first successful quantum mechanical explanation of a chemical bond, specifically that of molecular hydrogen, in 1927. Their work was based on the valence bond model, which assumes that a chemical bond is formed when there is good overlap between the atomic orbitals of participating atoms. These atomic orbitals are known to have specific angular relationships between each other, and thus the valence bond model can successfully predict the bond angles observed in simple molecules.

Physical Properties of Covalent Compounds

Physical Properties	Covalent Compounds
States(at room temperature)	Can Be a solid, liquid, gas
Electrical conductivity	No
Boiling point and Melting Point	Low
Solubility in water	Variable(usually lower than ionic compounds)
Thermal conductivity	Usually low

Polarity of covalent bonds

Covalent bonds are affected by the electronegativity of the connected atoms. Two atoms with equal electronegativity will make non-polar covalent bonds such as H-H. An unequal relationship creates a polar covalent bond such as with H-Cl.

Subdivision of covalent bonds

There are three types of covalent substances: individual molecules, molecular structures, and macromolecular structures. Individual molecules have strong bonds which hold the atoms together, but there are negligible forces of attraction between molecules. Such covalent substances are gases. For example, HCl, SO_2, CO_2, and CH_4. In molecular structures there are weak forces of attraction. Such covalent substances are low boiling temperature liquids (such as ethanol), and low melting temperature solids (such as iodine and solid CO_2). Macromolecular structures have large numbers of atoms linked in chains or sheets (such as graphite), or in 3-dimensional structures (such as diamond and quartz). These substances have a high melting and boiling points.

3. Metals

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.

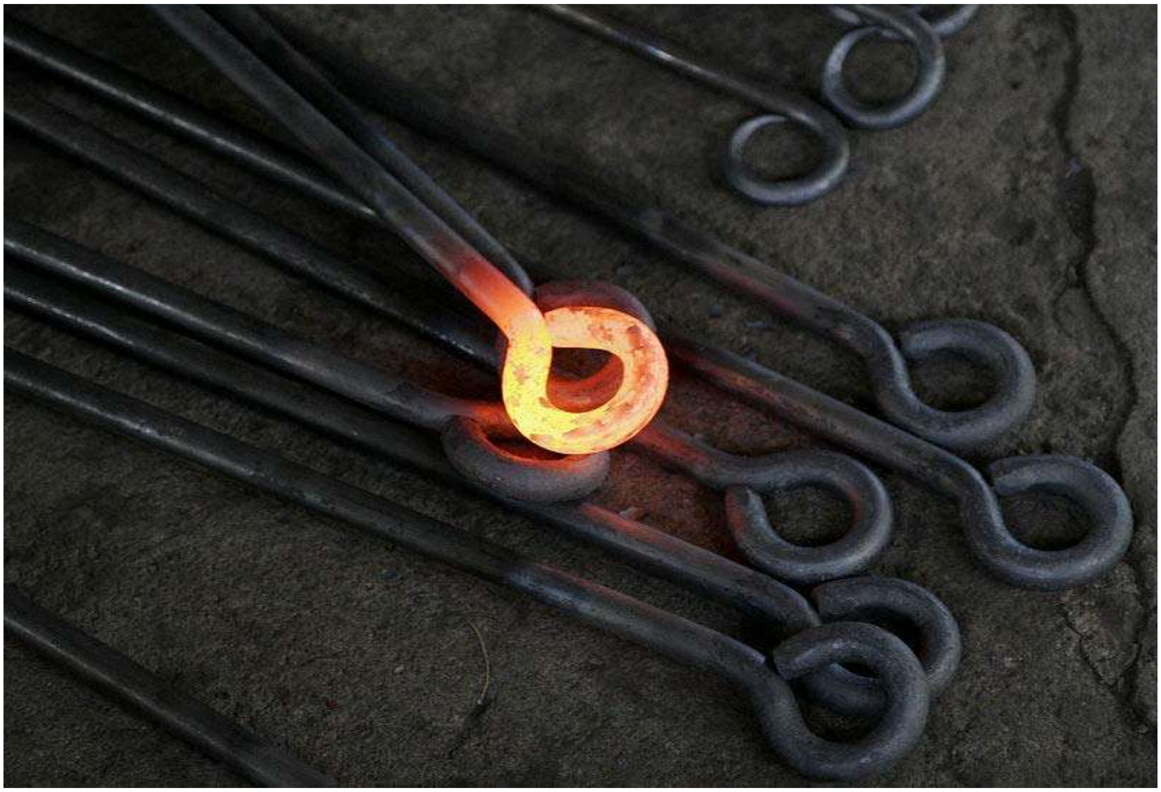
When considering the exact band structure and binding energy of a metal, it is necessary to take into account the positive potential caused by the specific arrangement of the ion cores - which is periodic in crystals. The most important consequence of the periodic potential is the formation of a small 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

An alloy is a mixture of two or more elements in solid solution in which the major component is a metal. Most pure metals are either too soft, brittle or chemically reactive for practical use. Combining different ratios of metals as alloys modifies the properties of pure metals to produce desirable characteristics. The aim of making alloys is generally to make them less brittle, harder, resistant to corrosion, or have a more desirable color and luster. Of all the metallic alloys in use today, the alloys of iron (steel, stainless steel, cast iron, tool steel, alloy steel) make up the largest proportion both by quantity and commercial value. Iron alloyed with various proportions of carbon gives low, mid and high carbon steels, with increasing carbon levels reducing ductility and toughness. The addition of silicon will produce cast irons, while the addition of chromium, nickel and molybdenum to carbon steels (more than 10%) results in stainless steels.

Other significant metallic alloys are those of aluminium, titanium, copper and magnesium. Copper alloys have been known since prehistory—bronze gave the Bronze Age its name—and have many applications today, most importantly in electrical wiring. The alloys of the other three metals have been developed relatively recently; due to their chemical reactivity they require electrolytic extraction processes. The alloys of aluminium, titanium and magnesium are valued for their high strength-to-weight ratios; magnesium can also provide electromagnetic shielding. These materials are ideal for situations where high strength-to-weight ratio is more important than material cost, such as in aerospace and some automotive applications.

Alloys specially designed for highly demanding applications, such as jet engines, may contain more than ten elements.

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

Noble metals are metals that are resistant to corrosion or oxidation, unlike most base metals. They tend to be precious metals, often due to perceived rarity. Examples include tantalum, gold, platinum, silver and rhodium.

Precious metal

A gold nugget

A *precious metal* is a rare metallic chemical element of high economic value.

Chemically, the precious metals are less reactive than most elements, have high luster and high electrical conductivity. 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 gold and silver. While both have industrial uses, they are better known for their uses in art, jewelry, 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. Plutonium and uranium could also be considered precious metals.

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. Palladium was, as of summer 2006, valued at a little under half the price of gold, and platinum at around twice that of gold. Silver is substantially less expensive than these metals, but is often traditionally considered a precious metal for its role in coinage and jewelry.

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.

4. Intermetallics

Intermetallics or **intermetallic compounds** is a term that is used in a number of different ways. Most commonly it refers to solid state phases involving metals. There is a "research definition" adhered to generally in scientific publications, and a wider "common use" term. There is also a completely different use in coordination chemistry, where it has been used to refer to complexes containing two or more different metals.

Although the term *intermetallic compounds*, as it applies to solid phases, has been in use for many years, its introduction was regretted, for example by Hume-Rothery in 1955.

Note that many intermetallic compounds are often simply called alloys, even though strictly speaking they are not. For example, complex metallic alloys are intermetallic compounds with large unit cells.

Definitions

Research definition

This was stated by Schulze in 1967, and defines intermetallic compounds as solid phases containing two or more metallic elements, with optionally one or more non-metallic elements, whose crystal structure differs from that of the other constituents. Under this definition the following are included

- Electron (or Hume-Rothery) compounds
- Size packing phases. e.g. Laves phases, Frank-Kaspar phases and Nowotny phases

- Zintl phases

The definition of a metal is taken to include:

- the so-called poor metals, i.e. aluminium, gallium, indium, thallium, tin and lead
- some, if not all, of the metalloids, e.g. silicon, germanium, arsenic, antimony and tellurium.

Alloys, which are a homogeneous mixture of metals, and interstitial compounds such as the carbides and nitrides are excluded under this definition. However, interstitial intermetallic compounds are included as are alloys of intermetallic compounds with a metal.

Common use

In common use the research definition, including poor metals and metalloids, is extended to include compounds such as cementite, Fe_3C. These compounds, sometimes termed interstitial compounds can be stoichiometric, and share similar properties to the intermetallic compounds defined above.

Complexes

The term intermetallic is used to describe compounds involving two or more metals such as the cyclopentadienyl complex $Cp_6Ni_2Zn_4$.

Intermetallics involving two or more metallic elements

Intermetallic compounds are generally brittle and high melting. They often offer a compromise between ceramic and metallic properties when hardness and/or resistance to high temperatures is important enough to sacrifice some toughness and ease of processing. They can also display desirable magnetic, superconducting and chemical properties, due to their strong internal order and mixed (metallic and covalent/ionic) bonding, respectively. Intermetallics have given rise to various novel materials developments. Some examples include alnico and the hydrogen storage materials in nickel metal hydride batteries. Ni_3Al, which is the hardening phase in the familiar nickel-base superalloys, and the various titanium aluminides have also attracted interest for turbine blade applications, while the latter is also used in very small quantities for grain refinement of titanium alloys.

Properties and examples

- magnetic materials e.g. alnico; sendust; Permendur, FeCo
- superconductors e.g. A15 phases; niobium-tin
- hydrogen storage e.g. AB_5 compounds (nickel metal hydride batteries)
- shape memory alloys e.g. Cu-Al-Ni (alloys of Cu_3Al and nickel)
- coating materials e.g. Nitinol, NiTi; NiAl

- high temperature structural materials e.g. nickel aluminide, Ni_3Al
- dental amalgams which are alloys of intermetallics Ag_3Sn and Cu_3Sn

The formation of intermetallics can cause problems. Intermetallics of gold and aluminium are a significant cause of wire bond failures in semiconductor devices and other microelectronics devices. There are 5 of them. $AuAl_2$ is known as "purple plague". Au_5Al_2 is known as "white plague".

History

Examples of intermetallics through history include:

- Roman yellow brass, CuZn
- Chinese high tin bronze, $Cu_{31}Sn_8$
- type metal SbSn

German type metal is described as breaking like glass, not bending, softer than copper but more fusible than lead. The chemical formula does not agree with the one above; however, the properties match with an intermetallic compound or an alloy of one.

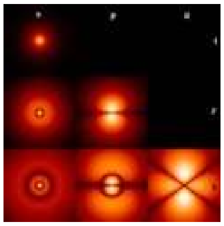
5. Semiconductors

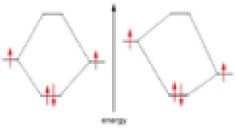
Explaining semiconductor energy bands

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

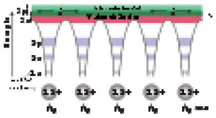
- Band structure

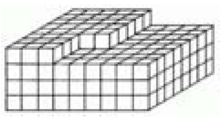
atoms – crystal – vacuum

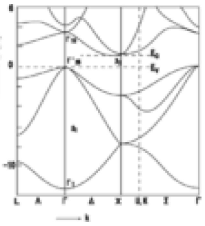

In a single H-atom an electron resides in well known orbitals. Note that the orbitals are called s,p,d in order of increasing circular current.

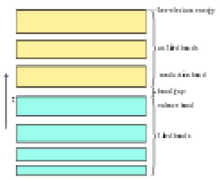


Putting two atoms together leads to delocalized orbitals across two atoms, yielding a covalent bond. Due to the Pauli exclusion principle, every state can contain only one electron.

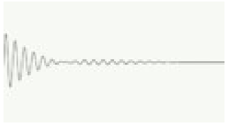

This can be continued with more atoms. Note: This picture shows a metal, not an actual semiconductor.


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.

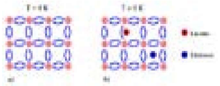


Integrating over the k axis gives the bands of a semiconductor showing a full valence band and an empty conduction band. Generally stopping at the vacuum level is undesirable, because some people want to calculate: photoemission, inverse photoemission



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 the semiconductor materials is nearly filled under usual operating conditions, thus causing more electrons to be 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.

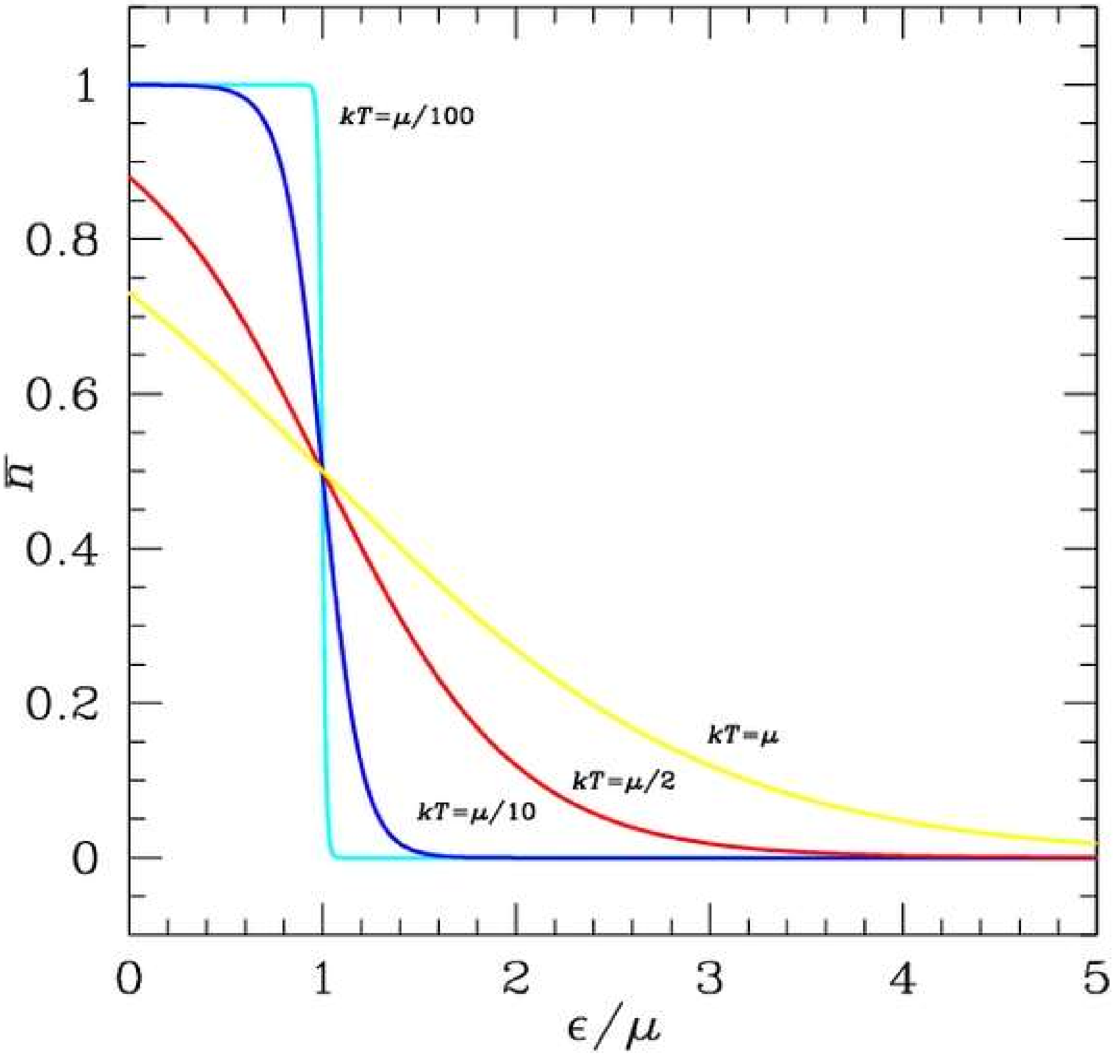
With covalent bonds, an electron moves by hopping to a neighboring bond. The Pauli exclusion principle requires the electron to be lifted into the higher anti-bonding state of that bond. For delocalized states, for example in one dimension – that is in a nanowire, for every energy there is a state with 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 contrast, some conductors like solutions of salts, or plasma. 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,

$$n = p = n_i.$$

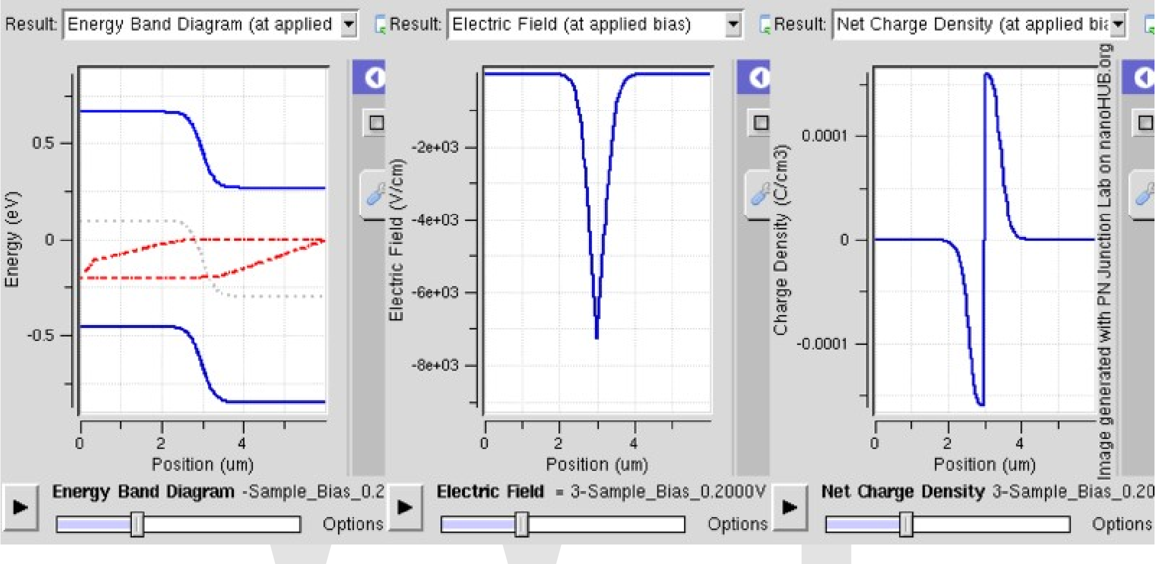
If we have a non-intrinsic semiconductor in thermal equilibrium the relation becomes:

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

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/cm^3. 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.

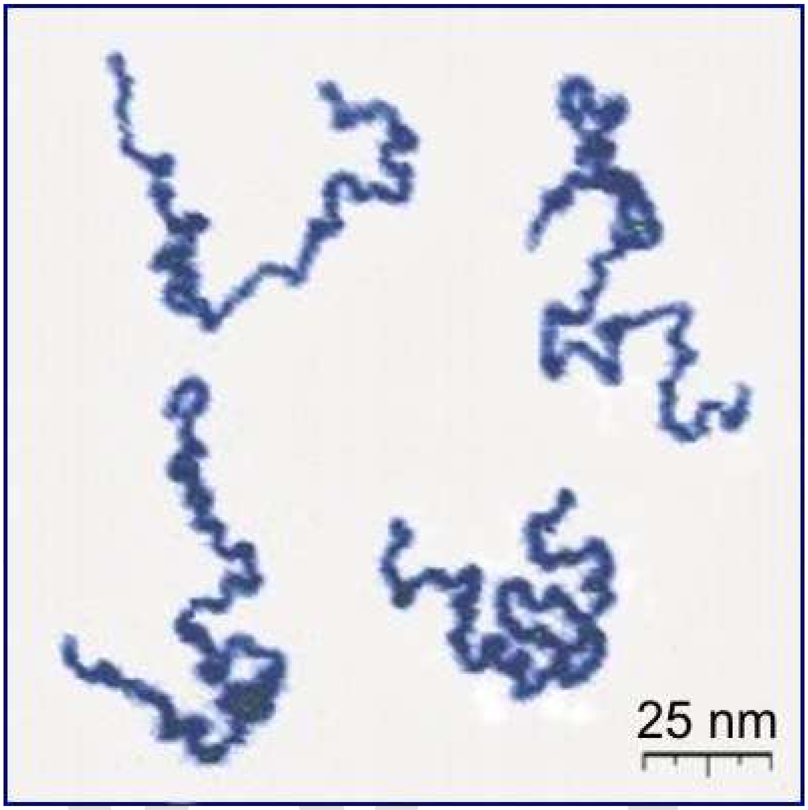
Preparation of semiconductor materials

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.

6. 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.

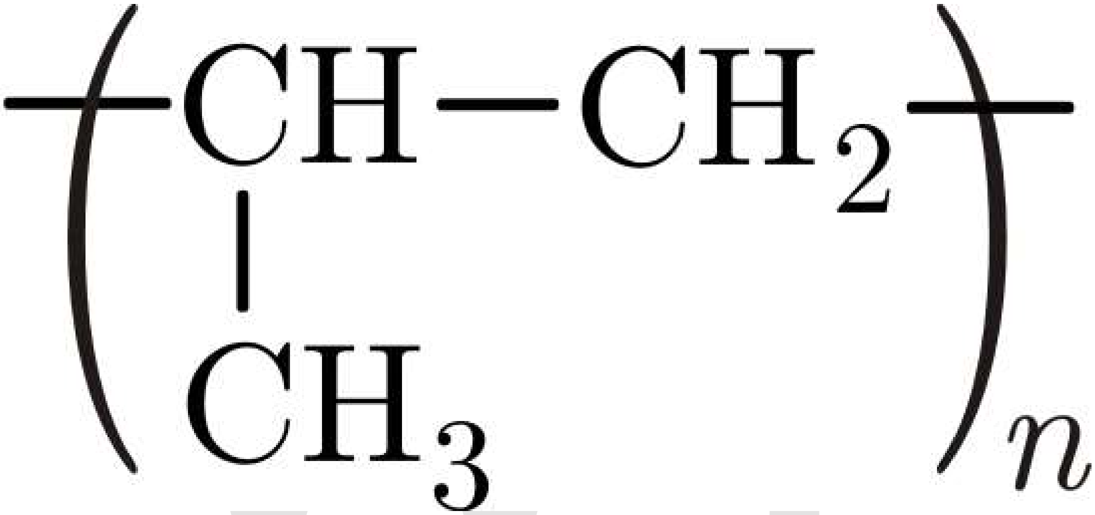
Historical development

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



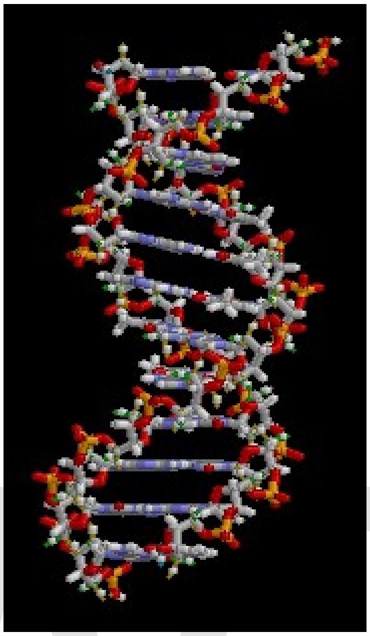
The repeating unit of the polymer polypropylene

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

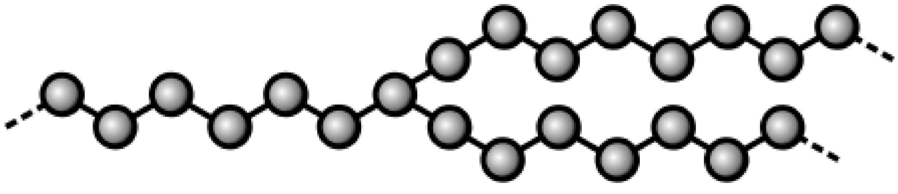
The identity of the monomer residues (repeat units) comprising a polymer is its first and most important attribute. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer. Polymers that contain only a single type of repeat unit are known as homopolymers, while 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

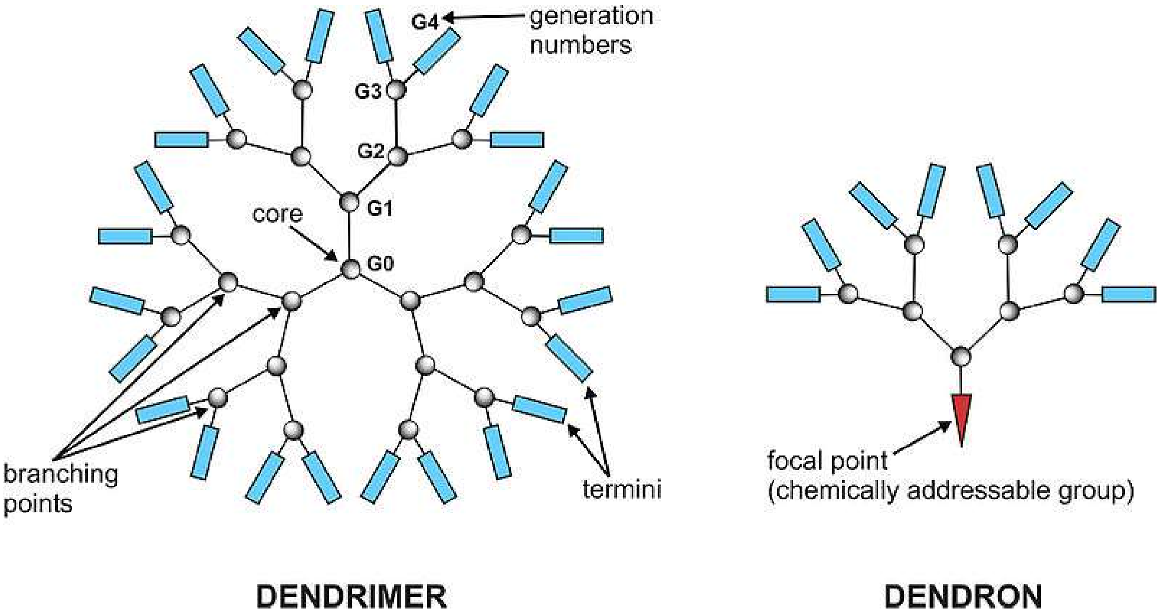


Branch point in a polymer

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

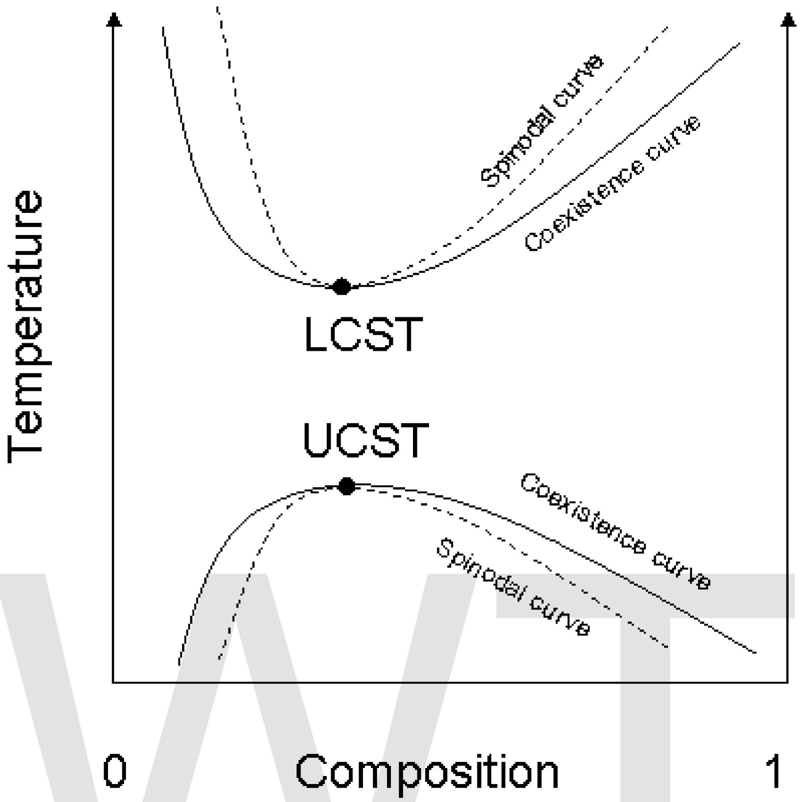
Melting point

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:

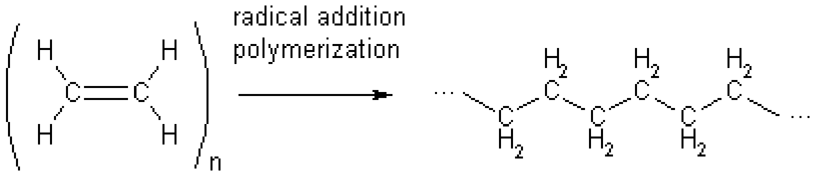
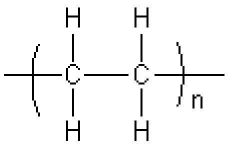


Fig 1: The polymerisation of ethene in to poly(ethene)

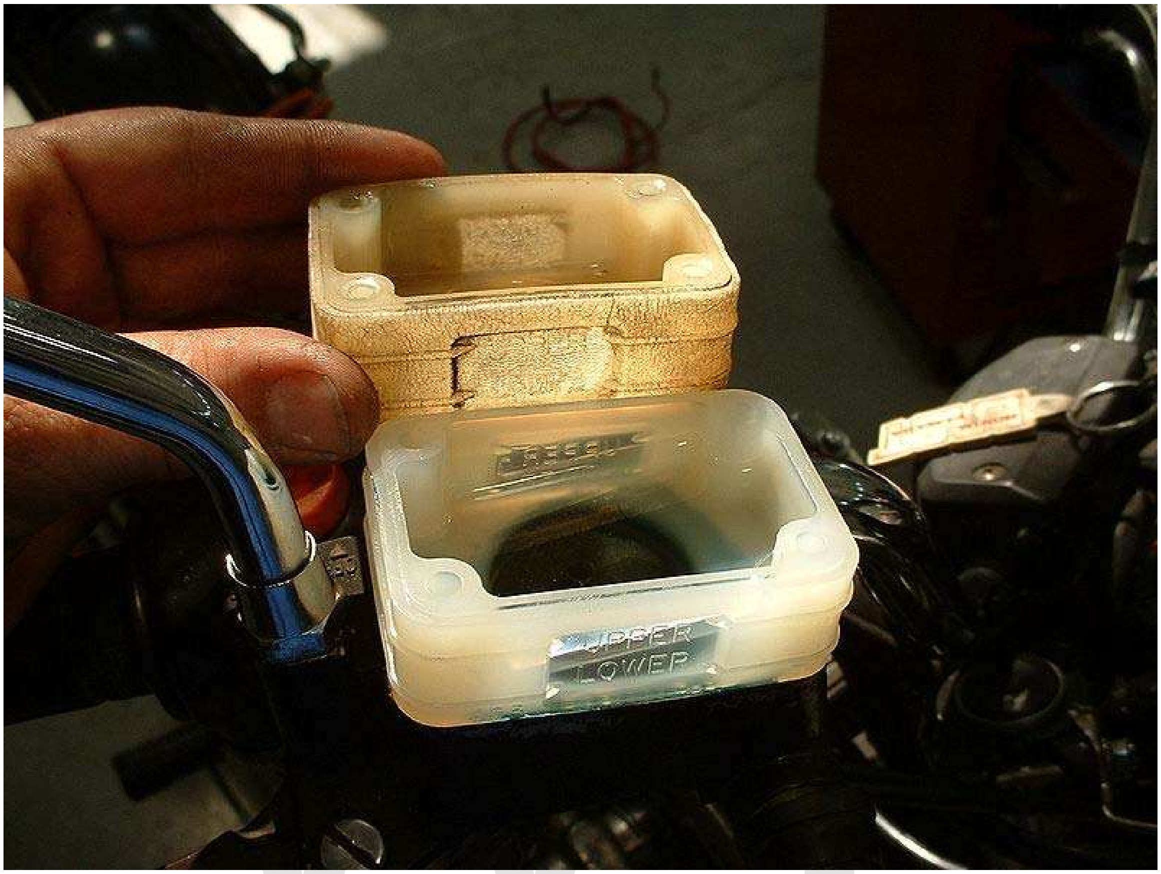


Polymer characterization

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.

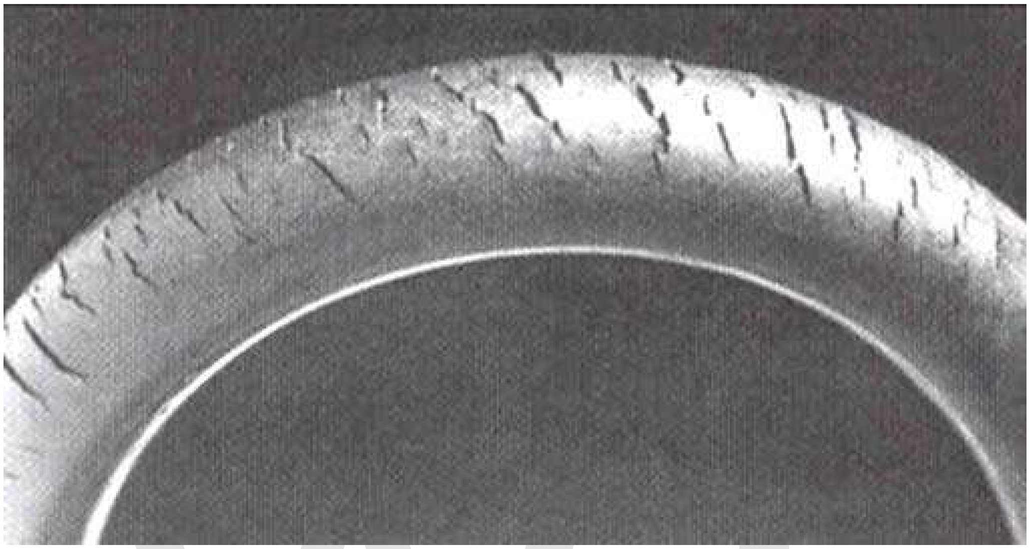
The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. The degradation of polyethylene occurs by random scission—a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When heated above 450 °C it degrades to form a mixture 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.



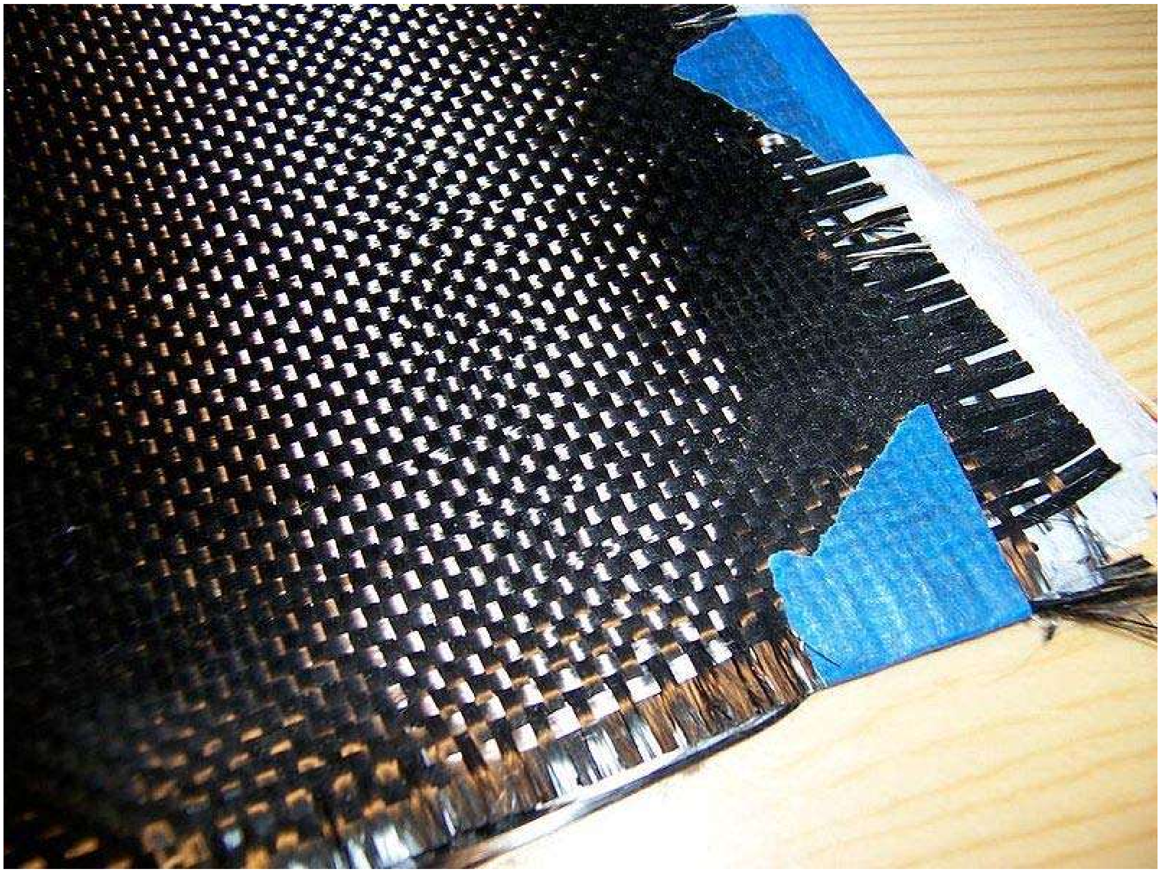
Ozone-induced cracking in natural rubber tubing

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- 4

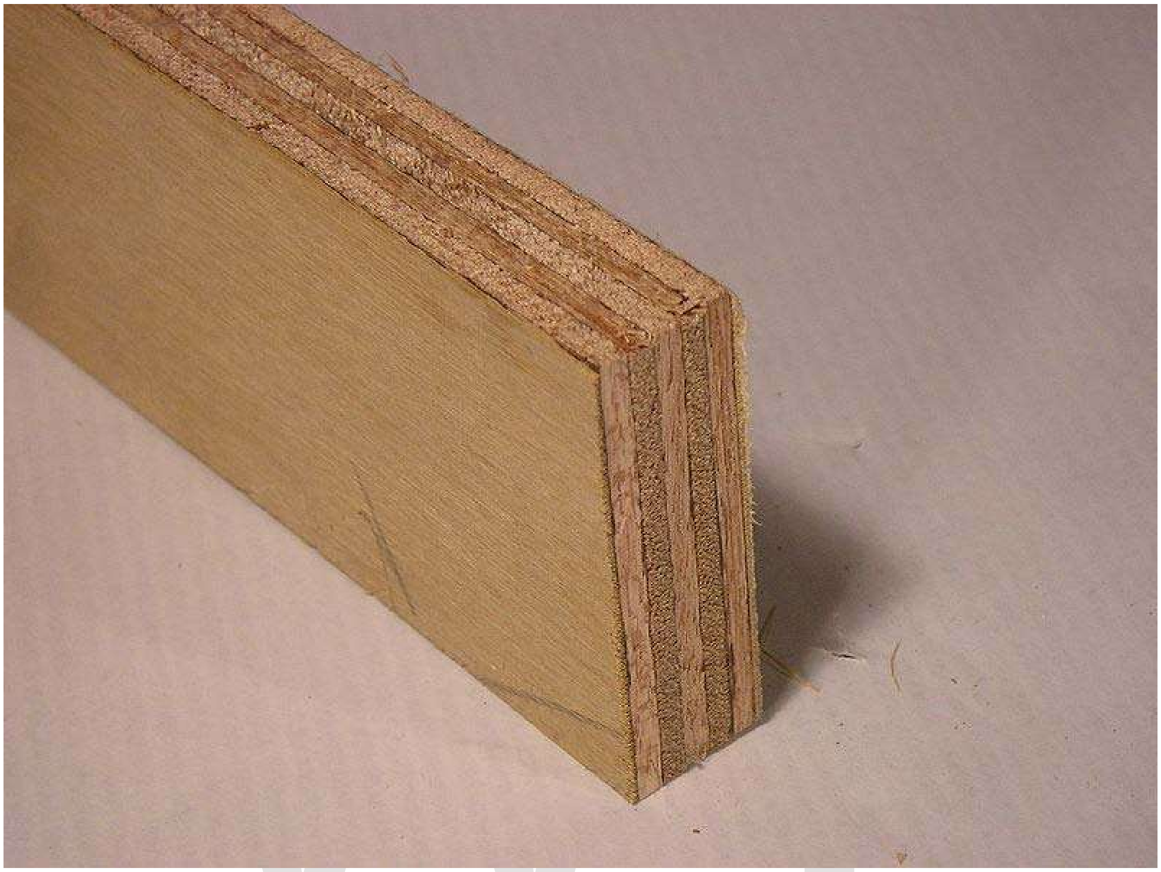
Composite Materials



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.

History



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. The most advanced examples perform routinely on spacecraft in demanding environments. The most visible applications pave our 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.

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.

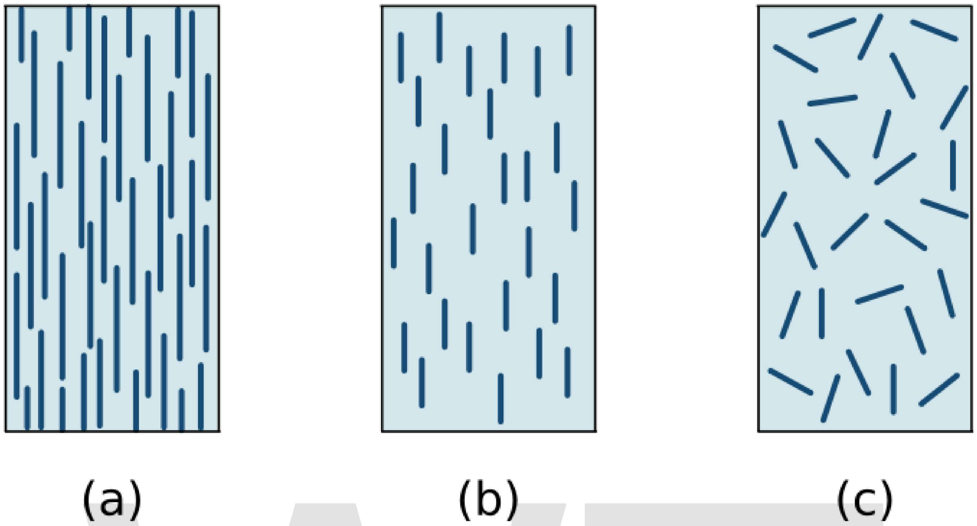
Polyester resin tends to have yellowish tint, and is suitable for most backyard projects. Its weaknesses are that it is UV sensitive and can tend to degrade over time, and thus generally is also coated to help preserve it. It is often used in the making of surfboards and for marine applications. Its 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 fibre-reinforced composite materials



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

Fibre-reinforced composite materials can be divided into two main categories normally referred to as short fibre-reinforced materials and continuous fibre-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 fibres 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.

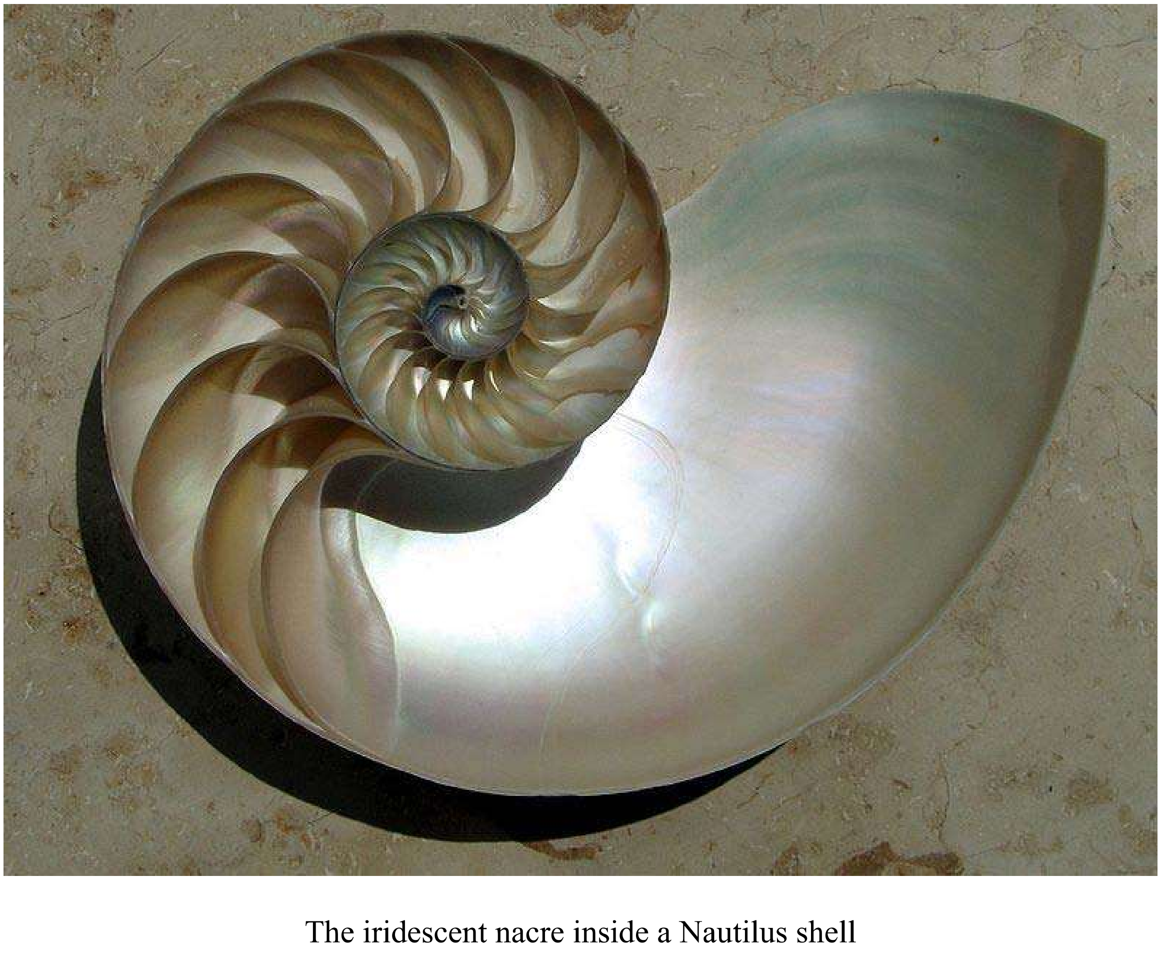
Many composite layup designs also include a co-curing or post-curing of the prepreg with various other mediums, such as honeycomb or foam. This is commonly called a sandwich structure. This is a more common layup process for the manufacture of radomes, doors, cowlings, or non-structural parts.

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.

Chapter- 5

Biomaterial

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.

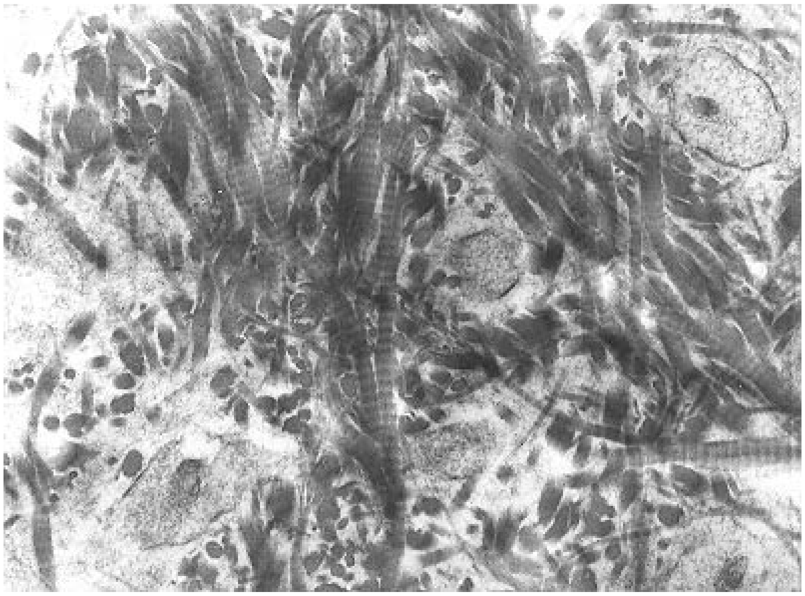
Biomineralization

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.

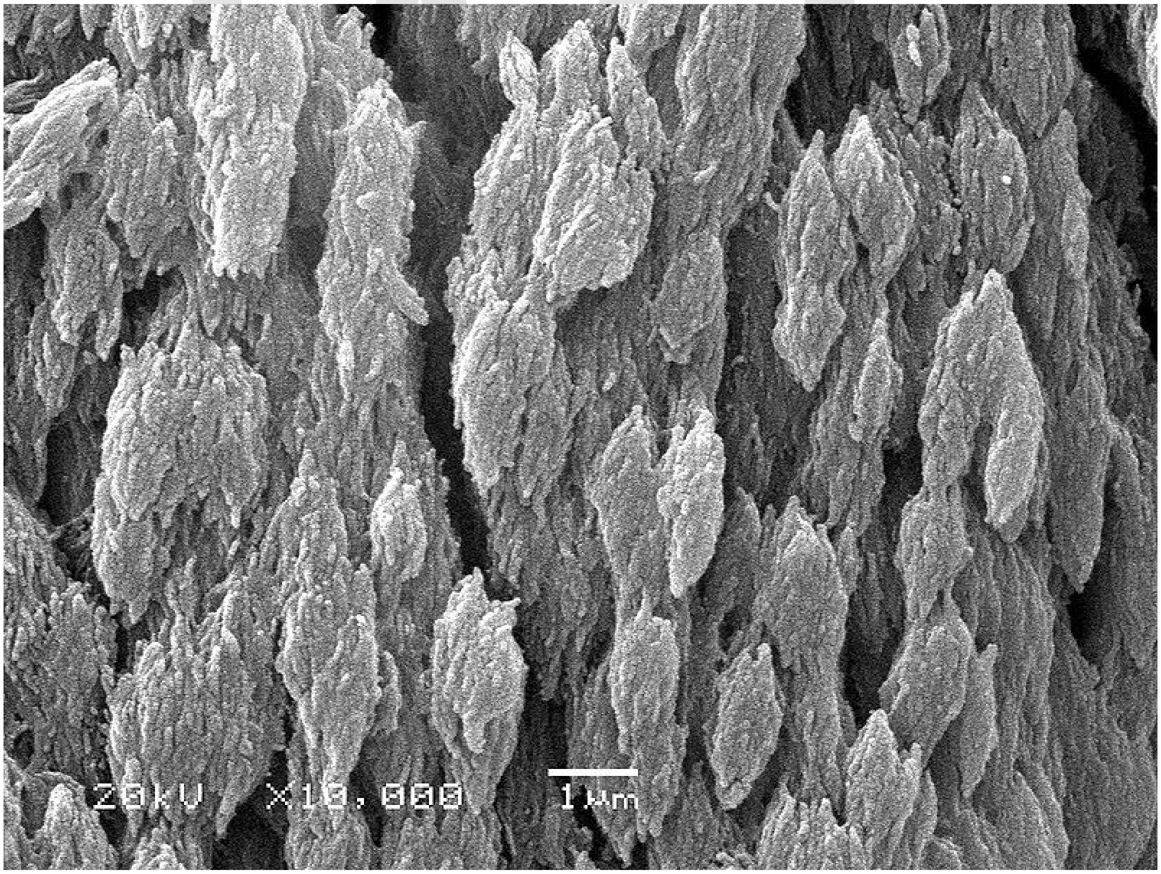
Sand from Pismo Beach, California including quartz, shell and rock fragments

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.

Bio-based material

A **bio-based material** is simply an engineering material made from substances derived from living matter. These materials are sometimes referred to as biomaterials, but this word also has another meaning. Strictly the definition could include many common materials such as wood and leather, but it typically refers to modern materials that have undergone more extensive processing. Unprocessed materials may be called biotic material. Bio-based materials or biomaterials fall under the broader category of bioproducts or bio-based products which includes materials, chemicals and energy derived from renewable biological resources.

Bio-based materials are often biodegradable, but this is not always the case.

Examples include:

- cellulose fibers-Fibers made from reconstituted cellulose.
- casein-A phosphoprotein extracted from milk during the process of creating low fat milk, it is processed in various ways to make: plastic, dietary supplements for body builders, glue, cotton candy, protective coatings, paints, and occurs naturally in cheese, giving it a creamy texture.
- polylactic acid-A polymer produced by industrial fermentation
- bioplastics-including a soy oil based plastic now being used to make body panels for John Deere tractors
- engineered wood-products such as oriented strand board and particle board
- zein-a natural biopolymer which is the most abundant corn protein
- cornstarch-the starch of the maize grain, used to make packing pellets
- grease- lubricants made from vegetable oils, including soybean oil, that can replace petroleum based lubricants