

Materials Science and Engineering

5.1 Introduction and basic principles

Everything around us is made up of materials, and they are basic substances that have mass and occupy space. The air we breathe, the water we drink and the food we eat and so on. They can be natural or human-made. Natural materials are materials that come from animals, plants and rocks and manufactured materials are those obtained from natural materials through chemical processes. A wide range of materials in nature form an essential part of the ecosystem in multiple ways. The materials that are used not only in the field of engineering, but on a day to day basis because of their properties are called engineering materials. Material engineers develop and test new materials for different specific applications. A wide range of new products like computer chips, recreational equipment (golf clubs, bicycles), and building materials for houses, bridges, cars, and aircraft will be created. Advanced materials refer to all new materials and modifications to existing materials to obtain superior performance in one or more functional features that are critical for the application under consideration. The functional materials perform specific functions within a system. Some recent advances include shape memory alloys and nanomaterials. Supermaterials of the future include aerogel, carbon nanotube, transparent alumina, e-textiles, metamaterials, nano-diamond and amorphous metal. Graphene is the thinnest material ever invented-only one atom thick yet stronger than steel. Every material has a set of physical and chemical properties that define it. The physical properties include melting point, boiling point, color, hardness, density and so forth. The chemical properties include reactivity with water, oxygen, acids, bases, and others. Traditionally, materials were developed keeping in mind a particular set of properties and were mainly used for making components and structures. With the advancement of materials science, they are expected to perform the role of an 'intelligent' structure. An excellent example of this would be applications of shape memory alloys, and they can be used to make deployable antennas. These materials enable people to explore the design and use of new products to improve the quality of life. Modern materials are employed in the primary production or manufacturing of a good, and there are about 3,00,000 different known materials. These include specialty and bulk chemicals, beverages and food products, metal products and alloys, wood and paper products, rubber and plastic products, textile and consumer goods, and those used in mining and metallurgy, and printing and publishing industries.

The kind of questions that a student in materials science would like answers to include the following; What is the densest crystal packing that can be achieved? How do intermolecular attractions arise? Why is glass transparent and brittle while copper opaque and ductile? Why is a diamond an efficient thermal conductor, but electrical insulator? Why is it easier to bend the Al rod as compared to the steel rod? Why is a wire of copper conducting, while a piece of dry wood non-conducting? How can we change properties like hardness, flexibility, biocompatibility in a material? Why does the electrical conductivity of Ag decrease on heating, while that of Si increases? Why does naphthalene (para-dichlorobenzene) solid evaporate? How can we explain the fact that good thermal conductors are also good electrical conductors? How can one understand the observations that when we release the load on a rubber band/spring, it comes back to its original shape while a bent aluminum rod would not come back? Why is it essential for some objects being transparent? Why is glass transparent to visible light, but opaque to UV light? Why can aluminum oxide exist as a transparent, translucent or opaque a material? What are the reasons for the viscosity of honey, mercury and paraffin oil? Why are composites used instead of metals, ceramics, or polymers? What is the mechanism behind functional smart materials? What does material science offer to society? Who can deny the role of materials in human existence? The answers to such questions could lead the learner to take the subject to higher levels of understanding, an understanding of the complex structure-property relationships, molecular mechanisms of material transformations, the development of an active system, to arrive at practical science-based solutions, and finally better materials management solutions.

Materials technology includes a range of materials used for manufacturing products, machines, and structures. For example, plastics are used in solid form as synthetic fibers for textiles, a film for packaging and in composites like fiberglass. Metals like iron or aluminum continue to be essential for building machines and structures. Concrete is the prime material for building civil structures such as bridges. Some building materials like steel, concrete, and bricks are structural while others, such as ceramics and glass are mainly decorative. Appropriate technology serves local needs using local resources such as stone and wood. Rubber is used for the soles of shoes and motor tires because of its resilience and elasticity. It is also used in rubber gloves and rainwear due to its flexibility and waterproof property. Plaster of Paris (POP) has the distinct feature of setting into a hard mass on wetting with water. It is used to make castings for statues, toys and decorative materials, for setting broken or fractured bones in the right position and as a fireproofing material. Thin-film materials are used

extensively in sensor applications. Thin film solar cells like amorphous silicon, cadmium telluride, copper indium gallium selenide and dye-sensitized solar cells are other examples of important novel materials. The nano-scale effects on sterical and biological properties include increased selectivity for specific drug transportation and controlled release, increased permeability through membranes, and improved biocompatibility. The role of materials science research, technology and innovations extend to almost all fields of human activity, and this particular domain has a transformational effect on the development in many areas which include healthcare, food processing, housing, energy, metals and minerals, and aerospace. The future of materials engineering is to obtain optimal performance by combining material design innovation with advances in technology involving several smart features.

Some materials are hard; others are soft. Some are strong; others are weak. Different materials have various properties because they contain different elements (atomic structure) and various combinations of ingredients, contain different types of chemical bonds (bonding between atoms and molecules, have different sizes of units (crystalline structures). The solid-state structure (microstructure + macrostructure) may include different types of assemblies, e.g., molecular packing arrangement may be different, or the geometry of linkage in an extended 3D structure may vary. Physical properties include mechanical and thermal properties (hardness, tensile strength, influence of coating, velocity of sound, thermal data and thermodynamic properties, thermal conductivity), electrical and magnetic properties (electron paramagnetic resonance, nuclear magnetic resonance, electrical conductivity, switching effect, thermoelectric power, magnetic susceptibility, magnetoresistance, optical and spectroscopic properties (index of refraction, dielectric constant, infrared spectra, Raman spectra, absorption in UV and visible range (EMR), photoconductivity, color dichroism, photoluminescence, The chemical properties include reactions of atoms, adsorption of gases, reactions with hydrogen/halogens, and reactions with main group/transition metals. The following factors put together determines the properties of the material; composition, phases present and their distribution, defect structure (in the phases and between the phases) and residual stress. The properties of materials also depend on the properties of individual components, the relative amount of particles, their size, shape, distribution, orientation and the degree of bonding. The goal of materials science and engineering is to design materials with a predetermined set of properties using suitable processing techniques, which gives them a particular microstructure and desired performance. The role of engineers has become very important for meeting the complex and specific challenges of making materials with desired functional characteristics

and solve technical issues with a specialized skill set and knowledge. The specific objective of this chapter is to provide students the vast subject in a structured and useful manner to equip them with a basic familiarity with materials science and engineering. It is a learning journey through the fundamental principles underlying the materials science and engineering and provides the essential vocabulary of these engineering sciences through inspirations, experiences, practices, and evolutions.

Classification of Materials

All materials used for engineering application can be put into six broad categories; pure substances (Cu, Ni, Fe), alloys (brass, NiAl), polymers (polyethene, polyvinyl chloride, polypropylene) ceramics (alumina, glass, zirconia), composites (wood, golf club shaft, bricks), and miscellaneous materials (lime, gypsum, tiles). The common types of engineering materials can be classified into different categories based on various parameters. Based on phase (state of matter) a given material can be divided into gases, liquids or solids. The solid state is a rigid state, the particles of liquids can move with greater freedom and gas particles have total freedom of motion. What distinguishes the crystalline state from the liquid and gaseous states is the nearly perfect positional order of the particles in crystals. Based on the structure of particles (arrangement of atoms/molecules/ions) materials can be classified into crystalline (quartz), quasicrystalline (Al-Pd-Mn alloy) or amorphous (glass). Liquid crystals and solid electrolytes have the properties in between liquids and crystals. Supercritical fluids have properties in between liquids and gases. Homogeneous materials include pure substances and solutions that have fixed, specific features. Heterogeneous materials can be separated into their components by purely mechanical means such as filtration, decantation, extraction, centrifuging and so on. Based on the size of the particles in question we can find nanocrystals, nano-quasicrystals, and bulk materials. Materials can be divided into paramagnetic, diamagnetic, ferromagnetic, ferrimagnetic, and antiferromagnetic materials based on the magnetic states of matter. Based on electrical conduction, we can categorize the materials into conductors (Cu, Al, Ag), semiconductors (Ge, Si, GaAs) and insulators (Al_2O_3 , $-(\text{CH}_2-\text{CH}_2)_n$). Based on ductility, we can have two categories- ductile (metals, alloys) and brittle (ceramics, glasses). Materials can be acoustic conductors (bronze) or acoustic insulators (cotton fiber) based on the capacity to transmit sounds. Materials can be classified based on the behavior when light strikes as transparent (clear glass windows, clear plastic food wrap), translucent (frosted glass, wax paper) and opaque materials (aluminum foil, wood). Based on the bonding,

solids can be classified into ionic (table salt, calcium chloride) molecular (ice, solid carbon dioxide) covalent network (diamond, quartz), and metallic solids (iron, silver). There are other categories of materials such as raw materials, in-process materials, finished products, bulk materials, value-added products, and packaging materials. Further classification of chemicals includes bulk chemicals (sulfuric acid), fine chemicals (ibuprofen) and specialty chemicals (adhesives).

Metals can be further classified into ferrous (steel, stainless steel, cast iron) and non-ferrous (aluminum, copper, tungsten) metals. Plastics can be further subdivided into thermoplastics (polyethene, polyvinyl chloride, teflon), thermosets (bakelite, melamine, vulcanized rubber) and elastomers (natural rubber, silicones, styrene-butadiene rubber) based on the response to heat. They can be classified into linear, branched, cross-linked (based on molecular structure), natural, semisynthetic, synthetic (based on origin), addition and condensation (based on the method of formation), plastics, elastomers, fibers and resins (based on applications). Ceramic materials can be categorized into glasses, clay products, refractories (acid, neutral, basic) abrasive materials, cement and advanced ceramics by an application. Composites are classified according to the matrix material into ceramic, metal, and polymer matrix materials, and based on reinforcement geometry into particulate-reinforced, fiber-reinforced and structural composites. Liquid crystalline materials can be subcategorized into calamitic, discotic, polycatenar, and bent-core types based on the shapes, and thermotropic and lyotropic liquid crystals based on the response to temperature or concentration. The classification of smart materials includes piezoelectric, electrostrictive, magnetostrictive, thermoelectric, shape memory alloys, photochromic and thermochromic materials. The classification of biomaterials based on the materials used include polymeric, metallic, ceramic and composite categories. Nanomaterials could be of natural or synthetic based on origin and zero, one, two and three-dimensional based on dimension. Electronic materials are classified into conductors, superconductors, semiconductors, and dielectrics. Based on their behavior in an applied field, superconductors are classified into two types; Type-I – soft and Type-II -hard. There are nine classes of hazardous materials; explosives, flammable gases, combustible liquids, flammable solids, oxidizers, toxic, radioactive, corrosive and miscellaneous materials.

The research and development of various kinds of materials have been exponential, and in the future, these types of materials will be used more extensively to meet the needs of the society. Material design is of vital importance in the development of different functional engineering systems, and it depends on multiple factors, including certain microscopic

structural features, texture, sizes, shapes, and density. Understanding how structural patterns are controlled and how that affects the properties gives engineers greater insight into the preparation of materials with predetermined properties. The materials have conveniently been grouped into various classes, and a combination of these materials will give a variety of other new materials. Apart from the standard categories of materials, future materials include smart materials, nanomaterials and advanced materials for specialized applications. There is a need for well-planned effort to synthesize and explore materials with unique property and use. This overview of the topic should make us think about the identity, composition, structure of materials in question and study the structure-property relationships, mechanism of change and its control, and finally the question about benefits, costs, and risks involved. We also have to take into consideration the ecological properties related to the impact they have on the environment and the function of biological systems can be exploited to find meaningful solutions to engineering problems. The qualities of successful material design include material quality, desired characteristics, ease of use, precision, attractiveness, cost of manufacture, development cost, development time, and enhanced development capacity. A multi-step investigation by researchers, exploration of eco-friendly approaches, preparation of semi-synthetic materials, and preference to use of local materials would go a long way in promoting sustainable and responsible discovery of novel materials and the development of new technological methods. We can achieve success in offering world-class materials through our expertise and experience by doing exceptional and result-oriented, hard work involving systematic and target-based planning with predictable outcomes. The quality of materials and their performance in processes and systems is probably the surest guide to the quality of research in materials science and engineering. These multiple perspectives might help the right-thinking people ask the right questions on the topic and to create future ideas, innovations and stable, sustainable, smart and high-quality materials that power the world through the scientific transformation and paves the way for severe developmental changes.

Effect of Bonding on Properties

The two important contributing factors to the properties of materials are the atomic structure and the nature of bonding. The properties of solids depend both on the arrangements of particles and on the attractive forces between them. A chemical bond is defined as a force that acts between two or more atoms to hold them together in a stable arrangement. Bonding in materials could involve strong interactions such as ionic, covalent and metallic bonds and weak interactions like van der Waals forces and hydrogen bond. Solids can be classified

according to the nature of the bonding between their atomic or molecular components into ionic solids, covalent network solids, molecular solids and metallic solids. Typical examples of these classes have distinctive electron distributions and binding energies, and thermodynamic, electronic, and mechanical properties. We have to note that this is not a rigid classification scheme and bonding in solids can be of mixed or intermediate kinds.

Ionic bond: A net electrostatic attraction between the positive (cation) and negative (anion) ions formed by transfer of electrons from metal to a non-metal atom constitutes an ionic bond (electrovalent bond). There are no rigid, directional bonds in an ionic material and the strong ionic bonding continues throughout the solid crystal resulting in giant structure. Some examples of ionic compounds include MgCl_2 , CaO , ZnS , Al_2O_3 . The characteristic properties of ionic compounds are the following; They are solids at room temperature. The crystals of ionic solids are hard and brittle. They possess high melting and boiling points. They do not conduct electricity in the solid state but are good conductors of electricity in the molten state or aqueous solution. They are soluble in polar solvents, but insoluble in nonpolar solvents. They do not exhibit isomerism. More common structures are the Rock salt structure which has a face-centered cubic (f.c.c.) unit cell and the Cesium chloride structure, which has a body-centered cubic (b.c.c.) unit cell. Less common structures include the Zincblende structure, Wurtzite, Fluorite, and Rutile structures. An ionic solid consist of cation and anions arranged in such a way that each ion is surrounded by as many nearest neighbors of opposite charge as possible and there is local neutralization of charge. There could be partial ionic character in predominantly ionic bonds in compounds with large anions, small cations, high charge on one of either ion, and non-noble gas electron configuration of the cation.

Covalent bond: Covalent bonds are formed by an overlap of atomic orbitals and mutual sharing of electrons. A covalent bond is typically formed by two non-metals having similar electronegativities and each bonded atom may contribute one electron to the shared electron pair or one atom may contribute both electrons. Covalently bonded compounds usually form molecular structures. Molecular solids are collections of distinct molecules held together by intermolecular forces such as dispersion forces, dipole-dipole forces, and hydrogen bonds. Typical examples of covalent molecular crystals include the noble gases, oxygen, nitrogen, the halogens, CO_2 , H_2O , $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, I_2 , and the vast majority of organic compounds. Depending on the number of shared electrons covalent bonds can be single (F_2), double (O_2) or triple bond (N_2) types. The common spatial arrangements of atoms in covalent molecular solids include linear, angular, trigonal plane, trigonal pyramid, tetrahedron, square plane and octahedral

structures. A covalent network solid has atoms at the crystal lattice sites that are linked together by covalent bonds into a three-dimensional array, e.g. C (diamond), SiO₂ (quartz). These solids are hard and high melting. Silica is the most abundant covalent solid in nature and carborundum (SiC) is the most common synthetic solids. The characteristic properties of covalent molecular compounds are the following; they are gases, liquids or solids at room temperature. Covalent solids are soft and easily deformed. They have low melting and boiling points. They are soluble in organic solvents. They are rigid and directional and can cause stereoisomerism. They do not conduct electricity in any state.

Metallic bond: The bonding which holds the metal atoms firmly together by force of attraction between metal ions and the mobile electrons is called metallic bond. Typical examples of metals include Na, Fe, Cu, Mg and Al. A metallic solid has metal atoms that occupy the crystal lattice sites in hexagonal close-packed (h.c.p.), cubic-close-packed (c.c.p.) or body-centered cubic (b.c.c.) structures. If many metal atoms are brought together, the outer electrons of each can merge together and overlap. These valence electrons are shared by nuclei of all the atoms that make up the solid (giant structure). These electrons have become delocalized and hence more stable. A block of metal can be thought of as an array of positive ions immersed in a sea of delocalized electrons. The great cohesive forces resulting from the delocalization is responsible for the great strength noted in metals. The type of bonding found in metals involves the manifold of closely spaced sublevels that can be regarded as a band. Using the band theory of metals, we can explain the properties of metals. The characteristic properties of metals include the following; they have bright metallic lustre. Metals are malleable and ductile. They have high electrical and thermal conductivity. The melting points vary according to the efficiency of metallic bonding and highest melting elemental metal, tungsten melts at 3410 °C. Those elements with intermediate electronegativity, exist as solids on the border between metallic and covalent, called metalloids. Silicon and germanium are semiconductors, with electrical conductivities significantly lower than those of metals, but far higher than those of true insulators like a diamond.

Intermolecular forces: To explain the properties of different materials, it is necessary to consider several types of intermolecular forces. These bonds are weaker than the intramolecular covalent bonds (for example, it takes only 1.2 kJ to overcome a mole of Ar-Ar interatomic attractions but it takes 239 kJ to break a mole of Cl-Cl covalent bonds). Intermolecular forces are much less directional than covalent bonds and they operate at longer range than covalent bonds. It is useful to distinguish types of forces based on their strength, directionality, and range. It exists in the inert gases, and between molecules in covalent molecular solids that arise

from atomic or molecular dipoles. All inert gas materials are gaseous at high temperatures as the high kinetic energy of the molecules disrupts all possible attractions. At lower temperatures, where materials are in the liquid state, molecules are close together and details of the intermolecular potential energy determine the properties of materials. The physical properties of molecular solids and liquids are because of intermolecular forces. The boiling and melting points of different substances reflect the strengths of the intermolecular forces. The stronger the intermolecular attractive forces, the higher is the boiling point of the liquid and the melting points of solids increase as the strengths of the intermolecular forces increase. The types of intermolecular forces include hydrogen-bonding forces, London dispersion forces, dipole-dipole interactions, and ion-dipole forces. The first three types are also known as van der Waals forces and all are electrostatic in nature.

Hydrogen bond: The electrostatic attraction between an H-atom covalently bonded to a highly electronegative atom X such as nitrogen, oxygen or fluorine and a lone pair of electrons on X in another molecule is called hydrogen bonding. The compounds like H_2O , NH_3 , and HF have abnormally high boiling points because of hydrogen bonding. Water has a high melting point, a high specific heat and a high heat of vaporization because of the abnormally strong intermolecular forces between water molecules. The hydrogen-bond attraction can occur between molecules (*intermolecular*) or within different parts of a single molecule (*intramolecular*). The examples of intermolecular hydrogen bonding include $(\text{HF})_n$, $(\text{H}_2\text{O})_n$, $(\text{NH}_3)_n$ and $(\text{CH}_3\text{COOH})_2$. The examples of intramolecular hydrogen bonding include o-nitrophenol, 2-nitrobenzoic acid and o-fluorophenol. Though the H-bonds are weak forces, they are strong enough to influence physical properties such as boiling points, solubility, viscosity, and crystal structure. The energy associated with hydrogen bonding lies in between 15 to 40 kJ/mole, and they are much weaker than ordinary chemical bonds. These bonds help stabilize the structure of proteins and DNA in biological systems. Ice floats on the top of the water when a lake freezes in winter because of its lower density compared to liquid water, thereby insulating the water below and protecting most of the aquatic life. Hydrogen bonds tend to be the strongest type of intermolecular force.

Ion-dipole forces: This type of force exists between an ion and the partial charge on the end of a polar molecule, e.g. KBr/NaCl in water. The negative ions are attracted to the positive end of a dipole, and positive ions are attracted to the negative end. These are important for solutions of ionic substances in polar solvents.

Dipole-dipole bonds: The strongest secondary bonding type exists between adjacent polar molecules. The associated binding energies are significantly higher than for bonds involving

induced dipoles and they are weaker than ion-dipole forces. HCl, H₂S, and CH₃Cl are some examples of polar molecules. For molecules of approximately equal mass and size, the strengths of intermolecular attractions increase with increasing polarity. The positive end of one dipole attracts the negative end of the other. There is the overall effect of net attraction between the polar molecules because two molecules that are drawing each other spend more time near each other than do those that are repelling each other. Generally, such attractions are about 1 % as strong as a covalent bond. The boiling point increases as the dipole moment increases. They are sufficiently strong to influence melting points, and molecular orientations in solids.

Dipole-induced dipole bonds: Permanent dipole moments exist in some molecules by an asymmetrical arrangement of positively and negatively charged regions. The polar molecules will induce a dipole in adjacent nonpolar molecules, and a bond will form as a result of attractive forces between the dipole and induced dipole. The magnitude of this interaction depends on the magnitude of the dipole moment of the polar molecule and the polarizability of the non-polar molecule. Eg. Solution of polar solutes in nonpolar solvents.

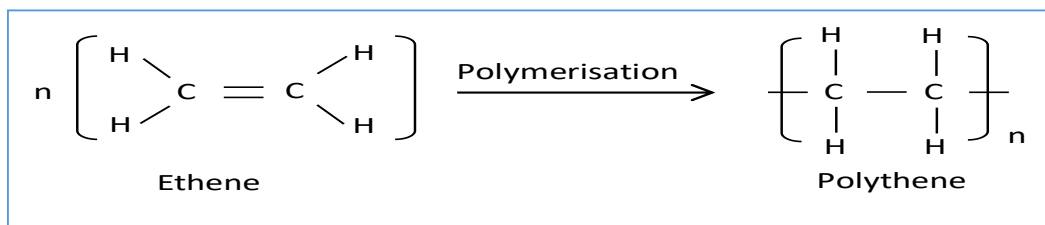
London forces: A dipole may be created or induced in an atom or molecule that is normally electrically symmetric; that is, the overall spatial distribution of the electrons is symmetric with respect to the positively charged nucleus. All atoms are experiencing constant vibrational motion that can cause instantaneous and short-lived distortions of this electrical symmetry for some of the atoms or molecules and the creation of small electric dipoles. One of these dipoles can, in turn, produce a displacement of the electron distribution of an adjacent molecule or atom, which induces the second one also to become a dipole that is then weakly attracted or bonded to the first. The momentary attraction between the molecules of a liquid caused by the instant dipole and induced dipole are called London Forces. These attractive forces may exist between large numbers of atoms or molecules, which forces are temporary and fluctuate with time. Liquefaction [e.g.Ar(l)] and, in some cases, the solidification of the inert gases and other electrically neutral and symmetric molecules such as H₂, I₂ (s) and Cl₂ are realized because of this types of bonding. Melting and boiling temperatures are extremely low in materials for which induced dipole bonding predominates; of all possible intermolecular bonds, these are the weakest. Dispersion forces operate between all polar and non-polar molecules. Polar molecules experience dipole-dipole interactions in addition to dispersion forces. The dispersion forces are approximately equal when the molecules have comparable molecular weights and shapes. The strength increases with increasing molecular weight, though molecular shape is also an important factor.

The Road Ahead

It is essential to study the effect of several environmental conditions such as heat, radiation, carbon dioxide, oxygen, water and various pollutants in finer detail to obtain the full picture. The study may reveal the number of critical molecules that can be exploited for both creating new materials and functional purposes. Finally, better technology using the finest ingredients and expert techniques to create innovative materials with practical utility and responsible sourcing becomes critical in this age of specialized domain expertise. Long-term stability and safety standards for new materials matters in some applications. The microscopic details make all the difference in the material world that turn ideas, dreams and the future into reality. Innovating in finding new ways of adding value to unique products makes the complex systems more efficient and make a positive transformation of society. Advanced material characterization remains a challenge because of several factors, including structure related (molecular geometry, 2D structure, perovskite structure), bonding pertaining (bond length, angle, strength, order), and condition/treatment-related (pressure, temperature, radiation) factors. Regular follow up of processes is essential from three perspectives. First, to understand if the method is working and what is the progress of material formation. Second, it helps to modify the method or alter treatment conditions based on the improvement. Lastly, if there are undesired events, necessary actions can be taken to prevent those. The sophisticated techniques such as wide angle X-ray diffraction, field emission scanning electron microscopy (FE-SEM), tensile strength tester, simultaneous TG-DTA/DSC apparatus, and acoustic material testing with impedance tube are used for characterization of final stable material. It remains to be seen that a multipronged approach to preparing modern materials soon could lead to better systems to enable sustainable development and the material progress of human beings.

5.2 Polymers

The word *polymer* is derived from two Greek words, *poly* and *meros*, where *poly* means many and *meros* means parts. Polymers are giant molecules formed by the combination of several simple molecules having two or more binding sites linked through covalent bonding.



The simple molecules which are repeating units of the polymer, are called monomers.

Eg: Polythene is formed by the combination of several ethene (ethylene) molecules.

Degree of polymerization (DP): Degree of polymerization is the number which expresses the total number of repeating units (n) in the polymer chain. Polymers with large number of repeating units are called high polymers and those with lower number of repeating units are called oligomers.

DP is used to determine the molecular weight of the polymer by multiplying the number of repeating units (n) with the molecular weight of repeated unit.

Functionality: The total number of functional groups, bonding sites or reactive sites present in the monomer is called the functionality of the monomer. The reactive functional groups can be

–OH, –COOH, –NH₂, –SH, –NCO etc.

Eg: In CH₃CH₂OH one reactive - OH group is present, hence functionality is one (monofunctional)

HO-CH₂-CH₂-OH has two –OH groups hence bifunctional

HOOC-CH₂-CH(COOH)-CH₂-COOH has three -COOH groups, hence trifunctional

The presence of double or triple bonds in the molecule imparts polyfunctionality to the molecules.

Eg: Ethylene - due to the presence of a double bond, it can take on two atoms of hydrogen or halogens. Depending upon the functionality of the monomers used linear, branched or three dimensional cross-linked polymers are formed.

Classification of polymers

Polymers can be classified in several ways, based on their

➤ origin

- structure
- methods of formation
- response to heat and crystallinity
- properties (or applications)

Based on their **origin**, polymers are broadly classified as

(a) Natural polymers (b) synthetic polymers.

Natural polymers are those which are obtained naturally. Eg: Cellulose, Silk, Starch

Synthetic polymers are those which are man-made. Eg: polythene, PVC, polyster, etc.

Semi-synthetic polymers are chemically modified natural polymers. Eg: cellulose acetate, cellulose nitrate, halogenated rubbers etc.

Based on their **molecular structure**, the polymers can be classified as

(a) Linear (b) Branched (c) Cross-linked

If all the monomeric units are identical and combine linearly with each other to form a polymer, it is called a *linear homopolymer*.

Eg. - M – M – M – M – M – M – M -

If the monomeric units are not identical, it is called a *linear co-polymer*.

Eg: -M – M1 – M – M1 – M – M1 – M -

If the linear co-polymers in which the units of each type form fairly long continuous sequences (blocks) are called *block co-polymers*.

Eg.,- M – M – M – M - M1 – M1 - M1 - M1 - M – M – M – M –

If the linear polymer branches out, then it is called a *branch polymer*.

The polymers can be classified as follows, on the basis of their **method of formation**

(a) Addition polymers (b) condensation polymers

Addition polymers are formed by a process of self-addition of monomers without the elimination of any byproducts. Eg: Polyethylene & synthetic rubbers.

Condensation polymers are formed by condensation reaction i.e., reaction between two or more monomer molecules with the elimination of simple molecules like water, ammonia, HCl etc.,
Eg: Urea-formaldehyde resins, phenol-formaldehyde resins & polyesters.

The polymers can be classified on the basis of their **response to heat** as follows.

(a) Thermo softening (b) Thermosetting

The polymers, which soften on heating and can be converted into any shape, which they can retain on cooling, are called as thermo softening or thermoplastic polymers. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Eg: polyethylene, nylons , sealing wax.

The polymers which undergo some chemical change on heating and convert themselves into an infusible mass are called as thermosetting polymers. Eg: bakelite, egg yolk.

Based on their **application and properties** polymers are classified as follows.

(a) Plastics (b) Elastomers (c) Fibers (d) Resins

Plastics are the polymers, which are soft enough at some temperature to be moulded into a desired shape and hardened on cooling so that they can retain that shape. Eg: polystyrene, polyvinyl chloride, poly methyl methacrylate.

Elastomers are polymers in which the structural units are either zig zag or helical chains. They undergo elastic changes when subjected to an external force, but readily regain their original shape when the force is withdrawn. Eg: natural rubber, silicone rubbers.

Fibres are characterized by their molecular chains arranged parallel to each other in a spiral or helical pattern which do not undergo stretching or deformation and the molecular length is at least 100 times its diameter. Eg: nylons, terylene.

Resins are much lower molecular weight polymers either in liquid or solid form used as adhesives or moulding powders. It has a glossy appearance. Resins constitute the major essential part of the plastics. Eg: Polysulphide sealants, epoxy adhesives.

Polymerization

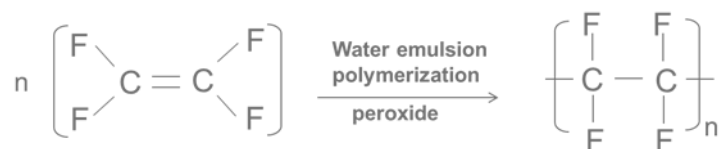
Polymerization is defined as the process by which the monomer molecules are linked to form a big polymer molecule.

Types of Polymerization:

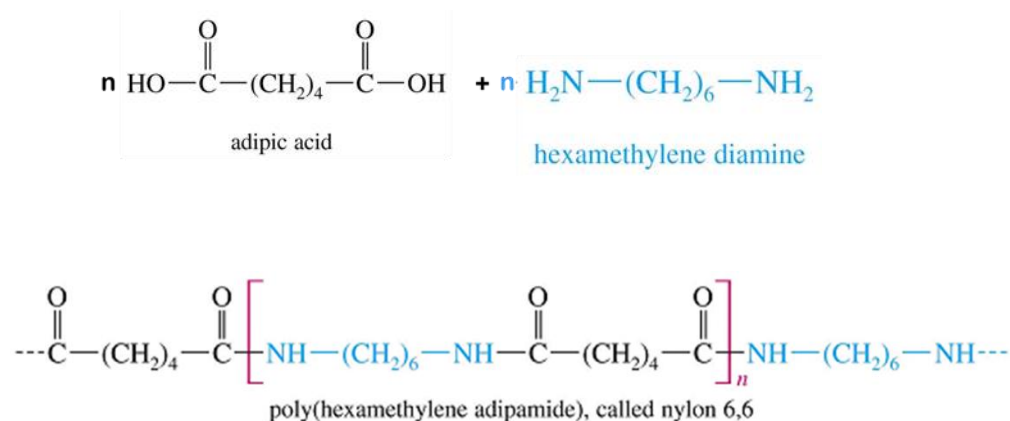
Polymerization occurs basically in two different modes.

1. Addition (chain growth) polymerization
2. Condensation (step growth) polymerization

Addition polymerization: The reaction in which self-addition of several olefinic monomers to each other takes place without elimination of by products is known as addition polymerization. The addition polymerization must be initiated by using heat or light or pressure or catalyst for the breakage of the double bonds of monomers.



Condensation Polymerization: The reaction in which monomers containing two or more reactive functional groups (hydroxyl, carboxyl, amino) condensing with each other.



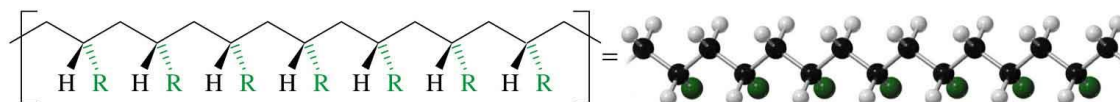
Distinguishing features of addition and condensation polymerisation

- | Addition polymerisation | Condensation polymerisation |
|---|--|
| <ul style="list-style-type: none"> ➤ Monomers undergo self addition to each other without loss of by products ➤ It follows free radical mechanism (Chain mechanism) ➤ Unsaturated vinyl compounds undergo addition polymerisation ➤ Monomers are linked together through C – C covalent linkages ➤ High polymers are formed fast ➤ Linear polymers are produced with or without branching ➤ Examples: polystyrene, plexiglass, PVC, etc. | <ul style="list-style-type: none"> ➤ Monomers undergo intermolecular condensation with continuous elimination of by products such as H₂O, NH₃, HCl, etc., ➤ It follows step mechanism ➤ Monomers containing the functional groups (-OH, -COOH, -NH₂) undergo this polymerization ➤ Covalent linkages are through their functional groups ➤ The reaction is slow and the polymer molecular weight increases steadily throughout the reaction ➤ Linear or cross linked polymers are produced ➤ Examples: nylons, terylene, PF resins, etc. |

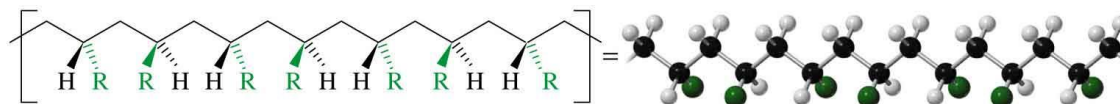
Stereo regular polymers (Tacticity in polymers)

This classification is based on the position of the substituent groups in the polymer chain. Depending on the position and regularity of the repeating substituent groups, three different arrangements can be visualized- isotactic, syndiotactic and atactic.

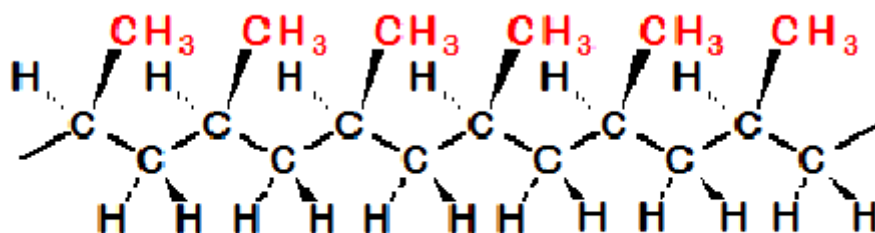
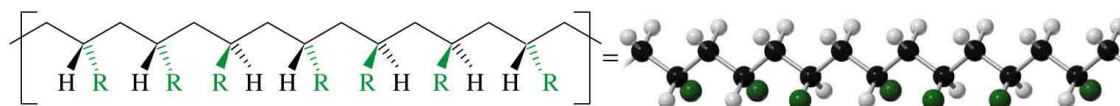
An isotactic polymer (side groups on the same side of the backbone)



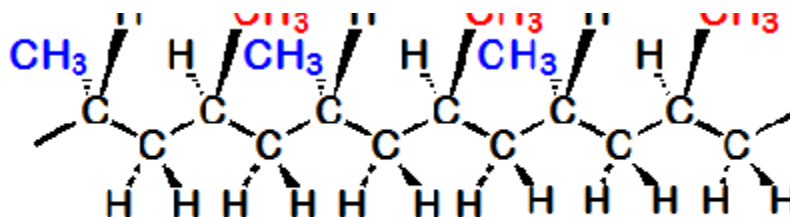
A syndiotactic polymer (side groups on alternating sides of the backbone)



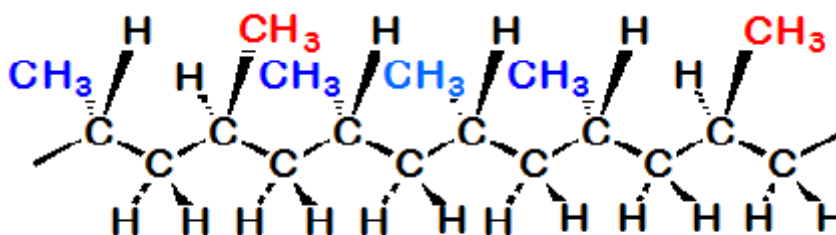
An atactic polymer (side groups on random sides of the backbone)



ISOTACTIC all methyl groups on the same side



SYNDIOTACTIC methyl groups alternate sides



ATACTIC methyl groups randomly oriented

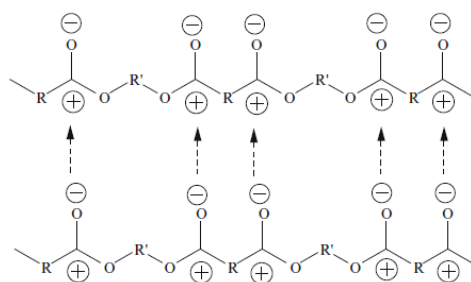
Structure and properties of polymers

The structure of a polymer has profound influence on some of the properties of polymers. The properties such as crystallinity, tensile strength, elasticity, resistance to chemicals and plasticity depend mostly on the polymer structure and are discussed below.

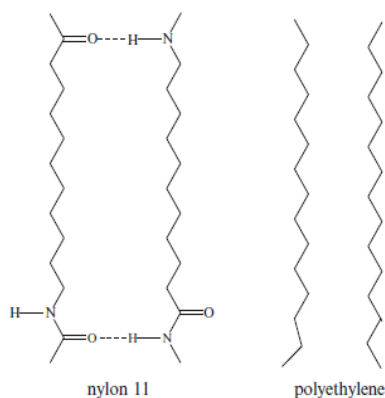
Strength: This property is discussed based on forces of attraction and slipping power.

Based on forces of attraction: Strength of the polymer is mainly determined by the magnitude and distribution of attraction forces between the polymer chains. These attractive forces are of two different types viz., primary or covalent bond and secondary or intermolecular forces.

In case of straight chain and branched chain polymers, the individual chains are held together by weak intermolecular force of attraction. But in these polymers, strength increases with increase in chain length (increase in molecular weight) i.e., attains mechanical strength if the chain length is greater than 150 – 200 carbon atoms in the chain. Less than these numbers, the polymers will be soft and gummy, but brittle at low temperature. Intermolecular forces can be increased by introducing polar groups like carbonyl & hydroxyl.



In cross-linked polymers, monomeric units are held together only by means of covalent forces. Hence possess greater strength than straight and branched chain.



Based on slipping power: Slipping power is defined as movement of molecules one over the other. Eg: polyethylene molecule is simple and uniform, hence movement of molecule one over

other is possible, i.e., slipping power is high. Hence it has lesser strength. But in case of polyvinyl chloride (PVC), bulky chlorine atoms are present along the chain length hence, movement is restricted, i.e., slipping power is less. Hence it has higher strength compared to polyethylene. But in case of cross-linked polymer, movement is totally restricted because of the presence of covalent bond. Hence these products are strong, rigid and tough.

Plastic deformation: When a polymer is subjected to some stress in the form of heat or pressure or both, permanent deformation in shape takes place, which is known as plastic deformation. This property actually helps in moulding of plastics. Slippage is more in case of linear molecules than branched and cross-linked, because of the presence of weak intermolecular forces and hence they show greatest degree of plastic deformation. At high pressure and temperature the vander Waal's forces acting between molecules become more and more weak. No slippage occurs in case of cross-linked polymers, because only strong covalent bonds are present throughout the entire structure. However, when considerable external force or temperature exceeding the stability of material is applied, it will result in total destruction.

Crystallinity: Based on the relative arrangement of polymer chains with respect to each other, polymer can exhibit amorphous and crystalline nature. An amorphous state is characterized by completely random arrangement of molecules and crystalline form by regular arrangement of molecules. The crystallization tendency of a polymer depends on the ease with which the chains can be aligned in an orderly arrangement. Crystalline regions of a polymer are formed when the individual chains are linear (without branching), contain no bulky substituents and are closely arranged parallel to each other. The chains of polymer may be held together by vander Waal's forces, hydrogen bonding or polar interactions. A polymer with high degree of crystallinity will have high tensile strength, impact and wear resistance, high density and high fusion temperature. Polymers with a long repeating unit or with low degree of symmetry do not crystallize easily, hence forms amorphous structure e.g., polystyrene. Crystallization imparts denser packing of molecules due to increase of intermolecular forces of attraction. Such type of polymers will have sharp softening point, greater strength and rigidity. e.g PVC, Polypropylene. Polymers are in general, amorphous with some degree of crystallinity.

Chemical Resistance: Chemical resistance of polymer depends upon the chemical nature of monomers and their molecular arrangement. A polymer is more soluble in structurally similar solvent. For example, polymers containing polar groups like – OH, - COOH, usually dissolve in polar solvents like water, alcohol etc but are chemically resistant to non-polar solvents. Similarly non-polar compounds like hydrocarbons dissolve only in non-polar solvents like benzene & toluene.

As a general rule, the tendency of solubility in a particular solvent decreases with increase in molecular weight of the polymer- (i) high molecular weight polymer on dissolving yield solutions of high viscosities (ii) crystalline polymers exhibit higher resistance than less crystalline polymers of similar chemical character (iii) greater the degree of crystallinity, lesser is its solubility.

Today several drugs and essential oils are stored in plastic bottles for long shelf life. If they disintegrate or change in their chemical composition they may render the drug ineffective or may cause it to react adversely when used, leading to specific disorder. Therefore, chemical resistance of plastic bottles is important to prevent drug polymer interactions.

Elasticity: Elastic nature in polymers results due to the uncoiling and recoiling of the molecular chains on the application of force. In an unstretched elastomer we can observe a peculiar configuration of irregularly coiled and entangled snarls in a random fashion, indicating the amorphous state. In a stretched state snarls disentangle and straighten out in a proper chain orientation, indicating the crystalline state. The crystallinity in a stretched rubber band can be observed from its opaqueness and warmth it produces when touched by lips. The main criteria for a polymer to show elastic nature is that, the individual chains should not break even after prolonged stretching. This can be done by introducing suitable crosslinking in the chains, by allowing nonpolar groups or side groups in the repeating unit.

Glass transition temperature T_g

Amorphous polymers do not have sharp melting points. They possess softening point. At low temperature, polymers exist as glassy substances. Since the molecular chains cannot move at all easily in this state, the solid tends to shatter, if it is hit. If the solid polymer is heated, eventually it softens and becomes flexible. This softness and flexibility is obtained at the glass transition temperature. After this temperature, crystalline and amorphous thermoplastic polymers behave differently. Heating has little effect on thermosetting polymers and at a high temperature, they are destroyed.

So the **glass transition temperature** can be defined as the temperature below which an amorphous polymer is brittle, hard and glassy and above the temperature it becomes flexible, soft and rubbery.

Glassy state	—————>	rubber state
(Hard brittle plastic)		(soft flexible)

In the glassy state of the polymer, there is neither molecular motion nor segmental motion. When all chain motions are not possible, the rigid solid results. On heating beyond T_g segmental motion becomes possible but molecular mobility is disallowed. Hence flexible,

Factors affecting glass transition Temperature

Glass transition temperature of a polymer depends on parameters such as chain geometry, chain flexibility, molecular aggregates, hydrogen bond between polymer chains, presence of plasticizers and presence of substrates in the polymer chains.

A polymer having regular chain geometry show high glass transition temperature, the bulky groups on chain increases the T_g of the polymer. E.g., polyethylene has T_g -110 °C. The T_g is quite low because there are no strong intermolecular forces and no bulky side groups are present, the side chain is only hydrogen atom. But nylon 6 has T_g 50 °C because of the presence of large number of polar groups in the molecule leading to strong intermolecular hydrogen bonding.

The T_g of a polymer is influenced by its molecular weight. However, it is not significantly affected if molecular weight is around 20000. With increase in molecular mass, the temperature (T_g) will be higher.

In crystalline polymers the polymer chains are arranged in a regular parallel fashion. Each chain is bound to the other by strong forces like H-bonding. Hence crystalline polymers have higher T_g than amorphous polymers.

The added plasticizers reduce the T_g of the polymer by reducing the cohesive forces of attraction between the polymers. e.g., dibutyl phthalate, diacetyl phthalate etc.,

The glass transition temperature is an important parameter of polymeric material. This helps in choosing the right processing temperature. It is a measure of flexibility of a polymer and also gives the idea of the thermal expansion, heat capacity, electrical and mechanical properties of the polymer.

Molecular weight of polymers

A polymer comprises of molecules of different molecular weights and hence, its molecular weight is expressed in terms of an 'average' value. Eg. In ethylene gas each of its molecules has the same chemical structure and hence, a fixed molecular weight of 28. But upon polymerization, it forms polyethylene and we encounter an indefinite chemical structure of -- $(-CH_2 - CH_2 -)_n$ —where 'n' can change its value from one polyethylene molecule to another present in the same polymer sample.

When ethylene is polymerized to form polyethylene, a number of polymer chains start growing at any instant, but all of them do not get terminated after growing to the same size. The chain

termination is a random process and hence, each polymer molecule formed can have a different number of monomer units and thus different molecular weights. So a sample polymer can be thought of as a mixture of molecules of the same chemical type, but of different molecular weights.

In this situation, the molecular weight of the polymer can only be viewed statistically and expressed as some average of the molecular weights contributed by the individual molecules that make the sample.

So the molecular weight of a polymer can be expressed by two most and experimentally verifiable methods of averaging - (i) Number – average and (ii) weight – average.

Number – average molecular weight: Number average molecular mass of a polymer can be defined as the total mass of all the molecules in a polymer sample divided by the total number of molecules present.

Weight – average molecular weight: The sum of the fractional masses that each molecule contributes to the average according to the ratio of its mass to that of the whole sample.

White foam cups, clear plastic cups and ultrathin fishing line are made of polystyrene with different average molar masses while styrofoam cups are made from beads of polystyrene with an average mass of approximately 15000 g/mol. Clear plastic cups are made by melting polystyrene with average mass of approximately 250000 g/ mol. Ultrathin fishing lines are composed of polystyrene with an average mass of 1000000 g/ mol.

$$\overline{M}_n = \frac{\sum_{i=1}^N N_i M_i}{\sum_{i=1}^N N_i} = \frac{\sum_{i=1}^N w_i}{\sum_{i=1}^N \frac{w_i}{M_i}}$$

$$\overline{M}_w = \frac{\sum_{i=1}^N N_i M_i^2}{\sum_{i=1}^N N_i M_i} = \frac{\sum_{i=1}^N w_i M_i}{\sum_{i=1}^N w_i}$$

\overline{M}_n = Number average molecular weight
 \overline{M}_w = Weight average molecular weight
 N = Total number of molecules
 N_i = Number of molecules with molecular weight M_i
 w_i = weight fraction of all molecules with molecular weight M_i

Application of Average molecular mass (AMM)

It is used to characterize a polymer. Samples of the polymer prepared under different conditions may have different AMM. It affects the mechanical, solution & melt properties of the polymer. Chain length is related to the ease of processing of the polymer. The longer the chain, the more difficult the melt is to process. The polymer chain becomes more entangled as the molecules get larger and offer more resistance to flow at the molecular level. In most applications, the polymer must be able to flow so that it can be flattened into sheets, moulded into bottles and so on.

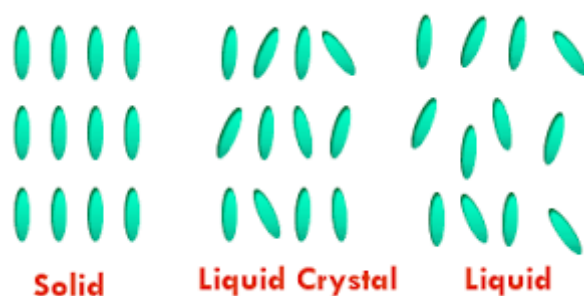
Numerical Problems

- 1) Calculate the number average & weight average molecular weight of a polymer sample in which 40 % molecules have molecular mass of 25000, 20 % have molecular mass of 30000 & rest have molecular mass of 55000.
- 2) A polymer sample contains 1, 2, 3 & 4 molecules having molecular weight 10^5 , 2×10^5 , 3×10^5 and 4×10^5 respectively. Calculate the number average & weight average molecular weight of the polymer.

5.3 Liquid crystals

Liquid Crystals (LC) possess properties of both the conventional liquids and solid crystals. They find application in the areas of science and engineering, particularly in display systems of modern electronic gadgets. Devices using liquid crystal displays have the advantage of low power consumption and hence are widely used in display devices of mobile communication appliances, aircraft cockpit, laptops and other electronic equipments.

In a crystalline state, the molecules (or atoms) are having a definite position and orientation in space in a regular repeated manner in a rigid arrangement and are immobile. They tend to orient in a preferred direction i.e., the molecules in solids have a positional and orientational order. In the liquid state, the molecules neither occupy specific positions nor remain oriented in a particular manner. The molecules are somewhat free to move at random and collide with one another, abruptly change their positions. The liquids have neither positional order nor orientational order. A liquid crystal (LC) is a state of matter exists between solids and liquids with both the properties. Normally when a low molar mass solid melts, it forms an ordinary liquid and is isotropic. Organic substances which are geometrically anisotropic i.e., long and relatively narrow molecular shape exhibits this intermediate state of order between solid crystals and isotropic liquids. They undergo more than a single transition in passing from solid to liquid through different intermediate states on heating. These intermediate states with different molecular ordering are also known as mesophases, derived from a Greek word, *mesos* meaning middle. In mesophase state either the individual molecules align with respect to each other or exhibit some regular position with respect to each other. The molecular arrangement in solids, liquid crystals and liquids can be represented as below.



In a liquid crystal, the molecules possess orientational order, i.e., the molecules tend to remain oriented in a particular direction. The direction of preferred orientation in a liquid crystal is called the **director** (\bar{n}) and may be imagined to be directed towards the top or bottom of the page. Since the molecules are in constant motion, in liquid crystal phase they spend more time pointing along the director than along any other direction. The extent of orientational order

can be described by taking an average. An average of 0° indicates perfect orientation and can be expected in solids. An average of greater than 45° indicates no orientational order and found in liquids. However, in liquid crystals, a smaller average angle with the director is observed which indicates orientational order.

The quality of any device using LCs depends mainly upon the **physical properties** of the LC molecules. To achieve a high performance of the LC device, it is essential to select the most appropriate LC material according to the specific requirements of the desired device. In general, the LCs must satisfy the following characteristic properties

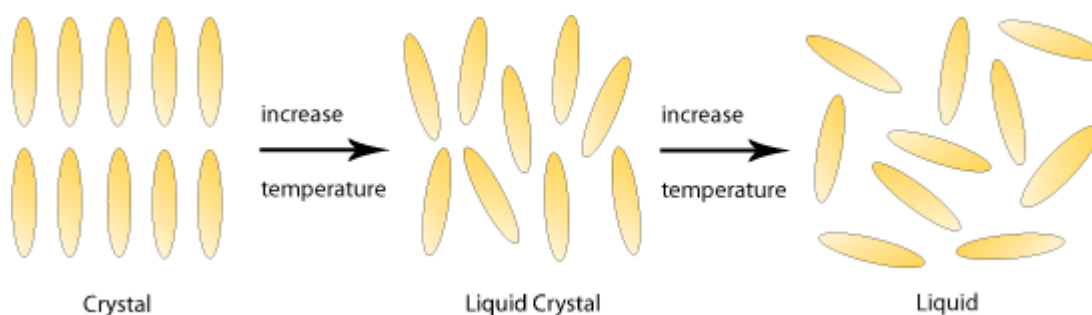
- a. Liquid crystalline nature should be at room temperature and the entire temperature range of the device operation
- b. Chemically, electrochemically, photochemically and thermally stable
- c. Permanent electric dipole
- d. Should possess easily polarizable substituents

6.3.1 Classification of Liquid Crystals

Based on the response to temperature or concentration, Liquid Crystals are broadly classified as

- ❖ Thermotropic LCs
- ❖ Lyotropic LCs

The liquid crystalline substances which undergo transitions by variation in temperature are called thermotropic LCs. Eg. p-azoxyanisole. The liquid crystalline substances which undergo transitions by the influence of solvents are called lyotropic LCs. Eg. sodium stearate. Both these systems can be characterized by anisotropic viscous, electrical, optical and mechanical properties. Organic molecules, which are able to form thermotropic as well as lyotropic mesophases, are termed as amphotropic LCs.



Thermotropic Liquid Crystals: Based on the mesophase, the TLCs are further classified as

- a. nematics
- b. smectics
- c. columnar
- d. cubic

Nematic: The properties of this phase are very close to liquid or they possess most liquid-like structure. The molecular axes are oriented parallel to one another, resulting in a long range of an orientational order. They do not possess positional order.

Smectic: The properties of this phase are very close to solid. They possess layered structures with many possibilities of the state of order inside the layers. They show long-range orientational as well as partial positional order.

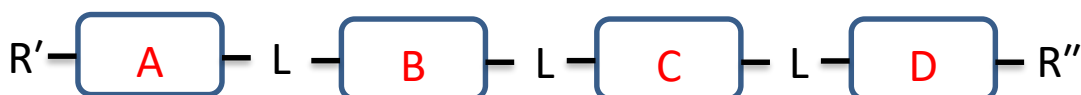
Columnar: Structures with columns consisting of parallel arranged disc-like molecules.

Cubic: Structures with micellar lattice units or complicated interwoven networks.

Based on the shape of the constituting molecules, the thermotropic LCs can be further classified as

- (i) Calamitic LCs
- (ii) Discotic LCs
- (iii) Polycatenar LCs
- (iv) Bent (Banana) LCs

Calamitic Liquid Crystals: The LC compounds possessing rod-like molecular shape belong to this category. The general molecular structure of a calamitic LC is as given below.

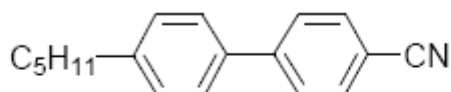


Where A, B, C, and D are called the rigid cores (containing a phenyl, biphenyl, naphthyl, cyclohexyl or five/six-membered heterocycles) of the molecule. In a Liquid crystal, there should be at least one rigid core.

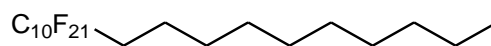
‘L’ is the linking group (an imine, azo, azoxy, ester, thioester, C=C, and C≡C)

R’ or R’’ is the end group/chain (a halo group, cyano, nitro, alkyl or alkoxy groups)

Some examples of the calamitic LCs are given below.

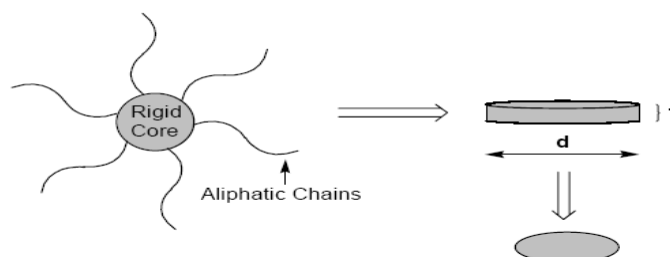


Molecular structure of 4-pentyl-4'-cyanobiphenyl

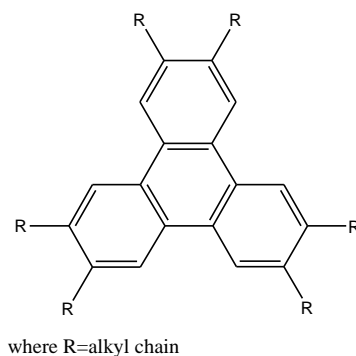


(perfluorodecyl)-decane

Discotic Liquid Crystals: Discotic compounds consist of flat and disc-like rigid cores which are surrounded by flexible chains such as alkyl, alkyloxy or alkanoyloxy. These discotic molecules can be stacked one over another in many ways so as to obtain different columnar structures like hexagonal, rectangular or oblique symmetry. Within the columns, the molecules can have a certain order or disorder. The general structure of discotic LCs can be represented with the following cartoon picture.



In discotic liquid crystals, the molecular diameter (d) is much greater than the disc thickness (t) to form anisotropy. A typical molecular structure of a discotic molecule is shown below.



Polycatenar Liquid crystals: Polycatenar mesogens are considered as a hybrid class of thermotropic LCs, as its molecular features lie intermediate between classical rod-like and disc-like mesogens. Schematically the central core of polycatenar LCs comprises a calamitic region, with half-discs on the extremities. This hybrid molecular structure allows them to exhibit both calamitic (nematics/smectic) and discotic (columnar) phases, depending on the specific molecular structure of the components. E.g., the tetracatenar mesogens (shown below), at shorter chain lengths exhibit nematic and/or smectic-C phases, while at longer chain lengths exhibit columnar phases. The numbers of the flexible end chains of the core can be indicated by using the term, m,n -polycatenary mesogen. The different polycatenar LCs can be represented with the following schematic diagrams.

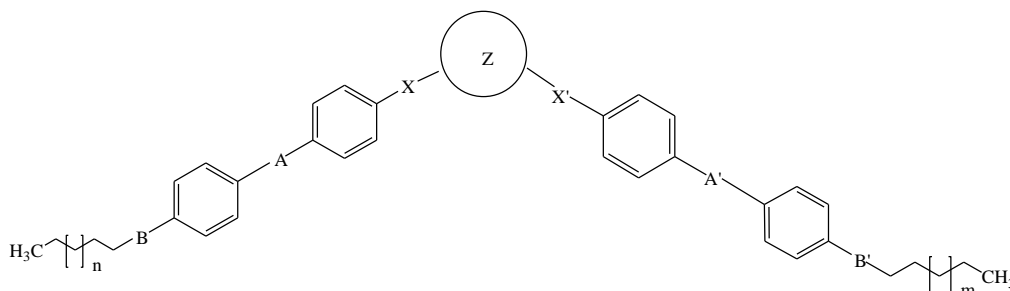


2,2-polycatenary mesogen



3,1-polycatenarymesogen

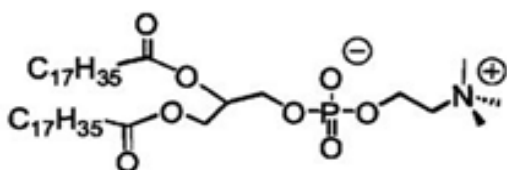
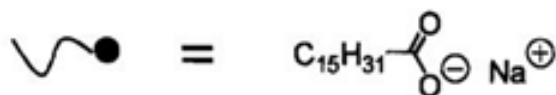
Bent (Banana) Liquid Crystals: Bent (Banana) shaped liquid crystals are constituted of two mesogenic groups linked through a rigid core in such a way that the molecule is not a linear (as shown in the following figure). The central rigid core (Z) may be a phenyl or biphenyl or naphthyl group. The mesogenic groups attached to the central core are mostly the calamitic molecules consisting of two (or more) aromatic rings with different linking groups (A, B, X, A', B', X') and a terminal chain/a substituent in para position to the linking group of the aromatic rings. The angle between the two calamitic wings (bending angle) is around 120° . In case of a benzene central core, the mesogens are connected in 1 and 3 positions (i.e., meta position to each other). If the central core is a naphthyl, the two calamitic wings are connected in 2 and 7 positions.



Lyotropic Liquid Crystals: Lyotropic liquid crystals form anisotropic aggregates when combined with a solvent, like water. The phase behavior is dependent on the concentration and polarity of solvent and also on the temperature. Molecules which form lyotropic phases are usually amphiphilic, having non-polar, hydrophobic "tails" at one end with a polar, hydrophilic "head" at the other end. Some examples are sodium stearate (soap) and phospholipids. The concentration of material in the solvent and the response of the amphiphile to the solvent environment dictate the type of lyotropic phase formed. For example, in a polar solvent like water, micelles are formed in which the hydrophobic tails assemble together and the hydrophilic heads groups are presented to the solvent. When combined with a non-polar solvent such as hexane, an inverse micelle is formed where the hydrophobic tails shield the

hydrophilic head groups from the non-polar environment. Under certain conditions, these micelles further aggregate to form more complicated assemblies, such as lamellar and hexagonal Phases, which generate lyotropic liquid crystal phases. Lamellar phases are particularly significant as they form the structural basis for biological membranes

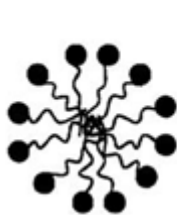
Examples of Lyotropic liquid crystals and their phase structures



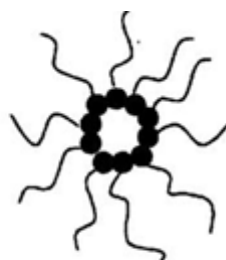
Sodium Sterate

Phospholipid

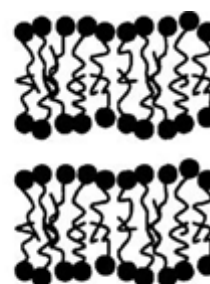
Micellar aggregates and phase structures formed by Lyotropic liquid crystals are shown below.



a.) micelle



b.) inverse micelle



c.) lamellar

6.3.2 Applications of liquid crystals:

Liquid crystal displays operate at low voltages (a few volts) and consume less power as compared to other displays and hence are used in:

1. Liquid crystal displays: Used in display devices such as watches, calculators, mobile telephones, laptop computers, and clocks.
2. Liquid crystal thermometers: Chiral nematic LCs reflect light and the color which is reflected is temperature dependent.

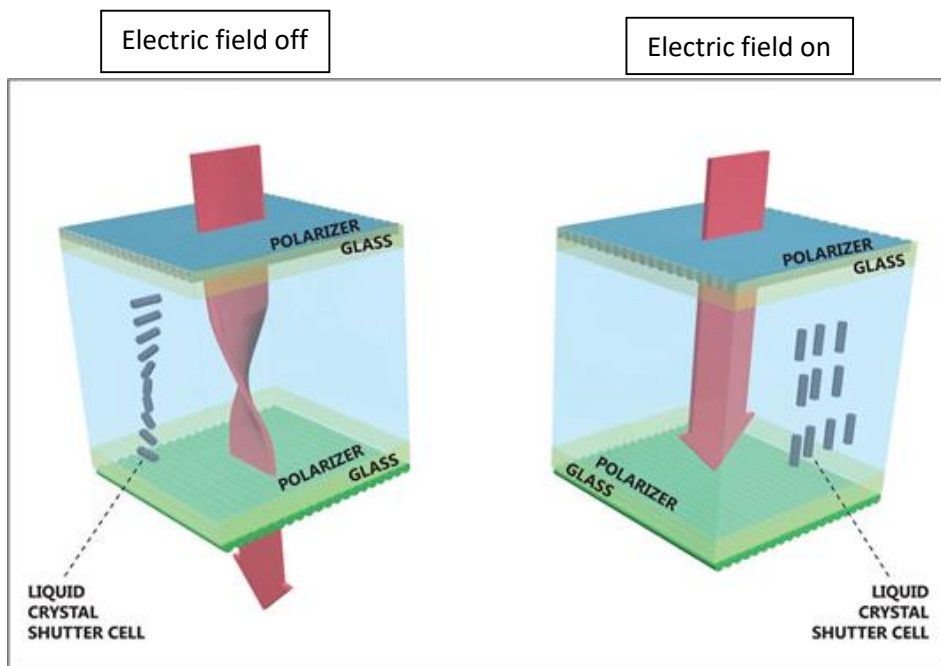
6.3.3 Liquid Crystals in Display systems

The electro-optic effect of liquid crystals controls the brightness/darkness of the light emerging from its elements and this is used in information displays. Information is passed on to the user

using LCs which control the brightness/darkness of the parts of a display. Liquid Crystal Displays are available in many sizes and can be used to display numeric, alphanumeric and graphic images. The numeric display has seven segments whereas alphabets are displayed using fourteen segments. More complex graphic images are formed using pixels (picture elements) which are closely packed array of dots in two dimensions.

A numeric display consists of seven segments for each digit. Light from the area of each of the seven segments is controlled independently and is used to create any one of the ten digits. When an electric field is applied to a segment, the liquid crystal in that segment undergoes deformation (is activated) and when polarized light is incident, the light is modulated depending on the deformation in that segment.

In twisted nematic displays (TND), the nematic LC is sandwiched between two ITO coated glass plates with parallel (homogeneous) alignment of its molecular director with the glass walls. However, the two glass plates are twisted by 90° relative to each other (as shown in the following figures).



In such geometry, the LC is forced to perform a 90° twist of the director resulting in a helical structure. The distance between the plates, hence the thickness of the LC film, is typically 6–10 μm . To complete the TND unit, a pair of crossed polarizers is placed on the outer side of the glass plates. In the absence of an external electric field, when linearly polarized light enters the device, the LC film rotates the polarization of the light by 90° . Thus, the light reaches the

second polarizer with its polarization plane parallel to the polarizer axis and is transmitted. In this configuration, the display appears bright (off-state). However, when an electric field is applied (on-state), the 90° twist in the cell is lost and the LC molecules reorient in order to align the molecular director with the external electric field, causing the helical arrangement to be unwound. As a consequence, the light passing through the LC film is not guided through 90° and is not able to pass through the second polarizer. The display looks dark and the observer can see the black character on a silver gray background.

5.4 Composite materials

A composite material is a material system composed of two or more macro constituents that differ in shape and chemical composition. Many modern technologies require materials with proper combinations of properties that cannot be met by conventional metal alloys, ceramics, and polymeric materials. This is especially true for structural materials that have low densities are strong, stiff and abrasion resistant and are needed for aerospace, underwater and transport applications. Other applications of these materials involve automotive, home appliance and sporting goods, industries.

Material property combinations and ranges have been extended by the development of composite materials. A composite is composed of two (or more) individual materials which come from the categories, namely metals, ceramics, and polymers. Thus ***Composites are artificially produced multiphase materials having a desirable combination of the best properties of the constituent phases.*** Usually, one phase (the matrix) is continuous and surrounds the other (the dispersed phase). The properties of composites are a function of the properties of the constituent phases, their relative amounts and the geometry of the dispersed phase.

Some composites occur in nature. For example, wood consists of strong and flexible cellulose fibers surrounded and held together by a stiffer material called lignin. However, most are synthetic composites. One of the most common and familiar composites is fiberglass, in which small glass fibers are embedded within a polymeric material (epoxy or polyester). The glass fibers are relatively strong and stiff (but also brittle), whereas the polymer is ductile. The plastic matrix holds the glass fibers together and also protects them from damage by sharing out the forces acting on them. It is still widely used today for boat hulls, sports equipment, building panels and many car bodies.

An optimum combination of properties is usually sought rather than one particular property, in selecting a composite material. For example, wings of an aircraft must be lightweight and be strong, stiff and sturdy. Several fiber-reinforced polymers possess this combination of properties. Adding significant amounts of carbon black to natural rubber increases its strength drastically.

Properties of composite materials are determined by three factors.

- i) The materials used as component phases in the composite
- ii) The geometric shapes of the constituents
- iii) The manner in which the phases interact with one another.

Classification of composites

Composites are classified into various types based on different parameters. One such classification is based on the matrix material, and the reinforcement geometry (particles, fibers, layers) and the simple scheme of such classification are shown below consisting of three main divisions.

I. Particle reinforced - Properties are isotropic

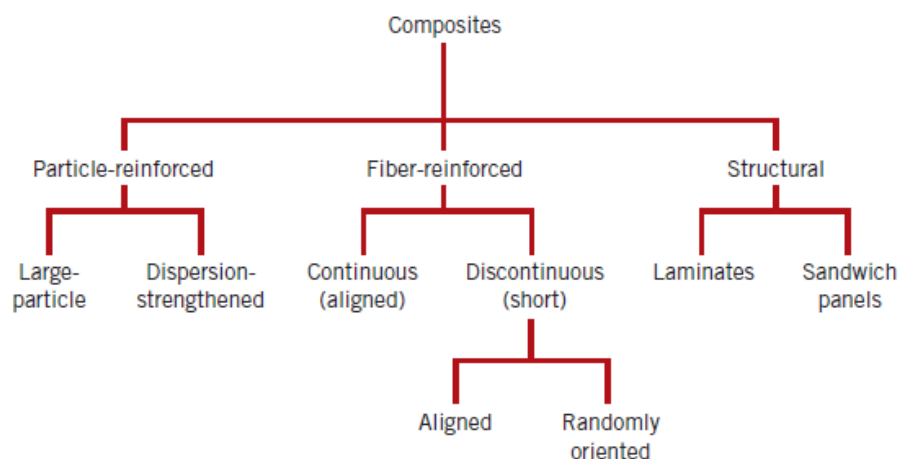
- Large particle
- Dispersion strengthened

II. Fiber reinforced - Properties can be isotropic or anisotropic

- Continuous (aligned)
- Discontinuous(short) – Aligned and Randomly oriented

III. Structural - Based on the build-up of sandwiches in layered form

- Laminates
- Sandwich panels

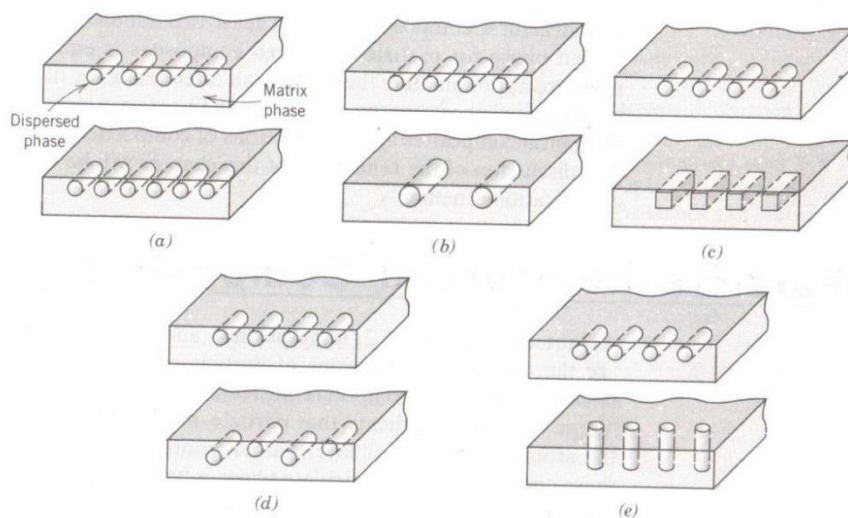


Particle reinforced:

The dispersed phase for particle reinforced composites is equiaxed (i.e., particle dimensions are approximately the same in all directions). Large particle and dispersion –strengthened composites fall within this category. The distinction between these is based upon reinforcement or strengthening mechanism.

For most of the large particle reinforced composites, the particulate phase is harder and stiffer than the matrix. In essence, the matrix transfers some of the applied stress to the particles, which bear the friction of the load.

For dispersion-strengthened composites, particles usually are much smaller. In this the matrix bears the major portion of an applied load, the small dispersed particles hinder the motion of dislocations. Thus plastic deformation is restricted such that yield and tensile strengths, as well as hardness improve.



Fiber reinforced:

The essential composites are those in which the dispersed phase is in the form of a fiber. The dispersed phase has the geometry of a fiber (large length to diameter ratio). Design goals of fiber reinforced composites often include high strength and /or stiffness on a weight basis. With these composites, an applied load is transmitted to and distributed among the fibers via the matrix phase. Based on diameter, fiber reinforcements are classified as whiskers, fibers, or wires.

Fiber orientation and concentration have a significant influence on the strength and other properties of fiber reinforced composites. With respect to orientation, two extremes are possible;

- i) a parallel alignment of the longitudinal axis of the fibers in a single direction and

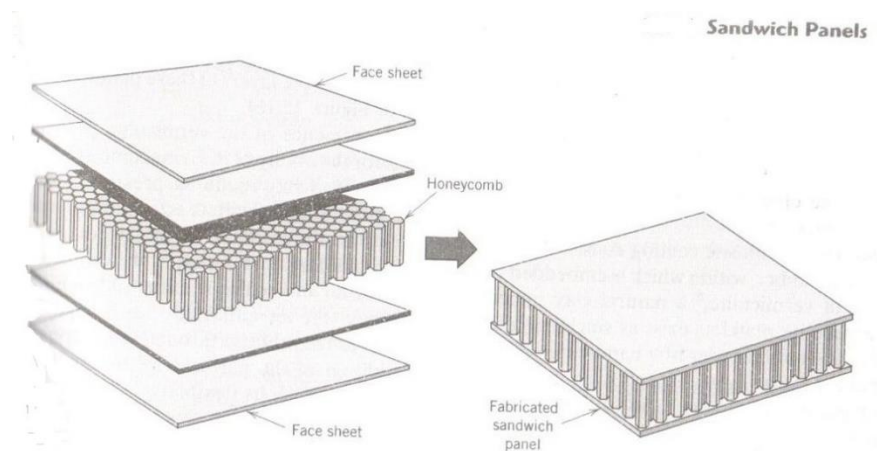
ii) a random alignment. Continuous fibers are generally aligned, whereas discontinuous fibers may be aligned randomly oriented or partially oriented. Better overall composite properties are realized when the fiber distribution is uniform.

Structural:

Structural composites are combinations of composites and homogeneous materials, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Laminar composites and sandwich panels are two of the most common structural composites.

The properties of laminar composites are virtually isotropic in a 2-D plane. This is made possible with several sheets of a highly anisotropic composite, which are cemented onto one another such that the high strength direction is varied with each successive layer.

Sandwich panels consist of two strong and stiff faces that are separated by a core material or structure. These structures combine relatively high strengths and stiffnesses with low densities.



Influence of length, orientation, concentration, and elastic behavior of fibers

Influence of fiber length

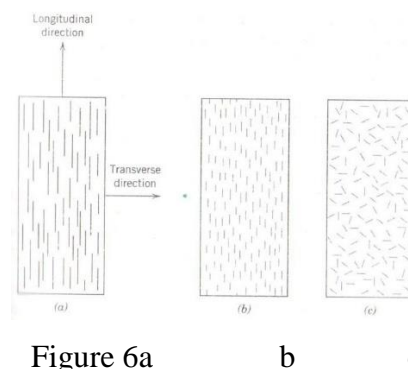
The mechanical characteristics of a fiber-reinforced composite depend not only on the properties of the fiber but also on the degree to which an applied load is transmitted to the fibers by the matrix phase, which in most cases is at least moderately ductile. Significant reinforcement is possible only if the matrix – fiber bond is strong. Based on diameter, fiber

reinforcements are classified as whiskers, fibers, or wires. Since reinforcement discontinues at the fiber extremities, reinforcement efficiency depends on fiber length. For each fiber – matrix combination, there exists some critical length; the length of continuous fibers dramatically exceeds this critical value, whereas shorter fibers are discontinuous.

For some glass and carbon fiber–matrix combinations, this critical length is on the order of 1 mm, which ranges between 20 and 150 times the fiber diameter.

Influence of fiber orientation and concentration

The arrangement or orientation of the fibers relative to one another, the fiber concentration, and the distribution all have a significant influence on the strength and other properties of fiber-reinforced composites. Concerning orientation, two extremes are possible: (1) a parallel alignment of the longitudinal axis of the fibers in a single direction, and (2) a random alignment. Continuous fibers are normally aligned (Figure 6a), whereas discontinuous fibers may be aligned (Figure 6b), randomly oriented (Figure 6c), or partially oriented. Better overall composite properties are realized when the fiber distribution is uniform.



Fiber arrangements are also crucial relative to composite characteristics. The mechanical properties of continuous and aligned fiber composites are highly anisotropic. In the alignment direction, reinforcement and strength are a maximum; perpendicular to the alignment they are minimum.

For short and discontinuous fibrous composites, the fibers may be either aligned or randomly oriented. Significant strengths and stiffness are possible for aligned short-fiber composites in the longitudinal direction. Despite some limitations on reinforcement efficiency, the properties of randomly oriented short fiber composites are isotropic.

Elastic Behavior—Longitudinal Loading

When the load is applied on the composite in the direction of the orientation of continuous fiber, then its modulus of elasticity is equal to the summation of the products of the modulus of elasticity (E) and volume fraction (V) of the respective phases.

i.e., Modulus of elasticity of composite, $E = (EV)_{\text{matrix}} + (EV)_{\text{fiber}}$

When the load is applied on the composite perpendicular to the orientation of continuous fiber, the inverse of the modulus of elasticity is equal to the summation of the ratio of volume fraction (V) and modulus of elasticity (E) of the respective phases.

i.e., $1/E = (V/E)_{\text{matrix}} + (V/E)_{\text{fiber}}$

$$\frac{1}{E} = \left(\frac{V}{E}\right)_{\text{matrix}} + \left(\frac{V}{E}\right)_{\text{fiber}}$$

Polymer – Matrix Composites

Polymer-matrix composites (PMCs) consist of a polymer resin as the matrix, with fibers as the reinforcement medium. These materials are used in diverse composite applications, as well as in the largest quantities, due to their room-temperature properties, ease of fabrication, and cost.

Polymer matrix materials:

The matrix materials used in composites are polyesters, vinyl esters, epoxies, polyetheretherketone (PEEK), polyphenylene sulfide (PPS), and polyetherimide (PEI). PEEK, PPS and PEI are the polymeric resins with potential aerospace applications.

The fibers, which are the reinforcing materials generally used are - Glass fibers, carbon fibers or aromatic polyamides (or aramids). Accordingly, they are classified into three categories.

- i) Glass Fiber-Reinforced Polymer (GFRP) Composites,
- ii) Carbon Fiber-Reinforced Polymer (CFRP) Composites, and
- iii) Aramid Fiber-Reinforced Polymer Composites.

The fiber is embedded in the matrix to make the matrix stronger. Fibre reinforced composites impart two important properties: (i) often stronger than steel (ii) less weight. This means that composites can be used to make automobiles lighter, and thus making them more fuel efficient.

Advantages of polymer composites: Polymer composite materials are preferred to conventional metals and materials for the following advantageous properties;

- Lightweight.
- High strength to weight ratio.
- More durable than conventional materials like steel and aluminum.
- Good corrosion resistance.
- High fatigue strength.
- High-temperature resistance.

Applications:

- Composites of phenolic resins and nylon are used in heat shields for space crafts.
- Automotive and railway applications.
- As the structural material in construction industries.

i) Glass Fibre Reinforced Plastic (GFRP):

Glass Fibre Reinforced Plastic is a typical polymer composite in which the reinforcing material is fiberglass. Its matrix is made by reacting a **polyester with carbon-carbon double bonds** in its backbone and **styrene** - a mix of the styrene and polyester over a mass of glass fibers.

The styrene and double bonds in the polyester react by free radical polymerization to form a cross-linked resin. The glass fiber is trapped inside, where they act as a reinforcement. The matrix adds toughness to the composite, while fibers have good tensile strength. The matrix gives compressional strength to the composite. Fiber reinforced composites are used in applications like car engine components, airplane parts.

ii) Carbon Fiber Reinforced Polymer (CFRP) Composite:

Carbon is a high-performance fiber material that is most commonly used reinforcement in advanced polymer matrix composites. The reasons for this are as follows:

1. Carbon fibers have the highest specific modulus and specific strength of all reinforcing fiber materials.

2. They retain their high tensile modulus and high strength at elevated temperatures; high-temperature oxidation, however, may be a problem.
3. At room temperature, carbon fibers are not affected by moisture or a wide variety of solvents, acids, and bases.
4. These fibers exhibit a diversity of physical and mechanical characteristics, allowing composites incorporating these fibers to have specific engineered properties.
5. Fiber and composite manufacturing processes have been developed that are relatively inexpensive and cost-effective.

Use of the term “carbon fiber” may seem perplexing since carbon is an element. Carbon fibers are not totally crystalline, but are composed of both graphitic and noncrystalline regions; these areas of non-crystallinity are devoid of the three-dimensional ordered arrangement of hexagonal carbon networks that is characteristic of graphite. Manufacturing techniques for producing carbon fibers are relatively complex and will not be discussed. However, three different organic precursor materials are used: rayon, polyacrylonitrile (PAN), and pitch. Processing technique will vary from precursor to precursor, as will also the resultant fiber characteristics.

Carbon-reinforced polymer composites are currently being utilized extensively in sports and recreational equipment (fishing rods, golf clubs), filament-wound rocket motor cases, pressure vessels, and aircraft structural components—both military and commercial, fixed wing and helicopters (e.g., as a wing, body, stabilizer, and rudder components).

iii) Aramid Fiber-Reinforced Polymer Composite:

Aramid fibers are high-strength, high-modulus materials that were introduced in the early 1970s. They are especially desirable for their outstanding strength-to-weight ratios, which are superior to metals. Chemically, this group of materials is known as poly(paraphenylene terephthalamide). There are some aramid materials; trade names for two of the most common are Kevlar™ and Nomex™.

Kevlar composites:

Kevlar is an aromatic polyimide (or aramid). The chemical composition of Kevlar is poly(para phenyleneterephthalamide). They belong to the family of nylons. Common nylons, such as nylon-6,6 do not have very good structural properties, so the incorporation of para-aramids

improve the properties. The aramid ring gives Kevlar its thermal stability, while the para structure gives it high strength and modulus. Kevlar is used as matrix material, whereas many fibers like carbon fiber or glass fiber are used as the reinforcing agent.

Advantages:

- Lightweight, high strength, Thermally Stable
- Resistant to impact and abrasion damage. It can be used as a protective layer on graphite laminates.
- Can be mixed with graphite to provide damage resistance and to prevent failure.

Disadvantages:

- Fibers themselves absorb moisture, so Kevlar composites are more sensitive to the environment than glass or graphite composites.
- Poor compression resistance.

5.5 Thin films

A thin film in general, refers to films with thickness ranging from 0.1 μm to about 300 μm . Coatings such as paint or varnish are typically much thicker. Thin film coatings have unique properties and hence make them desirable for a variety of reasons including materials conservation and design flexibility. A large number of materials which are used for coatings today range from the naturally occurring oxide layer (which protects the surfaces of many metals such as aluminum, titanium, and stainless steel), to those with very deliberate and controlled alloying additions to the surface to produce specific properties as follows;

- Chemically stable in the environment where it is used
- Adhere well to the substrate
- Uniform thickness
- Chemically pure or of controlled chemical composition
- The low density of imperfections
- Optical or magnetic properties, insulator or semiconductor as required for particular applications

As the film is inherently fragile, the bonding between the thin film and substrate provides the structural support. The bonding forces may be primary chemical in nature. Eg. The oxide lattices of the metal oxide and the glass blend at the interface forming a thin zone of intermediate composition. The bonding energies are in the range of 250 - 400 kJ/mol. In some cases, the bonds are based on intermolecular van der Waals and electrostatic forces. The energies are in the range of 50-100 kJ/mol. Eg. Deposition of polymer film on a metal surface

Uses of thin films

They are used as conductors, resistors and capacitors. They are widely used as optical coatings on lenses to reduce reflection and to protect the softer glass against scratching. Thin metallic films have been used as protective coatings on metals. Eg. Silver plating, chrome plating. Metal tool surfaces are coated with ceramic thin films to increase their hardness. The top of the drill bit is normally coated with a thin film of tungsten carbide to impart hardness and wear resistance. The films are applied to the glass to reduce scratching and abrasion and to increase lubricity.

Formation of thin films

The process of applying a thin film to a surface is known as thin-film deposition or fabrication. It is the technique for depositing a thin film of material onto a substrate or onto previously deposited layers. Thin films are formed by different techniques such as physical vapor deposition (PVD) or chemical vapor deposition (CVD). In PVD there is no change in the chemical nature of the source and coated material whereas in CVD due to chemical reactions occurring, the chemical identity of the source and the coated thin film materials are different.

Physical vapor deposition

PVD processes are atomistic deposition processes in which material is vaporized to form a solid or liquid source in the form of atoms or molecules, transported as vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. The material to be deposited is placed in an energetic, entropic environment so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to thousands of nanometers. The substrates can range in size from very small to very large, in shape from flat to complex geometries. The source-substrate geometry influences the ultimate film uniformity. Two principal methods for optimizing film uniformity over large areas involve varying the geometric location of the source and interposing static as well as rotating shutters between evaporation sources and substrates. The chemical purity of evaporated films depends on the nature and level of impurities that (1) are initially present in the source, (2) contaminate the source from the heater, crucible, or support materials, and (3) originate from the residual gases present in the vacuum system. Typical PVD deposition rates are 10-100 Å/s.



Fig. PVD: Process flow diagram

Vacuum evaporation is one of the important methods for depositing thin films using PVD technique.

Vacuum deposition: This method is used to form thin films of substances that can be vaporized without destroying their chemical identities. Eg. Optical lenses are coated with inorganic materials such as MgF_2 , Al_2O_3 and SiO_2 . During evaporation, a target consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions in a high vacuum chamber with a pressure of 10^{-5} torr or less. This dislodges atoms from the surface of the target, ‘vaporizing’ them. Vaporized atoms from the target move in a straight path to the substrate to be coated. Finally, the metal atoms get deposited on the substrate surface mounted at an appreciable distance away from the evaporation source. Uniformity is obtained by rotating the substrate to be coated.

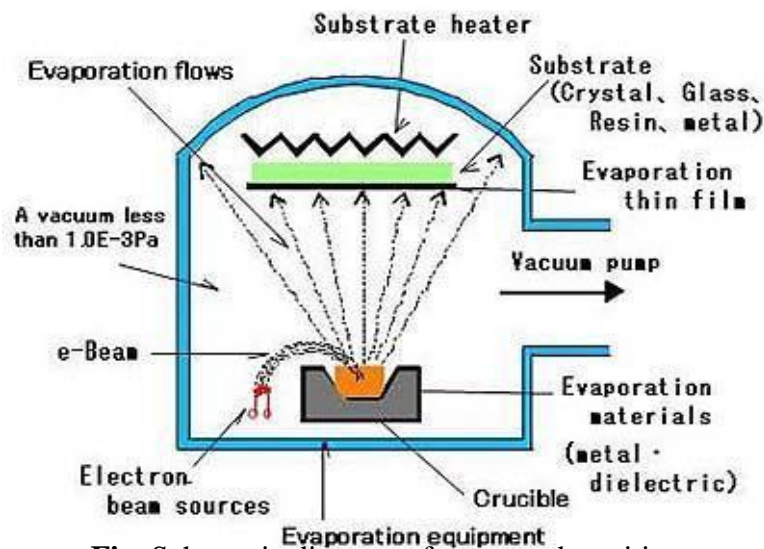


Fig. Schematic diagram of vacuum deposition

The vacuum environment may serve the following purposes by providing low pressure plasma environment, a means for controlling gas and vapor composition and a means for mass flow control into the processing chamber. And reducing the particle density of undesirable atoms and molecules (contaminants) so that the mean free path for collision is long

Advantages:

- PVD coatings are harder and more corrosion resistant than coatings applied by the electroplating process.
- Most coatings have high temperature and good impact strength, excellent abrasion resistance
- More environmentally friendly than traditional coating processes such as electroplating and painting.
- It is possible to change the target material without disturbing the system so that multilayer films can be formed.

Disadvantages:

- It is extremely difficult to coat undercuts and similar surface features
- High capital cost
- Some processes operate at high vacuums and temperatures, require skilled operators
- Processes involving a large amount of heat requires appropriate cooling systems
- The rate of coating deposition is usually quite slow

Chemical Vapor Deposition (CVD)

In this method, the surface is coated with a volatile, stable chemical compound at a temperature below the melting point of the surface. It involves the dissociation and /or chemical reactions of gaseous reactants in an activated (heat, light, plasma) environment, followed by the formation of a stable solid product. The deposition involves homogenous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions which occur on/near the vicinity of a heated substrate leading to the formation of powders or films, respectively. It has been used to produce ultrafine powders and thin films.

In general, the CVD equipment consists of three main components:

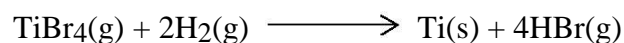
- (a) Chemical vapor precursor supply system: to generate vapor and deliver to the reactor.
- (b) CVD reactor component: consists of a reaction chamber equipped with a load-lock for the transport and placement of the substrate into the chamber, a substrate holder, and a heating system with temperature control. The main function is to heat the substrate to the deposition temperature.
- (c) Effluent gas handling system: This component consists of a neutralizing part for the downstream gases, and /or a vacuum system to provide the required reduced pressure for the CVD process.

Process principles and deposition mechanism: CVD process involves the following key steps:

1. Generation of active gaseous reactant species
2. Transport of these gaseous species into the reaction chamber.
3. Gaseous reactants undergo gas phase reactions forming intermediate species.
 - (a) At a high temperature above the decomposition temperatures of intermediate species inside the reactor, homogeneous gas phase reaction can occur where the intermediate species undergo subsequent decomposition and/or chemical reaction.

- (b) At temperatures below the dissociation of the intermediate phase, diffusion/convection of the intermediate species across the heated substrate surface occur. These intermediate species subsequently undergo steps (4-7)
4. Adsorption of gaseous reactants on to the heated substrate and the heterogeneous reaction occurs at the gas-solid interface (i.e. heated substrate) which produces the deposit and by-product species.
 5. The deposits will diffuse along the heated substrate surface forming the crystallization center and growth of the film takes place.
 6. Gaseous by-products are removed from the boundary layer through diffusion or convection.
 7. The unreacted gaseous precursors and by-products will be transported away from the deposition chamber.

Examples: Titanium tetrabromide is evaporated and the gaseous TiBr_4 is mixed with hydrogen. The mixture is then passed over a substrate heated to about 1300°C , such as silica or alumina. The metal halide undergoes reaction with hydrogen to form a thin film of titanium metal



Films of silicon are formed by decomposing SiCl_4 in the presence of H_2 at 1200°C .

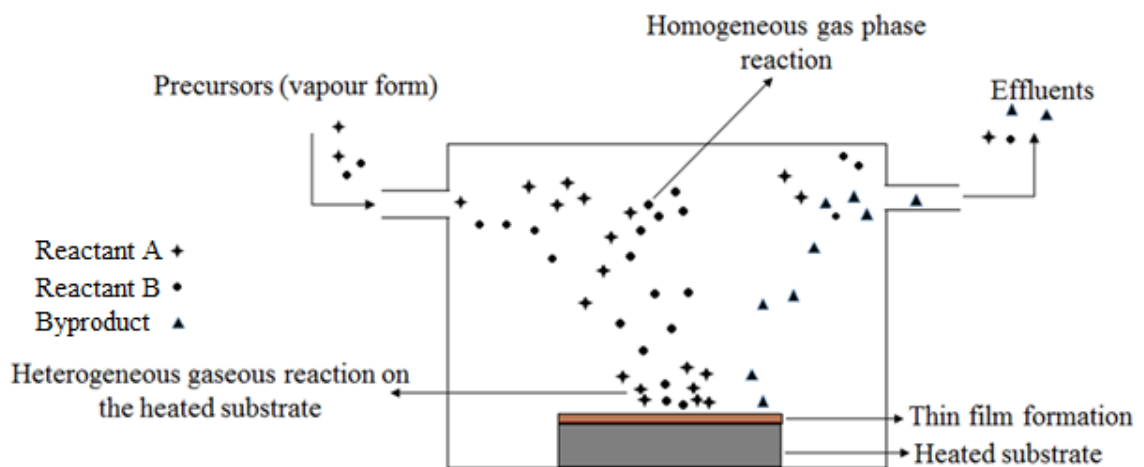
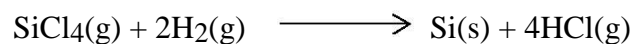


Fig. Schematic diagram of simplified CVD reactor

Advantages

- Capable of producing highly dense and pure materials without carbon or oxygen impurities.
- Produces uniform films with good reproducibility and adhesion at reasonably high deposition rates.
- Has good throwing power and hence can be used to uniformly coat complex shaped components and deposit films.
- Able to control crystal structure, surface morphology and orientation of the products by controlling the process parameters.
- Deposition rate can be adjusted readily. The low deposition rate is favored for the growth of epitaxial thin films for microelectronic applications. The deposition of thick protective coatings is favored by a high deposition rate.
- Reasonable processing cost using the CVD technique.
- The flexibility of using a wide range of chemical precursors such as nitrides, borides, organometallics which enable the deposition of a large spectrum of materials including metal carbides, nitrides, oxides and sulfides.

Drawbacks

- Chemical and safety hazards caused by the use of toxic, corrosive, flammable and/or explosive precursor gases.
- Difficult to deposit multicomponent materials with well-controlled stoichiometry using multisource precursors because different precursors have different vaporization rates.
- The use of more sophisticated reactor and /or vacuum system by CVD variants such as low pressure or ultrahigh vacuum CVD, plasma-assisted CVD and photo-assisted CVD tends to increase the cost of fabrication.

Applications:

- Production of high-quality optical fibers suitable for long distance applications.
- Diamond thin films: They are used as heat sinks for microelectronics and optoelectronics, sensors, microwave devices, coatings for IR windows in nuclear detectors, UV imaging, cold cathodes. The potential applications of diamond films

involve speaker diaphragms which are coated with thin films of diamond to provide improved acoustic properties.

Comparison between PVD & CVD

Features	PVD	CVD
Mechanism of deposition	Thermal energy	Chemical reaction
Deposition rate	High	Moderate
Deposited species	Atoms & ions	Precursor molecules dissociate into atoms
Energy of deposited species	Low (0.1-0.5 eV)	Low; can be high with plasma-assisted CVD
Throwing power	Poor	Good

Nano-materials

Nanoscience and nanotechnology deal with objects that have dimensions in the range from 1 nm to about 100 nm. Nano-materials are materials which have at least one of their dimension in the nanometer ($1 \text{ nm} = 10^{-9} \text{ m}$) range. The physical and chemical properties of nano-materials differ significantly from those of their bulk counterparts. The new properties are the result of an increase in the ratio of surface area to volume. This will change the surface effects such as those that give rise to catalysis, adsorption, adhesion and photonic effects. The reason for this is that the electrons in nanomaterials are confined within such a small volume that quantum effects now dominate optical and electronic behavior. Nano-fibers, nano-wires, nano-scale particles, Nano-channels and nano-tubes are some of the important nanostructures. The nano-science field is progressing so rapidly that it is probably hard to find any technical areas that are not useful.

The most important aspects of this field are connected with four issues;

- i) The way in which nanoparticles interact with their neighbors in solid arrays or with the second phase in composite materials.
- ii) Miniaturization of electronic circuits below the micro-scale to pack an increasing number of features into an integrated array.

- iii) Development of methods to produce nano-fibers that are of interest in geological tissue engineering, advanced textiles and filtration technology.
- iv) Use of micelles with diameters in the nano range for controlled drug delivery.

Classification

(a) Based on origin

(i) Natural nanomaterials

(ii) Artificial nanomaterials

Natural nanomaterials are those which are obtained naturally. Examples:- Carbon-nanotubes and fibers. Artificial nanomaterials are those which are synthesized artificially. Examples:- Au/Ag nanoparticles, Polymeric nano-composites.

(b) Based on dimension

This classification is based on the number of dimensions which are not confined to the nanoscale range (<100nm). They may be amorphous or crystalline, single crystalline or polycrystalline, made up of one or more elements, metallic, ceramics or polymers.

(i) *Zero-dimensional*: Materials wherein all the dimensions are within the nanoscale range are called zero-dimensional nanomaterial. Eg: quantum dots.

(ii) *1 dimensional*: Here two dimensions are at the nanoscale range, another dimension is not. This leads to needle-like nanomaterials. Eg: nanotubes, nanorods, nanowires.

(iii) *2 dimensional*: Here one dimension is at the nanoscale range, the other two dimensions are not. They exhibit plate-like shapes. Eg: nanocoatings, nanofilms

(iv) *3 dimensional*: These materials are not confined to the nanoscale in any dimension. These are characterized by having three arbitrarily dimensions above 100 nm. They are also known as bulk nanomaterials. 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nano wires/ nanotubes as well as multilayers. Eg: Nanocrystalline materials, nanospheres.

There are other types of classifications based on their field of application, shapes, properties, structures, manufacturing process and morphologies.

Preparation of nanomaterials:

Nanomaterials can be synthesized by two different approaches. They are “Bottom-up” and “Top-down methods”. Top-down methods start with micro – or macro scale materials, which are then broken down chemically or physically to nanoparticles. Methods that are used include ball milling, chemical etching, electrospinning and the vaporization of metals using plasmas. They

are slow, not cheap, and not suitable for large-scale production. Bottom-up methods involve the assembly of very small units (atoms, molecules or small nanoparticles) to create larger nanomaterials and systems. The fabrication is much less expensive.

“Bottom-up” Approach:

Sol-gel method

The sol-gel process is a wet-chemical technique used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for the preparation of gel by either discrete particles or network polymers. The process usually consists of five steps:

1. Preparation of a precursor solution: The desired colloidal particles are dispersed in a liquid to form a sol. Typical precursors are metal alkoxides, which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.
2. Deposition of the sol onto a substrate: The sol solution is coated on a substrate by spraying, dipping or spinning.
3. Formation of gel: The particles in the solid state are polymerized through the removal of the stabilizing components. This can be done either by heating the sol at a low temperature or allowing it to stand for a certain duration. This results in the formation of a gel.
4. Drying process: Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification.
5. Heat Treatment: After drying, a thermal treatment, or firing process, is often necessary to favor further poly-condensation reaction and enhance mechanical properties, structural stability of the gel.

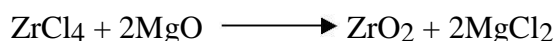
The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used as a means of producing very thin films of metal oxides for various purposes. Examples include Gallium based nano-materials, Dye-doped gel Glasses, Glass dispersed liquid crystals, Synthesis of glass-metal nano-composite, Metal-silica and Metal oxide-silica nanocomposites.

“Top Down” Approach:

Ball Milling

In this process, small balls are allowed to rotate around the inside of a drum and drop with gravity force on to a solid enclosed in the drum. The significant advantage of this method is that it can be readily implemented commercially. The grinding of ceramics can reduce them to a fine powder with each individual particle having nanoscale dimensions. It is difficult to avoid contamination of the nanoparticles by the materials used in the abrasion process and the particle sizes are not uniform. Polymers cannot be reduced to nanoparticles by grinding because of their molecular structure and their impact resistance. Ball milling can be used to make a variety of new carbon types, including carbon nanotubes. It is useful for preparing other types of nanotubes, such as boron nitride nanotubes and a wide range of elemental and oxide powders. For example, iron with grain sizes of 13-30 nm can be formed. Ball milling is the preferred method for preparing metal oxides.

To successfully prepare metal oxides, it is important to keep the crystallites from reacting and to have an understanding of the kinetic energy transferred during crushing. However, a by-product can sometimes be useful. In the production of nanocrystalline Zirconia (ZrO_2), zirconium chloride is treated with magnesium oxide during milling to form zirconia and magnesium chloride:



The by-product, magnesium chloride, acts to prevent the individual nanocrystallites of zirconia agglomerating. It is washed out at the end of the process.