



### 10.1 Introduction:

In this chapter some important modern engineering materials like Polymers, Ceramics, Super strong materials, High temperature materials, Cermets, Electrets, Thermoelectric materials and Nuclear Engineering materials have been discussed with their properties and applications.

### 10.2 Polymers:

Polymers are solids composed of long molecular chains. The long molecular chains are made up of relatively simple molecules. The most common polymers are made from compounds of carbon and consist of long molecular chains with strong bonds joining the atoms in the chain but with the relatively weak Van der Waals bonds joining the chains to each other. Along with natural polymers, we have synthetic organic polymers and synthetic inorganic polymers.

Types

1. Plastic
2. Elastomers (Rubber)
3. Fiber

### General Properties:

1. Polymers are made of large molecules and their molecular weight may vary upto several millions. These large molecules are made up of small molecules called monomers and are joined together through polymerisation reaction.
2. Polymers can be classified as plastics (resins), elastomers (rubber) and fibers (nylon and terylene).
3. When we heat polymers, they pass through five general states: glassy, leathery, rubbery, viscous rubbery and liquid.
4. Polymers have high tensile strength and modulus of elasticity.



5. The properties of polymers are depending upon molecular configuration, the degree of polymerization, branching and cross linking. Further the properties are also depending upon the mode of production. In cross linked polymers all structural units are connected by strong covalent bonds resulting in giant molecule extended in three dimensions. In branched chain polymers the chains are held together by intermolecular forces of attraction which increase with molecular weight or the chain length. The higher molecular weight polymers are toughers and more heat resistant. The lower molecular weight polymers are quite soft.
6. Polymers are strengthened by crystallization, cross linking and chain stiffening.
7. The dielectric behaviour of polymers is due to polarizable structure of polymers. Further the covalent bonds of all polymers prevent electrical conduction. They possess high insulation resistance and have low thermal and electrical conductivities.

### Plastics:

→ Notes

Plastics are generally organic high polymers and are available in natural form as resins, lac, casein etc. They are also manufactured synthetically as polystyrene, Polyvinyl chloride (P.V.C.) polyacrylic etc. Plastics have high corrosion resistance, high dielectric strength, good toughness and have low electrical and thermal conductivities. There are two types of plastics:

---

#### Thermosetting plastics

1. These are the polymers which require heat and pressure to mould them into shape. These polymers gets softened, when heated and can be given any shape; on further heating these undergo a permanent chemical change and set hard. Once done so, they cannot be softened again by the

#### Thermoplastics

These are the polymers which soften on the application of heat with or without pressure but they require cooling to set them to shape and hard. It can be resoftened and remolded by the application of heat and pressure.



2. These are hard, rigid and stronger.

These are comparatively softer and less strong.

3. These can be used at high temperature without damage.

These can not be used at high temperatures as they will tend to soften under heat.

Examples:

Examples:

- a) Bakelites (Phenolics)
- b) Polyster

- a) Polyethylene
- b) Polyvinyl chloride (PVC)

Uses:

Uses:

T.V. and Radio cabinets, telephone receivers, electric plugs etc.

Toys, electric insulation tapes, photographic films etc.

Rubbers (Elastomers): *Noted*

Properties:

- a. Elastomer is a polymer which sustains reversible elongations of several hundred percent and thus possess a high elastic yield strain.
- b. The material is soft and plastic. Among the plastic materials, it has more elastic modulus.
- c. Even for small stress, we can get large strains and the strain is reversible.
- d. They possess high dielectric properties.
- e. They have low tensile strength and it can be increased by vulcanizing.
- f. Structurally elastomers are non crystalline polymers at room temperature and is above its glass transition temperature.

All natural and synthetic rubbers fall in the category of elastomers. The natural rubber is obtained from the tree Hevea Brasiliensis in the form of a milky liquid known as latex. It is a linear molecule. During



vulcanisation (addition of sulphur) some cross links between adjacent molecules are formed and hence hardness is increased. Ebonite is a full vulcanised rubber. Synthetic rubbers are made from the coagulum of a polymerisation process. These possess different chemical structures but resemble natural rubber in many physical properties.

#### Wood:

Wood is a natural polymer and is composed of crystalline cellulose chains which are bonded together with amorphous lignin. Wood possesses fibrous structure and has greater strength in the longitudinal direction than in the transverse direction because celluloses are oriented along the axis of fibre. Plywood is formed by mixing a polymer with wood and is less liable to warp and is equally strong in all directions. Teak, sal and chir are important types of wood, used as common construction materials.

#### 10.3 Ceramics:

Ceramic materials are those materials which consist of phases which are compounds of metals & non metals. Ceramics are hard, strong & dense. These are completely stable even at high temperatures and are chemically inert. They have high compression strength and possess excellent dielectric properties. Already we have seen that the different types of ceramics and their uses as insulating materials in dielectric materials. Now let us see some of the ceramic tool materials with superior properties. The drawback of ceramics as tool materials is that they lack toughness and resistance to both mechanical and thermal shock; this has limited the use of ceramic tool materials in the past. In recent years, there have been significant developments in such materials. There are three categories of ceramic tool material available today: (i) The traditional ceramic tool material has been aluminium Oxide-alumina which is coming under the pure oxide ceramics. It is white and can be manufactured by cold pressing powder in a die with subsequent sintering. The modern alumina ceramic contains a proportion of Zirconium oxide - Zirconia, which toughens the material. A major disadvantage with pure oxide ceramics is that they have a low thermal conductivity that makes them very susceptible to thermal shock. (ii) In mixed ceramics oxide plus carbide and nitride are mixed.



ceramics, in addition to being harder and able to retain their hardness at high temperatures. (iii) The third class of ceramic tool material is that based on silicon nitride. Silicon nitride has a very low coefficient of thermal expansion which reduces the stresses set up between the hotter and cooler parts of an insert, so its thermal shock resistance is excellent. Sialon ceramics are silicon nitride plus alumina.

The present day use of ceramics for steel machining is largely confined to turning of hardened or low alloy steels and both pure oxide and mixed ceramics are used. Nitride ceramics find their most suitable application in rough-turning the intermittent operations whereas pure oxide ceramic is likely to give the longest tool life in semifinishing good quality castings under stable continuous cutting conditions. For finishing operations mixed ceramic is the best choice. The mixed ceramic is also used for high speed machining of heat resistant steels. Thus ceramics can offer increased metal removal rates, extended tool life and an ability to machine hard work piece materials.

#### 10.4 Super strong materials:

Due to the rapid development of Materials Science and Materials Technology today we have so many super strong materials to make cutting tools, aircraft parts, dies, crank axles, shafts, gears etc. Strong materials should have the following properties:

high tensile strength, high shear strength and high cleavage strength along with necessary ductility, weldability and machinability. In some cases, it should have the desired high resistance to corrosion, high creep resistance and high thermal shock resistance. Even though covalently bonded solids, like diamond and sapphire ( $Al_2O_3$ ) have high strength, from the view point of the engineer, the covalently bonded solids are not important, but the metallic ones are important because of the nonmachinable, poor ductility and brittle character of covalent solids.

##### a) New high strength steels:

A single crystal of very pure iron has a strength of about 26.3 MN  $m^{-2}$  whereas mild steel (which has



about  $340 \text{ MN m}^{-2}$ , and conventional quenched and tempered alloy steels may have strengths as high as  $2.1 \text{ GN m}^{-2}$ . The precipitation - hardened iron alloys containing little carbon but many other alloying elements - the so called 'maraging' steels - have reached a level of  $2.4 \text{ GN m}^{-2}$ . Metallurgists have obtained strengths as high as  $3.1 \text{ GN m}^{-2}$  by applying both mechanical and thermal treatments to relatively simple carbon steels with suitable alloying additions in the so called 'austforming' process.

### 1) Maraging Steels:

The new, high strength maraging steels contain virtually no carbon and the final hardening is produced by the precipitation of compounds containing iron, titanium, aluminium and molybdenum, which are added in small quantities when the alloy is prepared. The base alloy is iron containing between 18 and 22 percent of nickel by weight which is heated like the conventional steels, until it transforms into austenite. The transformed material is finally heated to about  $500^\circ\text{C}$  when precipitation of the compounds referred to above take place. This precipitation produces a very high density of particles which more than doubles the yield stress of the alloy. The change from austenite to martensite takes place when the alloy is cooled fairly slowly. These are used for solid propellant vessel in a rocket motor. It possesses excellent welding properties. But it is relatively high cost and has small corrosion resistance.

### II) Austformed Steels:

The process of 'austforming' a steel to develop high strength involves interrupting the quench to subject the steel to very severe plastic deformation, such as rolling or extrusion while it still possesses the austenite structure and the transforming it to martensite. At least three percent by weight of chromium is usually added to the steel in order to make it susceptible to this treatment. The density of dislocations in austformed steels is very high and very uniform, which contributes to the strength through work hardening. However the alloy also has a very fine grain size and substantial hardening also results from finely dispersed particles of alloy carbides throughout the structure which apparently form when the metal is being deformed. There is little decrease in the strength of an aust-



ment the steel has appreciable ductility. These are used in lorry springs and suitable for parts which can be shaped by deformation.

#### b) Nickel based alloys (Nimonic alloys):

These are used for creep resistance at higher temperatures. That is these are in materials which are working at higher temperatures.

#### i) Super alloys:

Nimonic 80A is an important super alloy which consists of Nickel and Chromium mainly. Chromium gives excellent resistance to Oxidation. Titanium and Aluminium are added to increase strength through precipitation hardening. Carbon and Cobalt are also added in small quantities. In super alloys we can achieve high strengths at temperatures in the range 700-850°C. But beyond this temperature range, the rate of fall of strength with increasing temperature is very steep so that the material is very weak at 950-1100°C. This effect arises because of the increasing solubility of the  $\text{Ni}_3(\text{Ti,Al})$  particles with increasing temperatures - so that the particles progressively disappear into solution once more as the temperature is raised which is the basic limitation of all age hardening systems. So in super alloys, the strengthening agent dissolves at high temperature.

#### ii) Powder Metallurgical TD nickel alloys:

To withstand the strength even at high temperatures these TD Nickel alloys are used. Necessary compounds are washed, dried and finally subjected to a chemical process which reduces the base material to metal and the dispersoid to Oxide, in the form of a powder in which the phases are intimately. This is subsequently compacted, sintered and forged to produce a dense solid. TD Nickel consists of nickel containing a volume fraction of about 2 percent of thoria - the particle diameter varying between  $10^{-8}$  and  $10^{-7}$  m. The mean interparticle spacing is less than  $3 \times 10^{-7}$  m. Eventhough the strength of TD Nickel is relatively low at low temperatures when we compare with super alloys, its strength is very large at 1100°C and its properties are superior to those of super alloys at this temperature.



### c) Fibre composite materials:

Composite materials constitute combination of two or more materials which are used in combination to rectify the weakness of one material with the strength of another. A good combination of strength and ductility is obtained by embedding fibres in a ductile material. Fibre strengthened plastics have been established as engineering materials for many years and more recently the basic idea has been applied to metal matrices. Fibre reinforced metals can be manufactured by molten metal infiltration and coating of fibres with a layer of metal. In molten metal infiltration method, a fibre bundle is placed in contact with the metal which is then heated to its melting point. In the other method, coating fibres with a layer of metal is taking place and the fibres are assembled and the composite is hot pressed to densify it. Carbon fibre strengthened composites have enormous strengths even at very high temperatures. By means of hydrazine electroless plating carbon fibres ( $7\ \mu\text{m}$  in diameter) is coated on pure Nickel or Aluminium. This pre-coating technique offers several advantages in addition to preventing filament - filament contact and thus fibre damage; excellent uniformity of fibre distribution in the composite is obtained because of the uniformity of thickness of the metal coating. Further electroplating, chemical vapour deposition and flame spraying are the other processes used to coat fibres. Al - 60% C fibre and Ni-50% C fibre are important fibre composite materials which have high strengths at all temperatures from 0 to  $1200^\circ\text{C}$  without changing in the value of their strengths. So these are superior to those super alloys and Ti-Nickel alloys. In National Physical Laboratory, New Delhi, manufacture of super strong materials using carbon fibres is under active research. To achieve high strengths in fibre composites, fibre of low density is desirable and the metal matrix and the fibre material must be mutually compatible so that no interaction leading to degradation of strength occurs.

### 10.5 Cermets:

Cermets are the composite materials consist of combination of metals and ceramics. The metal acts as a binder. These are made by powder metallurgy; the sintering temperature is above the melting point of the metal powder. In the finished cermets, the metal contributes high toughness and thermal shock resistance, while the ceramic contributes higher refractory properties, creep resistance, superior chemical stability and



abrasion resistance. These properties are depending upon the ratio of combination of metal and ceramics. Generally two types of cermets are available based on type of ceramics used.

- Types
- Oxide ceramics based cermets, in which ceramics are bonded by iron, chromium and tungsten.
  - Carbide ceramics based cermets, in which ceramics are bonded by iron, nickel and cobalt.

#### Uses:

- Due to their higher hardness, these are used to cut and shape many refractory materials such as glass, procelain and high temperature resistant brittle alloys which are considered to be unmachinable.
- These are also used to manufacture cutting tools and dies in metal working industry and rotating drills in the mining industry.
- Further high speed, heavy duty cutting tips and inserts are made from cermets.

#### 10.6 High temperature materials:

The high temperature materials used in machine parts and structural components should have high thermal shock resistance and high creep resistance. Thermal shock resistance is a property of a material which indicates its ability to be subjected to rapid temperature changes without physical failure. So by means of this property a material can retain its shape and not distort, crack or shalter, due to a sudden change in its temperature. Creep is a time dependent strain occurring under stress. Creep can take place and lead to fracture at static stresses much smaller than those which will break the object when loaded quickly. Normally creep rate is enormous at high temperatures. Creep resistance is a property by which the material can withstand without fracture at high temperatures and during quick loading. To obtain creep resistance at high temperatures, we must use metal with high melting point and FCC structure with low stacking faulty energy. To improve the creep resistance in high temperature materials, dispersion hardening method is adopted. For high temperature applications,



the fine grained materials and materials with grain boundaries are not useful since they have very weak creep resistance and generally the coarse grained materials are more useful since they show a better creep resistance.

Refractory Oxides such as  $MgO$  and  $Al_2O_3$  have high melting points and so they are very suitable for high temperature use. Further these materials should not react with the materials that they are in contact with. The Austenitic stainless steels are used for continuous service upto  $1100^\circ C$ . It contains 74% iron, 18% chromium and 8% nickel. The commonly used high temperature alloys are iron-base, nickel-base and cobalt-base alloys:

- Fe 62%, Ni 34% & Cr 4% alloy is mainly used as a resistance wire and has maximum working temperature of  $700^\circ C$ .
- Ni 80% and Cr 20% alloy is used for heaters and has a maximum working temperature of  $1150^\circ C$ .
- The alloy consisting of chromium, nickel and cobalt has high strength and corrosion resistance even at temperatures upto  $1200^\circ C$ . Normally chromium based alloys are called heat resistant alloys which are used in high temperature applications.

In various heat engines and energy conversion devices like MHD generators and nuclear reactors, high temperature materials are used.

### 10.7 Thermoelectric materials:

Thermoelectric materials are used to construct thermocouple. In a thermocouple, a voltage is induced between the hot and cold junctions of two dissimilar metals which increases with increasing temperature differences between hot and cold junctions. If we connect thermocouples in series, then that system can act as a voltage generator. Now-a-days thermocouples are widely used for temperature measurement, refrigeration, heating and generation of electrical power.

A good thermocouple which develops more voltage is defined by its figure of merit 'Z'

$$Z = \frac{S^2 \sigma}{K}$$



where  $S$  is called thermoelectric power which is the thermoelectric voltage developed per unit degree rise of temperature. This is a constant in each metal. Further according to Wiedemann-Franz Law, in metals the ratio between thermal conductivity ' $K$ ' and electrical conductivity ' $\sigma$ ' is directly proportional to absolute temperature.

$$\text{i.e. } \frac{K}{\sigma} = \frac{1}{3} \left( \frac{\pi k}{e} \right)^2 T$$

$$\text{(or) } \frac{K}{\sigma T} = \frac{1}{3} \left( \frac{\pi k}{e} \right)^2 = L$$

where  $L$  is called Lorentz number and it is a constant. Its value depends upon the absolute temperature of the metal. So at a particular temperature  $\frac{K}{\sigma}$  is a constant. The possibilities of increasing efficiency of metallic thermocouples by increasing  $Z$  are very limited. Similarly common semiconductors like Germanium and Silicon have high thermal conductivity and so they are unsuitable for thermoelectric applications. But there are some semiconductor alloys in which larger thermoelectric effects occur than in metals. (Bismuth and Antimony tellurides or selenides have high figure of merit.)

The Semiconductor alloys such as 75% of  $\text{Bi}_2\text{Te}_3$  + 25% of  $\text{Bi}_2\text{Se}_3$  and 50% of  $\text{Bi}_2\text{Te}_3$  + 50% of  $\text{Sb}_2\text{Te}_3$  have lower thermal conductivities but substantially high electrical conductivities. Similarly lead telluride semiconductor (where lead is the  $n$  type semiconductor and tellurium is the  $p$  type semiconductor) with 61.9% of  $\text{Pb}$  + 38.1% of  $\text{Te}$  is a very good thermoelectric material. For the electrical power generation or refrigeration, the maximum thermoelectric efficiency is about 10% only.

### 10.8 Electrets:

Electrets are ferroelectric materials and are electrostatic analog of permanent magnets in that they possess a gross permanent electric dipole moment. They are manufactured from certain types of waxes, plastics and ceramics. When these waxes are subjected to high electric fields ( $\approx 10^6 \text{ V/m}$ ) they are polarized in their molten state and retain a permanent polarisation after solidifying even though the external polarising field is removed. Some barium titanate ceramics and carnauba waxes can be polarised in this way. A number of new electret applications are based on the piezoelectric or pyroelectric effects in polarised



polymers. The interest in polymer electrets is due to the fact that these show extremely good charge storage capabilities and are available as flexible thin films. Polytetrafluoroethylene and polyvinylidene fluoride are important polymer electrets.

#### Applications:

- a) These are used in capacitor microphones. Here there is an electret diaphragm with metal layer at its top for electrical connection purpose. Further there is an air gap in between the back metal plate and bottom end of the electret diaphragm. If a sound wave impinges on diaphragm, it undergoes deflection and hence change in thickness of air gap is produced. The output voltage developed which is taken between the top metal layer and bottom metal back plate through a load is directly proportional to the frequency of sound waves. The same technique is also used in earphones. Here alternating voltage applied between the top and bottom of the earphone produces sound waves. Thus these are acting as electro acoustic transducers in an efficient manner with higher sensitivity and fidelity.
- b) An electret recorder is a recorder in which events lasting as little as 0.1 micro seconds are stored as electrets on the surface of plastic foil by a puncture of a thin air gap. The foil is not damaged and can be erased after readout.
- c) These are also used in gas filters which use corona charged electret fibres to capture submicron particles by electrostatic attraction.
- d) Further these are used in motors, relay switches, optical display systems, electrophotography and radiation dosimeters.
- e) In medical field, electrets are used in so many ways. It was shown that foil electrets placed in contact with bones of animals in vivo cause accelerated growth of callus, necessary for fracture healing. Moreover electret bondages put on skin incisions considerably improve the tensile strength of the wound over a given period of time and thus speed the healing process.
- f) Now-a-days so many piezoelectric transducers and pyroelectric devices are manufactured from electrets.



## 10.9 Nuclear Engineering Materials:

The materials used in Nuclear reactors may be classified into the following main groups:

- i) Fuel materials
- ii) Moderator materials
- iii) Fuel cladding materials
- iv) Control materials

### i) Fuel materials:

- a) Uranium: Uranium is very reactive and easily oxidised. In pure form it is heavy, hard and nickel like metal. It retains its hardness at much higher temperatures. In natural uranium, the following isotopes are present:

Uranium - 238 (99.3%) and Uranium - 235 (0.7%). Uranium-238 is a fertile material. But it can be converted into fissionable material as Plutonium - 239 by neutron bombardment. Uranium - 235 is a fissionable material. It is used as a fuel in most thermal reactors. Enriched uranium which contains slightly increased percentage of uranium - 235 in natural uranium is also used as fuel. Uranium Oxides or carbides are also used as Nuclear fuels in some reactors.

- b) Plutonium: Plutonium - 239 is very reactive, easily oxidised and highly toxic. It is a concentrated nuclear fuel and is not found in nature. It is produced from uranium - 238. It can undergo fission chain reaction even by fast neutrons. So Plutonium reactors would not use moderator to thermalize the fast neutrons.

- c) Thorium: It is a radio active material. Thorium-232 is a fertile material. It can be converted into fissionable Uranium - 233 by neutron bombardment. Thorium is less susceptible to irradiation damage. In pure form it is soft and weak. In India, Thorium is available in Kerala sea shores.



**ii) Moderator materials:**

*Speed can be reduced by* Moderators are used to thermalize the fast neutrons and by that way the fission yield can be increased. Any reactor with moderator is a thermal reactor. Nuclear fuel rods are surrounded by moderator material. Deuterium ( $D_2O$ ) and graphite are very good moderators since they have high moderating ratio. Beryllium is the best metallic moderating substance as it occupies small space and has low absorption cross section for neutrons. Moderators are also helpful in controlling and stabilizing the reactor power level during its operation. In some reactors moderators can also act as coolant and reflector.

**iii) Fuel cladding materials:**

Fuel cladding materials are used to improve the mechanical strength of fuel rods and to increase their corrosion resistance. They should not absorb any neutrons and should be stable even at high temperatures. They should possess higher thermal conductivity. For thermal reactors aluminium, magnesium beryllium and zirconium are preferred. For high power reactors zirconium and stainless steel are used since they can withstand at high temperatures.

**iv) Control materials**

The power level of the reactor or neutron flux in the reactor is controlled by inserting <sup>number of</sup> control rods which are high neutron absorbers. These are made from boron, silver and cadmium.

**SUMMARY**

1. Polymers are solids composed of long molecular chains. Polymers are classified as plastics, elastomers and fibers.
2. Ceramics are those materials which consist of phases which are compounds of metals and non-metals.
3. Super strong materials have high tensile strength, high shear strength and high compressive strength.