POLYMERIZATION

Polymers are macromolecules of high molecular weight which are formed by linkage between large numbers of small molecules called monomers, *e.g.*, polyethylene is made up of the monomers ethylene.

There is no limit to theoretical length of the polymer, but the polymer ceases to grow for many practical reasons. The number of repeating units in a polymer is called the "degree of polymerization".

Types of polymerization

- 1. Addition or chain polymerization. Monomers (M) having the general formula, CH_2 =CHY (Y=X, CO_2R , CN etc.,) undergo polymerization, *i.e.*, these monomers having double or triple bonds polymerize without the liberation of small molecules. There are three ways of addition polymerization:
 - (i) Head to tail type

$$--$$
CH $_2$ CHY $--$ CH $_2$ CHY $--$ CH $_2$ CHY $---$

(ii) Head to head type

(iii) Random type

Mechanism of addition polymerization:

(a) Free radical polymerization is the first type which involves the following steps:

Initiation. The first step of which involves two reactions. The first is the spontaneous decomposition of an initiator into free radicals. A variety of peroxides act as initiator such as benzoyl peroxide, tertiary butyl hydroperoxide etc.

$$\begin{array}{cccc}
COOOOC & COO' \\
\hline
\end{array}$$

$$\begin{array}{cccc}
& & & \\
\end{array}$$

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The next part of initiation involves the addition of this radical to the monomer molecule (M) to initiate the chain.

$$2R^{\bullet} + M \longrightarrow M^{*}$$
Free Monomer radical

The M* is the initiator radical or primary radical.

Propagation. The mechanism of propagation is the reaction of the radical M* with its own monomer M.

$$M^* + CH_2 = CHY \longrightarrow M-CH_2CHY^*$$

Continuous addition of new monomer in this manner will finally produce a polymer chain in which the substituents are located on alternate atoms.

Terminations. The most common terminations are the effect of

(i) Collision between two growing chains

- (ii) Collision of a growing chain with an initiator radical when the latter is proportionately in excess.
- (iii) Collision between a growing chain with impurities. Sometimes the chain length of the polymer is controlled by deliberately adding inhibitors.

More rarely, by disproportionation an H atom of one radical is transferred to another resulting in two polymers—one saturated and the other unsaturated.

(b) Ionic polymerization is an important class of addition polymerization which also involves the steps of initiation, propagation and termination but here, instead of free radicals, the unstable intermediates are either cations or anions.

Cationic Mechanism

Initiation

The initiators are Lewis acids like AlCl₃,BF₃, H₂SO₄ etc., in presence of water.

Propagation:

Termination:

If the medium is of dielectric strength, the overall effect leads to an increased polymerization rate and also increased degree of polymerization, since better charge separation of ion and counter ion occurs.

Anionic polymerization mechanism:

Initiation:

$$\mathbf{Z}^{(-)} + \mathbf{CH}_2 = \mathbf{CH} \xrightarrow{} \mathbf{ZCH}_2 - \overset{(-)}{\mathbf{C}} \mathbf{H}$$

$$\mathbf{Y} \qquad \qquad \mathbf{Y}$$
Corbonic

Propagation:

Termination:

$$Z \xrightarrow{\text{CH}_2\text{CH}} \xrightarrow{\text{CH}_2} \xrightarrow{$$

Polymerization of olefins with metallic sodium, sodium ethoxide takes place *via* this mechanism.

(c) Co-ordination polymerization or Ziegler-Natta polymerization. It was observed by Ziegler and Natta that in presence of a combination of transition metal halides (TiCl₄, ZrBr₃,

and halides of V, Zr, Cr, Mo etc.) along with organometallic compounds (triethyl/trimethyl aluminium) polymerization of olefins leads to stereospecific polymerization.

Mechanism of Ziegler-Natta polymerization:

Initiation:

$$Cat R' + CH_2 = CHR \longrightarrow Cat CH_2CH(R)R'$$

Propagation:

Termination:

By earlier free radical polymerization of ethylene, propylene yielded polymers of low density having highly branched chain polymer of low crystallinity and mechanically weaker structure like LDPE (low density polyethylene). Ziegler-Natta polymerization yielded stereospecific structure of high mechanical strength, unbranched, high melting and highly crystalline polymer like HDPE (high density polyethylene).

Stereochemistry of polymers

(i) *Isotactic polymers* have all the groups in one side of the polymeric backbone and the monomers are joined in a regular head to tail arrangement.

(ii) Syndiotactic polymers have similar head to tail arrangements but here Y groups appear on opposite sides of polymer backbone alternately.

(iii) Atactic polymers have Y groups arranged randomly along the polymeric backbone and the material is soft, elastic, rubbery.

Spatial arrangement of an atactic polymer: It is a form of *addition polymer*, such as polypropene in which the side groups along the *polymer* chain are randomly orientated. Atactic polypropene is an *amorphous*, rubbery polymer of little value unlike isotactic polypropene (Fig. 20.1).

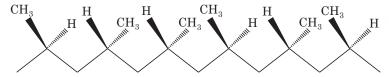


Fig. 20.1 Part of a chain of atactic polypropene.

Condensation polymerization

It is the type of reaction occurring between monomers containing polar groups which form polymer along with the elimination of small molecules like H_9O , HCl etc.

In this type of polymerization, as it takes place through the functional groups, when any monomer may contain two or three functional groups cross-linked polymer structure will be formed.

Co-polymerization

Two or more monomers undergoing joint polymerization is called copolymerization reaction such as the production of SBR (Styrene butadiene rubber).

$$n(\cdot \text{CH}_2 = \text{CH}_\text{CH} = \text{CH}_2) + n$$
butadiene
$$\text{SBR (GRS-rubber)}$$

$$\text{CH} = \text{CH}_2$$

$$\text{Copolymerization}$$

$$\text{CH}_2\text{CH} = \text{CH}_\text{CH}_2$$

$$\text{CH}_2\text{CH} = \text{CH}_\text{CH}_2$$

Influence of structure of polymer on its properties

Strength of polymer

In cross-linked polymer, the units are linked by interchain covalent bonds forming giant, three dimensional structure and they are strong and tough as the movement of inter molecular chains are totally restricted.

Strength of straight chain polymers depends on the chain length. Polymers of low mol. wt. are soft and gummy but brittle. But higher-chain length polymers are tougher and more heat resistant. Presence of polar groups along the chain length also increases the intermolecular forces and increases the strength of polymer.

Highlights:

Types of polymerization

• Addition polymerization:

The product polymer is exact multiple of the original monomeric molecule *e.g.*, polythene from ethene.

• Condensation polymerization:

Combination through different functional groups of monomers with elimination of small molecules like $\rm H_2O$.

• Copolymerization:

Joint polymerization of two or more types of monomers. As for example SBR.

- Mechanisms of addition polymerization are:
 - (a) Free radical mechanism.
 - (b) Ionic mechanism.
 - (c) Co-ordination polymerization (Ziegler-Natta polymerization).

Plastic deformation

Polymers consisting of linear-chain molecules are always soluble and *thermoplastic*, even for very high molecular weight.

Three-dimensional polymer molecules are insoluble in any conventional solvent and are *thermosetting*. Hence, thermoplastic and thermosetting qualities of polymer depend on structure of the polymers. Artificially creating crosslinking converts thermoplastic material into thermosetting.

Physical state

Random arrangement of molecules in the polymer leads to amorphous state whereas regular arrangements of molecules or chains in a polymer lead to crystalline state.

The regular arrangement increases the intermolecular forces of attraction and leads to higher softening point, greater rigidity, brittleness and strength of the polymer. The amorphous nature of polymer provides flexibility.

Very long chain polymers having free rotating groups form irregularly coiled and entangled snorts, which can be stretched and again returned back to its original state giving rise to elastic character to the polymer.

Solubility and chemical resistance

Polymer containing polar groups are more soluble in polar solvents like water, alcohol but are chemically resistant to non-polar solvents like benzene, toluene, ${\rm CCl_4}$ etc. Similarly, non-polar group containing polymers are chemically resistant to polar solvents but are soluble in non-polar solvents, particularly the greater the degree of cross-linking, less is the solubility of the polymer in a solvent.

Shapes and forms—mechanical properties

The internal arrangement of the long-chain molecules provides the forms in which the polymer may form *i.e.*, fibres, plastics and rubbers. If the internal forces between the molecules are low, molecules become bulky, form random arrangement and show rubbery character. If the internal forces are high they ultimately give rise to orderly arrangement and form fibrous nature. Intermediate forces lead to plastic nature.

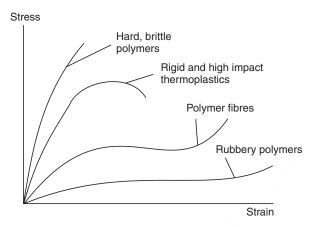


Fig. 20.2 Four types of stress-strain curves illustrating how polymers of different types behave (the lines end where the sample breaks).

The strength of the polymer is controlled by the length of the polymer chains and its cross-linking. Strength of a polymer is estimated from typical stress-strain curves for different polymers as shown in Fig. 20.2. On increasing strain continuously ultimately the polymer chains are uncoiled and fully stretched called *necking* and after this point the polymer reaches its *break point* and yields.

Effect of heat

Behaviour of polymer is controlled by the temperature. Amorphous polymers, which do not have melting point have softening points. At very low temperature both the crystalline and amorphous polymers behave like glass and on heating, the glass transition temperature is reached (T_g) after which they soften. Amorphous polymer becomes rubbery and then gummy and on further heating it liquefies. But the crystalline polymer on heating above T_g shows thermoplastic behaviour and finally liquefies.

PLASTICS (RESINS)

Plastics are a class of high polymers which can be moulded into any desired form by heat and pressure. Resins are actually the binders used for plastics and these two terms are used synonymously.

There are two classes of plastics or resins.

- 1. Thermoplastic resins soften on heating and harden on cooling and this change is not chemical but physical in nature, hence repeated heating and cooling also does not alter its nature.
- 2. Thermosetting resins are those which are heated during moulding and heating is continued until is set and hardened. This hardened material cannot be softened again, hence the setting is permanent and irreversible.

Compounding

Plastics for manufacturing of finished articles are always mixed with 4-10% of other materials, which impart some durable properties to the moulded material. These materials are known as additives which not only impart some properties to plastics but also make the processing easy. The process of mixing these additives to virgin plastics is called *Compounding*. Additives and their functions are discussed below:

(i) **Resin** is the binding constituent, which binds all the additives together. Thermosetting resins are added as linear low molecular weight polymers, which actually form crosslinking during the moulding process in presence of catalyst.

(ii) **Fillers.** Fillers can modify the properties of plastics to give the final plastic, better hardness, tensile strength, finish and workability.

Fibrous fillers such as wood flour, cotton fibre, chopped rags impart improved mechanical strength to the plastic; asbestos increases heat resistance; mica or slate powder improves electrical properties. Percentage of fillers may vary and can be upto 50%.

Solidified filaments of glass are bundled into strands, compressed to produce a glass mat. Plastics embedded with these mats are known as fibre reinforced plastics (FRP). FRP is very strong and can be used to make gates of dam, corrosion-resistant pipes and tanks, safety helmets, jeep bodies.

PVC laminated to steel or aluminium are called 'Composites'.

- (iii) Plasticizers. Plasticizers are small molecules which penetrate into the polymer matrix and neutralize a part of the intermolecular forces of attraction between macromolecules and increase the mobility of the polymer segments so that chains can slide over each other. Thus, plasticizers act as an internal lubricant and improve the plasticity and flexibility of the polymer. Commonly used plasticizers include vegetable oils, camphor, dibutyl/dioctyl phthalate etc.
- (*iv*) Waxes, oils, stearates and soaps are used to improve the finish and reduce the sticking tendency of the plastic to the moulds.
- (v) Colouring materials. To improve the appeal and to impart beauty to the finished materials, colours are added to them. Soluble organic dyes are added to the transparent variety and inorganic pigments are added to the nontransparent plastics. To give UV protection to the colours some compounds are added which preferentially absorb UV light.
- (vi) Other additives. Sometimes antioxidants are added to prevent oxidative degradation of polymers. Catalysts like H₂O₂, benzoyl peroxide, ZnO, NH₃, Ag, Cu, Pb etc. are added to accelerate the cross-linking of the thermosetting plastics while they are in the moulds.

Stabilizers like Pb, Pb-silicate, Pb chromate etc., are added to improve the thermal stability of polymers during processing.

Antistatic agents like amines, amides etc., are added to dissipate the electric charge developed by conducting it away.

Processing of plastics

- (i) Calendering. For production of continuous films or sheets this process is adopted. The compounding material is run between two highly polished metallic rollers rotating in opposite direction. While passing through the gap between the rollers the sheet is formed, whose thickness varies with the gap. Engraved rollers offer beautiful designs of embossed plastics.
- (ii) **Die casting.** This cheap technique is used for acrylics, polyesters, phenol and urethans. Compounded material is poured into die cavities made up of metals or plaster of paris and it is heated when the crosslinking takes place and finally the finished material is cooled.
- (iii) Film casting. A compounded solution in a suitable solvent is continuously dropped on a moving belt, the solvent evaporates and films are obtained. Cellophane papers and photographic films are produced by this process.

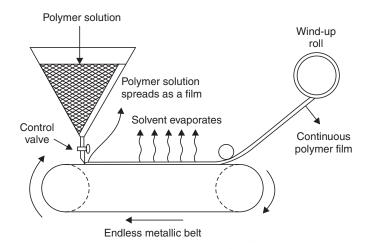


Fig. 20.3 A schematic representation of the film casting machine.

(iv) Compression moulding. This method is applicable for both thermosetting and thermosplastic materials. The mould consists of two halves. The compounding material in definite proportion fills the gap between the two pieces of mould, which are moved relative to each other. Heat and pressure applied. The cavities get filled with fluid plastic, two halves are closed slowly. Finally curing is done by heating (for thermosetting) and cooling (for thermoplastic). Furniture handles, telephone parts etc., are made by this process.

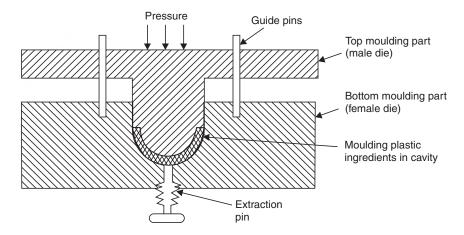


Fig. 20.4 Compressing moulding of plastics.

(v) **Injection moulding.** This process is applicable for thermoplastics only. Plastic powder is fed into a hot cylinder and then injected by a piston plunger into a tightly-locked mould with the help of a screw arrangement. The mould is cooled for curing and finally the half of the mould is opened for the ejection of the article. The whole process is automatic. Buckets, bowls, furniture parts are made by this process.

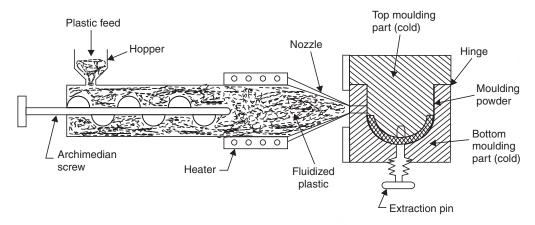


Fig. 20.5 Injection moulding of plastics.

- (vi) **Blow moulding.** A hot softened tube of thermoplastic is placed between the two halves of mould and compressed air is blown whereby the thermoplastic takes the shape of the mould to form hollow articles like bottles, jerrycans etc. The mould is cooled and the article taken out.
- (vii) Extrusion moulding. This process is used for continuous moulding of thermoplastics. The powder compounded material is introduced and electrically heated. In plastic condition, it is pushed by screw conveyer into a die whose shape is acquired by it and finally cooled.

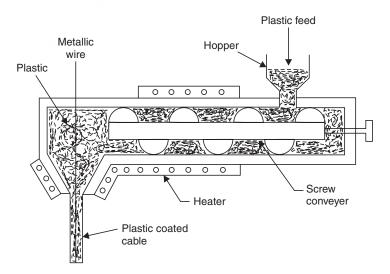


Fig. 20.6 Moulding of insulated electric cable by vertical extrusion moulding.

(viii) **Thermoforming.** This process is used to obtain three-dimensional articles from two-dimensional sheets. The thermoplastic sheet is heated and softened and placed between two halves of a metal die. The sheet is compressed between the die to the desired shape. Sometimes, vacuum is also applied so that the sheet sticks to the shape of the mould.

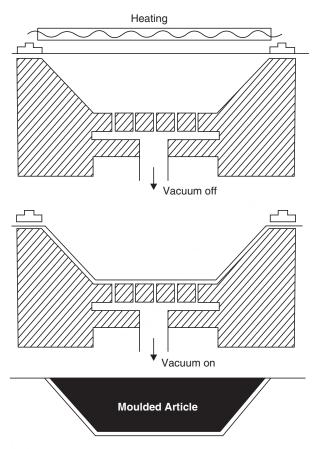


Fig. 20.7 Vacuum forming process.

Important Thermoplastics

Polyethylene

Polythene is polymerised ethylene. Ethylene is colorless gas at ordinary temperature. It is prepared in the lab by dehydration of ethyl alcohol at 160°C with concentrated H_2SO_4 . Industrially dehydration of ethyl alcohol is the process for ethylene production*.

Polyethylene is manufactured by gas-phase polymerization. The ethylene gas is compressed to 1500 atmosphere and passed through a reactor maintained at 200°C in the upper and 120°C in the lower parts. O_2 (0.01%) or peroxides act as catalyst. Ethylene is polymerised into polythene, a waxy solid, which comes out from the perforated bottom of the vessel. The unreacted gas is recycled.

Two types of polyethylenes are available—LDPE (Low density polyethylene) and HDPE (high density polyethylene). HDPE is produced by using low pressure methods (31 kgf/cm²) using ionic catalysts whereas LDPE is produced by using high pressure methods (1050-2000 kgf/cm²) using free radical initiator.

Properties. Polyethylene is a rigid, waxy, white, translucent non-polar material. It has good chemical resistance against acids, alkalies and salt solutions, good insulating property but it is susceptible to organic solvents, particularly kerosene.

*
$$C_2H_4 \xrightarrow{Polymerize} (C_2H_4)_n$$

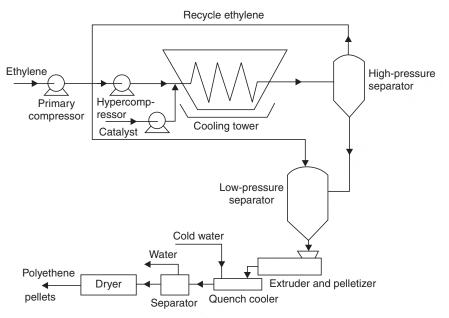


Fig. 20.8 Low-density polyethylene by high-pressure processing (LDPE).

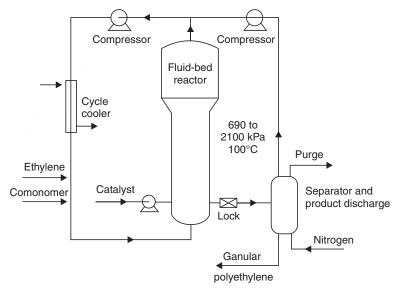


Fig. 20.9 High-density polyethylene by low-pressure resins (HDPE).

Polyethylene has highly symmetrical structure so it crystalizes easily. The degree of crystallinity varies from 40-95% depending on degree of branching. LDPE has a branched structure and hence is flexible and tough. It has low sp. gr. It has low hardness *i.e.*, about 1/10th of bakelite.

HDPE is a completely linear polymer, it has better chemical resistance, higher softening point, greater rigidity but low impact strength and it is opaque and relatively brittle.

Uses. Polythene sheets, tubes are manufactured, which are used for domestic purpose. It is also used to prepare toys, coated-wires and cables, bags for packing, bottles, caps, insulator parts.

Polypropylene

Polypropylene is obtained by polymerizing propylene in presence of Ziegler-Natta Catalyst *i.e.*, organo metallic halide with transition metal halide.

$$\mathrm{CH_{3}CH} = \mathrm{CH_{2}} \xrightarrow{\mathrm{Polymerize}} [\mathrm{CH_{3}CHCH_{2}}]_{n}$$

Properties. Polypropylene is also an isotactic, highly crystalline polymer. It is superior to polyethylene w.r.t. resistance to chemicals, hardness, strength, moisture proofing quality etc. It is lightest among all high polymers.

Uses. Fibres of polypropylene are very strong and hence fibres are used for making ropes, carpets, blankets, bags, apparels etc. It is also used for packing of pharmaceutical and cosmetic products, for making sterilizable hospital equipments, washing machine parts, pipes, TV, radios, moulded luggage, colorful furniture etc.

Polyvinyl Chloride (PVC)

Vinyl chloride is the monomer for PVC and the monomer is produced by direct addition of HCl to acetylene at 60°C-80°C.

$$\mathrm{CH} \equiv \mathrm{CH} + \mathrm{HCl} \xrightarrow{\ \ \mathrm{HgCl} \ \ } \mathrm{CH}_2 \equiv \mathrm{CHCl}$$

The polymerization of the gaseous monomer (b.p. 13.9°C) can be done in solution, emulsion and in suspension. The polymer is obtained in the form of fine powder and is soluble only in special solvents like dibutyl phthalate, benzyl benzoate etc. Increased solubility of the polymer is also attained by solution polymerization at high pressure and temperature.

$$n\mathrm{CH}_2 = \mathrm{CHCl} \xrightarrow{\mathrm{Polymerize}} -(\mathrm{CH}_2\mathrm{CHCl})_{\overline{n}}$$

Properties: PVC is a colorless, odorless, non-flammable, chemically-inert powder. It contains 53-55% Cl₂ and softens at around 80° C.

It is resistant to water, light, ${\rm O_2}$, inorganic acids and alkalies, oil, petrol etc., but soluble in hot chlorinated hydrocarbons.

Uses. It is the most widely used plastic. It has high rigidity and chemical resistance but brittle, so, its use is mainly in making cables, water hoses, toys, rain coats, rexin, pipes of petroleum industry, floor covering, refrigerator components, tyres, cycles and motor cycle mudguards etc.

Polytetrafluoroethylene (TEFLON)

It is obtained by polymerization of water-emulsion of tetrafluoro ethylene, under pressure and in presence of benzoyl peroxide as catalyst.

$$n(\operatorname{CF}_2 = \operatorname{CF}_2) \xrightarrow{\operatorname{Polymerize}} \begin{array}{c} \begin{bmatrix} F & F \\ | & | \\ | & F \end{bmatrix} \\ \begin{bmatrix} F & F \\ | & | \\ F & F \end{bmatrix}_n \end{bmatrix}$$

Properties. Due to the presence of highly electronegative fluorine in the regular polymer structure of TEFLON strong interchain forces are present which give the material extraordinary

properties like extreme toughness, high softening point (350°C), high chemical resistance, low coefficient of friction and waxy touch, good mechanical and electrical properties. Due to all these qualities, the polymeric material can be machined. It softens at about 350°C, hence at this high temperature it can be moulded applying high pressure.

Uses. It can be used for insulating motor, transformers, cables, wires etc. Non-stick cookware coatings are made of TEFLON. It can also be used for making gaskets, pump parts, tank linings, pipes and tubes for chemical industry, non-lubricating bearings and to make non-reactive coating.

Polyurethane

$$(i) \begin{picture}(2000){\line(1,0){CH}_3$} \\ NH_2 \\ NH_2 \\ N = C = O \\ N = C = O \\ 2, 4, tolulene di-isocyanate \\ \end{picture}$$

$$(ii) \ \mathrm{CH_3-CH_2-CH_2} \xrightarrow{\mathrm{OH}^-} \ \ \begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{HOCH-CH_2-O} \\ \end{array} \xrightarrow{\mathrm{CH_2}} \ \begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_2-CH-O} \\ \end{array} \xrightarrow{\mathrm{CH_2}} \ \mathrm{CH_3} \\ | \\ \mathrm{Poly(oxypropylene) \ glycol} \end{array}$$

Polyurethanes are a varied range of crosslinked polymers made from two liquids—a polyol and an isocynate.

$$-O - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{H} \\ | \\ -\mathrm{C} - \mathrm{N} \end{pmatrix} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_2O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3O} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3O} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3O} - \mathrm{CH_3O} - \mathrm{CH_3O} \end{pmatrix}_{n} - \begin{pmatrix} \mathrm{CH_3} \\ | \\ -\mathrm{CH_3O} - \mathrm{CH_3O} - \mathrm$$

Properties. It can be foamed like polystyrene but unlike thermocoal, is soft, spongy known as 'U-foam'. It has low thermal conductivity. Its greatest advantage lies in the fact that it can be made where they are needed without any complex machinery—the two liquid ingredients can be mixed and moulded.

Uses. It is used as insulating material in refrigerators. Due to its spongy nature, it is used for making pillows and matresses. A coating of polyurethane is applied over leather, which improves the appearance and quality of the leather and hence the bags made of these look attractive and the shoes feel comfortable. It is also used to make chairs etc.

Nylon-66

Polyamides are synthetic polymers, having recurring amide groups, which have a structure similar to that of polypeptides. Nylon belonging to this class is used for making fibres.

Nylon 66 is obtained by the polymerization of adipic acid with hexamethylene diamine. Adipic acid is commercially produced by oxidation of cyclohexane derived from either benzene or petroleum.

Hexamethylene is made by final hydrogenation of the adiponitrile.

$$\begin{aligned} \text{HOOC(CH}_2)_4 \text{COOH} + 2\text{NH}_4 \text{OH} &= \text{H}_4 \text{NOOC} - (\text{CH}_2)_4 \text{COONH}_4 \\ & & & & \text{Distilled with} \\ & & & & & \text{V} \\ & & & & & \text{P}_2 \text{O}_5 \end{aligned}$$

$$\begin{aligned} \text{H}_2 \text{N(CH}_2)_6 \text{NH}_2 &\longleftarrow & \text{NC} - (\text{CH}_2)_4 - \text{CN} + 4\text{H}_2 \text{O} \\ \text{Hexamethylene} & & \text{Adiponitrile} \end{aligned}$$

Adipic acid and hexamethylene diamine mixed in equimolecular proportions in aqueous solution in an autoclave and heated at 100°C. The compounds react to form nylon salt in solution. Nylon salt is then heated at 265°C with Dow therm vapours to remove water and molten nylon results. Nylon fibre is obtained by *melt spinning process*.

Nylon can be extruded as a heavy ribbon, in an atmosphere of nitrogen which is chilled and chipped. The polymer can be remelted to spin into fibre and can be used for extrusion of molded objects.

Properties: Nylon is strong, tough, elastic and can be dyed easily. Nylon possesses high abrasion resistance and is chemically stable. It possesses high temperature stability and also high melting (160°C-264°C). It is insoluble in common organic solvents but soluble in phenol, formic acid.

Uses: The polymer can be run directly to spinning machines to produce fibre, hence nylon 66 is primarily used for fibres, which find use in making socks, undergarments, dresses, carpets etc.

Important Thermosetting Resins

Phenolic resins

The most important of this class is *bakelite* or phenol-formaldehyde resin.

It is prepared by condensing phenol with formaldehyde in presence of acid-alkaline catalyst in an aqueous solution. In presence of acid catalyst, the first step leads to the formation of *o*-and *p*-hydroxy methyl phenol, which forms linear polymer.

In the second step a small amount of hexamethylene tetramine added and at the steam temperature, the chain length increases and also three-dimensional resin is formed, which crosslinks the structure. Thus, the soluble novolac gets converted to insoluble *bakelite*.

$$\begin{array}{c|ccccc} OH & OH & OH \\ \hline \\ CH_2 & CH_2 \\ \hline \\ CH_2 & CH_2 \\ \hline \\ OH & OH \\ \\ \end{array}$$

Properties. These phenolic resins are rigid, hard, water resistant. They are resistant to non-oxidising acids, organic solvents but are susceptible to alkalies. Solubilities and melting point of the resin gradually change with rise of molecular weight. These resins possess electrical insulating properties.

Uses. It can be widely used as metal substitute where high tensile strength is not necessary. As an inert material it can substitute for glass. It can be used for making insulator parts like switches, plugs, heater handles. It can be moulded to cabinets for TVs and radio and telephone parts. It is used as adhesive also used in paints and varnishes, as cation exchanger resin for water softening, in paper industry as propeller shafts.

Epoxy resin

Epoxy resins are obtained from a poly condensation of epichlorohydrin with polyphenols or polyalcohols.

Monomers are:

(i) 2, 2-(bis)-4-hydroxy phenyl propane [bis-phenol]

Preparation of bisphenol

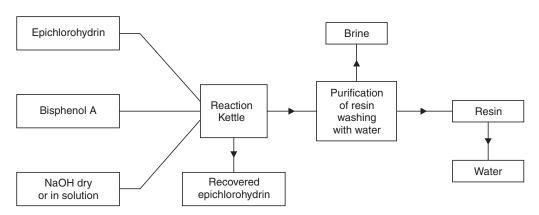
(ii) Epichlorohydrins

$$\begin{array}{c} \text{CH}_2 = \text{CH} - \text{CH}_3 + \text{Cl}_2 & \xrightarrow{400 \, ^{\circ}\text{C}} & \text{CH}_2 = \text{CH} - \text{CH}_2\text{Cl} \\ \text{Propylene} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\$$

(iii) Structure of epoxy resin

$$\begin{array}{c} \text{CH}_2\text{--CH}\text{--CH}_2\text{--} \\ \text{O} \\ \text{--} \\ \text{CH}_3 \\ \text{--} \\ \text{--} \\ \text{--} \\ \text{CH}_3 \\ \text{--} \\ \text{--} \\ \text{CH}_3 \\ \text{--} \\$$

Flow diagram for the production of epoxy resin:



Properties and Uses

Epoxy resins possess outstanding properties of

- Adhesion to various materials
- Flexibility
- Chemical inertness
- Toughness
- Stability at high temperature
- Low shrinkage during cure.

For the above properties, the epoxy resins are used as the major constituents of adhesives in paint industry and as insulator in electrical industry.

Polyester

Polyesters are the condensation products of dicarboxylic acid with dihydroxy alcohols. Terylene is the British name of Dacron, which is obtained by condensation of ethylene glycol and terephthalic acid. Ethylene is oxidised at high pressure and temperature in the presence of Ag as catalyst and the ethylene oxide is hydrolysed by dilute HCl to ethylene glycol.

(a)
$$CH_2 = CH_2 + \frac{1}{2}O_2 \longrightarrow CH_2 O$$

$$CH_2 + H_2O \longrightarrow CH_2 - OH$$

$$CH_2 - OH$$

$$CH_2 - OH$$

(b) Paraxylene obtained from coal tar fraction is oxidised by neutral permanganate solution or conc. HNO₃ (50%) at about 100°C to give terephthalic acid.

The equilibrium of the reaction is not favorable for the formation of ester hence to get high yield the byproduct must be continually removed from the reaction mixture. Better yields are obtained with dimethylterephthalate.

Properties. Since the structure of the polymer is symmetrical and a number of polar groups are present it forms fibre easily. The fibre has high tensile strength and resiliency and is stable to hydrolysis. The fabric made from the fibre is crease resistant.

Uses. It is mostly used for making synthetic fibres like terylene, dacron etc., which are finally used for making garments for men, women and children.

It can be blended with wool and used for making carpets, blankets, upholsteries, quilts etc.

It can be reinforced with glass to form safety helmets, aeroplane parts, paratroop, wire insulators, fighter parachute etc.

Terylene has several advantages over cotton in respect of

- (i) Resistance to acids
- (ii) Strength
- (iii) Crease resistance and
- (iv) Gives better finish and blendable with cotton or wool.

Silicones

Silicones have alternate silicon-oxygen bonds and organic radicals attached to the silicon atoms.

The monomers are prepared as

(i)
$$RCl + Si \xrightarrow{Cu} R_2SiCl_2$$

(ii) From Grignard reagent

$$SiCl_4 + RMgCl \longrightarrow RSiCl_3 + MgCl_2$$

The monomer is obtained by fractional distillation of the reaction products whereby different organo-silicon chlorides are obtained.

In the next step the chlorides are polymerized by hydrolysis involving the following steps-

$$\begin{split} &\equiv \text{SiCl} + \text{H}_2\text{O} \longrightarrow \equiv \text{SiOH} + \text{HCl} \\ &\equiv \text{SiOH} + \text{HOSi} \equiv \longrightarrow \equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{H}_2\text{O} \end{split}$$

Thus, the OH groups of Si are involved in polymerization hence when there is one or two —OH groups in Si, it leads to long chain polymers but when there are three OH groups, crosslinked polymers are formed. Reactions:

$$(i) \hspace{1cm} 2 \text{RCl} + \text{Si} \xrightarrow{\hspace{1cm}\text{Cu}} \text{R}_2 \text{SiCl}_2$$

(ii) From Grignard reagent

$$\operatorname{SiCl}_4 + \operatorname{RMgCl} {\longrightarrow} \operatorname{RSiCl}_3 + \operatorname{MgCl}_2$$

$$(iii) \hspace{1cm} \text{Me}_2 \text{SiCl}_2 \xrightarrow{\hspace{1cm} \text{H}_2 \text{O}} \text{Me}_2 \text{Si(OH)}_2$$

Structure of Silicone Polymers

$$\begin{array}{c} {\rm HO.SiMe_{2^{-}}[OSiMe_{2}]}_{n^{-}}{\rm OSiMe_{2}OH} \\ {\rm Silicone} \end{array}$$

Di-alkyl-di-chlorosilicane and alkyl trichloro silicone undergo hydrolysis and condensation polymerization to give a cross-linked silicone polymer.

http://keralatechnologicaluniversity.blogspot.com

Complete condensation of all the —OH give rise to hard, insoluble product, thus a mixture of monomers (containing one or more —OH groups) along with sufficient water for hydrolysis is heated for polymerization.

Different Types of Silicones

Depending on the proportion of various alkyl silicon halides used the final silicones may be liquids, viscous liquids, semi-solids and solids. Their properties and uses also differ accordingly.

(i) **Silicone fluids.** They are of relatively low molecular weight, sparkling clear fluids with an oily feel, insoluble in water but soluble in aromatic and chlorinated solvents. They have good resistance to heat and oxidation, low surface tension and show low change in viscosity with temperature.

Uses. They are used as autofoam agents, high temperature lubricants, in cosmetics, as damping and hydraulic fluids and to give water repellant finish to textiles and leathers.

- (ii) Silicone greases. These are formed from the oils by adding silica, carbon black etc. They are used as lubricants particularly for very high and low temperature applications.
- (iii) Silicone resins. They are highly cross-linked polymers, possess good insulating properties, heat resistance and good dielectric properties.

Uses. Used for high voltage insulators, high temperature insulating foams, siliconeglass laminates for high temperature application, for different electrical and electronic equipment parts manufacturing.

(iv) Silicone rubbers. Silicone rubbers are formed by reaction of dimethyl silicone fluid with peroxide and appropriate inorganic fillers like TiO_2 , ZnO , SiO_2 etc.

They retain rubbery properties over a much wider temperature span, good heat transfer properties, good resistance to dilute acids and alkalis. They are flexible in wide range of temperatures.

Uses. For tyre manufacturing of fighter aircrafts, as insulators of electric wires in ship, as adhesives for artificial heart valves, transfusion tubings, for special boots to be used at very low temperature, for making lubricants, paints, protective coatings etc.

Molecular weight of a polymer

Polymers are mixtures of molecules of different molecular masses, since the chain length varies. There are the following types of molecular weights for polymers.

(i) Number average molecular weight

The number average molecular weight $(\overline{\mathbf{M}}_n)$ is defined as the total mass (w) of all the molecules of polymer divided by the total number of molecules present. Thus

$$\overline{\mathbf{M}}_{n} = \frac{w}{\Sigma \mathbf{N}} = \frac{\Sigma \mathbf{N}_{i} \mathbf{M}_{i}}{\Sigma \mathbf{N}_{i}}$$

where N_i is the number of molecules of mass M_i . \overline{M}_n can be determined by measuring the colligative properties like lowering of vapor pressure, depression of freezing point etc.

(ii) Weight-average molecular weight

Weight average molecular weight $(\overline{\mathbf{M}}_{w})$ can be defined by the following relation:

$$\overline{\mathbf{M}}_w = \frac{\sum w_i \mathbf{M}_i}{\sum w_i}$$

where w_i is the weight fraction of molecules having mass M_i .

Also,

$$\overline{\mathbf{M}}_{w} = \frac{\sum c_{i} \mathbf{M}_{i}}{\sum c_{i}} = \frac{\sum c_{i} \mathbf{M}_{i}}{c} = \frac{\sum \mathbf{N}_{i} \mathbf{M}_{i}^{2}}{\sum \mathbf{N}_{i} \mathbf{M}_{i}}$$

where c_i = weight concentration of \mathbf{M}_i molecules and c = total concentration of all polymer molecules.

Now, $\overline{\mathbf{M}}_{w}$ is always greater than $\overline{\mathbf{M}}_{n}$.

 $\overline{\mathbf{M}}_w$ can be determined by light scattering measurements, viscosity measurements, diffusion measurements. $\overline{\mathbf{M}}_w/\overline{\mathbf{M}}_n$ is used as a measure of the molecular-mass distribution or "index of polydispersity" and it is 1.5 or larger for natural and synthetic polymers. $\overline{\mathbf{M}}_w = \overline{\mathbf{M}}_n$, in case all the polymer molecules are of identical molecular weight.

Degree of polymerization

The number of recurring units of monomers in a polymer chain is known as degree of polymerization (DP). In a polymer, actually the chain length varies, some may contain 100 to 200 monomers while others may contain 1000 or more. Hence, we use the term average degree of polymerization (\overline{DP}).

In a free radical polymerization, the overall rate of polymerization is proportional to the concentration of the monomer and the square root of concentration of the initiator.

$$-\frac{d(M)}{dt} = K[M][C]^{1/2} \quad M = \text{concentration of monomer}$$

$$C = \text{concentration of initiator}$$

At a certain stage of polymerization it is found that the number of active centres for polymerization is equal to the number of chain terminators. At this stage the average degree of polymerization is

$$\overline{\mathbf{D}}\mathbf{P} = \frac{\mathbf{K}.[\mathbf{M}]}{\left[c\right]^{1/2}}$$

This equation relates average degree of polymerization with monomer concentration as well as initiator concentration. The degree of polymerization influences the tensile strength of the polymer.

Highlights:

Classification of plastics

- *Thermoplastic* resins soften on heating and harden on cooling reversibly.
- Cellulose derivatives
- Polythene, Polypropylene, Polystyrene, Polyvinyl chloride, Polytetrafluoro ethylene (Teflon)
- Polyamides (nylon)
- ABS polymers.
- *Thermosetting plastics* are permanent setting resins which harden on heating during moulding and they cannot be softened again. Examples of this class include
 - (i) Bakelite obtained by polymerization of phenolic derivatives with aldehydes.
- (ii) Melamine obtained by condensing melamine with formaldehyde.
- (iii) Terylene (Polyester) are condensation products of dicarboxylic acids with dihydroxy alcohols
- (iv) Epoxy resins (araldite)
- (v) Silicone resins.

RUBBER

Rubbers are high polymers, which have elastic properties and can be stretched upto about 300 percent. The unstretched rubber is amorphous and the polymer chains are in a coiled state, which on stretching gets aligned causing crystallization. In releasing the stress the chains revert back to their original coiled state.

Natural rubber. Natural rubber is polymerized isoprene, which occurs in the latex of various trees. Natural rubber came into market first in early 19th century. The molecular weight of raw rubber is about 100,000-150,000 and is made from the latex of different plants like *Havea brasillians* and gangule found in tropical and subtropical countries. The latex is collected from the mature Havea tree by making deep cuts on the bark, and by allowing the latex stream to collect in a pot attached below the cuts. Tapping is done at intervals of about 6 months.

Coagulation of the latex. Latex is diluted to contain between 15-20% of rubber, filtered to make it free from dirt. Coagulation is then effected by adding acetic acid (1 to 2% on weight basis). Rubber coagulates as soft white mass which is washed and further processed.

The coagulum is allowed to drain and the absorbed serum is squeezed out through steel rollers upon which water is sprayed. The coagulum is converted to a sheet with uneven rough surface resembling crepe paper and called *crepe rubber*.

Smoked rubber sheets are made from thicker sheets than crepe rubber. Coagulation is carried out in large tanks and finally allowed to settle for 16 hours. The tough slabs are passed through rollers (embossed or ribbed) to obtain ribbed pattern. The embossed sheets are then hung up in a smoking house, where on the floor, wood or coconut husk is burnt to produce heat. Smoking is done at a temperature of 45°C-50°C, whereby the sheets get dried within 4 days.

The crude rubber obtained is translucent and amber in colour and is not attacked by micro-organisms.

Properties. Natural rubber is an amorphous solid, translucent, impervious to gases, elastic in nature. It is actually polymerized *cis*-isoprene.

Rubber slowly oxidises when exposed to air. On heating it softens and liquifies. It burns to form ${\rm CO_2}$ and ${\rm H_2O}$. On destructive distillation rubber first softens and then decomposes producing white fumes. When the destructive distillation is carried out at higher temperature the condensate contains mostly the isoprene dimers.

Raw rubber powder catalytically reacts with $\rm H_2$ gas, it decolorizes bromine water, forms ozonide with ozone, reacts with HCl. For each $\rm C_5H_8$ unit in rubber molecule, one molecule each of $\rm Br_2$, $\rm O_3$ and HCl reacts, thus there is only one double bond. But for decomposition product of

rubber
$$i.e.,$$
 isoprene there is two double bonds $\mathrm{CH_2=\!C-\!C=\!CH_2}$. $\phantom{\mathsf{CH_2=\!C-\!C}=\!CH_2}$. $\phantom{\mathsf{CH_2=\!C-\!C}=\!CH_2}$

During the process of linking, head and tail linking of isoprene molecule occurs.

$$\begin{bmatrix} H & H \\ | & | \\ -C - C = C - C - \\ | & | & | \\ H & CH_3 H & H \end{bmatrix}_n$$

Structure of natural rubber (cis-polyisoprene)

Rubber is attacked by strong alkalies and oxidising agents. Strong HNO₃ attacks rubber.

Limitations of natural rubber

Natural rubber softens at high temperature and becomes brittle at low temperature, it is attacked by acids, oxidising agents, non-polar solvents, it is oxidised by air. Also on excessive streteching it gets permanently deformed. To overcome these limitations rubber is vulcanized.

Vulcanization of rubber

During 1839, Charles Good Year developed the method of vulcanization of rubber by which the properties of natural rubber can be improved to a large extent. Vulcanization is a process which is essentially compounding rubber with different chemicals like, sulfur, $\rm H_2S$, benzoyl chloride etc. The method is basically heating raw rubber with sulfur at 100° C-140°C, when the sulfur enters into the double bonds of rubber forming crosslinks between the chains and this gives the structure toughness. The toughness or the stiffness of vulcanization depends on the amount of sulfur included. For flexible tyre rubber, sulfur content is from 3-5% whereas for tougher variety like ebonite, content of S is 32%. Ebonite is so tough that it can be machined, it has very good electrical insulation property.

	Property	Raw rubber	Vulcanized rubber
1.	Elasticity	very high	low, depending on percentage of sulphur
2.	Tensile strength	200 kg/cm^2	2000 kg/cm^2
3.	Useful temperature range	10°C-60°C	40°C to 100°C
4.	Chemical resistance	very poor	higher
5.	Water absorption tendency	high	low
6.	Resilience	good	much better

Comparative study between natural and vulcanized rubber

Synthetic Rubbers

9. Tackiness

10. Durability

11. Quality

Insulation property Resistance to

organic solvents

7.

Synthetic rubber is artificially produced rubber-like polymers which can be stretched to at least twice its length and on releasing the stress, it returns to its original shape and size. Some important examples are:

Low

marked

less

inherent

(i) GR-S or Buna-S. This variety is the most important synthetic rubber and it is obtained by copolymerization of butadiene and styrene.

$$xn\mathrm{CH}_2 = \mathrm{CH} - \mathrm{CH} = \mathrm{CH}_2 + n$$
butadiene
$$\text{Copolymerization}$$

$$\text{Copolymerization}$$

$$\text{CH} = \mathrm{CH}_2$$

SBR-Styrene butadiene rubber

much higher but swells

can be controlled by vulcanization

low

better

Properties. SBR is similar to natural rubber in processing character and also as finished product. It possesses high resilience and good and tough mechanical properties. But unfortunately it is easily attacked by oxidising agents, mainly ozone. It also swells in organic solvents. It can be vulcanized as natural rubber.

Uses. It is mainly used for the manufacture of tyres. It is also used as soles and other components of shoes, for insulating wires and cables, as adhesives and lining for vessels.

(ii) GRA or Buna-N. It is a copolymer of butadiene and acrylonitrile

$$x \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + n \text{CH}_2 = \text{CHCN} \xrightarrow{\text{Copolymerization}} - \left[\text{CH}_2 - \text{CH} = \text{CHCH}_2 \right]_x \left[\text{CH}_2 - \text{CHCN} \right]_n$$

Properties. It is highly resistant to heat, sunlight, acids, oils etc. but due to the presence of —CN group, it is much more susceptible to alkali than natural rubber. The good qualities increase as the proportion of acrylonitrile is increased and it can be vulcanized to better heat resistant variety.

Uses. Its use is versatile. It is used to manufacture parts for automobiles, aircraft. It is also used for making conveyer belts, adhesives and oil resistant foams.

(iii) GR-M or Neoprene. It is made by polymerization of chloroprene or α chlorinated butadiene.

$$n \text{CH}_2 = \text{C} - \text{CH} - \text{CH}_2 \xrightarrow{\text{Polymerize}} - \begin{bmatrix} \text{Cl} \\ | \\ \text{CH}_2 \text{C} = \text{CH} - \text{CH}_2 \end{bmatrix}_n$$
Chloroprene

Properties. The only difference of the structure of chloroprene and natural rubber is a single chlorine atom instead of an H atom which brings about marked resistance to temperature, atmospheric change and to oils. It can be vulcanized by heating alone. Its properties can be changed by compounding to ZnO or MgO.

Uses. It is used for making conveyer belts, adhesives, gaskets, as linings for reaction vessels and for making pipes to carry corrosive gases and oils.

Reclaimed Rubber

It is obtained from the waste rubber articles by the process of reclaimation.

Process. The waste rubber articles like tyres, tubes, footwares, gaskets etc. are cut and powdered in a cracker. The unwanted ferrous materials are separated by electromagnetic separator and then charged to an autoclave and digested with caustic soda solution at 200°C under pressure for 8-15 hours. The fibres get hydrolysed *i.e.*, devulcanization takes place. Sulphur is removed as sodium sulfide. It is washed, dried and finally reinforced with carbon black etc.

Properties: Reclaimed rubber has inferior tensile strength, elasticity etc. compared to natural rubber but has improved ageing properties. It is cheaper and easier for fabrication.

Uses. Reclaimed rubber is used for making tyres, tubes, belts, shoe soles, floor mats etc.

Compounding of rubber

Compounding is mixing of raw rubber with different chemicals to impart special properties for application.

Process. Synthetic or natural rubber is mixed with *vulcanizing agents* like sulfur, *plasticizers* like vegetable oils, waxes etc., *antioxidants* like amines and phosphites, *fillers* like C-black, *accelerators* like benzothiazole, mercaptans, and *coloring matters*. It is then repeatedly passed through hot roll mills rotating in opposite directions to soften and break down and the process is called *mastication*. Finally the material forms soft plastic mass.

Highlights:

Rubber

- Natural rubber is *cis*-polyisoprene
- Gutta percha is *trans*-polyisoprene.

Vulcanization

• The process discovered by Charles Good Year in 1839 to improve the quality of rubber by introducing sulfur at 100°C-140°C to the double bond of rubber.

 $\overline{(Contd.)}$

Synthetic rubber

- An elastomer produced artificially, which can be stretched to twice its length, but returns to its original shape.
 - Styrene rubber (GR-S)
 - Nitrile rubber (GR-A)
 - Neoprene (GR-M)
 - Thiocol (GR-P)
 - Hypalon
 - Polyurethane

Compounding of rubber

• Mixing of raw rubber with plasticizers, antioxidants, vulcanizing agents, fillers, colours etc. to impart specific properties to the finished products.

MISCELLANEOUS POLYMERS

- 1. **Laminate.** It is obtained by joining two or more layers of solid materials with the help of an adhesive. If the grains of the layers are parallel to each other, it is called *parallel laminate* and when they are at right angles to each other, it is called *cross laminate*.
 - (a) Plywood. Odd numbers of layer of wood (0.5-10 mm thick) are bonded such that grains of alternate layers are at right angles to each other (cross-laminate). By this process the plywood produced has uniform properties, length and widthwise, thus splitting of wood, shrinkage etc., are minimised and becomes more strong compared to wood of equal thickness.

Uses. Plywood is used for making railway coach, cabinets, false-ceilings and in other house building purposes.

(b) Laminated Plastics. Paper, cloth, asbestos fibre, glass, metal etc., are impregnated with thermosetting resin like phenol-formaldehyde or urea-formaldehyde solution in solvent and dried at a temperature much lower than the curing temperature of the resin, then they are cut into suitable size and then subjected to curing in a hydraulic press at about 180°C and pressure, when the resin becomes hard. The finished laminated plastics are light but strong and impermeable to water, oil etc. They are machineable and chemical resistant.

Uses. They are used for electrical and insulating materials, pump parts etc. They are also used for decorative purposes on table tops and wall panellings etc.

(c) Laminated glasses. Two glass sheets are joined by a plastic sheet in between to form laminated glass. For transparency, polyvinyl-butyl resin can be used as adhesive. Bullet proof or splinter proof laminated glass is obtained by curing the laminates in an oven under heat and pressure.

Conducting Polymers

Polymers obtained by the usual methods of polymerization are mainly insulators. Conducting polymers are made by special powders and are classified as

(a) π -electrons conducting polymer. In these polymers the backbone of the polymer is made up of molecules that contain conjugated π -electrons which extend the entire polymer and make the polymer conducting.

(b) Conducting element-filled polymer. In this type of polymer the polymer acts as binder, which binds the conducting elements like carbon black, metal oxides, metallic fibres that conduct electricity.

- (c) *Inorganic polymer*. A metal atom with poly dentate ligand, which is a charge transfer complex is bound to the polymer to make it conducting.
- (d) Doped-conducting polymer. The polymer is made conducting by exposing the surfaces to charge transfer agents in gas or in solution place.
- (e) Blended conducting polymer. This type of polymer is made by blending a conventional polymer with a conducting polymer.

Industrially important conducting polymers are: Polyquinoline, polyanthrylene, polythiophene, polybutadienylene etc.

Uses. Conducting polymers are used for making (*i*) button cells, (*ii*) photovoltaic devices, (*iii*) sensors and (*iv*) biomedical devices.

SHORT QUESTIONS AND ANSWERS

Q. 1. What is functionality of a monomer?

Ans. It is the number of bonding sites of monomer.

Q. 2. What is gel point?

Ans. The monomers of alkyl resins possess functionality greater than two. During condensation polymerization it gets transformed from viscous material to a gel and the transformation is sudden. This point of transformation is the gel point. The cause of gelation is the formation of an infinite network of polymer and at this phase the resin becomes tough and less extensible.

Q. 3. What is ageing of rubber?

Ans. Ageing is the autooxidation of rubber with time due to the presence of double bond and due to this rubber becomes hard.

Q. 4. When is vulcanization done? Mention some of the uses of vulcanized rubber.

Ans. Vulcanization is done after shaping the article. The shaping is done with raw rubber along with suphur and other ingredients like accelerators, antioxidants, fillers etc.

Uses. Vulcanized rubber is used in vehicle tyres, hose, conveyer belt, electrical insulation.

Q. 5. What is the basic difference between nylon 6 and nylon 66?

Ans. Nylon 6 is an additional polymer whereas nylon 66 is a condensation polymer.

In nylon 6, the composition of the monomer is the same as that of the polymer, but nylon 66 is formed with the elimination of water molecules.

Q. 6. Differentiate between a homopolymer and copolymer?

Ans. A homopolymer consists of many identical monomer units whereas a copolymer consists of monomers of different chemical structures.

Q. 7. Differentiate between addition and condensation polymerization.

Ans. Addition polymerization is a reaction that gives a polymer, which is an exact multiple of the original monomers.

Condensation polymerization takes place through different functional groups of monomers with elimination of small molecules like $H_{\circ}O$ etc.

Q. 8. What is copolymerization?

Ans. Copolymerization is the point polymerization of two or more monomers, *e.g.*, butadiene and styrene to yield GR-S rubber.

Q. 9. What is polydispersity index of a polymer?

Ans. Polymers are different from other small sized molecules as they are mixtures of molecules having different molecular masses. *Polydispersity index* (PDI) of a polymer is a measure of the molecular mass distribution of a polymer.

Q. 10. What is an elastomer?

Ans. Any rubber-like elastic polymer, which can be stretched to thrice its size and after removal of the stretching force it returns to its original shape is called an elastomer.

Q. 11. Why is the density of HDPE different from LDPE?

Ans. HDPE is completely a linear polymer and hence packing of the chains is efficient and hence its density is high. But for LDPE, due to its branched structure, packing efficiency is low and hence density is low.

Q. 12. Why thermosetting plastics cannot be reused?

Ans. In thermosetting plastics, the monomers are bound to each other by strong covalent bonds, which cannot be broken on heating. Thus by heating it cannot be softened to reshape and reuse.

Q. 13. What is natural rubber and what is gutta-percha?

Ans. Natural rubber is long-coiled chains of polycisisoprene and gutta-percha is horny and tough form of polytransisoprene.

Q. 14. Why is teflon highly chemical resistant?

Ans. In teflon the most electronegative element F contributes to the strong attractive force within the chains and hence is non-reactive towards other chemicals.

Q. 15. Why is PVC soft and flexible but bakelite is hard and brittle?

Ans. In PVC the molecular chains are bonded to each other by Van der Waal's forces and hence these long chains are flexible and can slip or twist on applying force but in the case of bakelite the thermosetting polymer chains are crosslinked by covalent bonds, so, it is hard and no deformation can take place on applying force. When the force becomes too large the covalent bonds are broken and it becomes brittle.

Q. 16. Why is natural rubber compounded?

Ans. Natural rubber possesses many undesirable properties and so to improve its properties it is usually compounded with different ingredients like plasticizers, antioxidants, filler, colorant etc.

Q. 17. Why is natural rubber vulcanized?

Ans. Raw rubber has high elasticity, tackiness, poor chemical resistance, poor strength, large water absorption capacity etc. Vulcanization i.e., adding some sulfur at 100°C-140°C causes saturation of the double bonds by S and hence stiffening of the polymer takes place. Vulcanization, thus, improves all the above properties.

Q. 18. What changes take place with polymers near glass transition temperature?

Ans. Below the glass transition temperature, the polymer is brittle and above it, they would deform but not break.

Q. 19. How can cross-linked silicone be produced?

Ans. Cross-linked silicone can be produced by adding a calculated quantity of trifunctional methyl silicon trichloride to the condensing polymer.

Q. 20. What are alkyd resins?

Ans. The basic reaction of alkyd formation is esterification. Phthalic anhydride is used instead of an acid and alcohol is polyfunctional alcohol, glycerol. The final cross-linked polymer is shown below:

$$O = C \qquad C = O \\ O \qquad O \qquad CH_2 \qquad CH_2 \\ CHOR \qquad CHOR \qquad O \\ CH_2OH \qquad CH_2-O-C \qquad C = O \\ O \qquad O \qquad O \\ CH_2-CH-CH_2 \\ O \qquad C = O \\ O \qquad O \\ CH_2-CH-CH_2 \\ O \qquad C = O \\ O \qquad O \\ C = O \\ O \qquad O$$

Alkyd resin (R = fatty acid chain)

Uses:

- As insulators
- As film formers in emulsion paints
- Automobile parts manufacture
- Switches manufacture.

Q. 21. What is polymethyl methacrylate (Trade name: Perspex)?

Ans. Here monomer is: Methylmethacrylate

Polymer is:

$$\begin{array}{c|c} \operatorname{CH}_3 & \operatorname{CH}_3 & \operatorname{CH}_3 \\ -\operatorname{CH}_2 - \operatorname{CH} & \operatorname{CH}_2 - \operatorname{C} & \operatorname{CH}_2 - \operatorname{C} \\ \operatorname{CH}_3 \operatorname{OOC} & \operatorname{COOCH}_3 & \operatorname{COOCH}_3 \end{array}$$

Properties and uses

It is a glass-like plastic. It is used for making transparent sheets, rods etc. and also for making binoculars, camera lenses, table lamp shades. It is a component of *emulsion paint*.

Q. 22. What is polyvinyl (Trade name: Fevicol) alcohol?

Ans. Monomer is: CH₂=CH—OH (Vinyl alcohol)

Polymer is: $-\text{CH}_2$ —CH(OH)—CH $_2$ CH(OH)—CH $_2$] $_n$

It is a water soluble polymer which is soft and gummy. It is used as an adhesive.

Q. 23. What do you mean by biodegradation of polymers?

Ans. Biodegradation is a process by which refuse mixes with environment by microorganisms. This biodegradation process is completely absent in the case of high polymers. Development of biodegradable polymer 'biopol' is now a challenge to scientists. Polyhydroxybutyrate is a 'biopol' which degrades within a few months in soil but it is too costly to be used very soon.

EXERCISES

- 1. Write short notes on (i) free radical polymerization (ii) cationic polymerization (iii) silicone resin.
- 2. Discuss various methods of plastic processing.
- 3. (a) Write short notes on
 - (i) addition polymerization

- (ii) condensation polymerization
- (iii) thermoplastic and thermosetting plastics
- (iv) number average and molecular weight.
- (b) Write the structures, two properties and uses of:
 - (i) PE, (ii) PP, (iii) PVC, (iv) PTFE, (v) Nylon 66.
- 4. Write the structures of five addition polymers and five condensation polymers, with their respective monomers.
- Explain with example: (i) addition polymerization, (ii) co-polymerization, (iii) vulcanization of rubber.
- **6.** Write short notes on:
 - (i) Rayon

- (ii) Synthetic rubber
- (iii) Types of plastics.
- 7. (a) Discuss the effect of structure of polymers on their physical properties in detail.
 - (b) Give the preparation and properties of
 - (i) Nylon 6,
- (ii) Neoprene rubber
- (iii) SBR
- (iv) Silicone rubber.
- 8. (a) What is a heterochain polymer? Give one example.
 - (b) Define the term functionality of monomers. Explain its significance with suitable examples.
 - (c) Discuss the preparation of bakelite and PVC plastic.
 - (d) What are the functions of fillers and plasticizers in plastic industry?
- 9. Discuss briefly the application of plastic in engineering and industry.

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- **10.** (a) Define the terms
 - (i) Degree of polymerization.
- (ii) Co-polymerization.
- (b) What is the effect of polymer structure on the strength and crystalline nature of polymer?
- (c) Give four uses of rubber.
- (d) What are silicones? Draw the polymer obtained by hydrolysing dichlorodimethyl silicone and give its use.
- 11. (a) Explain the terms with example
 - (i) addition polymerization
 - (ii) co-polymerization
 - (iii) condensation polymerization.
 - (b) Give an account of one (i) Crepe rubber, (ii) butyl rubber.
 - (c) How are the following produced: (i) Buna S (ii) thiokols? Mention their properties and uses.
- **12.** (a) What do you understand by vulcanization of rubber? What are the advantages and disadvantages? Give the structural unit of vulcanised rubber.
 - (b) Give the preparation and industrial application of PVC and neoprene.
- **13.** (a) Give a brief account of vulcanization of rubber.
 - (b) Give the manufacture and uses of
 - (i) teflon (ii) nylon 66.
 - (c) What is an Epoxy group? Give the preparation and uses of a common Epoxy resin. Give the structure of bakelite.
- 14. (a) Outline the general method of preparation of urethanes and state their applications.
 - (b) List out the difference between HDPE and LDPE.
 - (c) Write note on glass reinforce plastic.
 - (d) What is meant by compounding of plastic?
- 15. Define the term crystallinity of polymer. How is it related to the chemical structure?
- 16. List the difference between addition and condensation polymerization.
- 17. Describe with a neat sketch the process of compression moulding. How does it compare with injection moulding?
- **18.** (a) Discuss the mechanism of addition polymerization.
 - (b) Define monomer, homopolymer, copolymer, graft polymer.
 - (c) Write note on silicone.
- **19.** (a) Discuss the preparation of natural rubber.
 - (b) Discuss the methods of preparation of urea-formaldehyde resin and polyurethane and mention their uses.
 - (c) Describe the methods of preparation of neoprene and silicone rubber. Mention their uses.
- 20. Write short notes on bakelite, thiokol.
- **21.** (a) What is latex? How is natural rubber isolated from it?
 - (b) What is vulcanization? How does it improve the property of natural rubber?
- 22. Write preparation, properties and uses of
 - (i) Phenol-formaldehyde resin, (ii) Silicone rubber (iii) Polyethylene.
- 23. Distinguish between the following with examples:
 - (i) Natural and synthetic rubber
 - (ii) Addition and condensation polymerization
 - (iii) Thermo plastic and thermosetting plastic.

- 24. Write short notes on
 - (i) Teflon (ii) Cellulose acetate (iii) Silicone (iv) SBR.
- **25.** (a) Define and give examples for
 - (i) Monomer (ii) Functionality (iii) Degree of polymerization (iv) Co-polymer.
 - (b) Explain how the polymers are classified on the basis of their thermal behaviour and method of polymerization. Give example of each class.
- 26. Distinguish between
 - (i) Thermoplastic and thermosetting plastic.
 - (ii) Addition and condensation polymerization.
- 27. Write note on thermoplastic and thermosetting resin.
- 28. What is an elastomer?
 - (a) Write short notes on preparation, properties and uses of (i) bakelite, (ii) epoxy resin.
 - (b) Name a polymer containing fluorine. Give its structure, properties and uses.
- 29. Distinguish between nylon 6 and nylon 66.
- 30. Write short notes on
 - (i) Polypropylene
 - (ii) Plexi glass.
- **31.** Give preparation, properties and uses of (i) nylon 6, (ii) nylon 66, (iii) polyester or dacron, (iv) silicone resin.
- **32.** (a) What are bakelite and PTFE? Name any four commercial thermoplastics.
 - (b) What are the materials from which an epoxy adhesive is prepared?
- **33.** (a) Bring out the differences between thermoplastic and thermosetting plastic.
 - (b) Explain–Vulcanization of rubber.
 - (c) Explain-Injection moulding with a diagram.
 - (d) Explain the chemical resistant and thermal resistant polymers.
- 34. Give the representative formula and two important uses of each of the following:
 - (i) Plexi glass, (ii) Teflon, (iii) PVC.
- 35. Write a note on reclaimed rubber.
- **36.** (a) What is meant by co-ordination polymerization? Explain with two examples.
 - (b) Write short notes on (i) Plastic deformation, (ii) Moulding techniques.
- **37.** Write short notes on structure, method of preparation and uses of (i) HDPE, (ii) PVC, and (iii) Plexi glass.
- 38. Give a brief account of
 - (i) Vulcanization of rubber, (ii) Compounding of rubber.
- **39.** What is the difference between-plastic, rubber, and fibre?
- **40.** Write short notes on (i) rayon, (ii) nylon, and (iii) dacron.
- **41.** (a) How is natural rubber obtained from latex?
 - (b) Explain compounding and vulcanization of rubber.
- 42. What is Zeigler-Natta polymerization?
- **43.** Give the structures of syndiotactic, isotactic and atactic polymers.
- 44. How do the properties of polymer change with Zeigler-Natta polymerization?
- **45.** (a) Mention the technical tests of polymers.
 - (b) Mention the influence of molecular characteristic on the properties of polymers.
- **46.** What is biodegradation of polymers?