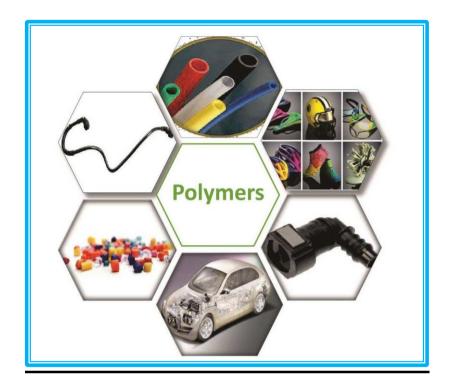
# **POLYMER AND PLASTICS**



Polymers (Greek Poly-many; mers-units or parts) are macromolecules (giant molecules of high molecular masses) formed by linking/joining together of a large number of small molecules (called monomers).

Eg: Polythene is a polymer formed by linking together of a large number of ethane  $(C_2H_4)$  molecules.

$$n \left( H_2C=CH_2 \right) \xrightarrow{POLYMERIZATION} \leftarrow \left( CH_2 \leftarrow CH_2 \right) \frac{}{n}$$
Ethene (monomer) Polyethene, PE (polymer)

Where 'n' is the degree of polymerization.

# **Functionality of Polymer**

Functionality means the number of bonding sites in a monomer. For a substance to act as a monomer it must have at least two reactive sites or bonding sites. In an olefin, the double bond can be considered as a site for two free valencies when the double bond is broken, two single bonds become available for combination.

Bifunctional monomers examples: They undergo polymerisation by condensation to give a polymers.

Ethene can be considered as bifunctional monomer:

Hence ethylene can be considered bifunctional.

## **Classification of Polymers**

Polymers can be classified in the following ways:-

#### 1. Classification on the basis of source

 a) Natural polymers:- Polymers which are found in nature in animals and plants are called Natural Polymers
 eg: Starch (a polymer of α-D-glucose), cellulose (a polymer of β-D-glucose), proteins (polypeptides and polyamides), nucleic acid, natural rubber (a polymer of cis-isoprene).

n 
$$H_2C$$
  $CH_3$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_3$   $CH_2$   $CH_2$   $CH_2$   $CH_3$   $CH_2$   $CH_2$   $CH_2$   $CH_3$   $CH_2$   $CH_2$   $CH_3$   $CH_2$   $CH_3$   $CH_4$   $CH_2$   $CH_4$   $CH_5$   $CH_5$ 

#### Structure of starch and cellulose

b) **Synthetic Polymers:-** Man made polymers are called synthetic polymers Eg: Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), nylon, terylene, Bakelite.

#### Structure of polystyrene

$$\begin{array}{c} \text{CH=CH}_2 & \left(\begin{array}{c} \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\ \text{CH} & \text{CH} & \text{CH} \end{array}\right)_{n} \\ \\ \begin{array}{c} \text{Polymerisation} \\ \\ \text{monomer} \end{array}$$

#### Structure of Bakelite

#### 2. Classification on the basis of structure

**a)** Linear polymers:- Polymers in which monomeric units are joined in the form of long straight chains.

Eg: High density polyethylene (HDPE), nylon, polyesters. These polymers possess high melting point, density and tensile strength, due to close packing of polymer chain.

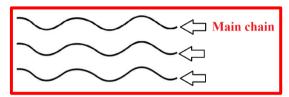


Fig: Linear chain polymer

Fig: Polyester (Polymer of terephthalic acid and ethylene glycol, PET)

b) Branched chain polymers:- Branched chain polymers are mainly linear in nature, but also possess branches along the main chain. These polymers possess low melting point, density and tensile strength compared to linear chain polymers due to poor packing off polymer chains in the presence of branches.

Eg: Low density polyethylene (LDPE), glycogen, amylopectin.

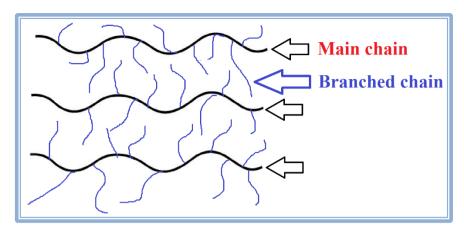


Fig: Branched chain polymer

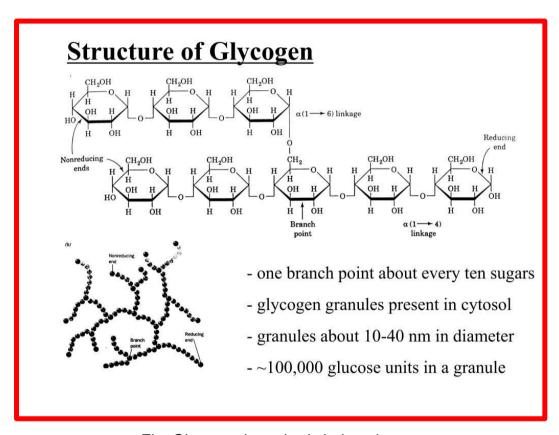


Fig: Glycogen branched chain polymer

c) Cross-linked or three dimensional network polymers:- It contains monomers molecules connected to each other by only covalent bonds. They are giant molecules in which movement of individual monomer units are prevented by strong cross-links. Due to the presence of strong cross-links, they are hard, rigid, brittle and do not melt, but burn on heating.
Eg: Bakelite, urea-formaldehyde, melamine-formaldehyde etc

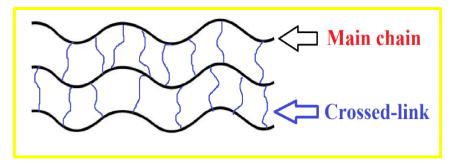


Fig: Cross-linked polymer

$$\begin{array}{c} O \\ H_2N \\ \text{ure a} \\ + \\ 3 \\ H_2C=0 \end{array} \\ \begin{array}{c} H_2O \\ HO \\ HO \\ \end{array} \\ \begin{array}{c} H_2O \\ HO \\ HO \\ \end{array} \\ \begin{array}{c} H_2O \\ HO \\ HO \\ \end{array} \\ \begin{array}{c} H_2O \\ HO \\ HO \\ \end{array} \\ \begin{array}{c} H_2O \\ HO \\ \end{array} \\ \begin{array}{c} H_2O \\ HO \\ HO \\ \end{array} \\ \begin{array}{c} H_1O \\ HO \\ \end{array} \\$$

Fig: Urea-formaldehyde cross-linked polymer

- **3. Classification on the basis of their methods of synthesis:-** Based on the methods of synthesis, the polymers are classified into two groups
  - a) Addition Polymers:- Addition polymers are obtained by addition polymerization method, which involves the repeat addition of monomers (unsaturated derivatives of ethane) to yield long chains. Their empirical formula is same as that of monomers.
  - Eg: Polyethylene, polypropylene, polystyrene, polyvinyl chloride etc.

**b)** Condensation polymers:- Condensation polymers are obtained by a series of condensation reaction generally involving two monomers. The condensation reactions usually results in the loss of small molecules like H<sub>2</sub>O, HCl, NH<sub>3</sub> etc. Eq: Nylon-66, Bakelite, polyester

O 
$$C - (CH_2)_4 - C$$
 O  $C - (CH_2)_4 - C$  O  $C - (CH_2)_4 - C$  O  $C - (CH_2)_4 - C$  O peptide bond  $C - (CH_2)_4 - C$  O  $C - (CH_2)_4 - C$  O  $C - (CH_2)_4 - C$  O  $C - (CH_2)_6 - C$  O  $C - (CH_2)_6$ 

Fig. Nylon-66

# 4. Classification on the basis of their behaviour when heated to processing temperature:-

Polymeric materials are broadly divided into two categories on this basis:

- a) Thermoplastic polymers:- Thermoplastic polymers are linear, long chain polymers which can be soften on heating and hardened on cooling reversibly, i.e their hardness is temporary property, subjected to change with rise or fall of temperature. Thus they can be processed again and again.
  - Eg: Polythene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylons, polytetrafluoroethylene (PTFE or Teflon) etc.
- b) Thermosetting polymers (or thermosets):- Thermosetting polymers are those polymers, which during moulding (by heating etc) get hardened and once they have solidified, they cannot be soften, i.e they are permanent setting polymers. Such polymers during moulding acquired three dimensional crossedlinked structures with predominantly strong covalent bonds. Thus a thermosetting polymer once moulded cannot be reprocessed.

Eg: Polyester (terylene), Bakelite, epoxy-resin, melamine resin, ureaformaldehyde.

Fig. Melamine polymer

 Classification on the basis of physical state:- A polymeric material can be amorphous (eg: LDPE, rubbers etc) or semi-crystalline (eg: HDPE, nylon, polyesters).

# Structural difference between thermoplastic and thermosetting polymers:-

Thermoplastic possess comparatively weaker intermolecular forces and then there is no cross-linking. Consequently they are flexible, and can be easily moulded on heating. On the other hand there is excessive cross-linking in thermosetting plastics and different chains held through strong covalent bonds forming a three-dimensional network. Hence once set cannot be remoulded. On heating they first fuse to form hard mass and then burn.

# Comparison between thermoplastics and thermosetting polymers:-

Thermoplastic Polymers	Thermosetting polymers	
They soften on heating readily.	They do not soften on heating.	
They consist of long chain linear macromolecules.	<ol><li>Their set molecules have three- dimensional network structure, joined by strong covalent bond.</li></ol>	
<ol><li>They are formed mostly by addition polymerization.</li></ol>	<ol><li>They are formed by condensation polymerization.</li></ol>	
<ol> <li>By reheating to a suitable temperature, they can be softened, reshaped and thus reused.</li> </ol>	<ol> <li>They retain their shape and structure, even on heating. Hence they cannot be reshaped and reused.</li> </ol>	
5. They are usually soft, weak and less brittle.	<ol><li>They are usually hard, strong and more brittle.</li></ol>	
6. They can be reclaimed from wastes.	6. They cannot be reclaimed from wastes.	
7. They are usually soluble in some organic solvents.	<ol><li>Due to strong bonds and cross-linking, they are insoluble in almost all solvents.</li></ol>	

**Polymerization:-** It is the process by which simple (monomers) molecules join together to form very large (polymer) molecules. Hence the system of large molecular weight polymer is termed as polymerization.

There are three different ways of doing polymerization:

#### (a) By opening a double bond:

$$n \left( H_2C=CH_2 \right) \xrightarrow{POLYMERIZATION} \leftarrow \left( CH_2 - CH_2 \right) n$$

Ethene (monomer)

Polyethene

Where 'n' is the degree of polymerization.

#### (b) By opening a ring:

#### (c) By using molecules having two functional groups

# Mechanism of addition polymerization

Polymerization reaction involves union of two or more small molecules to form a large molecule called polymer. Polymerization of ethylene and its substituted counterparts,

say CH<sub>2</sub>=CHSG (Where, Substituent Group, **SG = Ph, H, CI** etc) can be carried out by using any of the following mechanism:-

#### 1. Free radical polymerization mechanism:-

In free-radical polymerization, monomer is activated by its transformation into radical by the action of light (as in photochemically initiated), heat (as in thermally initiated), or by adding chemicals known as initiators (as in chemically initiated free radical polymerization.

Initiators are the compounds which readily decompose into free-radicals so that the monomer molecules can interact with these free-radical for their activation.

Examples of well-known initiators are benzoyl peroxide and azo bis isobutyronitrile (AIBN)

Figure 1: Radical formation using benzoyl peroxide.

Figure 2: Radical formation using AIBN.

Such reaction can be written as;

Free radical polymerization mechanism involves the following steps:

(a) Chain Initiation:- It is considered to involve two reactions. The first one is the production of free radical usually by homolytic dissociation of an initiator (or catalyst) to yield a pair of radicals R\*.

The second part of initiation involves the addition of these radical to the first monomer molecule to produce the chain initiating species  $M_1^*$ .

Thus the polymerization of monomer, H<sub>2</sub>C=CHSG takes in the form:-

(The radical are is often referred as an initiator radical or a primary radical).

**(b) Chain Propagation:** consist of the growth of M<sub>1</sub>\* by successive addition of large no. of monomer molecules according to equation

$$M_1$$
 +  $M$   $\longrightarrow$   $M_2$  ;  $M_2$  +  $M$   $\longrightarrow$   $M_3$  Chain initiating species OR in general term;  $M_n$  +  $M$   $\longrightarrow$   $M_{n+1}$ 

- **(c) Chain Termination:** At some point the propagating polymer chain stops growing and terminates by the following
  - Recombination: It consist of combination of two macro-radicals (chain initiating species)

At temperature, T = 60 °C, polystyrene and acrylonitrile chains terminate mainly by recombination

$$\begin{array}{c}
CH = CH_2 \\
n & \\
\hline
 & \\
CG_6H_5CO)_2O_2 \\
\hline
 & \\
Styrene
\end{array}$$

$$\begin{array}{c}
-CH - CH_2 - \\
\hline
 & \\
\hline
 & \\
Polystrene
\end{array}$$

**Disproportionation:** It involves the transfer of a hydrogen atom of one of the macro-radical to another to form two macromolecules, one of them with a double bond at its end.

At temperature,  $T \ge 60$  °C, PMMA and vinyl acetate chains terminate mainly by disproportionation.

methyl methacrylate

poly(methyl methacrylate)

**Reaction with polymer inhibitors:** Growing polymer chain can also be terminated by its reaction with polymer inhibitors like hydroquinone and trinitrobenzene.

Figure: Chain termination using polymerization inhibitor (hydroquinone). R radical is the growing polymer chain

#### iv) Reaction with solvent molecules: (say carbon tetrachloride)

# Ionic polymerization

a) Cationic mechanism of polymerization: Monomer with electron releasing substituents such as -OCH<sub>3</sub>, -OC<sub>2</sub>H<sub>5</sub> and -C<sub>6</sub>H<sub>5</sub> etc. undergo cationic polymerisation in the presence of Lewis acids and Friedel Craft catalysts (such as AlCl<sub>3</sub>, BF<sub>3</sub>, SnCl<sub>4</sub> etc.). Electron releasing substituents such as alkyl, alkoxy, and phenyl increase the electron density at the carbon-carbon double bond and facilitates its bonding to the cationic species. Moreover, these substituents stabilized the carbocation intermediates in propagation steps by resonance.

$$\begin{array}{c|c} -H_2 & & & & & \\ -C & -C & & & & & \\ \hline \\ \vdots & & & & \\ \end{array}$$

The mechanism of cationic polymerization can be explained by the polymerization of (a) Styrene using SnCl<sub>4</sub> as catalyst and (b) Isobutylene using BF<sub>3</sub> as catalyst and water as a co-catalyst (or protogen or initiator) since it supplies the proton which ultimately adds to the monomer to initiate polymerization. (Note that BF<sub>3</sub> alone cannot start polymerization).

(a) Polymerization mechanism of styrene

$$\begin{pmatrix} \mathsf{H_2C=CH} \\ \mathsf{\varphi} \end{pmatrix}$$

Where  $\phi$  stands for C<sub>6</sub>H<sub>5</sub> (Phenyl, benzene ring)

#### **Initiation:**

$$SnCl_4 + H_2O \longrightarrow \left[ SnCi_4 \cdot OH \right]^- + H^{\oplus}$$

#### **Propagation:**

#### **Termination:**

#### b) Anionic mechanism of polymerization

**Anionic Polymerization**, Monomers with electron-attracting substituents (such as -CN, -COOCH<sub>3</sub>, and C<sub>6</sub>H<sub>5</sub>, etc.) undergo anionic polymerization in the presence of sodium or potassium amide, alkali metals (such as Na, K) and Grignard reagent as catalysts. Thus, strong bases are typical catalysts.

Mechanism: In anionic polymerization, the catalyst interacts with the monomer to generate a carbanion as the active center for chain growth. As the intermediate carbanion is stabilized by the electron-withdrawing substituents hence anionic polymerization is favorable with the monomers having such substituents.

For example,

$$-CH_{2} - CH_{2} -$$

The mechanism can be explained by considering the steps for the formation of polymethyl methacrylate (PMMA) starting from methyl methacrylate.

#### **Initiation:**

$$H_{2}C = C \stackrel{CH_{3}}{\longleftarrow} + \stackrel{\downarrow}{K} \stackrel{\bar{h}_{2}}{\longrightarrow} \begin{bmatrix} CH_{3} \\ H_{2}N - CH_{2} - C \ominus \\ COOCH_{3} \end{bmatrix} \stackrel{\oplus}{K}$$

#### **Propagation:**

$$\begin{bmatrix} CH_3 \\ H_2N-CH_2-C\Theta \\ COOCH_3 \end{bmatrix} \xrightarrow{\mathbb{C}} + n H_2C=C \xrightarrow{CH_3} COOCH_3 \longrightarrow$$

#### **Termination:**

# Methods of polymerization:

 Addition polymerization: Polymer synthesis by addition polymerization has the same empirical formula as that of monomer. No molecule is evolved during polymerization and the polymer is an exact multiple of the original monomeric units.

$$\begin{array}{ccc}
 & n \left( \begin{array}{c} H_2C = CH \\ \downarrow \\ & SG \end{array} \right) & \xrightarrow{POLYMERIZATION} & \xrightarrow{} & \left( \begin{array}{c} CH_2 & CH \\ \downarrow \\ & SG \end{array} \right) \\
SG & SG
\end{array}$$
(SG=Substituent group)

2) **Condensation polymerization:** It takes place by the condensation of two different bi or poly functional monomers having functional groups which have affinity for each other, eg. –COOH and –OH or –COOH or –NH<sub>2</sub> carrying monomers undergo condensation polymerization. It is always accompanied with the elimination of small molecules like H<sub>2</sub>O, HCl etc.

# Molecular weight of polymer

All the molecules of the polymer sample don't have identical molecular weight, hence polymers are polydispersed. This is a consequence of the fact that in a polymerization reaction, the length of the chain formed is determined entirely by random events. In condensation reaction it depends on the availability of a suitable reactive functional growth.

#### Number average molecular weight $(\overline{M}_n)$ :

It is define as the total weight (w) of all molecules in a polymer sample divided by the total number of moles present:

$$\overline{M}_n = \frac{w}{\sum N_i} = \frac{\sum N_i M_i}{\sum N_i}$$

Where  $N_i$  is the number of molecules of molecular weight  $M_i$ .

#### Weight average molecular weight $(\overline{M}_w)$ :

When the molecular weight is averaged according to the weight of molecules of each type,  $M_w$  is obtained. It is determined by the light scattering measurements and sedimentation-equilibrium methods. Both the methods depend on the weight of the molecule present.

The weight average molecular weight  $\overline{M}_w$  is define by

$$\overline{M}_w = \frac{\sum N_i \ M_i^2}{\sum N_i \ M_i}$$

Where  $N_i$  is the no of molecules of molecular weight  $M_i$ .

# **Crystallinity in polymers:**

Even a polymer with regularity of molecular structure doesn't exist entirely in crystalline form. This is because of their large size. As solidification begins the

viscosity of the polymer rises and the molecules find more and more difficult in arranging there long chains in the regular pattern needed for crystal formation. In fact, polymers have regions of crystallinity called *crystallites* embedded in amorphous material. Crystallites provide hardness and amorphous region provides flexibility to the polymeric material. The density of the crystalline polymer is greater than that of a non-crystalline polymer because of more efficient packing of the former.

From density measurements, it is possible to determine the degree of (or percentage) crystallinity by using the following formula:

Percentage crystallinity = 
$$\frac{\rho c/\rho c - \rho a)}{\rho s/(\rho s - \rho a)} X 100$$

Where  $\rho c$  = density of perfectly cryslline polymer

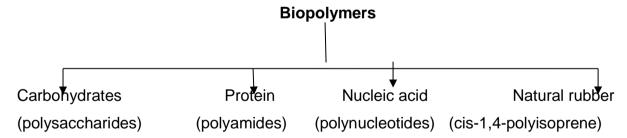
 $\rho a$ = density of amorphous polymer

 $\rho s$  = density of a specimen whose % crystallinity is to be determined

**Biopolymers:** The polymers present in living matter, animals and plants are termed as biopolymers.

Eg: polysaccharides (carbohydrates), protein, nuclei acid and natural rubber.

Broadly speaking there are four types of biopolymers viz:



# **Degradation of polymers:**

a) Oxidative degradation: It is caused by contact with oxidising agents, prolonged application of excessive heat etc. It results in embrittlement and stress cracking, deterioration in electrical insulation properties and loss of elasticity. It affects most thermoplastics to varying degrees, in particular PE, PP, PVC, nylons and unsaturated polymers like rubbers etc.

**b)** Thermal degradation: It causes adverse changes in mechanical and electrical properties of PVC, when PVC is heated to above 150°C in the presence of oxygen. The dehydrochlorination process results in the formation of conjugated polyene.

#### Commercially important thermoplastics and thermosets:

- 1) **Polyethylene:-** It is also known as polythene. It is prepared by the addition polymerization of ethylene (CH<sub>2</sub>=CH<sub>2</sub>). There are different types of polyethylene:
  - i) Low density polyethylene (LDPE):

Preparation: It is prepared by polymerizing ethylene at high pressure 1000-5000 atm and at 250 °C in the presence of free radical initiator (O<sub>2</sub>).

#### **Properties:**

- a) During the propagation steps large number of chain transfer reactions takes place resulting in the formation of branched structure. These branches are mainly short chain. These branches don't allow the molecules to pack efficiently and hence its density is low.
- b) Due to low density, crystallinity of LDPE is low (around 55%).
- c) As it is non-polar polymer, there are no strong intermolecular forces.
- d) It is chemically inert and has good chemical resistance.
- e) It has excellent electrical insulator properties.
- f) It is tough and flexible even at low temperature.

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#### ii) High density polyethylene (HDPE)

**Preparation:**- HDPE can be made by following two methods:

a) Using Zeigler-Natta catalyst, ethylene is polymerized under 6-7 atmospheric pressure at 60-70 °C in the presence of { TiCl<sub>4</sub>+Al(C<sub>2</sub>H<sub>5</sub>)} or catalyst.

$$\begin{array}{c} \text{Cl} & \text{Cl} \\ \text{CH}_3\text{CH}_2 - \text{Al} \xrightarrow{\text{H}_3\text{C}} & \text{H} \\ \text{Cl} & \text{CH}_3 \\ \text{Cl} & \text{Cl} \\ \text{Cl} & \text{Cl} \\ \end{array}$$

b) Using supported metal oxide catalyst, like CrO<sub>3</sub> supported on silicaalumina, ethylene is polymerized at 35 atm pressure and a temperature of 62-200°C.

#### Properties:

- a) HDPE molecules are linear and hence it has high densty (0.95-0.97g/cm³) and more percentage crystallinity (80-90%).
- b) Softening temperature of HDPE is also higher than LDPE.
- c) HDPE has excellent chemical resistance.
- d) It has excellent electrical insulation property.

#### 2) Polyvinylchloride (PVC):

PVC is made by addition polymerization, It is of two types.

#### a) Rigid PVC:

Preparation: It is made by vinyl chloride (in the form of emulsion of it in water) in the presence of small amount of benzoyl peroxide or hydrogen peroxide as catalyst under pressure in an autoclave.

#### b) Plasticized PVC:

Preparation: It is obtain by adding plasticisers such as DOP (dioctyl phthalate), dibutyl phthalate, tricresyl phosphate etc to rigid PVC.

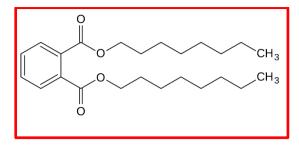


Figure 1: Dioctylphthalate

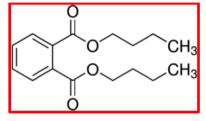


Figure 2: Dibutyl phthalate

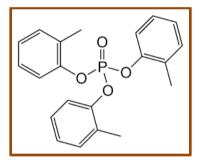


Figure 3: Tricresyl phosphate

#### 3) Polystyrene:

Preparation: Polystyrene is prepared by free radical polymerization of styrene in the presence of benzoyl peroxide as catalyst.

Figure: Benzoyl peroxide

#### Properties:

a) Because of the presence of bulky phenyl group, packing of PS chains is not efficient and hence it is an amorphous polymer.

- b) Due to chain stiffening effect of the benzene/phenyl ring, PS is hard but brittle.
- c) Being a non-polar amorphous polymer, its softening temperature is low (82-100°C).
- d) As it is non-polar, it has low tendency for moisture absorption.

#### 4) Polytetrafluoroethylene (PTFE) or Teflon:

**Preparation:** Teflon is prepared by the polymerisation of tetrafluoroethylene under pressure in the presence of benzoyl peroxide as catalyst.

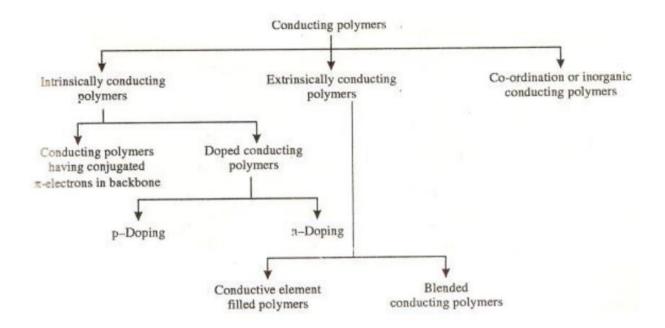
#### Properties:

Teflon has a two step zig zag structure with the fluorine atom packing tightly in a spiral around the carbon – carbon skeleton. Due to the presence of highly electronegative fluorine atom, there are very strong attractive forces between different chains. This strong attractive forces are responsible for its:

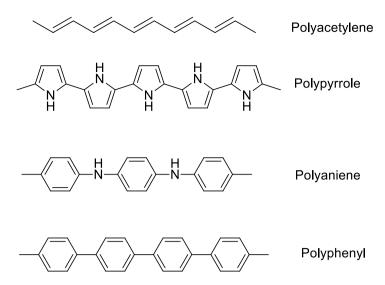
- a) High Density
- b) Chemical Inertness over a wide temperature range.
- c) Known adhesive characters.
- d) Excellent toughness and heat resistance

# **CONDUCTING POLYMERS**

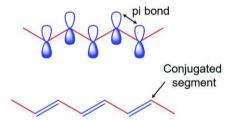
A polymer which can conduct electricity is termed as a conducting polymer. Conducting Polymers can be classified into following types:



- 1) Intrinsically conducting polymers: These polymers have extensive conjugation in the backbone which is responsible for conductance. These are of two types:
  - a) Conducting polymers having conjugate  $\pi$ -electrons in the backbone: Such polymers contain conjugate  $\pi$ -electrons in the backbone which increase the conductivity to a large extent. This is because, overlapping of conjugate  $\pi$ -electrons over the entire backbone results in the formation of valance bands as such as conduction bands which extends over the cationic polymer molecule. The valance band and conduction bands are separated by a significant band gap. Thus electrical conduction could occur only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower level of the conduction band. E.g.



#### Poly(acetylene)



- b) Doped Conducting Polymer: In comparison to conventional polymers the conducting polymers of type (a) can be easily oxidised or reduced as they have low ionization potentials and high electron affinities. Their conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. By analogy with semi-conductor technology, it is reformed to as doping and is of following two types:
- **1).** *p***-doping:** It is done by oxidation process, conducting polymers of type (a) is treated with Lewis acid or with iodine vapour or iodine in CCl<sub>4</sub>.

$$(CH)_x + A \longrightarrow (CH)_x^+ A^-$$
Polyacetylene Lewis acid p-doped polyacetylene

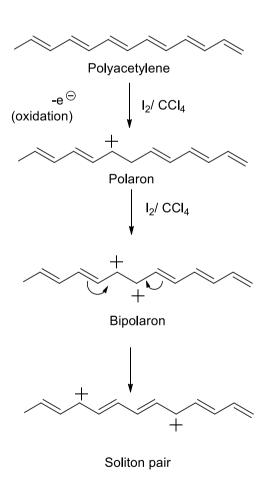


Figure: Mechanism of p-doping of polyacetylene

**2).** *n***-doping:** It is done by reduction process. In this process, the conducting polymer is treated with a Lewis base.

$$(CH)_x + B \longrightarrow (CH)_x B^+$$
  
Polyacetylene Lewis base n-Doped polyacetylene

Figure: Mechanism of p-doping of polyacetylene

#### Advantages of intrinsically conducting polymers:

- (i) Their conductivity
- (ii) Their ability to store a charge.
- (iii) Their ability to undergo ion exchange.
- (iv) They can absorb visible light to give coloured products.
- (v) They are transparent to X-rays.

#### Limitations of intrinsically conducting polymers:

- (i) Their conductivities are poorer than metals.
- (ii) Their improcessability.

- (iii) Their poor mechanical strength.
- (iv) They are less stable at high temperatures.
- (v) On storage they lead to loss in their conductivity.
- **2. Extrinsically conducting polymers:** Those conducting polymers which owe their conductivity due to the presence of externally added ingredients in them are called extrinsically conducting polymers. They are of two types:
- (i) Conductive element filled polymers: In this type, polymer acts as a binder to hold the conducting elements together in solid entity.

The minimum concentration of the conductive filler, which is added to let the polymer start conducting is called the percolation threshold.

Important characteristics of these polymers are: (a) They possess good bulk conductivity.

- (b) They are cheaper.
- (c) They are light in weight.
- (d) They are mechanically durable and strong.
- (e) They are easily processable in different forms, shapes and sizes.
- (ii) Blended conducting polymers: These types of polymers are obtained by blending a conventional polymer with a conducting polymer either physically or chemically. Such polymers can be easily processed and possess better physical, chemical and mechanical properties.

#### 3. Coordination or inorganic conducting polymers:

These polymers contain charge transfer complexes and are obtained by combining metal atoms with polydentate ligands.

# **PVC and CPVC: Synthesis, Properties and Applications**

### 1. Polyvinyl Chloride (PVC)

**Synthesis:** PVC is synthesized from vinyl chloride monomer (CH2=CHCI) using free radical polymerization (suspension, emulsion, or bulk). Initiators such as organic peroxides or azo compounds are used.

**Properties:** Thermoplastic, rigid or flexible with plasticizers, density ~1.3–1.45 g/cm³, high tensile strength, chemical resistance, poor thermal stability, good electrical insulator.

**Applications:** Pipes and fittings, electrical cable insulation, packaging films, flooring, synthetic leather, raincoats, medical devices.

#### 2. Chlorinated Polyvinyl Chloride (CPVC)

**Synthesis:** Produced by chlorination of PVC resin using UV light or thermal methods. Chlorine content increases from ~56% (PVC) to 63–69% (CPVC).

**Properties:** Higher glass transition temperature (~110–125 °C), improved fire and corrosion resistance, stronger at elevated temperatures, density ~1.55–1.65 g/cm³.

**Applications:** Hot and cold water pipes, industrial fluid handling, fire sprinkler systems, chemical equipment, automotive and aerospace parts.

# 3. Comparative Summary

Property	PVC	CPVC
Chlorine Content (%)	~56	63–69
Heat Resistance	Up to ∼60 °C	Up to ~90–110 °C
Mechanical Strength	Good	Higher (especially at high T)
Chemical Resistance	Moderate	Excellent
Main Use	General piping, packaging, wire	Hot water pipes, industrial uses

# **Composite Materials**

## 1. Definition

A **composite material** is a multiphase material obtained by combining two or more distinct materials (matrix + reinforcement) such that the resulting material exhibits properties superior to those of the individual constituents.

- Matrix phase: Continuous medium (polymer, metal, ceramic).
- **Reinforcement phase:** Dispersed medium (fibers, particles, flakes, whiskers).
- **Key idea:** "The whole is better than the sum of its parts."

#### **Examples:**

- **Polymer Matrix Composites (PMC):** Fiberglass, Carbon-fiber reinforced plastic (CFRP).
- Metal Matrix Composites (MMC): Aluminum–SiC, Titanium–Boron fibers.
- Ceramic Matrix Composites (CMC): SiC/SiC, Al<sub>2</sub>O<sub>3</sub>/SiC.
- Natural composites: Wood (cellulose + lignin), Bone (collagen + hydroxyapatite).

## 2. Classification

#### (a) Based on Matrix Material

- Polymer Matrix Composites (PMC)
- Metal Matrix Composites (MMC)
- Ceramic Matrix Composites (CMC)

#### (b) Based on Reinforcement

- **Fiber-reinforced composites:** Continuous, short, whisker.
- **Particle-reinforced composites:** Large particle, dispersion strengthened.
- Structural composites: Laminates, sandwich panels.

# 3. Requirements of a Composite Material

- Should consist of two or more distinct phases.
- Reinforcement must be **stiffer**, **stronger**, **or tougher** than the matrix.
- Strong interfacial bonding between reinforcement and matrix.
- Matrix should **transfer stress** and **protect reinforcement** from environment.
- The composite must show **synergistic properties** (better performance than either material alone).

# 4. Properties

- High strength-to-weight ratio.
- High stiffness-to-weight ratio.
- Excellent corrosion, fatigue, and wear resistance.
- **Tailorable** thermal, mechanical, and electrical properties.
- Often anisotropic (properties vary with direction).
- **Low density** → lightweight compared to metals.

# 5. Applications

- Aerospace: Aircraft fuselage, spacecraft panels.
- Automobile: Brake pads, body panels, drive shafts.
- Civil engineering: Reinforced concrete, bridge decks.
- Marine: Boat hulls, propellers.
- **Electronics:** Printed circuit boards, insulators.
- **Medical:** Prosthetic limbs, dental composites, bone implants.
- **Sports:** Tennis rackets, golf clubs, helmets, bicycles.