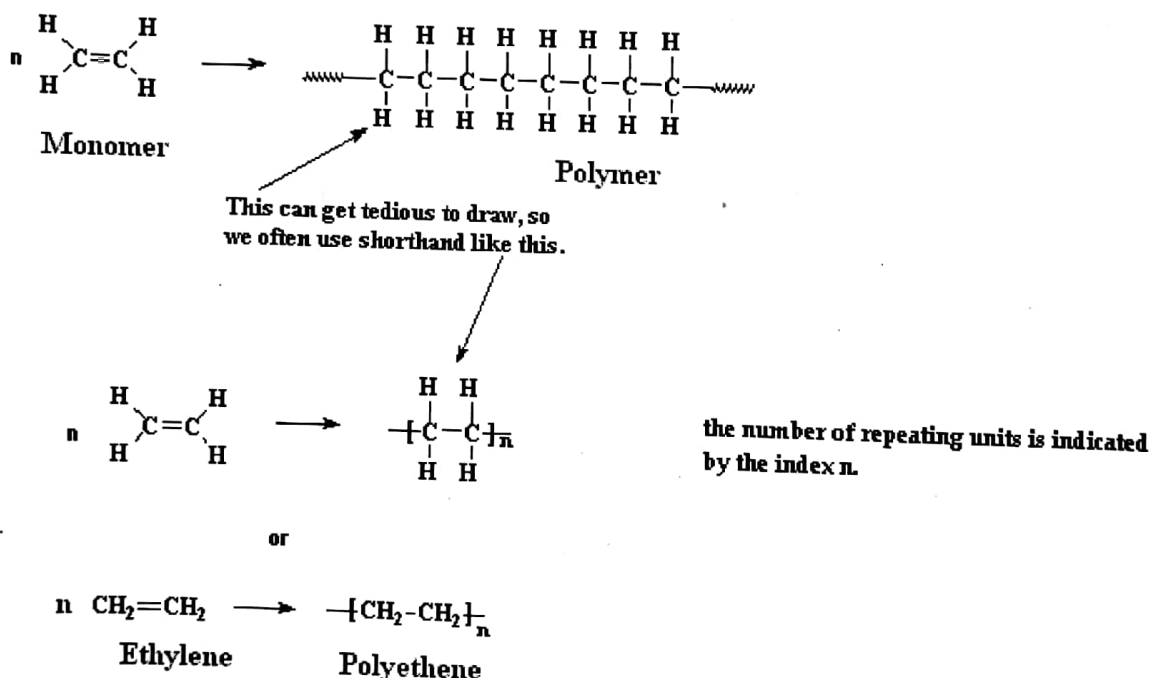


Unit - 2  
Polymers

### 1.1 Introduction

The word Polymer is derived from the Greek word *Poly* meaning "many" and *meros* meaning "parts", i.e., "a polymer is a long chain molecule that is composed of large number of repeating units (**monomer**) of identical structure joined together through covalent bonds in a regular manner" thus they are also known as macromolecules. Certain polymers such as proteins cellulose and silk are found in nature, while many others, including polystyrene, polyethylene and nylon are produced only by synthetic routes.

The process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains is known as **polymerization**. Consider the case of polyethylene polymer; it is synthesized from polymerizing ethylene as shown below:



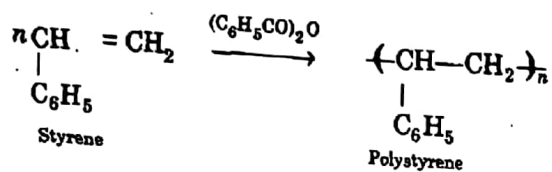
### 1.2 Some important terms:

**1.2.1 Monomer:** A molecule of low molecular weight capable of reacting with identical or different molecules of low molecular weight to form a polymer is called as monomer.

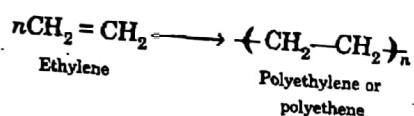
- The essential feature of monomer molecules is the ability to form chemical bonds with at least two other monomer molecules (polyfunctionality).
- Monomers link together by two basic methods: addition polymerization and condensation polymerization

- Examples of monomers and their polymers are

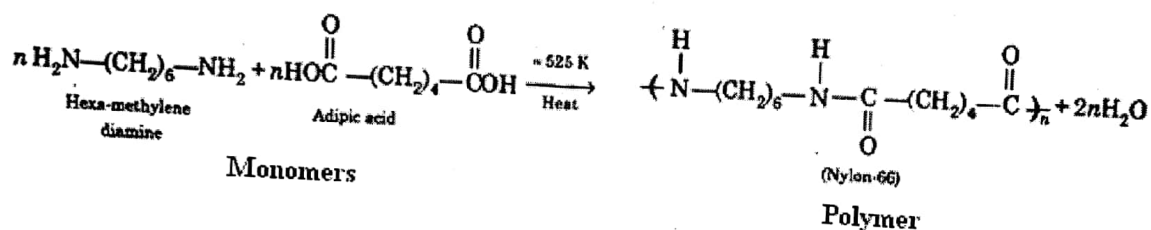
1) Styrene  $\longrightarrow$  polystyrene,



2) Ethylene  $\longrightarrow$  polyethylene



3) Hexamethylene diamine and adipic acid  $\longrightarrow$  Nylon 6,6



4) Amino acids  $\longrightarrow$  proteins

### Classification of Polymers:

Important classifications of polymers are shown in Table (1). The bases of classification and major classes of polymers along with examples are given below:

**Table-1 Classification of Polymers**

Basis Of Classification	Polymer Types
Chemical composition	Organic polymer, Inorganic Polymer
Origin	Natural, Semisynthetic, Synthetic
Chemical structure	Homopolymer, Copolymer)
Arrangement of monomers	Random copolymer, Alternate copolymer Block copolymer, Graft copolymer,
Thermal response	Thermoplastic, Thermosetting
Mode of formation	Addition, Condensation
Line structure	Linear, Branched, Cross-linked
Application and physical properties	Rubbers, Plastic, Fibres
Tacticity	Isotactic, Syndiotactic, Atactic

crystallinity

Non- crystalline (amorphous), Semicrystalline,  
Crystalline

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## 27 (a) Thermoplastic Polymers:

- They become soft on heating and can remould again and again. The polymer melt can be formed or shaped when in this softened state.
- They are soluble in organic solvents, soften on heating and stiffen on cooling.
- Thermoplastic polymers are usually linear i.e., not highly cross-linked. Only weak forces like Hydrogen bonding, Vander Walls forces or dipole-dipole forces occur between polymeric chains.
- They have lower melting, boiling points than thermosetting polymers.
- When thermoplastics are heated, weak bonds between molecules can be easily broken. This is why thermoplastic materials can be remelted.
- Examples include polyethylene and polypropylene. e.g., polyolefins, polystyrene, nylons, linear polyesters and polyethers, poly (vinyl chloride), etc. They remain soluble and fusible after many cycles of heating and cooling.

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## 27 (b) Thermosetting Polymers:

- These polymers have extensive **cross-linking** between different polymer chains forming the three dimensional network of bonds.
- On heating, they undergo some chemical changes and on cooling they convert themselves into an infusible mass. After cooling if the set article is again heated it will not soften again therefore **thermosetting plastics cannot be molded several times**.
- Thermosetting polymers are more rigid and generally have higher strength than thermoplastic polymers.
- For examples: phenolic resins (Bakelite), urea/melamine resins, epoxy resins, diene rubbers, unsaturated polyesters, etc.

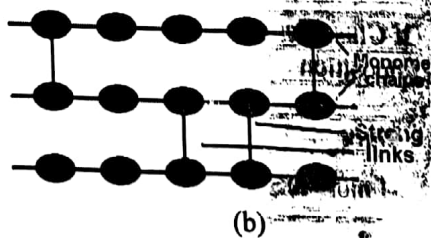
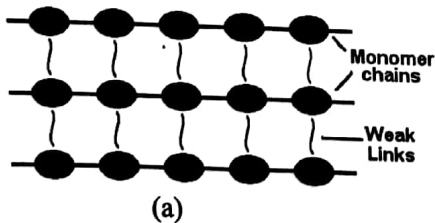
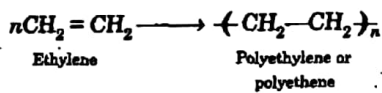
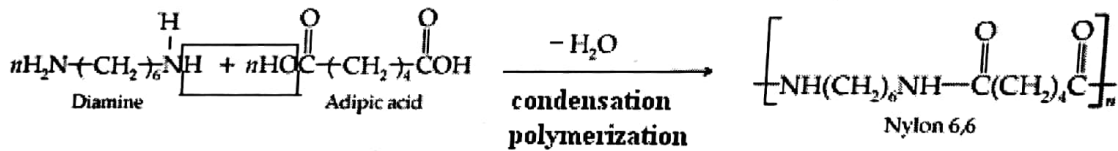


Figure: Structures showing (a) thermoplastic and (b) thermosetting plastic (having lots of crosslinks)

Table- Differences between addition and condensation polymers

Addition polymers	Condensation polymers
Formed by addition reaction.	Formed by condensation process with elimination of small molecules like $H_2O$ .
Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
Generally involve one monomer unit.	Generally involve more than one monomer unit.
Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
They are generally chain growth polymers.	They are generally step growth polymers.

**Example: Addition Polymerization****Example: Condensation Polymerization****Arrangement of monomers**

- a) **Alternate copolymer:** In which monomer units are arranged in alternate manner i.e one after one
- Nylon 6,6 is also the example of an alternating copolymer.
- b) **Random copolymer:** In random copolymers, monomer units are arranged randomly i.e not any specific arrangement.
- c) **Block copolymer:** In block copolymer a sequence or block of one monomer is followed by a sequence of other in the polymer chain.
- d) **Graft copolymer:** Polymers in which side chains of a given monomer are attached to the main chain of the second monomer are known as graft copolymer.

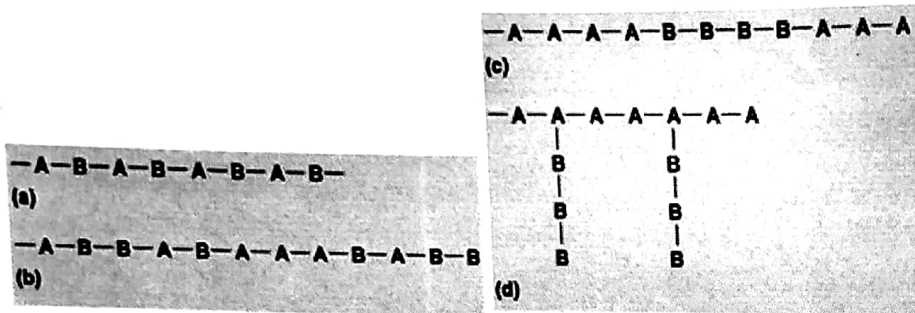


Figure: (a) Alternate copolymer (b) Random copolymer (c) Block copolymer. (d) Graft copolymer.

### Tacticity:

Depending upon the orientation of monomer units in a polymer molecule with respect to the main chain the polymers are classified as

**Isotactic:** If the side groups of the monomers lie on the same side of the chain, it is called an isotactic polymer.

(a) **Syndiotactic:** If the side groups are arranged in an alternate fashion, it is called syndiotactic polymer.

(b) **Atactic:** If the side groups are arranged in regular fashion or randomly around the main chain, it is called atactic polymer.

The different stereoisomers may have very different physical properties. For example, atactic polypropylene is a useless, gummy solid, while the isotactic version is a highly crystalline, tough plastic that can even be made into fibers.

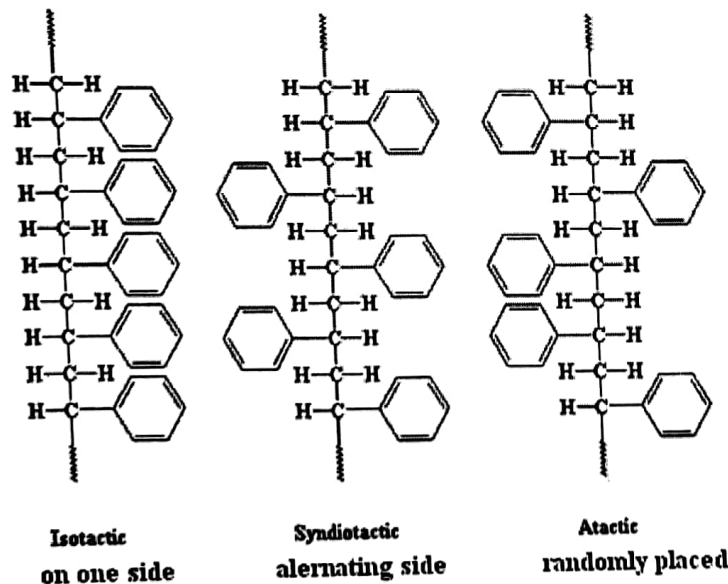


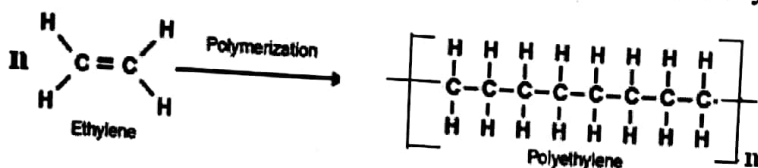
Figure: Structures showing stereochemically similar and different sequence of repeat units for Polystyrene.

## Organic Polymers

### Some Important Thermoplastic Polymers:

#### 1) Polyethylene:

Polyethylene is simplest addition polymer. Monomer unit is ethylene



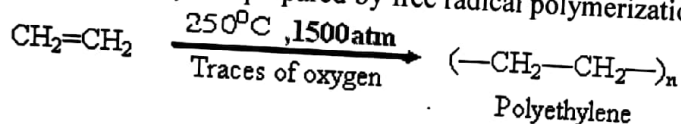
Polyethylene is an inexpensive and versatile polymer with numerous applications. It can be produced in many forms such as:

Low density polyethylene (LDPE)

High density polyethylene (HDPE)

#### Low density polyethylene (LDPE):

- It is prepared by heating ethylene ( $\text{CH}_2=\text{CH}_2$ ) to  $250^\circ\text{C}$  under very high pressure (1500 atm) in the presence of a trace of oxygen.
- This polymerization occurs by a free radical mechanism initiated by oxygen.
- The polyethylene thus produced has a molecular mass of about 20,000 and has a branched structure.
- These branched polyethylene molecules do not pack well and hence this type of polyethylene has low density ( $0.92 \text{ g/cm}^3$ ) and a low melting point ( $111^\circ\text{C}$ ). That is why polyethylene prepared by free radical polymerization is called low density polyethylene.



(a)



(b)

Figure: (a) A molecule of branched polyethylene, or LDPE; (b) A molecule of linear polyethylene, or HDPE

#### Properties of LDPE

- Having branched structure therefore low density ( $0.92 \text{ g/cm}^3$ ) and a low melting point ( $111^\circ\text{C}$ ).

- It is translucent to opaque.
- Excellent flexibility
- Excellent resistance (no attack) to dilute and concentrated Acids, Alcohols, Bases and Esters
- Poor resistance and not recommended for use with Halogenated Hydrocarbons

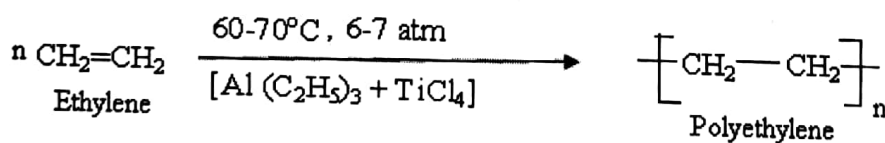
#### Uses:

- LDPE is ideally suited for a wide range of molded laboratory apparatus including wash bottles, pipette washing equipment, general purpose tubing, bags and small tanks.
- It is good for parts that require flexibility.
- Because of chemical resistivity, it is used in making trays & containers.
- In juice and milk cartons, LDPE and layer of aluminium foil is used to make inner layer
- Used in car covers, squeeze bottles, liners for tanks and ponds, moisture barriers in construction

#### ✶ High density polyethylene (HDPE):

- HDPE is linear polymer. The absence of branching results in a more closely packed structure. This better packing means that van der Waals attractions between the chains are greater and so the plastic is a higher density, melting point and somewhat higher chemical resistance than LDPE.
- HDPE is also somewhat harder and more opaque and it can withstand rather higher temperatures (120° C for short periods, 110° C continuously).
- High density polyethylene is suitable for blow molding, e.g. for bottles, cutting boards, dipping baskets, dippers, trays and containers.
- It is prepared by co-ordination polymerization of ethylene in presence of a catalyst such as

Trimethylaluminium and titanium tetrachloride  $[Al(C_2H_5)_3 + TiCl_4]$  called Zeigler-Natta catalyst.



#### Uses:

Good chemical resistance and high rigidity make it a good choice for trays, containers and fuel tanks for vehicles.

- Other uses include pipe fittings, Chemical resistant piping systems, Natural gas distribution pipe systems, Water pipes, for domestic water supply, Telecom ducts.
- One of the largest uses for HDPE is wood plastic composites (WPC)
- freezer bags, Plastic bags, wire and cable insulation, extrusion coating

- Bottles, suitable for use as refillable bottles
- Milk jugs, Watering cans, Folding chairs and tables

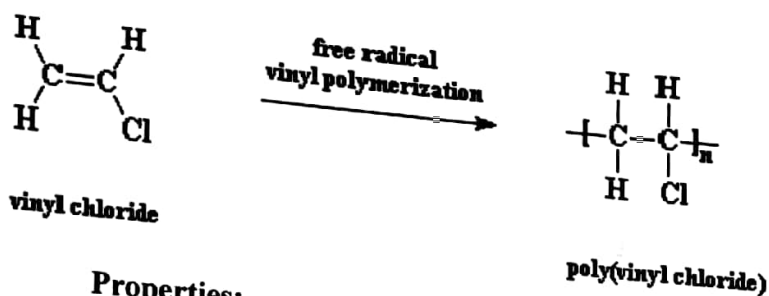
✍ Table: Difference between LDPE and HDPE

	LDPE	HDPE
1	It is polymerized by free radical polymerization	It is prepared by co-ordination polymerization
2	It is polymerized in presence of traces of oxygen under high pressure and temperature.	It is polymerized in presence of Ziegler-Natta catalyst or metal oxide under low pressure and temperature
3	It is not highly crystalline because of presence of side branches in it.	It is highly crystalline (>95% crystalline) due to its linear structure
4	0.91-0.94 g/cm <sup>3</sup> lower density than HDPE	0.95-0.97 g/cm <sup>3</sup> higher density than LDPE
5	LDPE can withstand temperatures of up to 95 <sup>o</sup> C.	HDPE can withstand temperatures of up to 120 <sup>o</sup> .
6	Low stiffness and hardness.	It is more stiff and hard than LDPE
7	It is transparent and flexible and is resistant to many different chemicals.	It is translucent and rigid and is more resistant to chemicals.
9	Because of the flexible nature of LDPE, it is used to make films, plastic bags. it is used to make plastic items that need to be molded, such as plastic bottles, wash bottles and tubing used in labs .	Because of the rigid nature and chemical resistance of HDPE it is used for making food product containers and chemical containers. Other uses for HDPE include trays, cutting boards, pipe fittings and tanks. It is most commonly used for items requiring blow molding techniques, such as toys, automobile parts and bottles.
10	Uses: sandwich bags, cling wrap, car covers, squeeze bottles, liners for tanks and ponds, moisture barriers in construction	freezer bags, water pipes, wire and cable insulation, extrusion coating

## 2) Polyvinyl chloride (PVC):

Polyvinyl chloride is also known as Koroseal. It is the third most widely produced plastic, after polyethylene and polypropylene .It is produced by the free radical polymerization by heating vinyl chloride at about 500<sup>o</sup>C in an auto clave in presence of 40% H<sub>2</sub>O<sub>2</sub>.





### Properties:

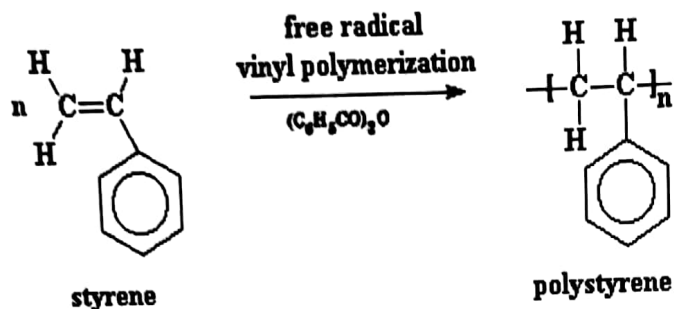
- PVC has water resistance.
- It has flame resistance property, too, because it contains chlorine. On burning chlorine atoms are released, and chlorine atoms inhibit combustion.
- The presence of chlorine unit in the Polyvinylchloride backbone causes configurational and conformational isomers of the polymer. The chlorine atom can be disposed in one side with respect to the backbone (isotactic), either sides of the backbone in a regular pattern (syndiotactic), or can be randomly distributed in both sides (atactic). The configurational and conformational isomerism of PVC has a direct impact on the crystallinity of the polymer.

### Applications:

- PVC is useful because of the resistance for: fire and water. Because of its water resistance it's used to make raincoats and shower curtains, water pipes, garden hose, baby paints, swimming-pool liners.
- Because of chemical resistant, bio-compatibility, and low cost of PVC, it has been widely used for surgery, pharmaceuticals, drug delivery and medical packaging. Some products include blood bags, medical containers, fluid bags, tubing, heart and lung bypass sets, masks, gloves, bottles and jars, drainage systems, ducting, etc.
- Useful for manufacturing household sewerage pipes and other pipe applications where corrosion would limit the use of metal. Around 50% the world's polyvinyl chloride resin manufactured annually is used for producing pipes for various municipal and industrial applications.
- It is also used in shoe soles and vinyl flooring.
- PVC is also used for making ceiling tiles. They can be glued onto an existing flat surface ceiling.

### 3) Polystyrene or Styron:

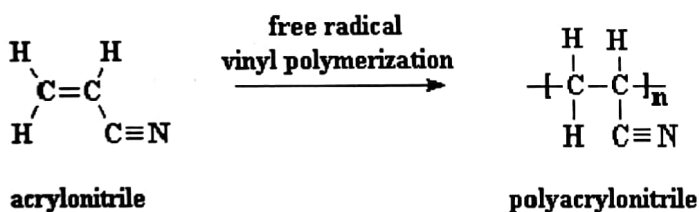
The monomer units are styrene molecules. It is prepared by free radical polymerisation of styrene in the presence of benzoyl peroxide. Polystyrene (PS) is a clear, colorless polymer used extensively for low-cost applications. It is available commercially in both pellet and sheet form. Polystyrene is sold under the name styrofoam or styron.



#### Properties and Uses:

- It is a white thermoplastic material which is transparent and floats on water. It is used for making toys, combs, model construction kits, ceiling tiles, packing for delicate articles and lining material for refrigerators and TV cabinets.
- The most serious deficiencies are low impact strength, poor weatherability and poor chemical resistance.
- Clear plastic drinking cups are made of polystyrene.

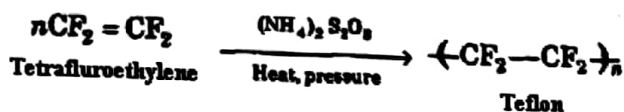
4) **Polyacrylonitrile (PAN):** Polyacrylonitrile is a vinyl\* polymer, and a derivative of the acrylate family of polymers. It is made from the monomer acrylonitrile ( $\text{CH}_2=\text{CH-CN}$ ) by free radical vinyl polymerization in presence of peroxide.



#### Properties and Uses:

- Polyacrylonitrile is a highly crystalline polymer having high melting point ( $319^\circ\text{C}$ ).
- PAN fibers can be chemically modified to make the carbon fibers, which are used in making civil and military aircraft primary and secondary structures, missiles, solid propellant rocket motors, pressure vessels, fishing rods, tennis rackets, badminton rackets & high-tech bicycles.
- It is also used in the manufacture of Orlon and Acrilan fibres for making clothes, carpets and blankets.

5) **Teflon or Poly Tetrafluoro Ethylene (PTFE):** The monomer unit is Tetrafluoro-ethylene molecules. It is prepared by heating tetrafluoroethylene under pressure in the presence of ammonium peroxosulphate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  by free radical vinyl polymerization.



### Properties:

- Polytetrafluoroethylene (PTFE) is a highly crystalline polymer.
- It is a very tough material and is resistant towards heat, action of acids or bases. Even it is unaffected by boiling acids and aqua regia. The reason of its inertness is the presence of fluorine atoms. The bond between the fluorine atom and the carbon atom is extremely strong. It is so stable that nothing will react with it. Even when it gets as hot as a frying pan, not even oxygen will react with it. In addition F atoms present in molecules at the surface of a piece of PTFE has a tendency to repel the molecules which try to come close to F atoms. This is why nothing sticks to PTFE.
- It is bad conductor of electricity. It also has extremely good thermal resistance at temperatures up to 250<sup>0</sup>

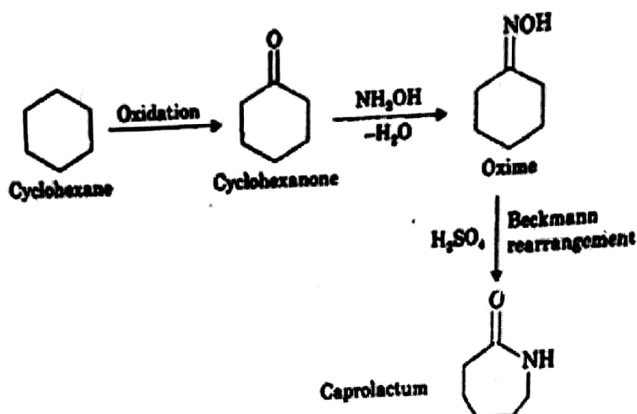
**Uses:** coating utensils to make them non-sticking, making seals and gaskets which can withstand high pressures, insulations for high frequency electrical installations.

**6) Polyamides:** Polyamides contain repeating amide groups (-NH-CO-) in the main polymer chain. They are capable of fiber formation. These polymers are commonly known as nylons. Various commercially important nylons are nylon 6; nylon 6,6; nylon 6,10; nylon 5,10 ; nylon 10,12 etc. The number against the nylon shows the number of carbon atoms in a one monomer unit, for example in nylon 6, only 6 carbon atoms in its monomer back bone. Similarly nylon 6,6 contains 6 and 6 carbon atoms.

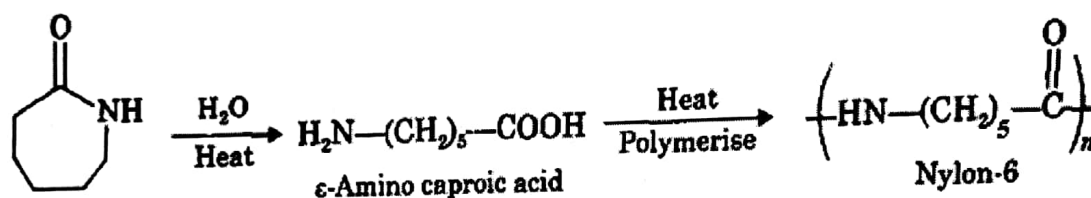
**Note:** Nylon was originally prepared in New York and London simultaneously (ny = New York, lon = London). This is how the polymer got its name.

#### 6.1 Nylon 6 (or Perlon):

Nylon-6 (PA6) is semicrystalline polyamide used most commonly in tire cord. It is manufactured by the ring opening; self condensation polymerization of caprolactum. Caprolactum needed for the purpose is manufactured from cyclohexane as described below:



Caprolactum on heating with traces of water hydrolyses to  $\epsilon$ -amino caproic acid which on continued heating undergoes self-condensation and polymerises to give nylon-6.



#### Properties:

- Nylon 6 fibres are tough, having high tensile strength, as well as elasticity and lustre.
- They are wrinkle-proof and highly resistant to abrasion and chemicals such as acids and alkalis.
- The fibres can absorb up to 2.4% of water, although this lowers tensile strength.

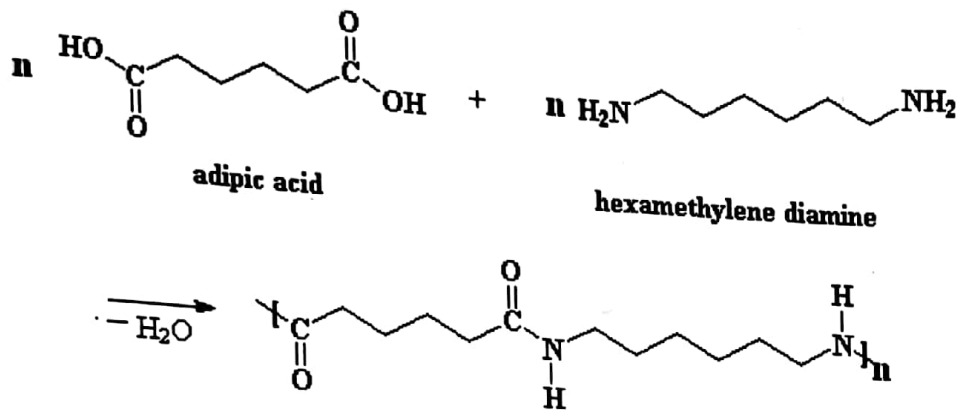
#### Uses:

Nylon-6 is used for the manufacture of tire cords, fabrics, nets and ropes as well as hosiery and knitted garments.

It is used as thread in bristles for toothbrushes, sutures for surgery and strings for acoustic and classical musical instruments, including guitars, violins, violas, and cellos.

#### gm 6.2 Nylon 6,6

It is manufactured by the condensation polymerization of adipic acid and hexamethylene diamine at about  $250^\circ\text{C}$  when water is lost as steam and the nylon is produced in the molten state. It is then cast into sheet or fibres by passing through a spinneret.



This polymer is known as Nylon 6,6 because of the 6 carbon atoms in both the hexamethylene diamine and adipic acid.

#### Properties:

- Nylon 6,6 is highly crystalline due to strong intermolecular H-bonding (figure 2).

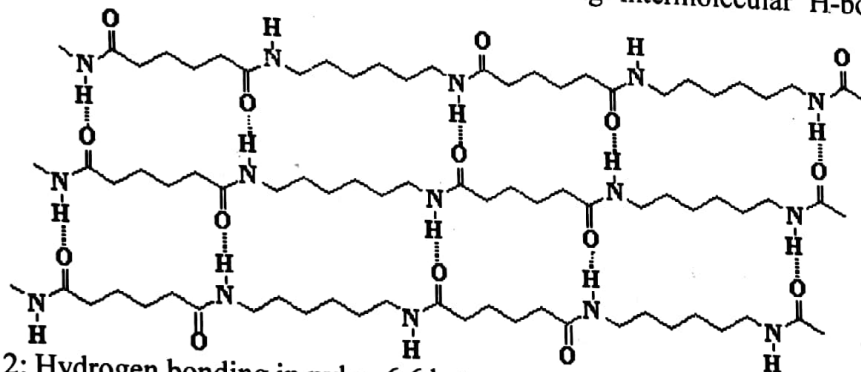


Figure 2: Hydrogen bonding in nylon 6,6 between carbonyl oxygen and amide hydrogen.

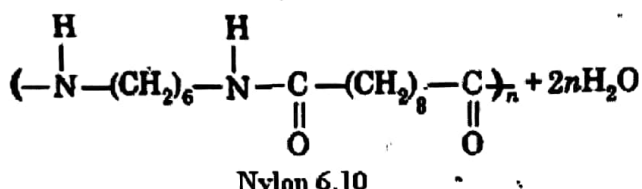
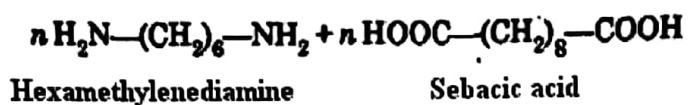
- It has a dense structure (due to H bonding) with small, evenly spaced pores. This means that nylon 6,6 is difficult to dye, but once dyed it has superior colorfastness and is less susceptible to fading from sunlight and ozone and to yellowing from nitrous oxide.

#### Uses:

- Nylon 6,6 is used to make Carpet fiber, Apparel, Airbags, Tires, Ropes, threads, britsles, Conveyor Belts, and Hoses

#### 6.3 Nylon 6,10 gm.

It is obtained by condensation of hexamethylenediamine and sebacic acid.

**Properties:**

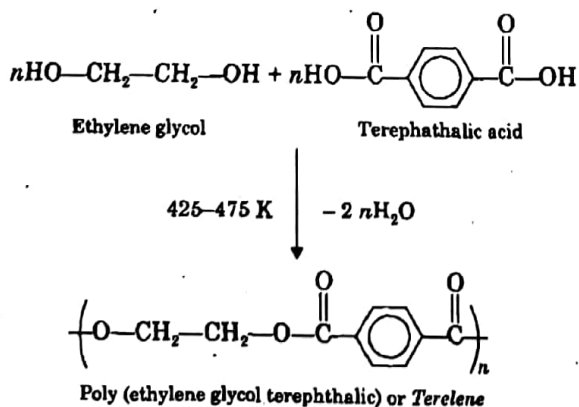
Nylon 6,10 (PA610) is semicrystalline polyamide. Due to its low moisture absorption compared to other nylons, it retains its properties better when wet. It possesses high tensile strength and is abrasion resistant. It also possesses some elasticity.

**Uses:**

- It is commonly used in monofilament form in applications such as bristles and brushes.
- It is also used in the manufacture of carpets, and textile fibres.
- Being tough it is used as substitute for metals in bearings and gears.

7) **Polyesters:** These are the polymers having ester linkage ( $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}$ ). Depending on the chemical structure, polyester can be a thermoplastic or thermoset. Some examples are:

**7.1 Poly (ethylene terephthalate) PET (or Terylene; Dacron):** Poly (ethylene terephthalate) PET may sometimes be known by a brand name like Terylene or Dacron. It is a polymer obtained by the condensation reaction between ethylene glycol and terephthalic acid Poly (ethylene terephthalate).



### Properties and uses.

- PET is semicrystalline polyester commonly used in packaging and fiber applications.
- It is used as a blend with cotton and wool in clothing. It is also used in seat belts and sails.
- used for making magnetic recording tapes.
- Dacron (and teflon) tubes are good substitutes for human blood vessels in heart by-pass operations.

### Elastomers (Rubbers):

- Elastomers are amorphous polymers having high degree of elasticity.
- They have the ability to stretch out many times (at least 150 %) of their original length and return to original position when the force is withdrawn. Thus, a rubber band can be stretched to 4 to 10 times to its original length.
- These polymers consist of randomly coiled molecular chains of irregular shape having a few cross-links (figure). When the force is applied, these coiled chains open out and the polymer is stretched. These chains are held together by weak Vander Walls forces of attraction.

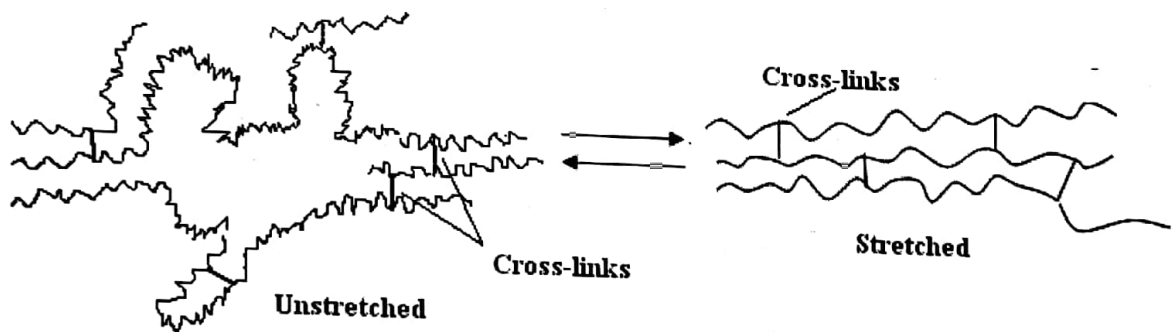


Figure: Unstretched and stretched forms of elastomers.

The most important example of elastomers is natural rubber.

#### 13.1.2 Vulcanization:

Raw rubber which is obtained from the rubber trees has following drawbacks:

- Uncured natural rubber is soft sticky, thermoplastic and deforms easily when warm, and is brittle when cold. So it can be used in the temperature range of 10 to 60°C only.
- It has low tensile strength and low elasticity and very little durability.
- It has large water absorption capacity.

- It is easily attacked by oxidizing agents like nitric acid, conc. sulphuric acid, and chromic acid etc.
- It destroys, due to oxidation in air.
- It possesses tackiness, i.e., when fresh raw rubber surfaces are pressed together, they coalesce to form a single piece.
- When stretched to a great extent, it suffers permanent deformation, because rubber is composed of long polymer chains. These chains can move independently relative to each other, and sliding or slippage of chains over each other results in the permanent deformation.

In this state raw natural rubber cannot be used to make articles with a good level of elasticity. To improve the properties of rubber, Charles Good Year (in 1839) invented the process of Vulcanization.

*"Vulcanization is a chemical process for converting rubber into more durable and useful materials via the addition of sulphur (or other additives like benzoyl chloride, hydrogen sulphide etc). In this process rubber molecules get cross-linked with each other by heating the liquid rubber with sulfur (see Figure). Cross-linking increases the elasticity and the strength of rubber by about ten-fold, but the amount of cross-linking must be controlled to avoid creating a brittle and inelastic substance". These additives modify the polymer by forming crosslinks (bridges) between individual polymer chains*

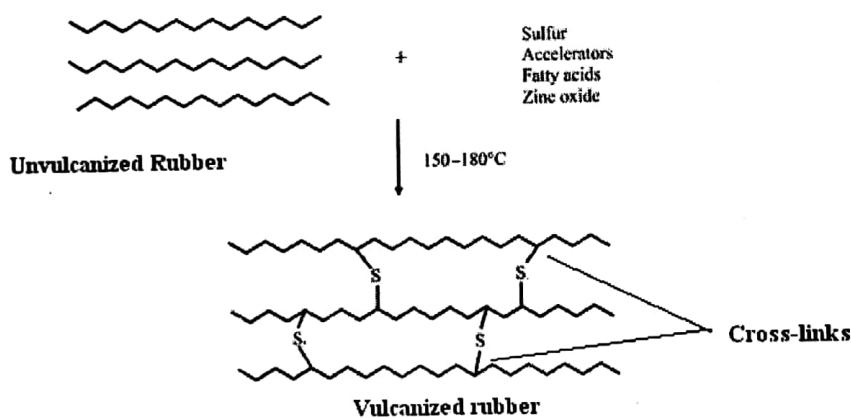
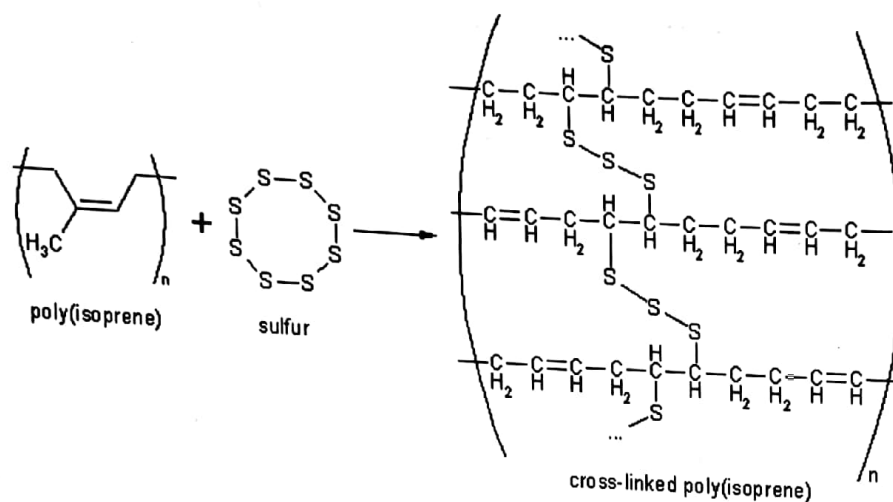


Figure: Vulcanization of rubber by sulphur.

**Process of vulcanization [The process is named after Vulcan, Roman god of fire.]:**

In the process of vulcanization, the added sulphur breaks some C-H bonds in polyisoprene (i.e. natural rubber) and replaced by C-S bonds. The process of vulcanization cross-links the chains of polyisoprene to each other. The cross-linked molecules create a three-dimensional network of rubber.





Vulcanized rubber is about 10 times stronger than natural rubber and is also about 10 times more rigid

#### Advantages of vulcanization:

- Vulcanized material is less sticky and has superior mechanical properties like high tensile strength and excellent elasticity.
- It possesses low water-absorption tendency.
- It has higher resistance to oxidation, abrasion, wear and tear than raw rubber.
- It has high resistance to organic solvents such as petrol, benzene, carbon tetrachloride, fats and oils. However, it swells in these liquids.
- It has useful temperature range of  $-40$  to  $100^{\circ}\text{C}$ .
- It is slight tacky, but can be molded into desirable shapes.

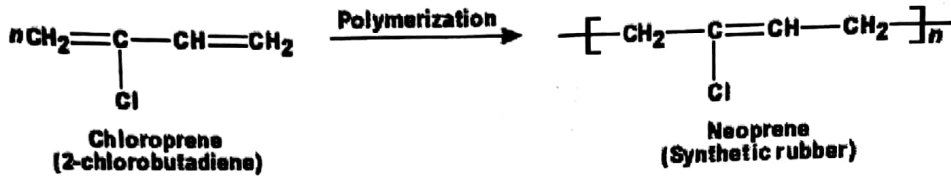
#### 13.1.3 Synthetic rubber:

Synthetic or artificial rubber is made from by-products of petroleum industry. Artificial rubber has many properties, which are much better than natural rubber and therefore they find wide use in industrial and domestic applications. There are number of synthetic rubbers, some of them are discussed below.

gm

##### a) Neoprene

The first commercially successful rubber substitute, manufactured in the US is neoprene (1931). Neoprene is made by polymerization of chloroprene or 2 chlorobutadiene in the presence of potassium persulphate.. The equation below shows the reaction.



### Properties of neoprene:

Neoprene is superior to natural rubber because of the following properties:

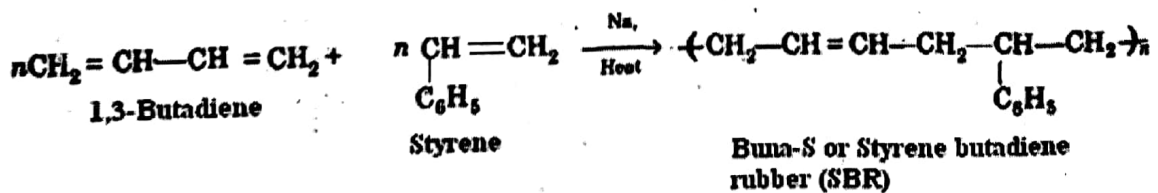
- Neoprene is resistant to oils, organic solvents, petrol and grease.
- Neoprene is non-inflammable. This property is opposite to that of natural rubber made from latex.
- Neoprene is unreactive to many industrial chemicals such as oil, grease, petrol, other solvents. Natural rubber is reactive to all these chemical agents. Natural rubber swells and rots in contact with these materials
- Neoprene is resistant to the action of oxygen and ozone. Natural rubber deteriorates when exposed to oxygen

### Uses of Neoprene:

- Neoprene is used as an insulating material for electrical connections, especially where the environment has chemicals.
- Neoprene is used to make conveyor belts, car belts, gaskets, printing rolls and flexible tubing for carrying oil and petrol.etc.
- Neoprene is used in petrol industry in the form flexible pipes or hoses. This is because neoprene is not attacked by petrol.
- It is used to make hoses, shoe heels, stoppers etc.

*GM* b) **Buna-S rubber (or Styrene butadiene rubber, SBR or GR-S):** The largest portion of the synthetic rubber industry centres on styrene-butadiene rubber (SBR), which is a copolymer of styrene and 1,3-butadiene. It is obtained by the polymerization of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium.

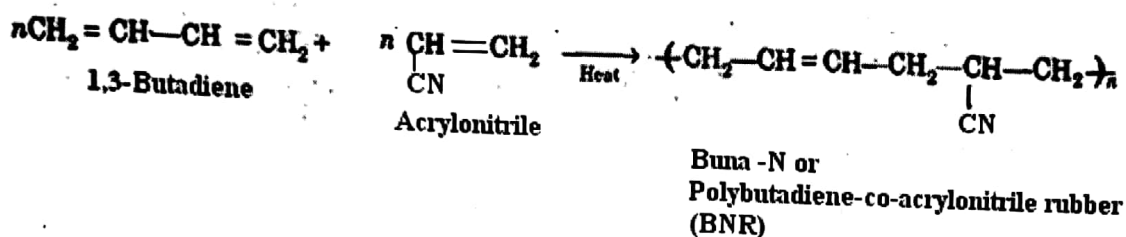
Note: In Buna-S, *Bu* stands for butadiene; *na* for sodium which is polymerizing agent and *S* stands for *styrene*.



**Characteristics and uses:**

Roughly 40% of the rubber used in the world today is SBR; another 35% is natural rubber that has been treated with sulfur. SBR has slightly less tensile strength than natural rubber. It is used in the manufacture of: automobile tyres, rubber soles, belts, hoses, etc.

*gm*  
c) Nitrile rubber (GR-N or Buna-N): It is copolymer of butadiene and acrylonitrile.

**Properties:**

- It has excellent resistance to heat, sunlight, oils, acids and salts, but it is less resistance to alkalis than natural rubber, because of the presence of cyano groups (-CN).
- As the content of acrylonitrile is increased, the resistance to acids, salts, oils, and solvents increases.
- Vulcanized nitrile rubber is more resistant to heat and ageing than natural rubber and may be exposed to high temperatures.

**Uses:**

It is used for making conveyor belts, high altitude aircraft components, tank-linings, hoses, gaskets, printing rollers, adhesives, oil-resistant foams and automobiles parts etc.

**Conducting Polymers**

A Polymer which can conduct electricity is termed as conducting polymer. Because of the conductivity, they are also known as synthetic metal.

*[The first conducting plastics were discovered by accident at the Plastics Research Laboratory of BASF in Germany. Scientists at this laboratory made polyphenylene and polythiophenes, which showed electrical conductivity of the order of 0.1scm-1. Since then, other conducting polymers have been discovered.]*

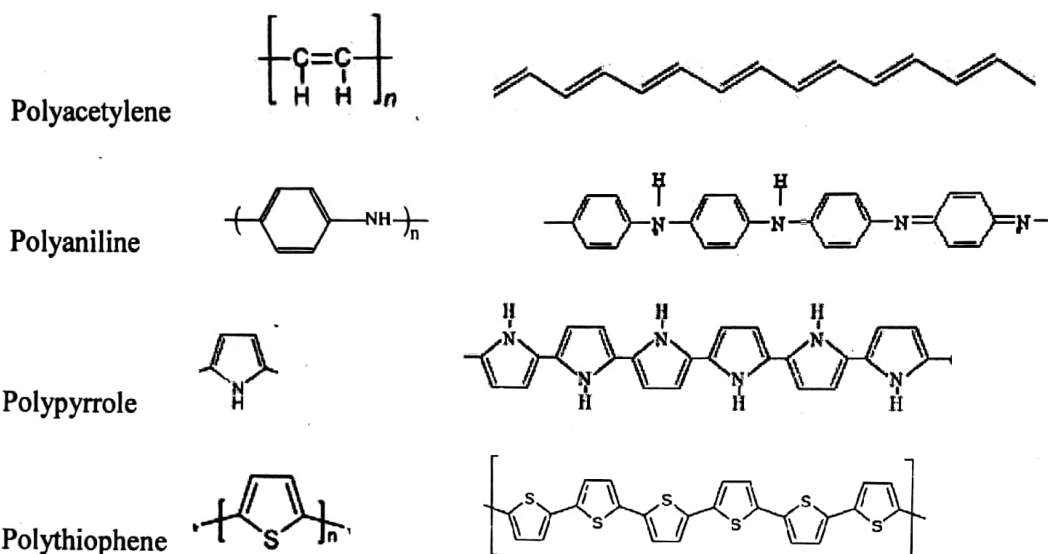
Conducting polymers can be classified into the following categories:

- 1- Intrinsically conducting polymers
- 2- Extrinsicly conducting polymers

**1-Intrinsically conducting polymers:** They are of two types:

- **Conducting Polymers having conjugated  $\pi$ -electrons in the back bone:** Such polymers contain conjugated  $\pi$  electrons along the backbone of the polymers, which are responsible for the formation of valence bands and conduction bands. If the band gap between the valence band and conduction band is narrow, the electrons from the valence band are excited to conduction band giving rise to its conductivity. If the band gap is too wide, the substance is an insulator.

Examples:



- **Doped Conducting Polymers:** The process of transforming a polymer to its conductive form via chemical oxidation or reduction is called 'Doping'. The process of doping can be carried out by two methods.
  - Oxidation:** In this process some e- are removed from the  $\pi$  bond of the conjugated double bonds, the holes so created can move along the molecule i.e., the polymer becomes electrically conductive. The oxidation process is generally brought about by Lewis acids such as  $\text{FeCl}_3$ .
  - Reduction:** In this type of doping some electrons are introduced into the polymer having conjugated double bonds. This process is brought about by adding Lewis bases.

**2-Extrinsically conducting polymers:** They are of two types

- Conducting element filled polymers:** These are the polymers which are filled with conducting elements, such as carbon black, metallic fibers, metallic oxides etc. These polymers possess reasonable conductivity, low in cost, and light in weight, mechanically durable and strong.

- ii- **Blended Conducting Polymers:** It is obtained by blending a non conducting polymer with a conducting polymer. Such Polymers possess better physical, chemical, electrical and mechanical properties.

### Application of Conducting Polymers:

- i. **Rechargeable Batteries:** The polymeric batteries have the properties of high reliability, light weight, no leakage of electrolyte solution and are small in size. Polyacetylene is used in researchable batteries. Polyacetylene's power density is 12 times that of ordinary lead acid batteries. Its energy density is also higher - about 50 wh/kg Vs 35 for lead acid batteries. They have the unique potential to be made of low-cost environmentally friendly materials. Supporters of this technology feel that a polymer battery can be part of the battery-powered car of the future.

- ii. **Conductive Polymers in Photography:** Photographic firms were facing a problem with the production of photofilms in the late 80s because static discharges induced by friction, produced the electric sparks which destroy the costly rolls of the company's film. To overcome this problem nowadays conducting polymer Polythiophene is used to coat photographic films.

- iii. **Conductive Polymers in Display Devices [Polymer Light-Emitting Diodes for Backlights & Displays]:** A polymer Light-Emitting Diode (LED) is a thin light source in which a polymer is used as the emissive (radiation) material. The simplest polymer LED consists of a polymer layer, which is sandwiched between two electrodes. The bottom electrode (anode) is a thin indium-tin oxide (ITO) layer that is deposited onto a glass substrate. A vacuum-deposited metal electrode serves as the top electrode (cathode).

A soluble derivative of the poly-phenylene-vinylene polymer is used as the emissive material. By changing the chemical structure of the polymer, the emission colour of the device can be varied from green to orange-red.

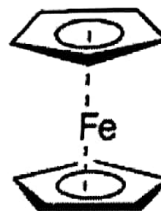
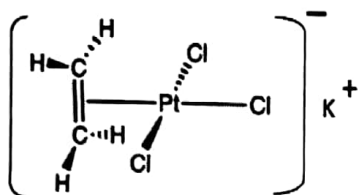
- iv. **Conductive Polymers for Medical Applications:** Medical applications using conductive thermoplastics include:
- Bodies for asthma inhalers. Because the proper dose of asthma medications is critical to relief, any static "capture" of the fine particulate drugs can affect recovery from a spasm.
  - Airway or breathing tubes and structures. A flow of gases creates triboelectric charge or decay. A buildup of such charges could cause an explosion in high-oxygen atmospheres.
  - Antistatic surfaces, containers, packaging to eliminate dust attraction in pharmaceutical manufacturing.

### Organometallic compounds

Organometallic compounds are such compounds in which a metal atom is bonded directly to a carbon atom of a hydrocarbon molecule or radical.

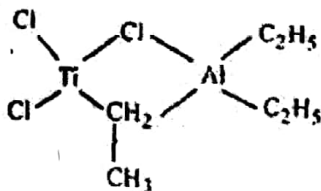
Examples:

- 1- Grignard Reagent (RMgX):  $\text{CH}_3\text{-Mg-Cl}$
- 2- Methyl lithium  $\text{Li CH}_3$ , Diethyl zinc  $\text{Zn (C}_2\text{H}_5)_2$
- 3- Zeise's salt: It is the first synthetic organometallic compound,



4- Ferrocene

5- Ziegler-Natta Catalyst  $\text{Al (C}_2\text{H}_5)_3 + \text{TiCl}_4$



6- Metal carbonyls: Iron pentacarbonyl  $\text{Fe (CO)}_5$ , Nickel tetracarbonyl  $\text{Ni (CO)}_4$

### Classification of Organometallic Compounds:

Organometallic compounds can be divided into simple and mixed compounds.

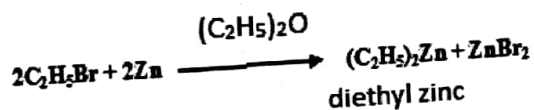
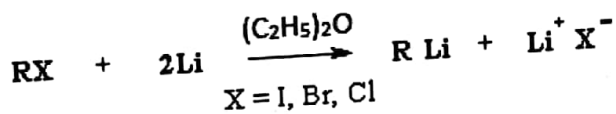
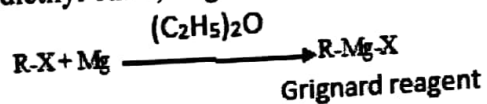
1. **Simple organometallic compounds:** These are such organic compounds which have only hydrocarbon radical or H atom bonded to the metal atom.  
For Example: Diethyl Zinc  $\text{C}_2\text{H}_5\text{-Zn-C}_2\text{H}_5$  ; Tetra ethyl lead  $(\text{-CH}_2\text{CH}_3)_4\text{Pb}$  ; Butyl ethyl mercury  $\text{C}_2\text{H}_5\text{-Hg- C}_4\text{H}_9$

They are further subdivided into:

- (i) **Symmetrical:** In symmetrical organometallic compounds the metal atom is bonded to same kind of hydrocarbon radicals. Like: Diethyl Zinc  $\text{C}_2\text{H}_5\text{-Zn-C}_2\text{H}_5$  ; Tetra ethyl lead  $(\text{CH}_2\text{CH}_3)_4\text{Pb}$
  - (ii) **Unsymmetrical:** In unsymmetrical organometallic compounds the metal atom is bonded to different kind of hydrocarbon radicals. Like: Butyl ethyl mercury  $\text{C}_2\text{H}_5\text{-Hg- C}_4\text{H}_9$
2. **Mixed Organometallic compounds:** These are such compounds which have also groups other than hydrocarbon radicals attached directly to the metal. Like: Grignard reagent  $\text{R-Mg-X}$ ,  $(\text{C}_4\text{H}_9)_2\text{-Sn-Cl}_2$  etc.

### Methods of Preparation of Organometallic compounds:

- 1- By the direct action of metal and alkyl halides (RX): When metals like Li, Na, K, Mg, Zn and Cd are treated with alkyl halides RX in presence of suitable organic solvent like diethyl ether, Organometallic compound is formed.

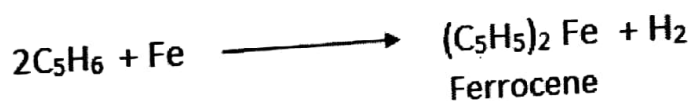


### 2- Preparation of $\pi$ -complexes:

- a) Preparation of Zeise's salt: It is prepared by reaction of ethylene and potassium tetrachloroplatinate (II).



- b) Preparation of Ferrocene: When cyclopentadiene ( $\text{C}_5\text{H}_6$ ) reacts with iron at 575 K, Ferrocene is obtained.

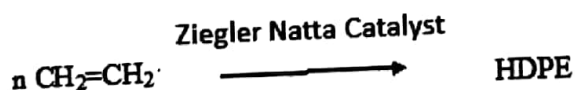


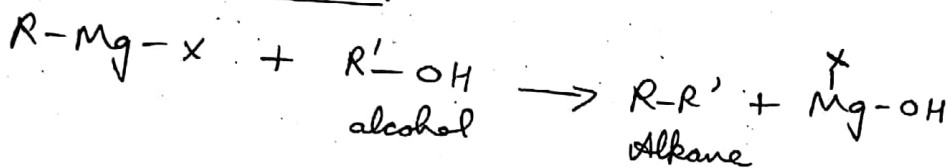
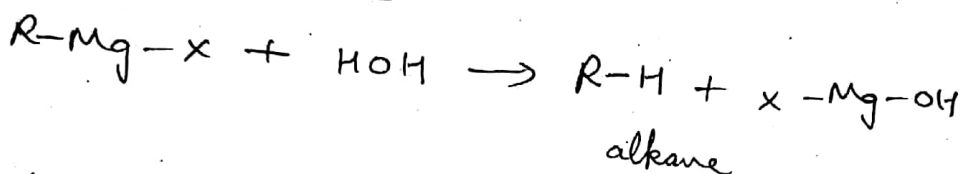
- c) Preparation of metal carbonyl: When finely divided nickel is treated with carbon monoxide at 325 K, nickel carbonyl is formed.



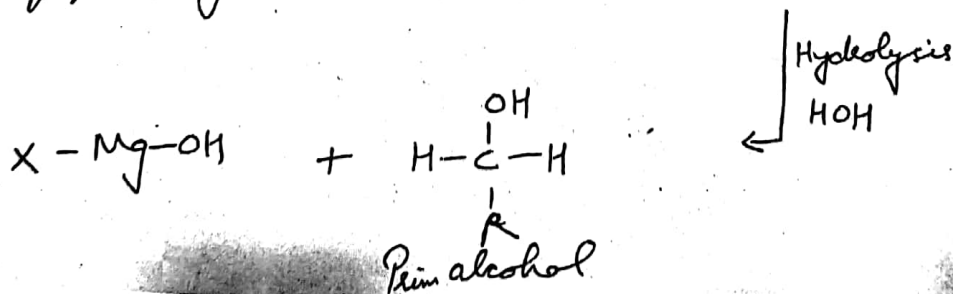
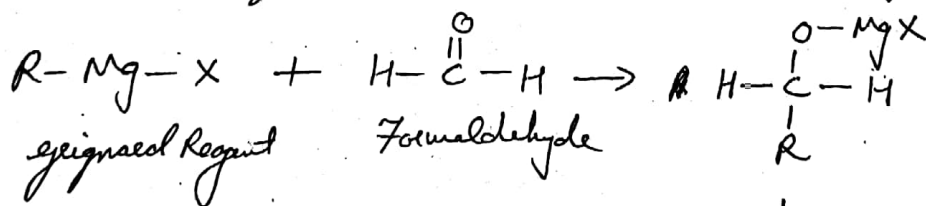
### Applications of Organometallic Compounds:

- a) Ziegler-Natta Catalyst  $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ : It is used in making High Density Polyethene (HDPE)



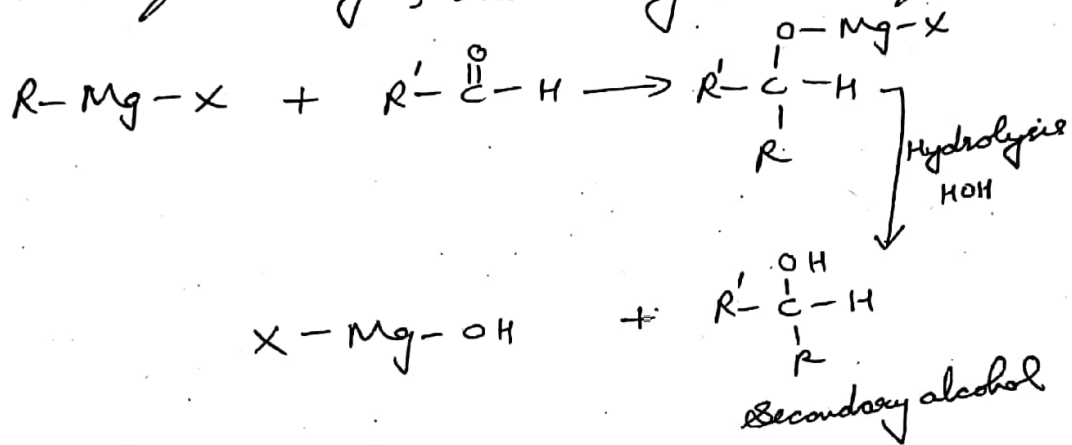
Application of Grignard Reagent RMgX:Applications of Grignard Reagent1) Formation of hydrocarbons (alkanes)Reaction with alcoholReaction with water2) Formation of alcohol

Primary alcohol: when a grignard reagent is treated with formaldehyde, a primary alcohol is formed

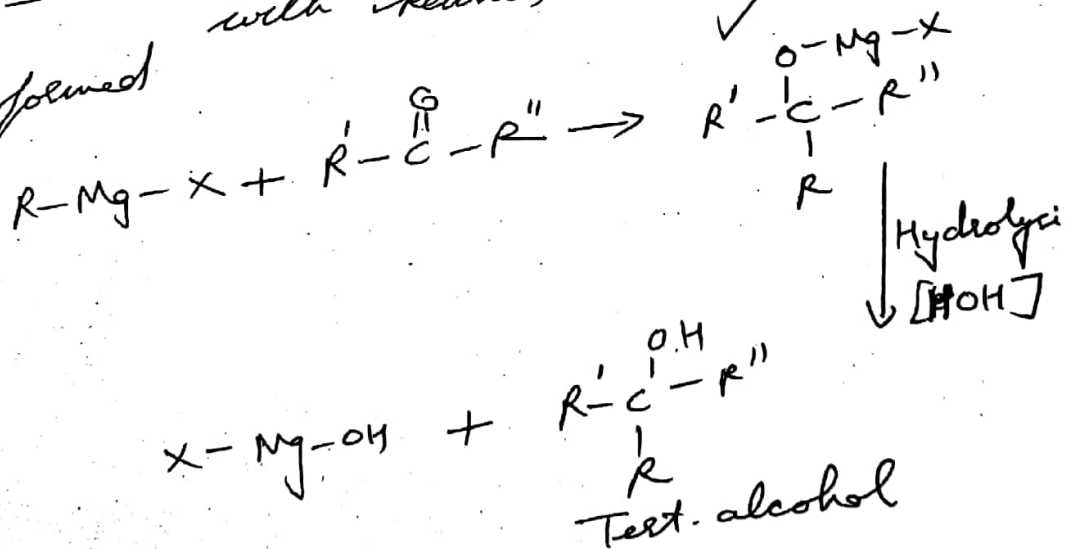




Secondary alcohol: When a Grignard reagent is treated with any aldehyde other than formaldehyde, a secondary alcohol is formed.

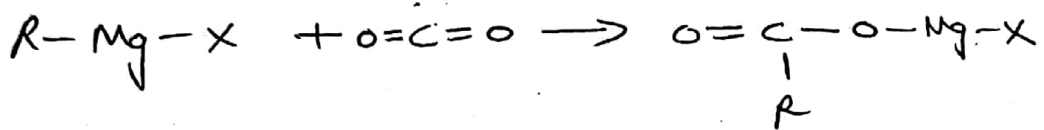


Tert. alcohol: When a Grignard reagent is treated with ketone, a tertiary alcohol is formed

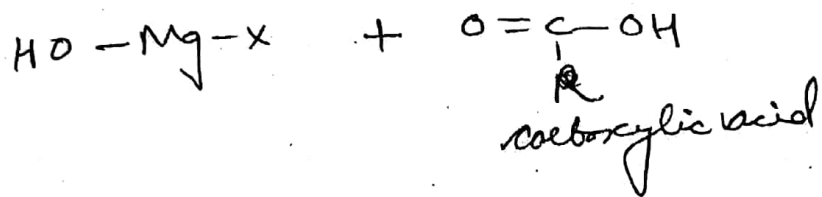


### 3) Formation of carboxylic acid

Reaction with  $\text{CO}_2$ : Grignard reagent reacts with  $\text{CO}_2$  and form carboxylic acid on hydrolysis of intermediate compound



↓ Hydrolysis  
[HOH]



### Biodegradable Polymers

These are those polymers which get decomposed under aerobic or anaerobic conditions, as a result of the action of microorganism/enzymes. The materials develop it like starch, cellulose, and polyesters. Aliphatic polyesters are the most commonly used polymers of this type.

Classification of biodegradable polymers based on the source

- 1) Synthetic biodegradable polymers: eg: Aliphatic poly(esters) Polyanhydrides Polyphosphazenes polyaminoacids Poly orthoesters etc.,
- 2) Natural biodegradable polymers: eg: Protein, carbohydrate, Albumin, Collagen, Dextran, Gelatin, Pectin, starch etc.,

#### Synthetic biodegradable polymers

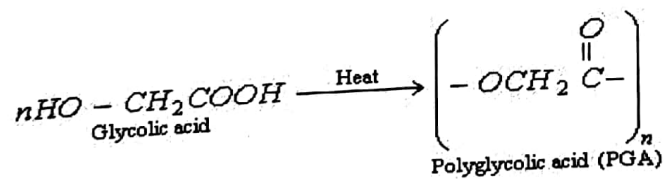
- 1) Aliphatic poly(esters): These are prepared by ring opening and polymerization of cyclic ester. e.g:

- a) Poly (glycolic acid)
- b) Poly (lactic acid)
- c) Poly (caprolactone)

#### a) Polyglycolic acid:

Polyglycolide or Polyglycolic acid (PGA) is a biodegradable, thermoplastic polymer and the simplest linear, aliphatic polyester.

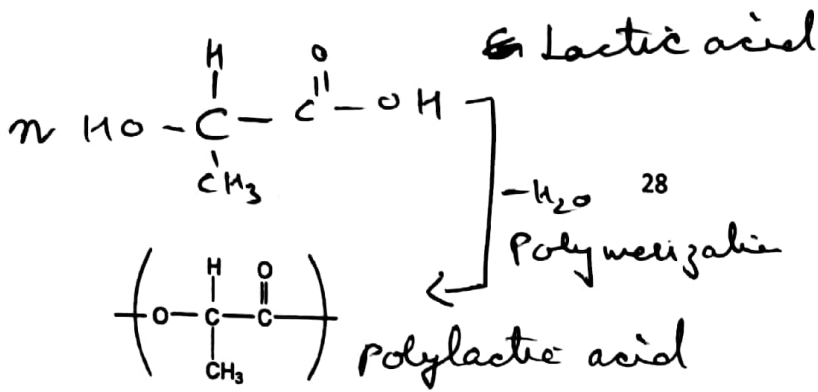
PGA Polyglycolic acid is obtained by the chain polymerization of glycolic acid,



- It is a tough fibre-forming polymer.
- Insoluble in water.
- polyglycolide is degraded by hydrolysis, and broken down by certain enzymes.

Applications – Used in drug delivery system – Examples of drugs delivered include steroid hormones, antibiotics, anti cancer agents etc.,

#### b) Polylactic acid:



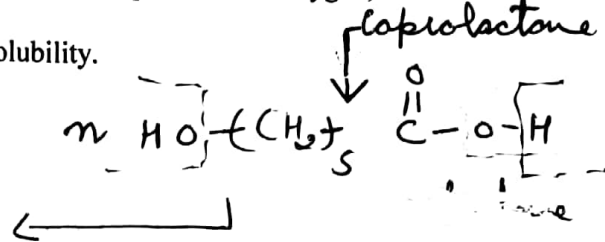
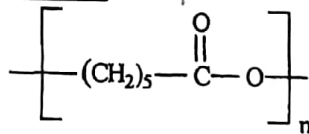
PLA is used in the preparation of sutures or orthopedic devices.

Poly(lactic acid) or polylactide (PLA) is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, or sugarcane.

- It can biodegrade under certain conditions, such as the presence of oxygen, and is difficult to recycle.

- Highly crystalline, high melting point, low solubility.

**c) Polycaprolactone**



Polycaprolactone (PCL) is a biodegradable polyester but slower degradation rate than PLA.

- It remains active as long as a year for drug delivery.

**Natural biodegradable polymers :** Derived from natural sources, Easily available and Relatively cheap eg: Carbohydrate, starch, Albumin, Collagen, Gelatin and Pectin etc.,

**Applications of biodegradable polymers:**

- In Drug delivery system
- Most of the biodegradable polymers find use in stitching wounds and cuts.
- In medical goods such as surgical sutures, adhesive and glues.
- In agriculture materials such as films, seed coatings. 3. In food wrappers, personal hygiene products, etc.
- For gene therapy
- On soil to improve aeration, and promote plant growth and health.

# Polymer blends and Composites

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## Polymer Blends

The development and commercialization of new polymer usually requires many years and is also extremely costly. Polymer blending is an easy and convenient way for the development of new polymeric materials, which combine the excellent properties of two or more existing polymers. This method is usually cheaper and less time consuming than the development of new polymers.

***“Blending is the mixing of two or more polymers having better properties than the component polymers”.***

- Polymer blend is a combination of two or more polymers, which are physically mixed to obtain a single phase. Usually strong chemical bonds between polymers blends are absent.
- Property of polymer blends is superior to those of component homo-polymers.
- Blending technology also provides attractive opportunities for reuse and recycling of polymer wastes.
- Blends are usually obtained in a molten state or by dissolving in solvents.
- Polymer blends are mainly classified as compatible, Partial miscible and incompatible polymer blends.
- Compatible polymer blends are miscible blends, where there are no separate phases, but a single phase. These type of blends provide superior mechanical properties. Eg. PS/PPO
- In partially miscible blends a small part of one blend component is dissolved in the other. Eg. PC/ABS blends
- For incompatible blends ( like Nylon6/ABS blends) some interfacial agents are used to reduce interfacial tension and allow the polymers to mix. These agents are called as compatibilizers or compatibilizing agents. SAGMA, ABS-g-MAH, and ABS-MA copolymer are used as comapatibilizer in making blends of Nylon6/ABS.

### **The various advantages of blending are:**

- Develop or improved properties of polymers to meet specific customer needs
- Producing materials having a full set of the desired properties at lowest cost
- Development of Light weight polymers
- The ability to improve the processability of materials which are otherwise limited in their ability to be transformed into finished products.
- Improvement of specific properties like Increased toughening ,Dimensional Stability
- Improved modulus and hardness
- Improved barrier property and flame retardant property
- Improved impact and environmental stress cracking resistance, etc.

In short, By blending of two or more polymers, unique materials are generated as far as its processability and or performance are concerned.

### **Five different methods are used for the preparation of polymer blends:**

Melt mixing, solution blending, latex mixing, partial block or graft copolymerization, and preparation of interpenetrating polymer networks (IPN)

## Composites:

**Composites** are combinations of two materials, in which one of the materials, called as reinforcing phase, is embedded in the other material, called matrix phase (figure 1). Materials used as reinforcing phase are generally in the form of fibres, sheets, or particles.



Figure 1: Microscopic structure of polymer composite.

### **General Characteristics**

- The reinforcing material and the matrix material can be metal, ceramic, or polymer. Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile, or tough, material.
- If the composite is designed and fabricated correctly, it combines the properties of both matrix and reinforcing material i.e., strength of the reinforcement and toughness of the matrix. This gives a combination of desirable properties, which are not available in any single conventional material.
- The properties of composites mainly depend on the physico-mechanical properties of their components and the strength of bonds between them
- Such composites are often more expensive than conventional materials.
- Examples of some current application of composites include the diesel piston, brake-shoes and pads, tires and the Beechcraft aircraft in which 100% of the structural components are composites.
- Composites are used because overall properties of the composites are superior to those of the individual components. For example: polymer/ceramic composites have a greater modulus than the polymer component, but are not as brittle as ceramics.

The following are some of the reasons why composites are selected for certain applications:

- High strength to weight ratio (low density high tensile strength)
- High creep resistance
- High tensile strength at elevated temperatures
- High toughness

The degree of reinforcement or improvement of mechanical properties depends on strong bonding of reinforcing phase to the matrix. Generally, in composites, as the reinforcement content increases, the strength also increases. In addition, the composite is often mixed with fillers and additives to facilitate processing and improve performance characteristics.

**There are three types of composites:**

- 1) Particle-reinforced composites
- 2) Fiber-reinforced composites

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### 3) Structural composites

**1) Particle Reinforced Composites:** Particles are used to increase the modulus of the matrix, to decrease the permeability of the matrix, to decrease the ductility of the matrix. Particles are also used to produce inexpensive composites. These can be further classified under two subgroups:

- a) Large particle composites
- b) Dispersion- strengthened composites.

a) **Large particle composites:** Some examples of large particle composites are given below:

- **Concrete:** Concrete is the example of large particle composites. Concrete is composed of cement (**the matrix**), and **sand and gravel (reinforcing particles)**.
- **Reinforcing rubber (automobile tire):** Another important example is an **automobile tire** which has **carbon black particles in a matrix of polyisobutylene elastomeric polymer**. When carbon black is added to vulcanized rubber, his material which is very cheap, enhance tensile strength, toughness, and tear and abrasion resistance
- **Cermets:** Cermets are composites of **ceramic particles (strong, brittle) in a metal matrix** (soft, ductile) that enhances toughness. For example: tungsten carbide or titanium carbide ceramics in matrix of Co or Ni. They are used for cutting tools for hardened steels.

b) **Dispersion- strengthened composites:** Metals and metal alloys may be strengthened and hardened by the uniform dispersion of several volume percent of fine particles of a very hard and inert material. The dispersed phase may be metallic or nonmetallic; oxide materials are often used.

### 2) Fibre-reinforced Composites:

In fibre- reinforced composites, fibres are used as reinforcing phase, which are embedded in a matrix.

**Fiber materials include:** Reinforcing fibers can be made of glasses, carbon fibers, polymers, ceramics, and metals.

**Glass** – glass is the most common and inexpensive fiber and is usually use for the reinforcement of polymer matrices. Glass has a high tensile strength and fairly low density (2.5 g/cc).

**Carbon-graphite (carbon fibre)** - In advance composites, carbon fibers are used. Carbon is a very light element, with a density of about 2.3 g/cc and its stiffness is considerable higher than glass. Carbon fibers can have up to 3 times the stiffness of steel and up to 15 times the strength of construction steel.

**Polymer** – Polymer fibres are also used because of the presence of the strong covalent bonds. For example: **Kevlar** is an aramid (aromatic polyamide) composed of oriented aromatic chains,

which makes them rigid rod-like polymers. Its stiffness can be as high as 125 GPa and although very strong in tension, it has very poor compression properties. Kevlar fibers are mostly used to increase toughness in otherwise brittle matrices.

### **3) Structural Composites:**

Example: modern ski and plywood.

They can be used in variety of applications which include roofs, floors, walls of buildings and in aircraft, for wings, fuselage and tailplane skins.

### **Applications of polymer composites:**

- Polymer composites are used to make very light bicycles that are faster and easier to handle than standard ones,
- Fishing boats that are resistant to corrosive seawater, and
- Lightweight turbine blades that generate wind power efficiently.
- New commercial aircraft also contain more composites than their predecessors. A 555-passenger plane recently built by Airbus, for example, consists of 25 percent composite material, while Boeing is designing a new jumbo aircraft that is planned to be more than half polymer composites.
- The hull of this sailing yacht is a sandwich structure with the outer skin made of an epoxy resin reinforced with Kevlar fibres. The core is expanded polyvinyl chloride foam. This composite material; system is lightweight but providing high impact strength and tear resistance. In addition, the sail is not mere cloth, but is instead a fiber-reinforced Mylar film (Mylar is an extraordinarily strong polyester film).

