

By

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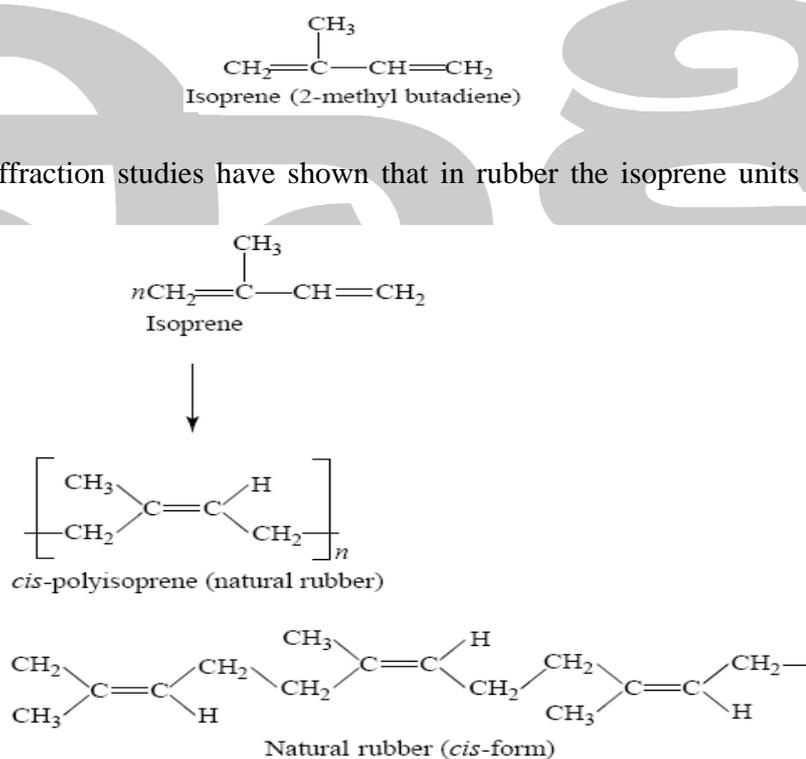
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RUBBERS

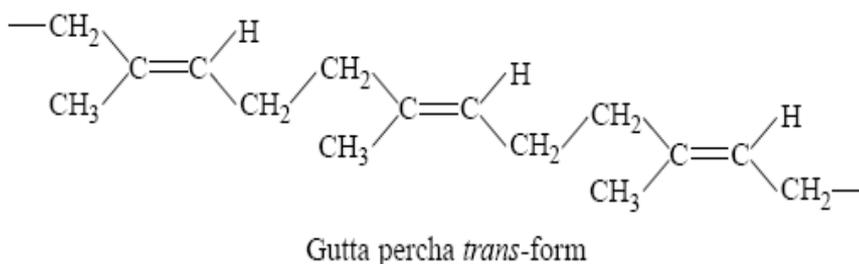
1) What is natural rubber? How is it extracted from latex? What is its composition?

Natural rubber is obtained from nearly 500 different plants, but the main source from which the commercial natural rubber is obtained is the tree *Hovea brazil ianesis*. The rubber is obtained from latex (milky sap) collected from the cuts made in the bark of the tree. The obtained latex contains hydrocarbon with impurities such as fatty acids, proteins and resins in an emulsified form. The latex is then coagulated with acetic acid or formic acid. The crude or raw rubber is composed of 95% hydrocarbons, 4% protein and 1% of resins. Destructive distillation of natural rubber gives isoprene as the main product

The X-ray diffraction studies have shown that in rubber the isoprene units are arranged in the *cis*-form.

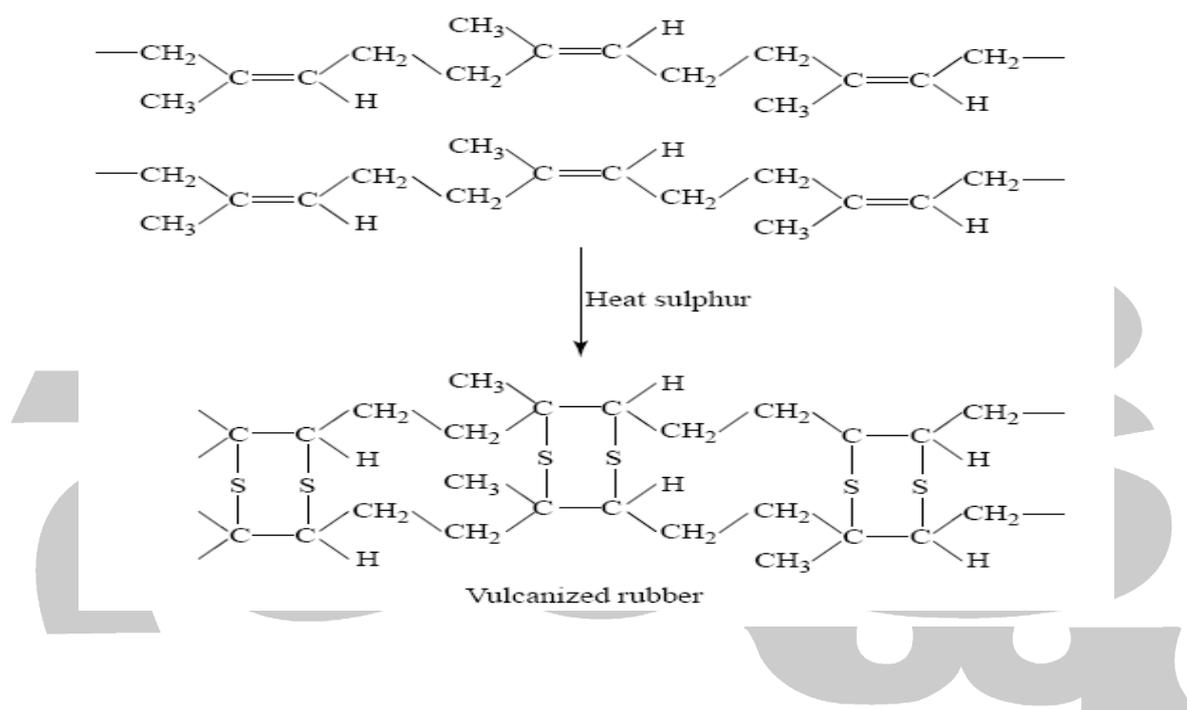


Gutta percha rubber is also a natural rubber in which isoprene units are arranged in the *trans* manner.



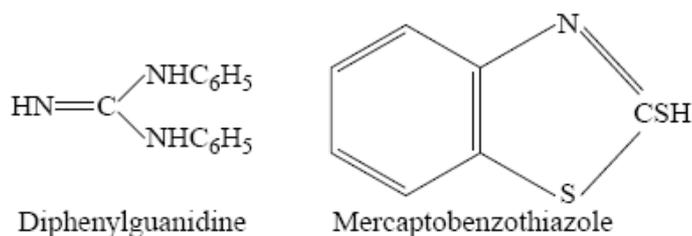
2).What is vulcanization? What are its advantages? Why rubber is vulcanized?

The raw or crude rubber is very little useful because it has very undesirable properties, such as low tensile strength, possesses elasticity only over a limited range of temperature and becomes softer, more plastic and sticky on heating and brittle on cooling. Its solubility in organic solvents (such as CHCl_3 , benzene and petrol) is of advantage for preparing rubber derivatives and adhesive solutions.



In order to give more strength and more elasticity, natural rubber is heated with sulphur or sulphur compounds at 150°C temperature for a few hours. The sulphur combines chemically at double bonds of different rubber springs and a crosslinked network is formed. This process is known as vulcanisation of rubber. The vulcanisation process is invented by Charles Goodyear in 1839. The vulcanization can also be accomplished with certain peroxides, gamma radiation and several other organic compounds.

The vulcanisation process can be enhanced in the presence of certain organic substances known as accelerators. The common accelerators contain nitrogen, sulphur or both, **E.g.**



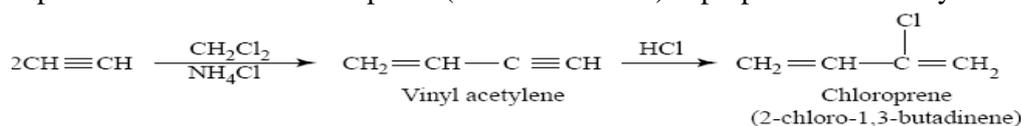
Advantages of Vulcanised Rubber

1. Vulcanised rubber has good tensile strength.

- The working temperature of vulcanised rubber is enhanced up to 100°C. Temperature range of raw rubber is 10–60°C.
- The elasticity of vulcanised rubber is very low.
- It has good resistance to organic solvents.

3) Give some examples of synthetic rubbers? Write their preparation, properties and uses?

- Neoprene:** It was the first synthetic rubber manufactured on large scale. It is also called duprene. Its monomer chloroprene (chlorobutadiene) is prepared from acetylene.



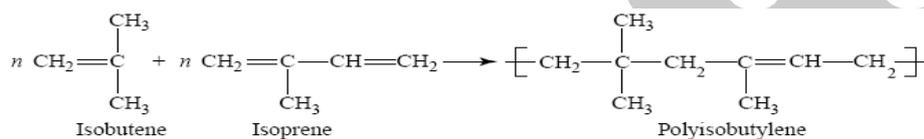
Chloroprene undergoes free radical polymerisation to form neoprene (poly-chloroprene).



Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils and other hydrocarbons. It is non-inflammable and resistant to sunlight, oxygen and heat.

Neoprene is used for making shoe-soles, automobile and refrigerator parts. It is also used in wire insulation and laboratory stoppers.

- Butyl Rubber (Polyisobutylene):** It is a copolymer of 98% isobutene and 2% butadiene or isoprene. The butadiene is added to introduce the necessary ethylenic linkages for vulcanization.



Butyl rubber is soluble in hydrocarbon solvents, such as benzene, but highly insoluble in polar solvents, such as alcohol and acetone. It has low degree of unsaturation and it is quite resistant to oxidation and chemicals. Because of the above properties, it is used in manufacturing the inner tubes for automobile tyres. It is also used for insulation of high-voltage wires and cables.

- Buna-S (Styrene Butadiene Rubber: SBR):** Buna is a copolymer of 75% butadiene (CH₂=CH-CH=CH₂) and 25% of styrene (C₆H₅CH=CH₂). The polymerisation is carried out at 50°C in the presence of peroxide catalyst.

the number of sulphur atoms present in it. The polymer behaves like elastomer when four sulphur atoms are present per monomer and it do not behave as elastomer if only two sulphur atoms are present per monomer. Thus in case of thiokol four methylene groups should be present in the dihalide to induce elastic properties. Some of the important properties are:

- (i) Thiokol is resistant to the action of oxygen and ozone.
- (ii) It is also resistant to the action of petrol lubricants and organic solvents
- (iii) Thiokols outstanding resistance to swelling by organic solvents but benzene and its derivatives cause some swelling.
- (iv) Thiokol films are impermeable to gases to a large extent.
- (v) Thiokols are vulcanized with metal oxides such as zinc oxide.
- (vi) But Thiokol has poor heat resistance and low tensile strength. The odour of thiokol is very bad. It tends to lose its shape under continuous pressure.

Uses:

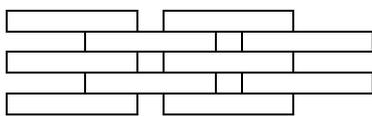
- (i) Thiokol mixed with oxidizing agents in used as a fuel in rocket engine.
- (ii) It is used to engine gaskets and other such products that come into contact with oil.
- (iii) Thiokols are used for hoses and tank lining for the handling and storage of oils and solvents.

4) What is the difference between polymer and plastic? Name the additives present in it? What is their importance?

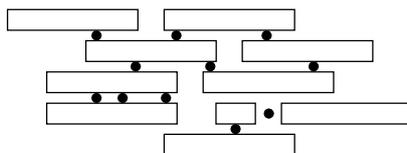
The pure material obtained from the process of polymerisation is known as polymer. The usefulness of long chain pure polymer is very little. After adding some materials, polymer becomes useful and termed as a *plastic*.

Following types of additives are found to be present in plastic:

- 1. Fillers:** These are substances that increase hardness, tensile strength and the mechanical properties of plastics. Some important fillers are carbon-black (C-black), chalk, china clay, cellulose fillers, metallic oxide (ZnO, PbO, etc.), metal powders (Al, Cu, Pb, etc.), carborundum, quartz, etc. Fillers also reduce the cost of the final compounds.
- 2. Binder (Resin):** In the plastics, binder holds different constituents together. They are generally of low molecular weight materials and withstand high temperature.
- 3. Plasticisers:** Plasticisers are generally small liquid molecules that are chemically similar to the polymer and create gaps between polymer chains for greater mobility and reduced inter-chain interactions. Commonly used plasticisers are camphor, some phosphateesters (dioctyl phthalate), etc.



Polymeric chain without plasticiser



Polymeric chain with plasticizer

4. Stabilisers: Stabilisers are used to improve the thermal stability of plastics, e.g. polyvinyl chloride. At moulding temperature, PVC undergoes decomposition and decolourisation. So during their moulding, stabilisers are used. The commonly used stabilisers are white lead, lead chromate, red lead, etc.

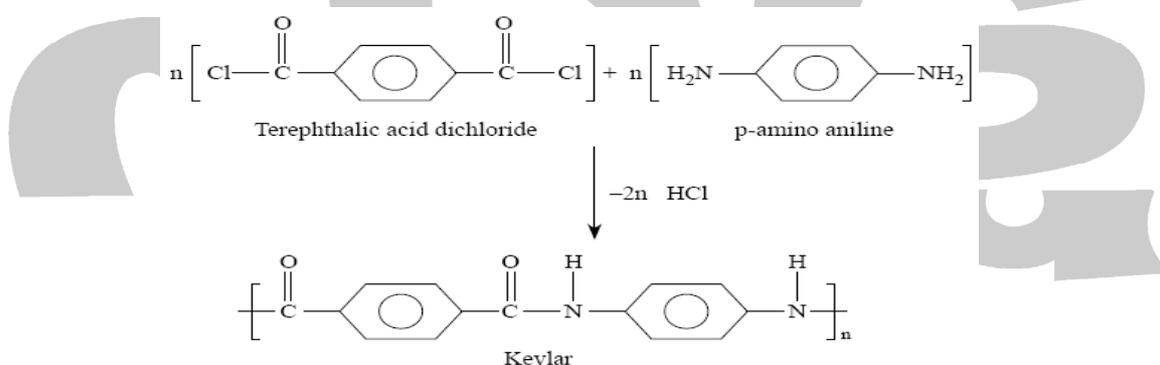
5. Colouring Materials: Organic dyestuffs and inorganic pigments are used as colouring materials.

5. what are liquid crystal polymers? Give an account of LCPS?

Liquid crystal polymers (LCP) are a class of aromatic polyester polymers. Liquid crystallinity in polymers occurs either by dissolving a polymer in a solvent (lyotropic liquid crystal polymer) or by heating a polymer above its glass transition temperature (Thermotropic liquid-crystal polymers). These show the characteristic of ordinary liquid crystals and also retaining the properties of polymers.

In the main chain of LCP's there are two distinct groups. The first group is characterized by stiff, rod like monomers and is usually made up of aromatic rings. The second group of LCP is the mesogen which is incorporated directly into the polymer chain. The mesogen acts just like the stiff areas in the first group, but are comprised of two or more aromatic rings, which give the necessary restriction for the polymer to display its liquid crystalline properties. The examples of liquid crystal polymers are Kevlar, poly-p-benzamide, polybenzyl-L-glutamate etc. The main example of lyotropic LCP (solid) is Kevlar (commercially known as aramid).

Preparation: In nylon when aliphatic chain is replaced by benzene ring, a aromatic polyamide is formed which is known as Kevlar. It is prepared by polycondensation between aromatic dichloride and aromatic diamines.



The chemical structure of the Kevlar consists of linearly substituted aromatic rings linked by amide groups.

Properties and uses:

- (1) They are extremely unreactive and inert towards organic solvents.
- (2) They are highly ordered but the degree of order is somewhat less than that of a regular solid crystal.
- (3) LCPs have a high mechanical strength at high temperatures.
- (4) They have excellent thermal properties especially heat resistance. (5) LCPs have high impact resistance.
- (6) Because of their various properties, LCPs are useful for preparing electrical and mechanical parts, food containers and many other applications requiring chemical inertness and high strength.
- (7) Liquid crystal polymers are used in making car parts, tyres and motor cycle helmets.

Extrusion: It is a manufacturing process in which plastic material is melted and formed into a continuous profile. This method of fabrication is generally used for the manufacture of pipes, tubes, window frame, rods etc. Plastic extrusion uses a single screw extruder to melt plastic pellets and molten plastic move through a pressurized screw mechanism and then is forced through a die having the required shape. In this method only thermoplastics are used as raw material.

6. write an account on moulding of plastics by 1. Injection moulding, 2. Transfer moulding, 3. Compression moulding and 4. Blow moulding processes?

1) **Injection Moulding:** The moulded plastic powder is heated in a cylinder and injected at a controlled rate into the locked mould by means of screw arrangement.

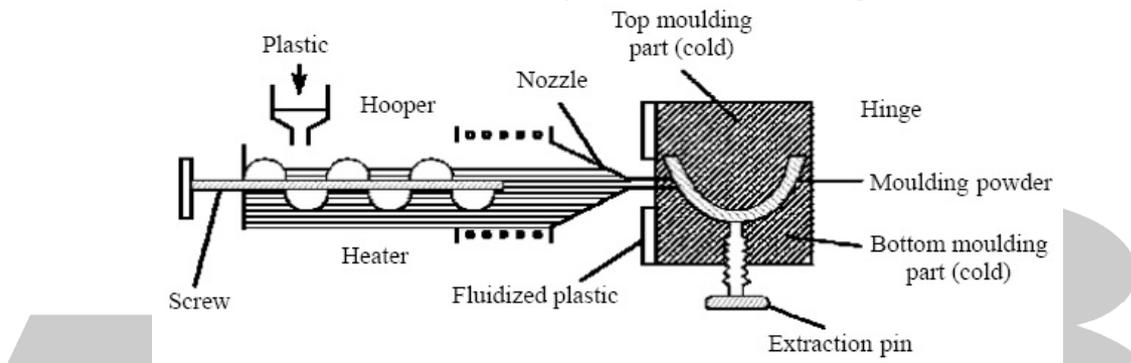


Fig 3.4 Injection moulding of plastics

The mould is kept cold so that the hot plastic becomes solid due to the phenomenon of curing. After sufficient curing, the mould is opened to allow the ejection of moulded object. This method is generally used for thermoplastics because of high speed production, low mould cost and minimum loss of material. Injection moulding is used to many things such as milk cartons, containers, bottle caps, pocket combs etc. The disadvantages of injection moulding are expensive equipment investment and high running cost.

2. Compression Moulding: In this method, the required amount of a raw material is placed in a closed mould. Then high pressure and high temperature are applied to complete the curing process. This technique is applied to thermoplastic as well as thermosetting plastics. Finally curing is done by heating in case of thermosetting resin while in case of thermoplastic curing is done by cooling. After curing, the moulded article is taken out by opening the mould parts.

The advantages of compression moulding are lowest cost moulds, lower labour cost, minimum amount of wasted material and minimum internal stress.

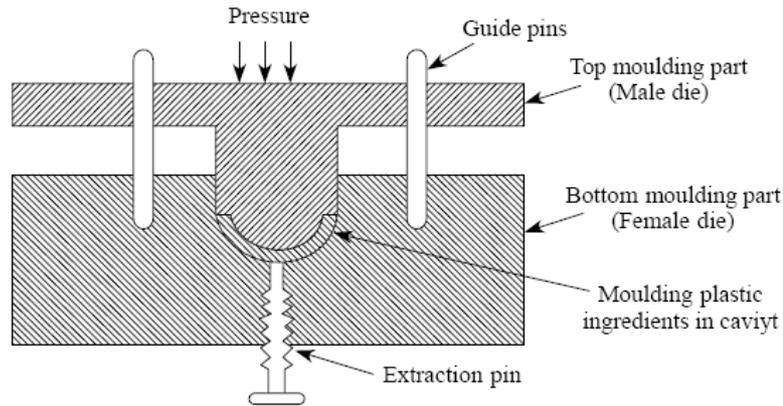


Fig. 3.5 Compressing moulding plastics

3. Transfer Moulding: This method is applied for thermosetting plastics and the technique is similar to injection moulding. The sample is kept in a heated chamber then injected through an orifice into the mould by a piston plunger at very high pressure. As the plastic mass (sample) passes through the orifice, due to friction, temperature of the material increases and moulding powder becomes liquid and drops quickly to the mould. Now curing takes place under the influence of heat and pressure and required shaped product is obtained.

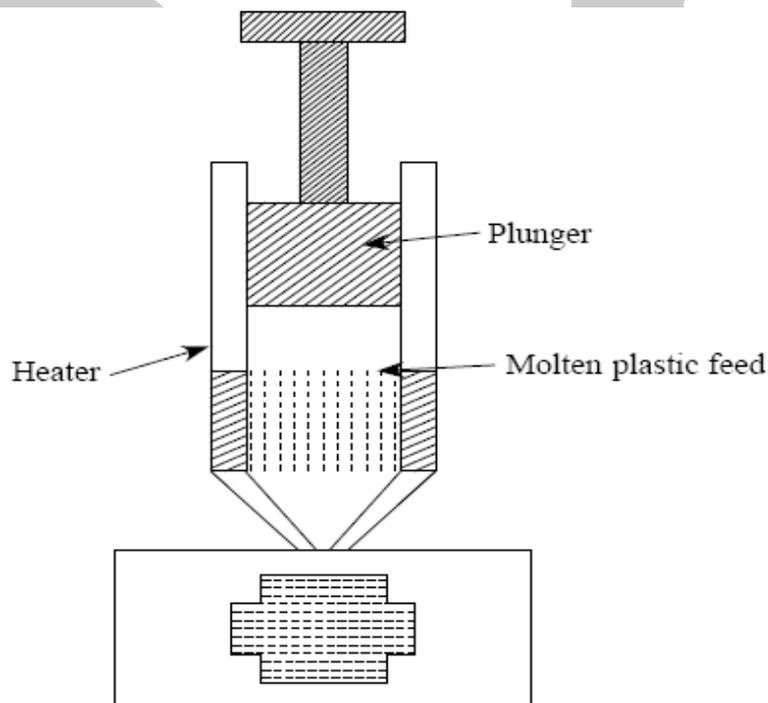
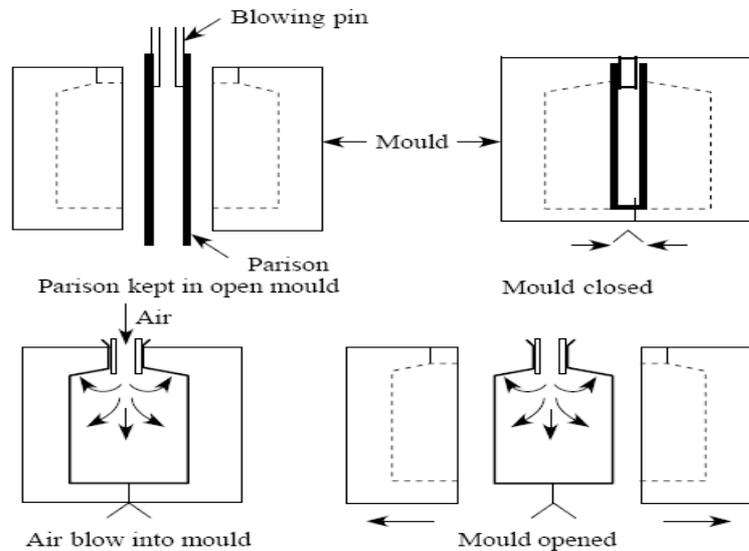


Fig. 3.6 Transfer moulding

4. Blow Moulding: Blow moulding produces hollow plastic materials like bottles, tubes, tanks and drums. Thermoplastic materials like PVC, polystyrene, polypropylene can be blow moulded.

In this process a tube is placed inside a two piece hollow mould. One end of the tube is completely closed in heated and simultaneously air is blown to fabricate the product having the shape of mould



7) What are Fibre-reinforced plastics. Give examples?

Fibre-reinforced plastics are a category of plastics that specifically use fibrous material to mechanically enhance the strength and elasticity of plastics. The plastic material without fiber reinforcement is known as matrix. Enhanced strength and elasticity in a fiber reinforced plastic depends on the mechanical properties of both the fiber and matrix, the fiber length and orientation within the matrix.

Fiber glass, carbon, graphite are the main reinforcing fibers used, while the common plastic material (matrices) used in FRPs are polyester, epoxy, vinylester and polyamides.

Fiber glass or glass fiber (SiO_2)_n is a material made from extremely fine fibers of glass. It has no melting point and it becomes soft at 2000°C. Mainly fiber-reinforced plastics are classified into two groups.

- (i) *Carbon fiber reinforced plastics (CFRP)*: When carbon is used as reinforcement material in FRP, it is known as carbon fiber reinforced plastic. It has many applications in aerospace and automotive fields, motorcycles, and specially used in civil engineering and applications include increasing the load capacity of old structures such as bridges.
- (ii) *Glass-Fiber reinforced plastics (GFRP)*: In this, fiber glass is used as reinforcement material. It is used in making storage tanks with capacities upto about 300 tonnes. The GFRPs are also used in house building market for the production of roofing laminate, over door canopies and window canopies.

GFRP pipe can be used for variety of applications such as cooling water system, drinking water system, waste water system etc.

There are various methods for producing fiber-reinforce plastic such as continuous lamination, pultrusion rotational molding, injection molding, hand lay up etc. Some methods are discussed below.

8). Write notes on Conducting polymers?

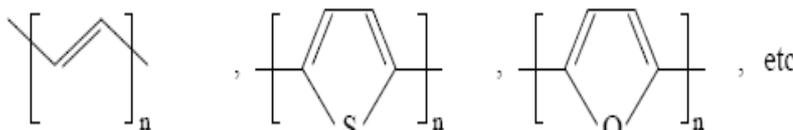
Generally polymers are insulators i.e. they do not conduct electricity or heat and due to this property the most common use of these is as insulator for electric wires. However scientists have discovered that certain class of organic polymers called conjugated polymers, which contain many double bonds in their structure and conduct electricity like semiconductors.

In 2000, the Nobel prize for chemistry was awarded to Alan Heeger, Alan Macdiarmid and Hideki Shirakawa for the discovery and development of electrically conductive polymers. A researcher in Shirakawa's group in Japan was attempting to make regular non-conductive polyacetylene, which is a black powder. However he accidentally added a thousand times the usual amount of catalyst, and the reaction produced a silver colour metallic looking film. Alan Macdiarmid heard of this discovery invited Shirakawa and they continued to investigate the usual properties of polyacetylene. They discovered that, by adding iodine or bromine to polyacetylene, its conductivity could be increased by a factor of ten millions. This technique is called chemical doping and is analogous to the doping of semiconductor. Conducting polymers can be classified into following groups.

- 1. Conjugated p-electrons conducting polymers:** Conjugated conducting polymers have alternating double and single bonds along the polymeric chain and each carbon atom is in sp^2 hybridised state. One valence electron (p) on each carbon is in a p_z orbital, which is orthogonal to other three sigma bonds.

The orbitals of conjugated p-electrons, overlap the entire backbone of the polymer and result the formation of valence, band and conduction band. The valence band is filled band and conduction band is empty. When the energy gap between these is low, the electrons from valence band are excited to conduction band and become mobile throughout the polymer and show conductivity.

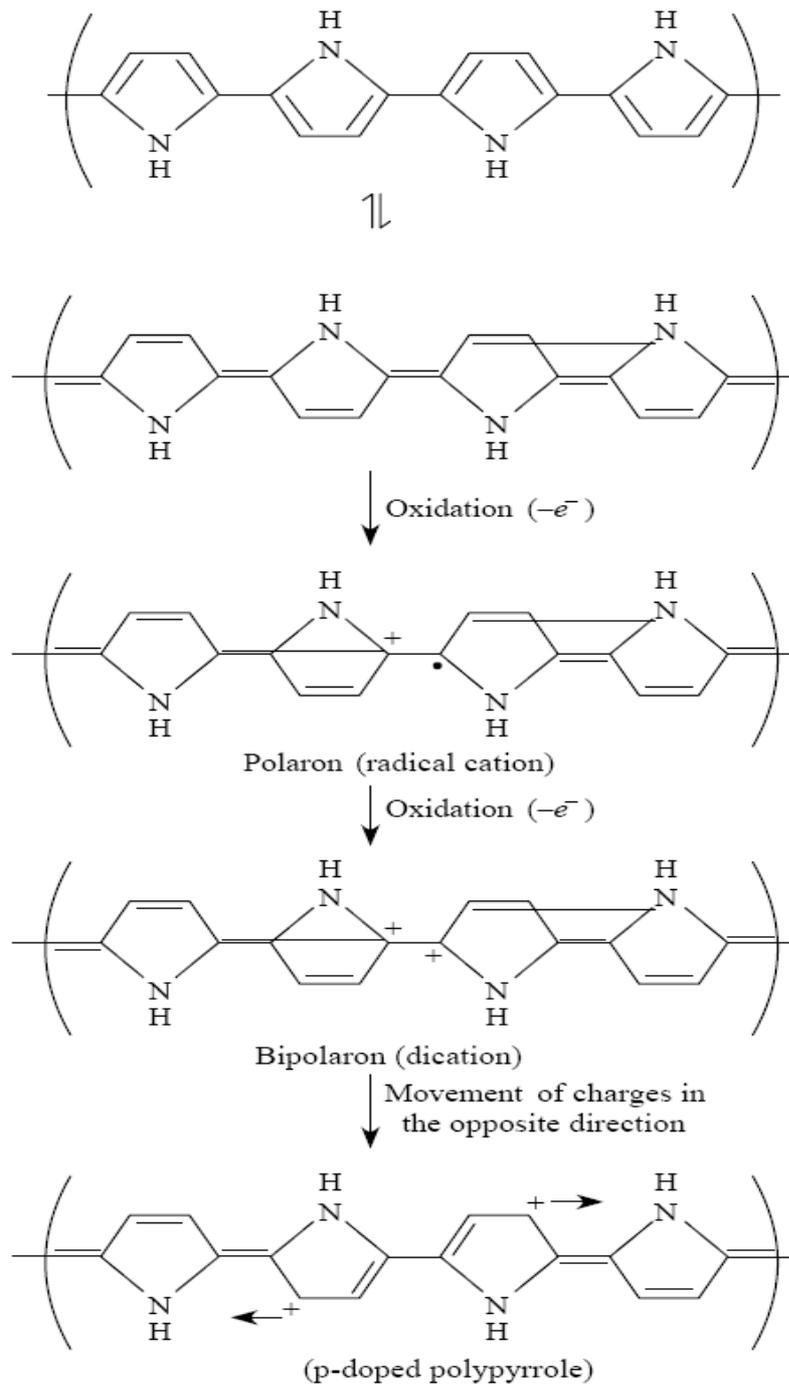
The examples of such type of conjugated polymers are:



2. Doped co

decreased Trans-polyacetylene, Poly thiophene, Polyfuran, etc. increased or
 oxidation process by adding some alkali metal ion or an electron acceptor, the conductivity
 so enhanced is said to be due to
 'p-doping', on the other hand the enhancement of conductivity due to reduction process
 by adding an electron donor is called 'n-doping'.

(i) *Oxidation process (p-doping):* Conducting polymers are oxidised by adding some oxidizing agents. In this process, p-electrons are removed from conjugated double bonds and positive hole or radical cation is created. The radical cation is called 'polaron' which stabilizes itself by polarising the medium. The positive holes (polaron) are mobile (delocalised) and this delocalisation of positively charged holes is responsible for the conduction of current in the polymers. The p-doping is generally brought by adding Lewis acids (such as $FeCl_3$), iodine, bromine arsenic penta-fluoride (AsF_5) etc.



role

(ii) *Reduction process (n-doping)*: In this type of doping some electrons are introduced into the polymer by reducing agent like sodium naphthalide or by adding Lewis base (electron donor). The movement of negative charges in n-doped polypyrrole is shown in Fig. 3.9

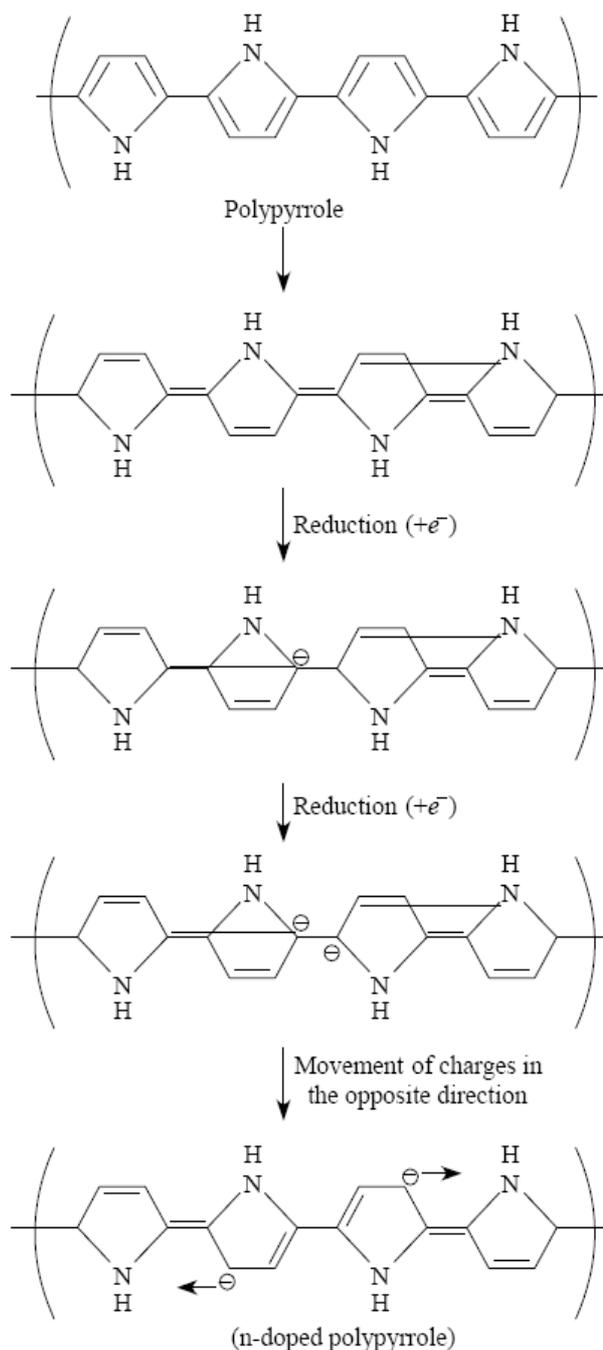


Fig. 3.9 Propagation of negative charges in n-doped polypyrrole

The n-doping is less common because on earth, atmosphere is oxygen rich, which creates an oxidising environment. An electron rich 'n-doped' polymer will react immediately with oxygen and converts into the neutral state by re-oxidising. Thus in the research field, electrochemical 'n-doping' is more common because it is easier to exclude oxygen from a solvent in a sealed flask. However there are likely no commercialized n-doped conducting polymers.

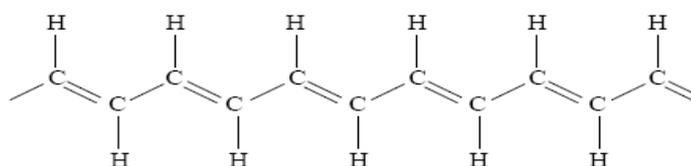
3. Blended Conducting Polymers: These are the polymers, which are obtained by mixing a non-conducting polymer with a conduction polymer either by physically or chemically. These blended conducting polymers have better physical, chemical and

mechanical properties.

Iodine and bromine used as dopant produce high conductivities but they are unstable and slowly evaporate from the material while organic acids, including trifluoroacetic acid, propionic acids and sulphonic acids produce doped conducting polymer with lower conductivities than iodine but with higher environmental stabilities. The structure and conductivity of some conducting polymers are given with doping materials.

9) How poly acetylene behaves as a conducting polymer? Give mechanism?

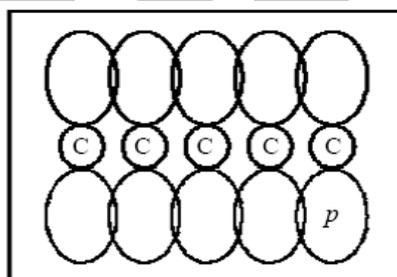
The conjugated polymer with the simplest chemical structure is poly acetylene.



Polymerisation of acetylene over Ziegler Natta catalysts give poly acetylene which in its form with inhaling temperature it gets transformed to more stable trans form. This polymer is infusible, insoluble and become brittle on exposure to air. The conductivity of poly acetylene is magnified by doping. Exposure of the film to dry ammonia gives a polymer with conductivity of 10^3 s cm^{-1} . Controlled addition of p-doping agents like AgF_5 , Br_2 , I_2 or HClO_4 could to still higher conductivities.

Conducting Mechanism in Poly Acetylene

The semi-conducting poly acetylene $(\text{CH}_2)_n$ has a typical carbon-carbon back structure.



The localized e's in 's' bonds form the backbone of the polymer chain and dominate the medicinal properties, while the electrons in the p bonds are delocalized along the chain and responsible for the electrical and optical properties of a conjugated polymer.

The s bonds form completely filled low lying energy bands that have larger energy gap than the p bond electrons.

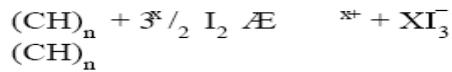
Before passing current, the electrons can flow along the molecule, one or more electrons have to be removed or inserted.

In presence of an electric field, the electrons constituting p-bonds can move along the molecular chain. The conductivity of the polymeric material, containing many chains of polymers will be limited by the fact that the e's have to jump from one molecule to the next. Hence the chains have to be packed in ordered row

10) Write an account on P-doping and n-doping with reference to poly acetylene? p-doping of Poly Acetylene

Poly acetylene possess alternate single and double bonds that give rise to mobile p-electrons when doped fig. become anisotropic metallic conductors. There are two types of doping oxidation or reduction. Ex.

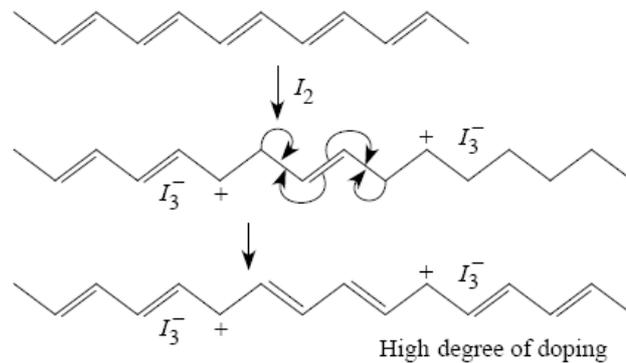
1. Oxidation with halogen – (p-doping)



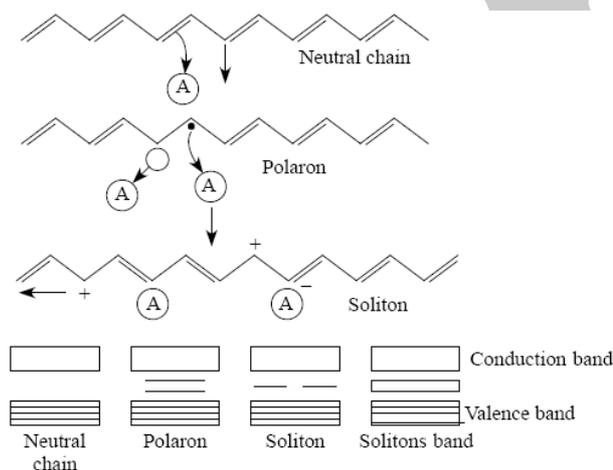
2. Reduction with alkali metal – (n-doping)



In reaction 1, the iodine molecules attracts an e^{-} from poly acetylene chain and becomes I_3^{-} . Now the poly acetylene becomes positively charged and termed as radical cation or polar on. The polarons on doping form solitons.

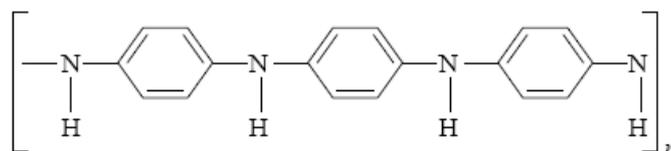


The solitons are responsible for the transport of charges along the polymer chains as well as from chain to chain on a macroscopic scale. The mobile solitons which enable spinless conductivity are unique to poly acetylene.



11). What is Poly Aniline? How is prepared?

Among the conducting polymers, poly aniline posses unique properties.



Poly aniline is a conjugated polymer and is reactive. Poly aniline is considered as an organic metal. Its specific conductivity is 55 cm^{-1} . Poly aniline is transparent in thin layers. It is stable in an. In conducting state it is green. It turns red under reducing conditions and blue under oxidizing or basic ones.

Poly aniline is a stable conducting polymer. It has a wide range of conductivity.

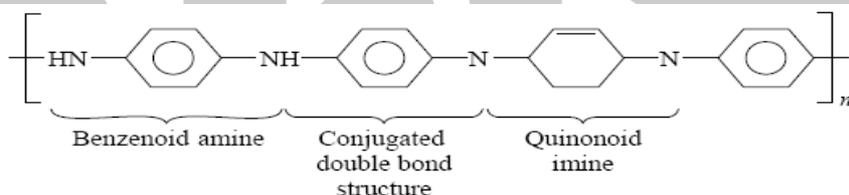
It shows multi colour electrochromism and chemical sensitivity.

It can be synthesized chemically (or) electrochemically as a bulk powder or film

Disadvantages

Poly Aniline

It is one of the oldest conductive polymers known. It was prepared by the anodic oxidation of aniline in H_2SO_4 . Its conductivity is due to the conjugated p-bond system formed by the overlapping of carbon p-orbitals and alternating C-C bond lengths extending over a large number of recurring monomer units. In poly aniline p-orbitals of nitrogen and carbon rings are also part of the conjugated system.



Conjugated double bonds permit the electron to move through out the molecule due to delocalized electrons.

In addition, it has a conjugated double bond structure between the benzenoid ring and the quinonoid imine structure.

Preparation of Poly Aniline

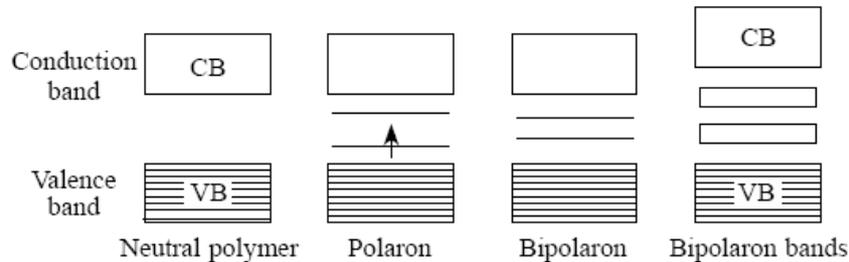
Poly aniline is prepared by the redox polymerization of aniline in protonic and aqueous solution in the presence of ammonium persulfate as oxidant or electrochemically. It can be regarded as a conducting polymer under certain stimulating conditions like UV light, heat or addition of a suitable dopant to the polymer.

Therefore, $s = n$.

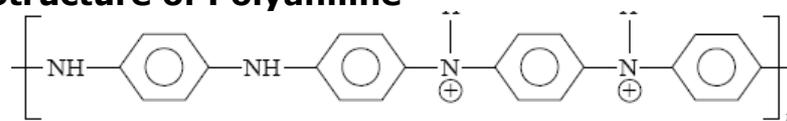
Properties of Poly Aniline

Due to the presence of extended p-bond system of conjugated polymers, it is highly susceptible to chemical and electrochemical oxidation or reduction. As a result the electrical and optical properties of the polymer are altered.

Electronically conducting polymers are extensively conjugated molecules and possess specially delocalized band line structure



Bipolaron Structure of Polyaniline



Dis advantages:

- (1) poly aniline decomposes prior to melting. Hence the difficult to process.
- (2) It is insoluble in common solvents except strong acids and N-methyl-2-pyrrolidone.
- (3) It has poor mechanical properties.

12) Write about engineering applications of poly aniline?

Applications

1. Poly aniline is used for corrosion, protection, sensors, smart windows, printed circuit boards, conductive fabrics and conductive pipes for explosives.
2. Poly aniline is used for coating of films and semi finished articles.
3. it is used as a secondary electrode in rechargeable batteries and electrochromic display devices due to its reversible electrochemical response during anodic oxidation and cathodic reduction.
4. Injection moulded products with poly aniline used to produce dispersion paints which are transparent and permanently antistatic.

13) Give an account on the Engineering Applications of Conducting Polymers?

There are variety of applications of conducting polymers in many fields.

1. **Smart Windows:** Smart windows are the windows which change colour in response to sunlight or temperature changes. The smart windows are made of two glass panes which are laminated together with a conducting polymer foil. The glass panes are coated with an electrochromic film. The conducting polymers which used in smart window are polyaniline, polythiophene etc.
2. **Light Emitting Diodes (LED):** Many outstanding properties of organic conducting polymers compared to inorganic semiconductor, create new business opportunities in

wide range of electronic devices such as transistors, light emitting diodes etc. The conducting polymer which used in LED, in 'bulky *p*-conjugated' poly (phenylenevinylene).

3. **Rechargeable Batteries:** The conducting polymers are also used in re-chargeable dry cell battery which is cheap, safe and compact in comparison to the conventional dry cell. The conducting polymer based rechargeable batteries are highly useful for portable microelectronic devices and house- hold appliances such as radio, transistors, tape-recorders etc.
4. The conducting polymers are used in lasers, flat television and solar cells.
2. These are also used in electroluminescence displays like in mobile phones etc.

MULTIPLE-CHOICE QUESTIONS

1. Natural rubber is
■ (a) poly isoprene (b) nitrocellulose
(c) polyethylene (d) bakelite
2. The repeating unit of PVC is
(a) ethylene (b) tetra chloroethylene
(c) acrylonitrile (d) vinyl chloride
3. Which of the following contains isoprene units?
(a) natural rubber (b) nylon-66
(c) dacron (d) polyethylene
4. Nylon is a
(a) vinyl polymer (b) polyamide
(c) polyester (d) chloroprene
5. Bakelite is made by the action of
(a) phenol and formaldehyde (b) melamine and formaldehyde
(c) urea and formaldehyde (d) ethylene and formaldehyde
6. Which of the following is a branched polymer?
(a) Low-density polythene (b) Polyester
(c) Nylon (d) PVC
7. Which of the following is a natural rubber?
(a) Polyester (b) Glyptal
(c) Starch (d) Nylon-6
8. Which of the following is a synthetic polymer?
(a) cellulose (b) PVC
(c) proteins (d) nucleosides
9. Heating of rubber with sulphur is known as
(a) galvanisation (b) bessemerisation
(c) vulcanisation (d) sulphonation
10. Buna-S is a polymer of
(a) butadiene (b) butadiene and styrene
(c) styrene (d) butadiene and chloroprene
11. Terylene is a

- (a) polyamide (b) polyethylene
 (c) polyvinyl chloride (d) polyester
12. Which one of the following is a thermosetting plastic?
 (a) PVC (b) PVA
 (c) bakelite (d) perspex
13. Polymer used in bullet-proof glass is
 (a) PMMA (b) lexan
 (c) nomex (d) kevlar
14. $F_2C = CF_2$ is a monomer of
 (a) teflon (b) glyptal
 (c) nylon-6 (d) buna-S
15. Soft drinks and baby-feeding bottles are generally made up of
 (a) polyester (b) polyurethane
 (c) polyamide (d) polystyrene
16. Which one is used to make 'non-stick' cookware?
 (a) PVC (b) polystyrene
 (c) poly(ethylene terephthalate) (d) polytetrafluoroethylene
17. Which of the following is not an example of addition polymer?
 (a) polystyrene (b) PVC
 (c) polypropylene (d) nylon
18. An example of branched polymer is
 (a) polyester (b) PVC
 (c) nylon (d) low-density polymer
19. Cellulose acetate is a
 (a) thermoplastic (b) thermosetting
 (c) both (d) none

Answers

1. (a) 2. (c) 3. (a) 4. (b) 5. (a) 6. (a) 7. (c) 8. (b) 9. (c)
 10. (b) 11. (d) 12. (c) 13. (b) 14. (a) 15. (c) 16. (d) 17.(d) 18. (d)
 19. (a)