GOKARAJU RANGARAJU INSTITUTE OF ENGINEERING & TECHNOLOGY

(*Autonomous Institute under JNTU, Hyderabad)*

UNIT – III POLYMERS

Introduction :

Polymers are giant molecules produced by the combination of smaller units(polymer is derived from Greek word(poly = many) and (mer= parts or units).

Hence polymer is giant molecule of high M.wt built up by linking together of a large no. of smaller molecules called monomers.

Nature is the first scientist to produce the polymers in tits "giant laboratory".

Ex: Evolution of earth by combination of elements like C, H, O & N.

- Protein is the polymer – synthesized by nature from methane, ethene, ammonia & CO_2
- Some natural polymers are wood, cotton, cellulose.
- Synthetic materials existing in form of polymer are plastics, fibers, gums, laminates, paints etc…

Some polymers have gone to the extent of replacing ailing hearts and other ones sensitive organs.

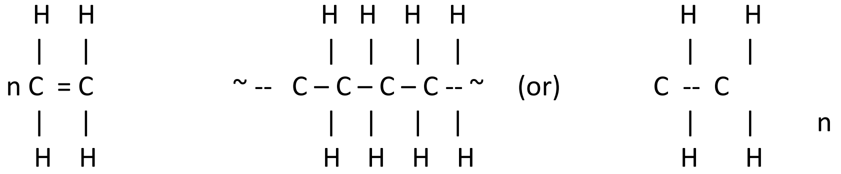
Polymers possess the desirable properties like high strength light wt., good flexibility, special electrical properties resistance t chemicals and fabrication into complex shapes in a wide variety of colors.

Naturally occurring macromolecules are cellulose, wood and rubber are very widely used in day today life.

Concept of polymerization :

The polymer (ie macromolecules) is the resulting structure comprises of repetition of relatively small molecular fragments referred to as repeating units.

Ex: polythene is made up of interlinking of ethylene



$$n\,\mathrm{H_2C{=}CH_2} \quad \sim\text{--}\,\mathrm{CH_2{-}CH_2{-}CH_2{-}CH_2}\,\text{--}\sim \quad \text{(or)} \quad \left[\mathrm{CH_2{-}CH_2}\right]_n$$

Ethylene monomer polyethylene Repeating unit

Depending upon degree of polymerization there are 2 types , Degree of polymerization of polythene is 100

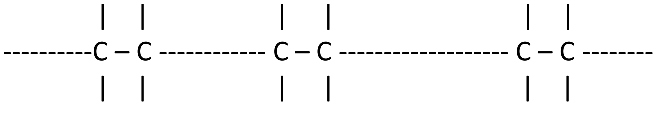
- Oligo polymers :- Polymers whose degree of polymerization is less than 600 are called oligo polymers.

  These do not posses engg. Properties.
- High Polymers :- Degree of polymerization of polymer is more than 600 they possess desired engg properties.

Functionality of Monomers :-

For a substance to act as a monomer, it must have at least two reactive sites or bonding sites. No of reactive or bonding sites in a monomer is called functionality

If x reactive sites are there in a monomer is bi functional – they form linear or straight chain molecules



$$\text{----------}\mathrm{C-C}\text{------------}\mathrm{C-C}\text{-------------------}\mathrm{C-C}\text{--------}$$

Vanderwalls forces of attraction

----------C – C ------------ C – C ------------------- C – C --------

| | | | | |

Strong covalent bond

.

A tri functional has 3 reactive sites then it forms a branched chain polymer

Covalent bond

|

------C --- C --- C ----------------- C --- C --- C ---------------- C --- C – C ---

------C --- C --- C ----------------- C --- C --- C ---------------- C --- C – C ---

------C --- C --- C ----------------- C --- C --- C ---------------- C --- C – C ---

Tri functional monomer

Formation of 3 dimensional network polymer

<u>Nomenclature of polymers</u> :-

- Polymer consists of identical monomers (or) monomers of diff. chemical Structure and they are called homo polymers and copolymers.

----M – M – M – M – M -------

Homo polymer (linear)

--- M_1—M_2 –M_1 – M_2 –M_1 –M_2 --

copolymer (linear)

|

M_2

|

M_1

|

----M – M – M – M – M -------

--- M_1—M_2 –M_1 – M_2 –M_1 –

Branching of same monomer

|

M

|

M

|

|

M_1

|

M_2

|

Branching of co monomers

Monomer Unit

----M – M – M – M – M -- M – M – M – M – M

| cross line |

M M

| |

(Graft Co-Polymer)

```
----M – M – M – M – M -- M – M –
         |                   |
         M                   M        Cross line
         |                   |
         M                   M
         |                   |
----M – M – M – M – M -- M – M – M --
  (strong & tough)          Cross linear homo polymer
```

The arrangement of co-polymers are arranged regularly, irregularly and alternatively

M_1—M_1 –M_2 – M_1 –M_1 –M_2 – M_1 –M_1 Soft and flexible (regular st arrangement)

M_1—M_2 –M_1 – M_1 –M_2 –M_1 – (soft & flexible st copolymer (arranged irregular)

M_1—M_2 –M_1 – M_2 –M_1 –M_2 – M_1 –M_2 (Alternate copolymer (soft & flexible)

Q) How are synthetic high polymers classified? (2010-R)

Classification of polymers :

Plastics
(property of plasticity
Fibers
(Drawn in form of filaments)
Ex: polyester Nylon
Rubber
(property of elasticity)
Ex: Buna –S, butyl rubber
Thermoset plastics
Ex: bakelite
Thermoplastics
Ex: polyethylene
Organic polymers backbone is C
Inorganic polymers (backbone of chain is made up of B,S, P, O, N & fi)
Ex: Polysulphurnitride
Elements organic polymers (combination of or. & inorg. Polymers
Ex: silicones
Organic polymers (backbone of polymer
Inorganic polymers (backbone of polymer is made of elements other than (like B, S, P, O, N & fi)
Synthetic
Natural
Polymers
mers

Rubber
(property of elasticity) Ex: Buna –S, butyl rubber (property of plasiticity

Polymerisation

Chain (or)Addition Polymerisation Step (or condensation polymerization.

Free Radical Ionic Co-ordination.

Cactionic
Chain polymerization

Anionic chain
polymerization.

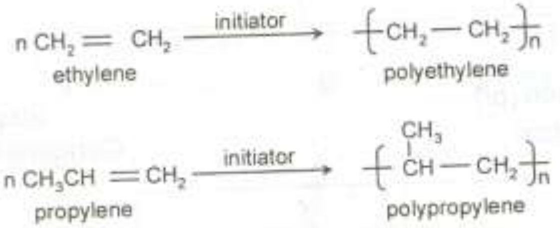
- Addition (or) chain Polymerization : -

Is a reaction that yields a product which is an exact multiple of the original monomeric molecule.

- It contains (or) more double bonds and it is bi functional.
- It must be initiated by light, Heat, Pressure (or) a catalyst for breaking down double covalent bonds of a monomer.

  Ex: Olefines, Vinyl compounds, Allyl and dienes.

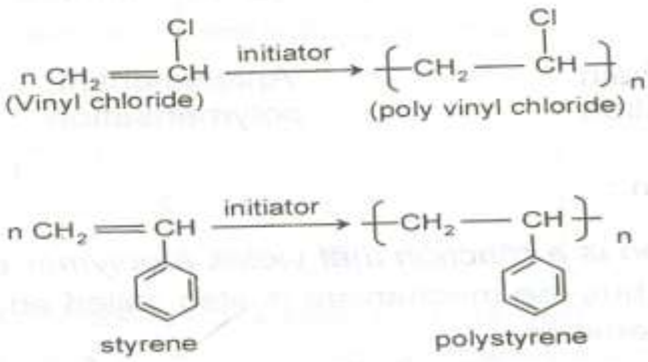
- Olefines:-



$$n\,CH_2{=}CH_2 \xrightarrow{\text{initiator}} \left[CH_2-CH_2 \right]_n$$

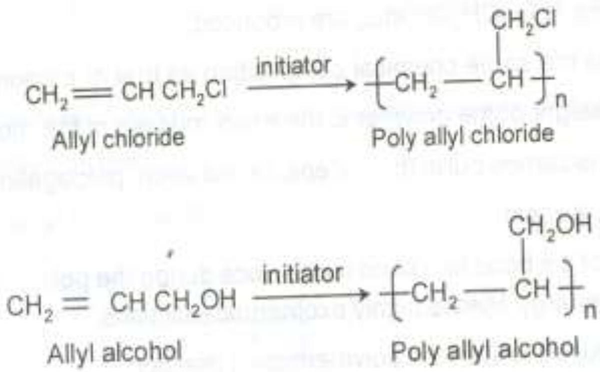
$$n\,CH_3CH{=}CH_2 \xrightarrow{\text{initiator}} \left[\overset{CH_3}{\underset{}{CH}}-CH_2 \right]_n$$

- Vinylcompounds:-



$$n\,CH_2{=}\overset{Cl}{CH} \xrightarrow{\text{initiator}} \left[CH_2-\overset{Cl}{CH} \right]_n$$

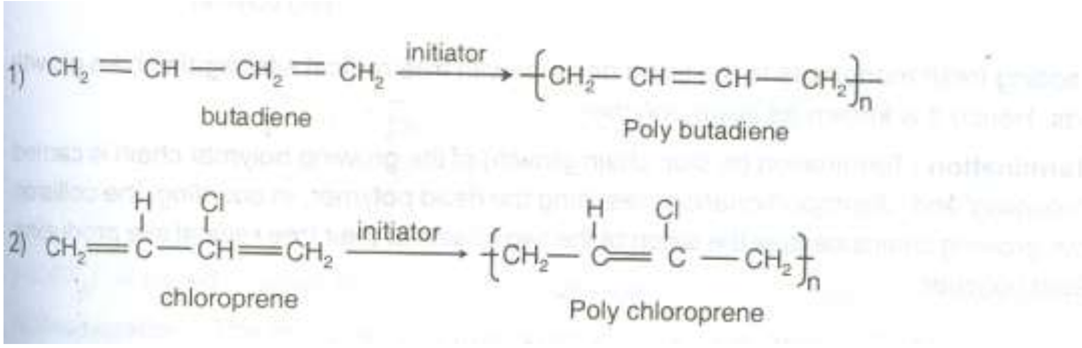
- Allyl compounds:-



$$CH_2{=}CH\,CH_2Cl \xrightarrow{\text{initiator}} \left[CH_2-\overset{CH_2Cl}{CH} \right]_n$$

$$CH_2{=}CH\,CH_2OH \xrightarrow{\text{initiator}} \left[CH_2-\overset{CH_2OH}{CH} \right]_n$$

- Diene compounds:-

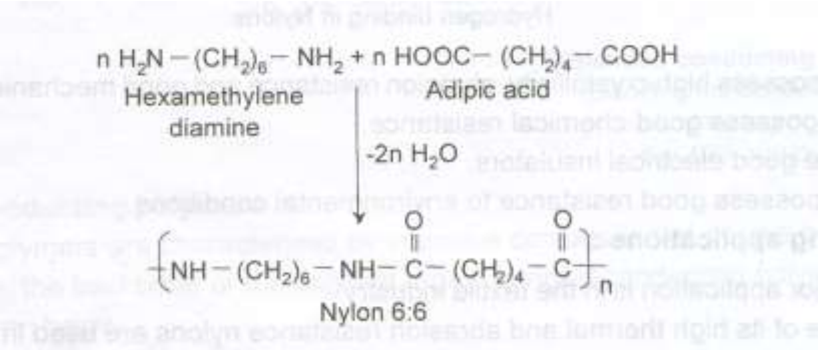


II. <u>condensation (or) step polymerisation</u> : -

It involves the reaction occuring b/w polar gps containing monomers with formation of polymer and elimination of small molecules like water, HC…

Ex: <u>Nylon 6:6</u> : -Hexamethylene diamine and adipic acid condense to from nylon 6:6

--NH_2 + -- C O O H -- NH --CO-- + H_2O
Polyamide



The types of functional groups, which are most important in condensation reactions are ,

--OH] + --COOH[-- OOC -- with elimination of H_2O

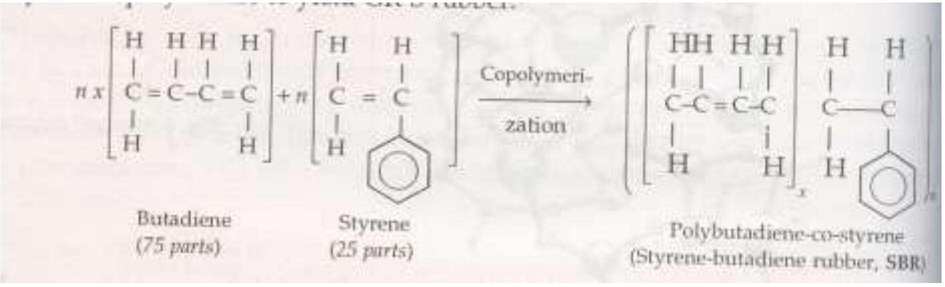
Ex: polyethylene terephthalate(terylene)

--NH_2 + -- C O O H -- NH --CO-- + H_2O
Polyamide

Ex: spandex fibre

III <u>copolymerization</u> : - (it is also addition polymerization high M.wt compounds obtained by copolymerization, are called copolymers.

2 diff. monomer units combine to form polymer



Polymerisztion like in addition and it requires special catalyst)

<u>Co – ordination Polymerisation (or) ziegler – Natta polymerization</u>

Ziegler & Natta proposed that presence of combination of transition metal halides like $TiCl_4$, $ZnBr_3$… with an organometallic compounds like $(C_2H_5)_3$ Al (or) $(CH_3)_3Al$ polymerization can be carried out. It explains the stereo specific type of polymerization.

Q) What is a plastic. Explain the differences between thermoset and thermoplastic materials. Give examples.

Plastics

Thermoplastic Resin , Thermosetting Resin

Plastics are polymers characterized by property of plasticity (permanent deformation in structure on applying some stress / force) and molded to desired shape upon subjected to heat and press in presence of catalyst.

Resin : - It's the product of polymerization and form the major part of plastics.

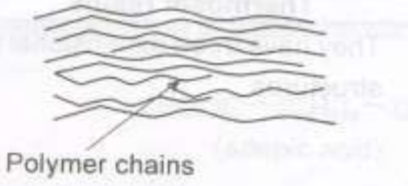
	Thermoplastic Resin	Thermoset Resins
1	They soften on heating readily	They do not soften on heating on prolong heating, they burn
2	Consists of long chain linear molecules	They have 3 –d network joined by strong covalent bonds
3	Formed by Addition polymerization	Condensation – polymerization
4	They are soft, weak & less brittle	They are hard, strong and more brittle
5	They can be reclaimed from wastes	Cant be reclaimed from wastes
6	Usually soluble in some org. solvents	Due to strong bonds & cross liking they are insoluble in all org. solvents

COMPOUNDING OF PLASTICS

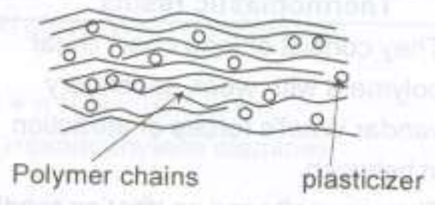
COMPOUNDING OF PLASTICS : - Polymer Resin is mixed with 4 to 10ingredients during fabrication to impart useful properties to the finished article, this is called compounding of plastics

- ***Resin*** : - it's a binder which holds the diff. constituents together. Thermoset resins are supplied as linear polymers of comparitively low M.wt. This is converted to cross linked infusable from during moulding.
- That are added to resins to increase their plasticity and flexibility.
- They neutralize the intermolecular forces of attraction b/w polymer chains.
- They impart greater freedom of movement b/w the polymeric molecules

2. ***Plasticizers*** decrease the strength and chemical resistance. commonly used plasticizers are vegetable oils, camphor, esters of stearicacid … tricresyl phosphate and trivinyl phosphate.



No plasticizer in a polymer



Plasticizer in a polymer

3.Fillers : -

- They are added to give final plastic better hardness, tensile strength, opacity and brittleness.
- They reduce cost of polymers
- Some special type of fillers are added to impart special properties to polymers like Ba salts make polymers impermeable to x-rays and Asbestos provides heat & Corrosion resistance to polymers

Percentage of fillers is upto 50% of total moulding mix commonly used fillers are wood flour, gypsum saw dust, marble flour, paper pulp , cotton fibres and metallic oxides like Zno & Pbo.

4.Lubricants ***: -*** *a.waxes oils stearates and soaps are employed to make the moulding of plastic easier*

b.They prevent plastic material from sticking to the fabrication equipment.

5.Calalysts or Accelerators :-

They accelerate the polymerization of fusible resin during molding operation into cross linked infusible form for thermosetting resins.

Commonly used catalysts for compounding of thermosetting resins are benzoyl peroxide, H_2O_2 acetyl H_2SO_4, metals like Ag, Cu & lead, metal oxide like Zno.

6.Stabilizers : -

__They improve thermal stability during polymerization.

- During moulding heat stabilizers are used

  Ex: opaque moulding compounds like salts of lead, lead chromate, litharge, red lead, lead silicate and lead naphthalene.

  Transparent molding compounds like stearates of lead, Cd and Ba.

- ***Colouring Materials*** ***:*** -
- Colouring is of high importance in high polymer articles.
- Colouring materials impart esthetic sense and appeal to plastics.
- Organic dyestuffs and opaque inorganic pigments are commonly used as colouring materials.

Summary of compounding of plastics

- Resin forms body of the plastics and binder for diff ingredients.

  Ex: Thermoplastic & Thermoset resin.
- Plasticizer gives plasticity and flexibility.

  Ex: Oils, water, tricresyl and triamyl compounds.
- Fillers | reinforced fillers give hardness, tensile strength, opacity, finish workability to plastics, reduces the cost.

  Ex: Ba salts, quartz, mica, ZnO, PbO, Al, Cu, Pb.
- Lubricants makes moulding easier fives flawless gloss finish to plastics.

  Ex: waxes, oils, stearates and oleates.
  - Catalysts | accelerators accelerates the cross linking of thermosetting resin.

  Ex: H_2O_2, Cu, Ag, Pb.
- Stabilizers increase thermal stability during fabrication

  Ex: Pb salts, Ca & Ba
- Colouring materials gives esthetic sense and appeal to plastics.

  Ex: organic dyes & opaque inorganic pigments

MOULDING OF PLASTICS INTO ARTICLES

To give suitable shape to plastic several methods of fabrications are in used.

The method chosen depend upon type of plastics (ie thermo or thermosetting plastics) and shape of finished product commonly used methods are given below.

Q) Explain different types of moulding techniques involved in preparation of plastics.(2008-R)

- Compression Moulding : -

Applicable to both thermoplastic and thermosetting resin. A known quantity of compounded plastic resin is filled in the cavity present in the cavity present in the bottom mould. Top mould and bottom mould are capable of being moved relative to each other when heat and press are applied according to specifications the cavities get filled with fluidized plastic.

The two mould (top & bottom in fig.) are closed tightly and curing (time given to polymer to set in the mould) is clone either by heating in case of thermoplastic resins or by cooling in case of thermoplastic resins

After curing the moulded article is taken out by opening the mould.

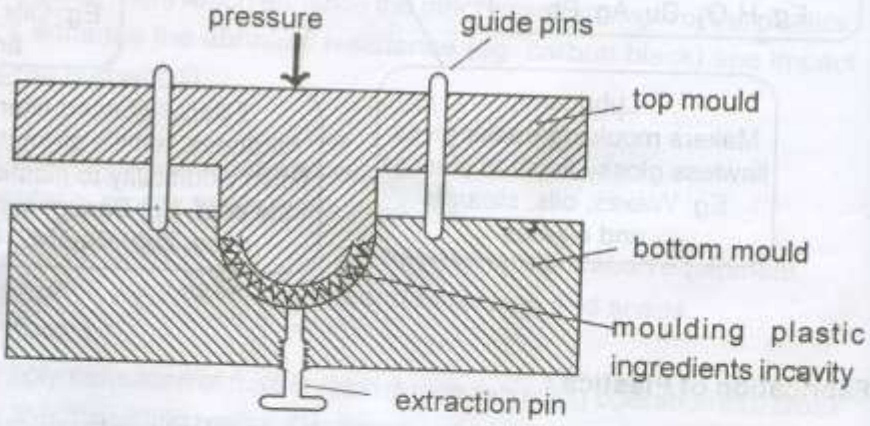


Fig. 3.2 Compressing moulding of plastics

USES : - used for manufacture of cylinders, gear handles.

- **INJECTION MOULDING** : - (Applicable to thermoplastic resins)

The moulding plastic powder is fed into heated cylinder from a hopper is fed into heated cylinder from where it is injected at a controlled rate into tightly locked mould by means of screw arrangement or by piston the mould is kept cold to allow hot plastic to cure and become rigid.

When material have been cured sufficiently half of the mould is opened to allow the injection of finished article without any deformation. Heating is done by oil or electricity.

Advantages : - Mainly useful for moulding of phno plastics because of high speed production, low mould cost, very low cost of material and low finished cost.

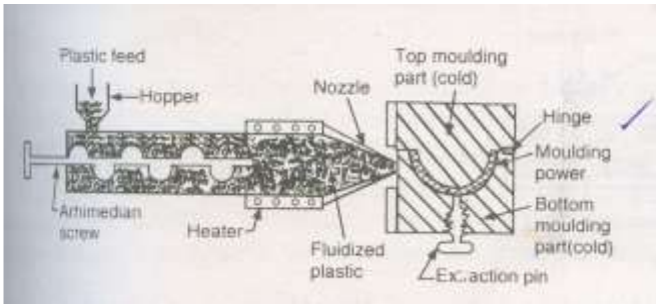


Fig. 18. Injection moulding of plastics.

Limitations : - large no. of cavities cant be filled simultaneously. So there is limitation of design articles to be moulded.

- **TRANSFER MOULDING** : - (for thermosetting Resins)

Moulding powder is placed in heated chamber maintained at min temp at which moulding powder just begins to become plastic material is injected through an orifice into the mould by a plunger working at high pressure.

Due to very great friction developed at the orifice, the temp of the material, at the time of injection from orifice, results such an extent that moulding powder becomes almost liquid and consequently, it flows quickly into the mould, which is being heated upto curing temp required for setting.

The moulded article is taken outside.

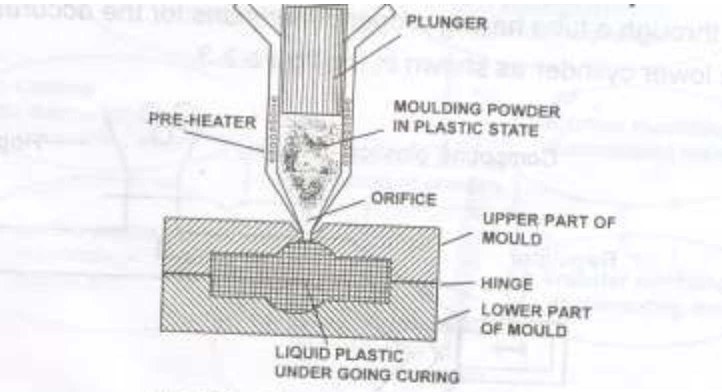


Fig. 3.4 : Transfer moulding of plastics

Advantages : -

- Plasticized mix flows very slowly into the mould very delicate articles with intricate shapes can be produced.
- Articles are free from flaw marks and thick pieces of article can be cured very slowly, completely and uniformly.
- Shrinkage and distortion are at minimum.
- Mould cost is less.

- **EXTRUSION MOULDING** : - (used for continuous moulding of Thermoplastic materials into articles of uniform cross section like tubes, rods, strips, insulated electric cables.)

The thermoplastic ingredients are heated to plastic condition and pushed by means of screw into die, having he required outer shape of the article to be fabricated.

The extruded article gets cooled due to atmospheric exposure or artificially by air jets or by water sprayer in a long convey or which carries a way the cooled product.

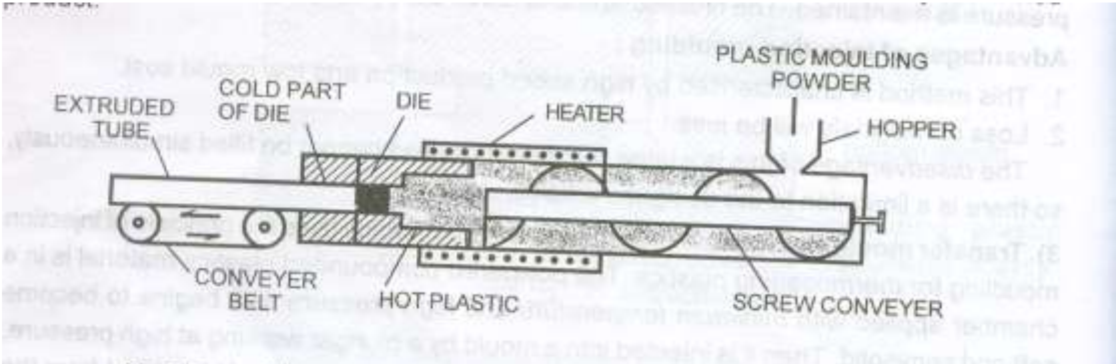


Fig. 3.5 : moulding of insulated electric cable by horizontal extrusion moulding

TEHRMOPLASTIC & THERMOSET RESINS

Q) Write the preparation properties and uses of LDPE and HDPE. (2010-R)

- **POLY ETHYLENE** : - $-- H_2C - CH_2 ---_n$

Polyethylene is commonly used polymer first produced by imperial chemical industries in 1933 by polymerizing ethylene monomer.

$$nH_2C = CH_2 \qquad --- CH_2 -- CH_2 ---_n$$

Preparation : -

- By hydrogenation of acetylene : -

$$HC = CH \xrightarrow{H_2\ |Pd} H_2C = CH_2$$

- By Dehydration of Ethanol : -

$$CH_3\ CH_2 - OH \xrightarrow[\text{catalyst}]{\text{Dehydration}} H_2C = CH_2 + H_2O$$

- By catalytic degradation or dehydrogenation of ethane.

$$H_3C -- CH_3 \xrightarrow[\text{catalyst}]{\text{Dehydrogenation}} H_2C = CH_2 + H_2 \uparrow$$

- From petroleum by cracking process :

Properties : - 1. It's a gas at room temp 2. Liquifies under high press (upto 1500 atm) and then pumped into a heated vessel maintaining of temp of 150 – 250^o C for chain polymerization.

Low density polyethylene : (0.092 gm/cc)

LDPE : is prepared by using free radical Initiator(benzoyl peroxide of 80 – 250^o temp)

$$nH_2C = CH_2 \xrightarrow[80 - 250^oC]{\text{Benzoyl peroxide}} ----------CH_2 - CH_2 ---_n$$

High density polyethylene (0.965 gm/cc)

HDPE :- prepared by using coordination chain polymerization mechanism.

$$nH_2C = CH_2 \xrightarrow[120^oC]{\text{Triethyl Al}} \underset{\text{HDPE}}{--- H_2C -- CH_2 ---_n}$$

Properties & uses : -

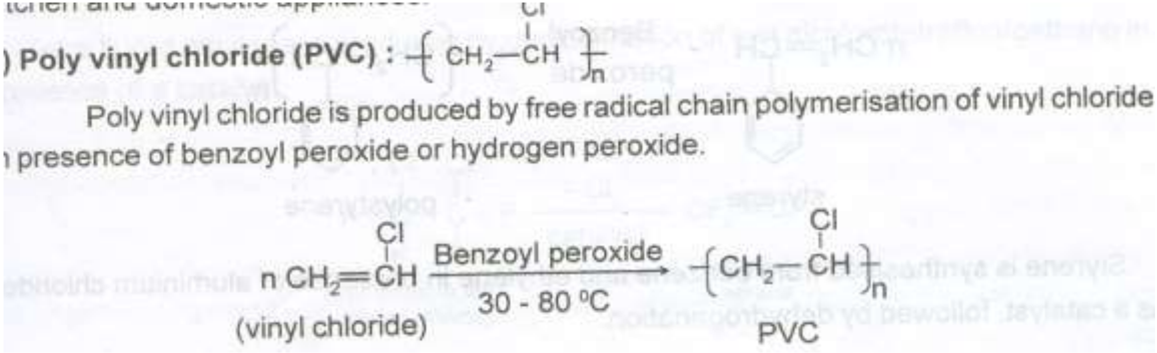
- Polyethylene is a rigid, waxy white, translucent, non – polar material with high symmetrical structure.
- Polyethylene is a good electrical insulator.
- Resistant to strong acids, alkalis and salt solution at room temp.
- Its soft flexible polymer
- Resistant to atmospheric conditions like O_2, CO_2, moisture.
- LDPE possess branched chain structure and its M.P is 81^{o}C
- HDPE has MP 144 - 150^{o}C it has higher tensile strength and hardness with less gas permeability

Engineering Applications:-

Polyethylene used for making high frequency insulator parts, bottle caps, packing materials, tubes, coated wires, in chemical plants for kitchen and domestic appliances.

Q) Mention the properties and uses of PVC. (2008-R)

- **Poly vinyl chloride:-**



tchen and domestic appliances.

) Poly vinyl chloride (PVC) : $-\!\!\left[\mathrm{CH_2{-}CH(Cl)}\right]_n\!\!-$

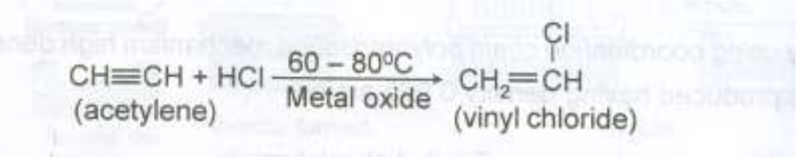
Poly vinyl chloride is produced by free radical chain polymerisation of vinyl chloride

presence of benzoyl peroxide or hydrogen peroxide.

$$\underset{\text{(vinyl chloride)}}{n\,\mathrm{CH_2{=}CH(Cl)}} \xrightarrow[30\,-\,80\,^{\circ}\mathrm{C}]{\text{Benzoyl peroxide}} \underset{\text{PVC}}{\left[\mathrm{CH_2{-}CH(Cl)}\right]_n}$$

Vinyl chloride is prepared by treating acetylene with HCl at 60-80°

In presence of metal oxide catalyst.



$$\underset{\text{(acetylene)}}{\mathrm{CH{\equiv}CH}} + \mathrm{HCl} \xrightarrow[\text{Metal oxide}]{60-80^{\circ}\mathrm{C}} \underset{\text{(vinyl chloride)}}{\mathrm{CH_2{=}CH(Cl)}}$$

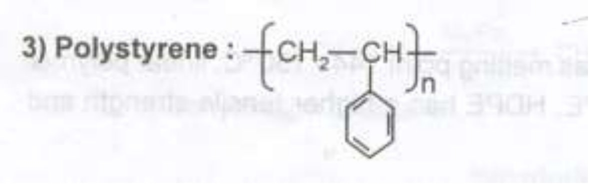
PROPERTIES: PVC is colourless, odourless, non inflammable and chemically inert powder. Pure resin posses greater stiffness and rigidity compared to poly ethylene.

It is brittle in nature.

Engineering applications:-

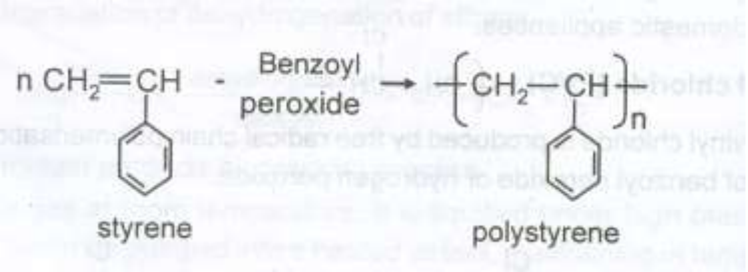
1. Used for electrical insulations.
2. Injection moulding articles like tool handles ,radio and telephone components.

- Used for making safety helmets, refrigerator components,tyres
- and motor cycle mudguards.



3) Polystyrene :

It is produced by free radical chain polymerization of styrene in presence of Benzoyl peroxide as an initiator.



styrene

polystyrene

PROPERTIES: Polystyrene is transparent, light – stable, excellent moisture resistant.

It is highly electric insulatingand highly resistant to acids.

It is brittle in nature.

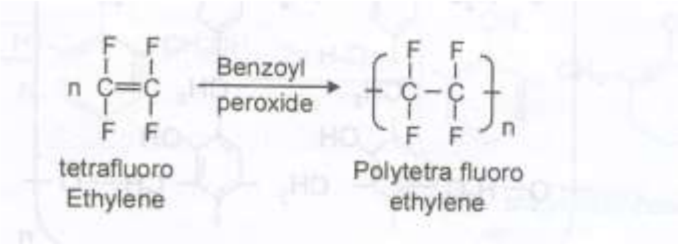
It has unique property of transmitting light through curved sections.

Engineering applications:-

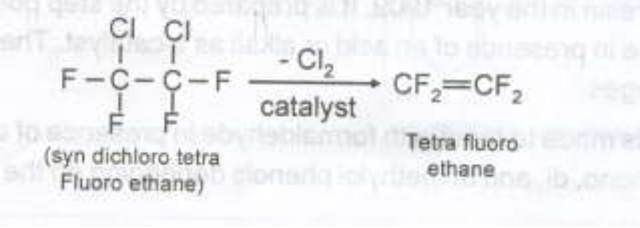
- It is used for moulding of radio and television parts, refrigerator parts.
- Used in high frequency electrical insulators , lenses and battery cases

4.TEFLON(Poly tetra fluoro ethylene) or Fluon:-

It is obtained by chain polymerisation of tetra fluoro ethylene in presence of benzoyl peroxide as an initiator.



Tetra fluoro ethylene is produced by dichloro tetrafluoroethane in presence of catalyst.



PROPERTIES: Due to presence of highly electronegative fluorine atoms results strong attractive forces between different chains gives the material extreme toughness high softening point and chemical resistant.

Engineering applications:-

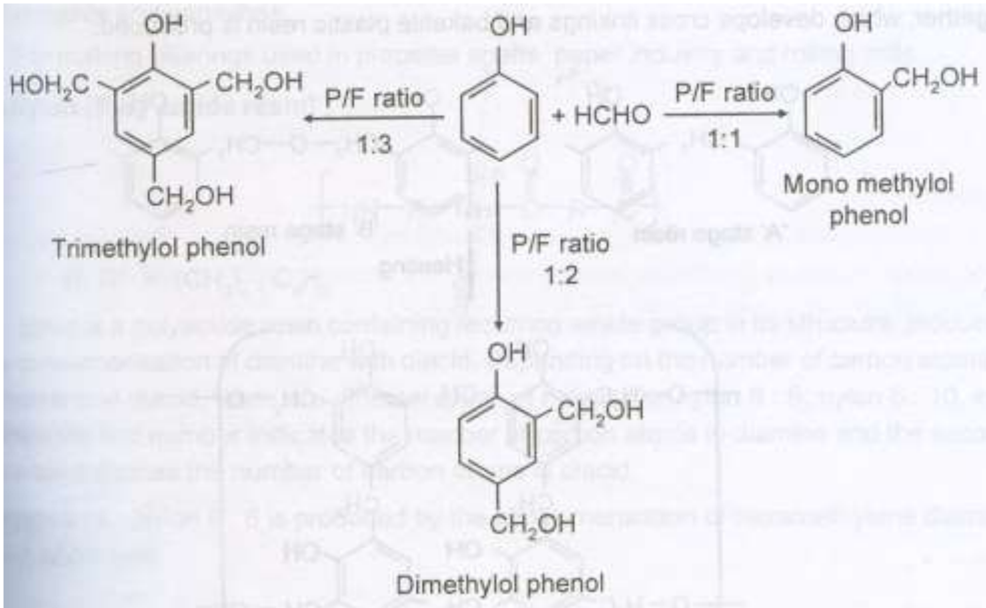
- It is a very good insulator insulating material for motors cables wires…
- Used for making gaskets , pumps, tank linings…
- Non lubricating bearings and nonstick stop cock for burettes are made up of TEFLON.

4. As an adhesive (binder) for grinding wheels etc.
5. In paints and varnishes.
6. For making bearings used in propeller shafts, paper industry and rolling mills.

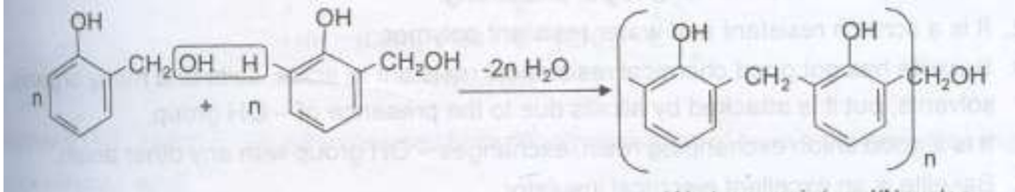
Q) Explin the preparation properties and uses of Bakelite.

5.BAKELITE:-(Phenol-formaldehyde resin). This belongs to thermoset resin.

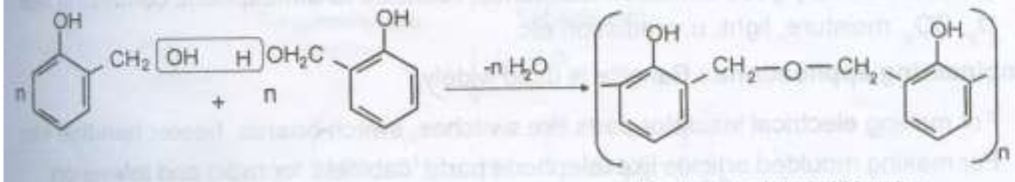
Phenol reacts with formaldehyde in presence of acid or alkali produces mono di and tri Methylol phenols depending on phenol formaldehyde ratio.



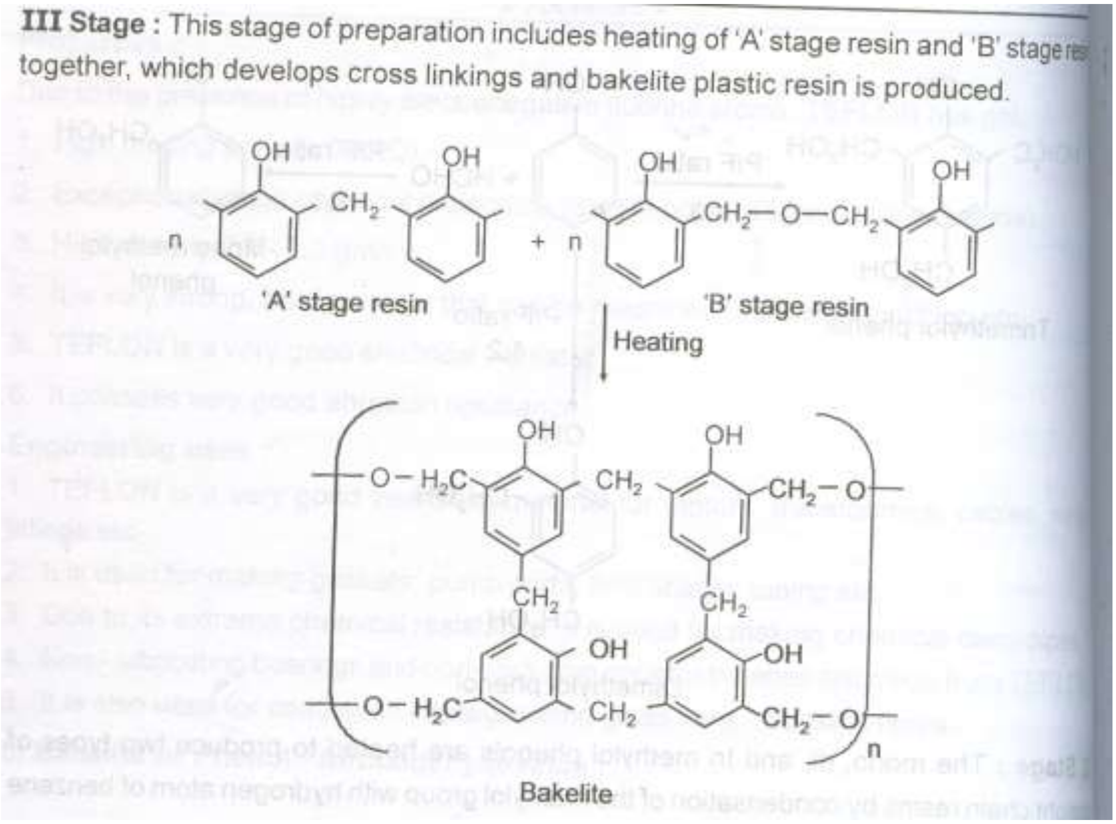
II Stage : The mono, di, and tri methylol phenols are heated to produce two types of straight chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.



'A' stage resin/resol/Novolac



'B' stage resin/resol/Novolac



III Stage : This stage of preparation includes heating of 'A' stage resin and 'B' stage res together, which develops cross linkings and bakelite plastic resin is produced.

Properties: phenolic resins set to rigid ,hard, scratch resistant, water resistant, insoluble solids, which are resistant to non oxidizing acids and many organic solvents.

Engineering applications:- a. *for making electric insulator parts like switches, plugs, switch boards etc…*

b. for moulding articles like telephone parts,cabinets for radio and television.

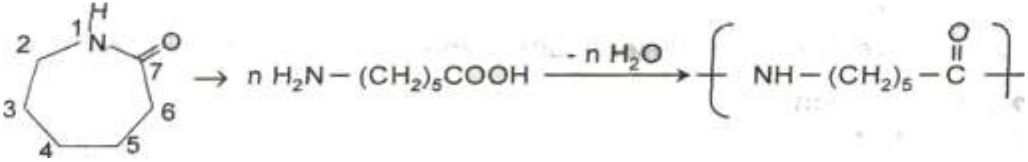
c. as adhesives for grinding wheels.

d. for making bearings,used in propeller shafts for paper industry and rolling mills.

Q) Write 4 examples of condensation polymers. (Or)

Write preparation properties and uses of nylon.

Nylon 6 : Nylon 6 is produced by the homo polymerization *of caprolactum.*



caprolactum

n H_2N — $(CH_2)_6$— NH_2 + n HOOC- $(CH_2)_4$- COOH
Hexamethylene Adipic acid
Diamine

-2n H_2O
O O

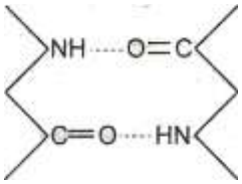
NH - $(CH_2)_6$ - NH- C- $(CH_2)_4$- C-
n

Nylon 6:6

Properties :

- Nylons possess high strength, hardness and high melting point. The high melting point of the nylons is due to the hydrogen bonding between the hydrogen atom of the amide group (-NH) and oxygen the C = O group.

C=0…..HN



Hydrogen binding in Nylons

- Nylons possess high crystallinity, abrasion resistance and good mechanical properties
- Nylons possess good chemical resistance,
- They are good electrical insulators.
- Nylons possess good resistance to environmental conditions.

Engineering applications :

- The major application is in the textile industry.
- Because of its high thermal and abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there
- Flexible tubings for conveying petrol etc are made from nylons.
- Nylons are used as electrical insulators.
- Nylon 6 is used for making tire cords.
- Nylons are used in auto mobile industry and telecommunication industry for making radiator parts and coil formers respectively.

Q) What are conducting polymers. Write their applications and uses.

3.6 CONDUCTING POLYMERS: Those polymers which conduct electricity are called *conducting polymers.* The conduction of the polymers may be due to unsaturation or due to the presence of externally added ingredients in them. The conducting polymers can be classified in the following way.

Conducting polymers

Intrinsic Conducting polymers

Extrinsic Conducting polymers

(conjugation due to presence of **(Due to externally added reagents)**

Double bond)

Intrinsic polymer with conjugation **Doped** Conducting polymers

Conductivity element **Blended Conducting polymers**

(Eg: Carbon black in polymers) **(Eg:- 40% polypyrrole)**

Intrinsic Conducting polymers: Due to presence of intrinsic conjugation of double bonds in their structure. It is classified into two types.

1 . Conducting polymers having **conjugation:**

polymers having **conjugative double bonds in backbone posses due to II electrons.**

Polymerization

n CH CH -------------------- CH = CH --------

acetyene **poly acetylene** **n** **trans poly acetylene**

2 . Doped Conducting polymers: Conducting polymers having II electrons can easily oxidize or reduce because of low ionization potential and high electron affinities. This can be done by 2 ways.

1 . p-doping (creating positive site on polymer backbone):-

It can be done by oxidation of conducting polymer like poly acetylene with lewis acid or iodine vapour. Also called as oxidative doping.

During oxidative doping removal of II electron from polymer backbone lead to formation of delocalized radical ion called as polar ion.

The second oxidation of polar ion results in two positive charge carriers called as bipolarion(dication).

$-e^-$ **+**

$+I_2$ -----------

CCl_4 **Polar ion(radical cation)**

+ **$-e^-$** **+**

+I_2 -----------

CCl_4 **+**

+e^- -2 .

------------->

n-doping:- It is carried out by reduction process by addition of electron to polymer backbone by using reducing agents like sodium naphthalide.

The electron added to polyacetylene by reductive doping causes bipolaron(dianion).The presence of electrons (holes) caused on the polymer backbone results the generation of conduction pathways. As a result conductivity increases**.**

$Na^+(C_{10}H_8)^-$ **Polar ion(radical cation)**

- **+e^-** **-** **-**

Extrinsically **Conducting polymers:-** (Due to externally added reagents).

Polymer acting as a binder to hold conducting element as carbon black, metallic fibres, metallic oxides… Minimum concentration of conducting filler is added so that polymer starts conducting.

APPLICATIONS:-

- The conducting polymers are used in rechargeable batteries.
- Used for making analytical sensors for pH ,O_2, SO_2, NH_3 and glucose.
- Used for electron beam lithography.
- They are applicable in photo voltaic cells.

ADVANTAGES:-Polymers posses good conductivity.

- They can store charge.
- They absorb visible light to give colored complex.

Nylon (Poly amide resin):

O O

HN— R— NH— C—R^l--- C

n

R, R' = $(CH_2)_n$, C_6H_5.

Nylon is a polyamide resin containing recurring amide group in its structure, produced by co polymerization of diamine with diacid. Depending on the number of carbon atoms in :!amine and diacid, there are different types of nylons like nylon 6 : 6, nylon 6:10, etc. where the first number indicates the number of carbon atoms in diamine and the second -umber indicates the number of carbon atoms in diacid.

Nylon 6 : 6 : Nylon 6 : 6 is produced by the co polymerization of hexamethylene diamine with adipic acid.n H_2N — $(CH_2)_6$— NH_2 + n HOOC- $(CH_2)_4$- COOH

Hexamethylene Adipic acid
Diamine

-2n H_2O

O O

NH - $(CH_2)_6$ - NH- C- $(CH_2)_4$- C-

n

Nylon 6:6

Nylon 6:10: Nylon 6:10 is synthesized from copolymerization of hexa methylene diamine with sebacic acid.

n H_2N — $(CH_2)_6$— NH_2 + n HOOC- $(CH_2)_8$- COOH
Hexamethylene Adipic acid
Diamine

-2n H_2O

O O

NH - $(CH_2)_6$ - NH- C- $(CH_2)_8$- C-

n

nylon 6:10

RUBBERS

- **INTRODUCTION**
- ***DEFINITION***
- *high polymers,which have elastic properties in excess of 300 percent*
- ***PROPERTIES***

posses elasticity i.e. they temporarily deform.

- ***STRUCTURE***

helix structure

HELIX STRUCTURE

WHAT HAPPENS TO THE STRUCTURE OF RUBBER WHEN IT IS STRECHED?

- *Since the structure of rubber is in helix form , not in a straight chain , when a stress is applied then the helix structure elongates into a straight chain . And on releasing the deforming stress , the chains get reverted back to their original helix or coiled state.*

STRAIGHT CHAIN OF RUBBER

NATURAL RUBBER

EXTRACTION: from cell sap or latex
= hevea brasiliensis
= guayule
= dichopsis percha\ palagum gutta

- **COMPOSITION**

main composition is polyisoprene.

Isoprene in natural rubber exists in two geometrical isomeric forms , cis and trans . Cis – polyisoprene is present in hevea rubber and trans – polyisoprene present in Gayule and percha rubber .

ISOPRENE UNIT OF NATURAL

RUBBER

COILED HELIX

STRUCTURE OF TRANS-POLYISOPRENE

STRUCTURE

OF CIS POLYISOPRENE

PROCESSING:

- ***NATURAL RUBBER FROM HEVEA BRASILIENSIS:***

1. CREPE RUBBER
2. SMOKED RUBBER

CREPE RUBBER

Latex from hevea brasiliensis.
diluted to 15%-20%
Filtered
Fed into rectangular tanks

Treated with acetic acid or formic acid and stirred
Inset vertical partition and allow for 16 hours
Rubber slabs
Passed between a series of rollers
Final roller giving ribbed-pattern sheet (3mm apart, 50cm wide)
Hanged in smoked chambers for 4 days
Crepe rubber

SMOKED RUBBER:

Latex from hevea brasiliensis
Diluted
Filtered (1m wide,30cm deep)
Treated with acetic acid and formic acid
Coagulation
Filtered
Coagulation (16 hours)
Washed with water (spraying)
Passed between two rollers(quick drying, preventing the adherence)
Rubber sheet
Dried in sun
Smoked rubber

PROCESSING OF GUTTA PERCHA:

Dichopsis gutta and palagum
Solvent extraction process
Grounded, heated with water 70c for half an hour and pour into cold water.
Floats on water
Extracted with carbon tetra chloride
Evaporated
Formation of sheets using rollers
Gutta percha has transpolyisoprene in its composition.

DISADVANTAGES:

Soft and plastic in nature
Brittle at low temperature
Swells in water
Easily attacked by organic solvents, acids, bases, non polar solvents like oils, benzene, gasoline
Poor Tensile strength
Atmospheric oxygen attacks the rubber and produces epoxides which gives a foul smell and sticking nature to the rubber.
Attack of carbon dioxide, moisture, light, u.v.radiation,
etc gives less durability.

EQUATION

Possess takiness
When a larger force is applied to stretch the rubber it gets permanent deformation because sliding or slippage of some molecular chains over each other
To improve the properties of rubber, CHARLES GOOD in 1839 compounded the raw rubber with some chemicals and heated to 100-140 degree C.

COMPOUNDING AND VULCANISATION

Q) Write a note on vulcanization. How can we improve the properties of rubber upon vulcanization.(2009-R) (2009-S)

COMPOUNDING AND VULCANISATION

1.vulcanisers
2.plasticizers
3.accelerators
4.anti oxidants
5.reinforcing agents
6.colouring agents

VULCANISERS:

CHEMICALS: SULPHUR , HYDROGEN SULPHIDE , SULPHUR DICHLORIDE , BENZOYL CHLORIDE AND ZINC OXIDE.

SULPHUR:

Combines chemically at the double bonds of different chains producing sulphur cross linking, imparting strength increases,the brittleness also increases.
Precentage : 0.5% - >35%.
Examples: tyres(3 to 5%), battery case (30%)
% of s >32% ebonite\vulcanite\hard rubber
Plasticizers:
(softners)
Great plasticity and Adhesion
Examples: vegetable Oil, waxes.

ACCELERATORS:

To Catalyse the process
Examples: litharge,magnesia and white lead
Percentage: 0.5 – 1%
zinc oxide(activator to accelerators)

ANTI OXIDANTS:

Retard the deterioration of rubber by light and air
Examples: complex organic amines : phenylnaphthylamine, phenolic substances and phosphites

REINFORCING AGENTS:

Gives strength, rigidity and toughness
Examples: ZnO,$MgCO_3$,$BaSO_4$, AND $CaCO_3$.

COLOURING AGENTS:

Lithophane,TiO_2 = white
Lead chromate = yellow
Caron black = black
Ferric oxide = red
Chromium trioxide = green
Ultra marine = blue

ADVANTAGES OF VULCANISATION:

Good tensile strength
Good elasticity depending on the extent of vulcanisation
Low water absorption tendency
High resistance to oxidation
Good electrical insulators (ebonite)
Abrasion resistance increases
Good impact resistance
Good resilience

PROPERTIES:

Strong and tough engineering material
Good resilience
Resistant
Abrasion resistant
Specific heat- 0.502
Density- 0.934
Rubber is heated with organic sulphonyl chloride or organic sulfonic acid at 130 ^{0} C it is converted into a thermoplastic resin known as thermoprene.
Rubber reacts with chlorine to give chlorinated rubber

APPLICATIONS OF NATURAL RUBBER:

Manufacture of tyres.
V belts for power transmission
Tanks lining in chemical plants
Reduce machine vibrations
Cushions, mattresses, paddings (foamed rubbers)
Toys and sports items (natural rubber)
Submarine cables, golf ball covers (gutta percha)
Synthetic rubbers or elastomers

BUTYL RUBBER:

GR-I
Produced by copolymerisation of isobutene + 1-5% of butadiene(anhydrous aluminium chloride in methyl chloride)

Properties:

Strong, tough, low permeability to air and other gases.
Excellent resistance to heat, abrasion, ageing, and chemicals such as inorganic solvents, polar solvents
Soluble in hydrocarbons solvents like benzene
Abrasion resistant
High resistant to atmospheric gases(ozone)
Good electrical insulator .

APPLICATION:

Cycle tyres, automobile parts and its tubes
Conveyor belt in food processing
Insulator for high voltage wires and cables
Tank lining

THIOKOL RUBBEER:

Polysulphide rubber or GRP
PERKINS english chemist
Thiokol rubber=(copolymerisation) sodium polysulphide+ethylene dichloride

PROPERTIES:

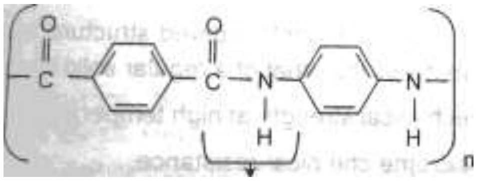
Strength, impermeable to gases
Cannot form hard rubber
Good resistance to mineral oils, fuels, oxygen, solvents, ozone and sunlight
Low abrasion resistance

APPLICATIONS:

fabric coated with thiokol used for barrage ballons, lift rafts and jackets which are inflated by carbondioxide.
Lining hoses for conveying gasoline and oil
Making gaskets and seals for printing rolls

LIQUID CRYSTAL POLYMERS(LCP)

Liquid crystals are materials that behave in some ways like solids and in some ways like liquids. The first known polymer liquid crystal solution was invented by Kwolek from a polyamide known as Kevlar .Its repeat unit had this following structure which forms very strong fibres.



N N

Amide group I

CH_3 CH_3

Tetra methyl Urea II

. When this polymer dissolved in tetramethyl urea(II) and calcium chloride, the polymer molecules behave strangely. The Kevlar molecules which were long, straight and stiff, lined up like logs floating down a river, because of the strange opalescent look of the solution .

Kevlar molecules lined up in solution normal Kevlar polymer solution

This is unusual because normally molecules in a solution or a pure liquid are not arranged in any orderly fashion. Molecules of solids materials are arranged in orderly fashion called crystals. Since Kevlar solution is a liquid, but its molecules are orderly arranged, the solution is called a liquid crystal. Liquid crystals can be classified into two types.

- **Lyotropic liquid crystasl polymers**: Liquid crystallinity in polymers may occur by dissolving a polymer in a solvent, which are called lyotropic liquid crystasl polymers Eg: Kevlar
- **Thermotropic liquid crystal polymers**:Liquid crystallinity in polymer may occur by heating a polymer above its glass transition temperature or melting transition point, which are called thermotropic liquid crystal polymers. Eg: Vectra having the following structure.

Properties of liquid crystal polymers:

- These polymers are capable of forming regions of highly ordered structure while in liquid phase. The degree of order is somewhat less than that of a regular solid crystal.
- The liquid crystal polymers have high mechanical strength at high temperatures.
- These liquid crystal polymers possess extreme chemical resistance.
- They possess inherent flame retardancy and good weatherability.
- They can be easily fabricated into a variety of forms.
- LCP can be welded. The lines created by welding are the weak points in the resulting product.
- LCP has high z- axis coefficient of thermal expansion.
- LCP resist stress cracking the presence of most chemicals at elevated temperatures.

Applications of LCP:

LCP are sometimes called 'super polymers'. Their wide range of exceptional properties and case of processing make them design for many demanding applications.

- LCP thermoplastic fibres possess exceptional strength and rigidity, suitable for industrial, electronic and also space applications as well as high performance ropes and tennis rackets.
- LCP finds extensive applications as coatings, composites and additives.
- The electrical motor components are made from LCP.
- LCP finds its applications in electronic industry as LED's and SMT components.
- LCP has an interesting application like information storage media.

FRP(Fibre Reinforced Plastic):-

They are produced by reinforcing plastic matrix with fibre materials such as glass graphite, alumina, C, B, Be and aromatic polyamide. Glass is drawn through threads or fibres in form of filaments. Then filaments are woven in form of mats. The fibre material is suitably bonded with plastics to be reinforced. The common plastic resins used are polyesters, epoxy, silicone…

T he various processing techniques involved are,

1 . Injection moulding:- Mix of short resins and fibres are forced by a screw into the mould and allowed to cure. This is for reinforced thermoplastics only.

2 . Matched metal dye moulding:- The moulding can be done under a temperature of 235-260^{o}F and 200-300 psi pressure. The upper mould containing resin and reinforcing fibre is pressed on lower mould.3 . Centrifugal casting:- Fibres and resins are placed inside a mandrel and is rotated inside a oven.

APPLICATIONS:-

- They find extensive use in space crafts, aeroplanes, boat nulls, acid storage tanks, motor cars and building materials.
- FRP is used for making baskets.

ADVANTAGES:-

- Low efficient of thermal expansion
- High dimensional stability.
- Low dielectric constant.
- Low cost of production.
- It is corrosion and chemical resistance.

Biodegradabe polymers: polymers are not attacked by environmental conditions including biological attack.polymers are degradaded by oxidation , u.v radiation etc..but not by bacteria.

Biodegradable polymers are defined as degradable polymer in which degradation results from the nature of naturally occurring microorganisms such as bacteria fungi and algae The biodegradable polymers may be naturally occurring or they may be synthesized to chemicals.

- Naturally occurring biodegradable polymers : they are classified into four groups.

Polysaccharides	proteins	polyesters	others
Ex: starch and Cellulose	Ex: gelatin,ceasin silk,wool.	Ex:polyhydroxy alkanoils.	Ex:lignin, shellac, Natural rubber.

Natural polymers are for environment degradation. The rate of degradation depends upon the structural complexity of material and environmental conditions.

Synthesisezed Biodegradabe polymers: polymers derived from petrochemicals or biological sources are biodegradable. They are used in dissolving suture material in medical field , and biopolyesters.because of their high prices new type of polymers were developed of chemicals derived from farming of particular crops, which laid foundation to new synthetic biodegradable polymers.

Exs: 1. Polyalkaline esters 2. Polylacticacid and its copolymers

- Polyamide esters 4.polyvinyl esters 5. Polyvinyl alcohol
  6.poly anhydrides

All the above biodegradable polymers posses particular properties and potential applications.

Applications: 1. biodegradable polymers are synthesized from the processing of crops or from petrochemical feed stock with normal or conventional processing methods.

- The compostable bags help in the disposal of vegetable matter being converted to CO_2 and CH_4.
- The problem of land fills by solid waste can be reduced.

Drawbacks: They are more expensive than the products manufactured from commodity resins.

BIO DEGRADABLE POLYMERS:

A variety of natural, synthetic, and biosynthetic polymers are bio and environmentally degradable. A polymer based on a C-C backbone tends to resist degradation, whereas heteroatom-containing polymer backbones confer biodegradability. Biodegradability can, therefore, be engineered into polymers by the judicious addition of chemical linkages such as anhydride, ester, or amide bonds, among others. The usual mechanism for degradation is by hydrolysis or enzymatic cleavage of the labile heteroatom bonds, resulting in a scission of the polymer backbone. Macro organisms can eat and, sometimes, digest polymers, and also initiate a mechanical, chemical, or enzymatic aging.1

Biodegradable polymers with hydrolysable chemical bonds are researched extensively for biomedical, pharmaceutical, agricultural, and packaging applications.2 In order to be used in medical devices and controlled-drug-release applications, the biodegradable polymer must be biocompatible and meet other criteria to be qualified as biomaterial-processable, sterilizable, and capable of controlled stability or degradation in response to biological conditions.3 The chemical nature of the degradation products, rather than of the polymer itself, often critically influences biocompatibility. Poly(esters) based on polylactide (PLA), polyglycolide (PGA), polycaprolactone (PCL), and their copolymers have been extensively employed as biomaterials.4,5 Degradation of these materials yields the corresponding hydroxy acids, making them safe for in vivo use.

Other bio- and environmentally degradable polymers include poly(hydroxyalkanoate)s of the PHB-PHV class, additional poly(ester)s, and natural polymers, particularly, modified poly(saccharide)s, e.g., starch, cellulose, and chitosan. Please refer to the Natural Polymers section for a list of available poly(saccharides).

- Naturally occurring biodegradable polymers: they are classified into 4 groups.
- Polysaccharides. Ex:starch and cellulose
- Proteins. Ex: gelatin, casein, silk and wool.
- Polyesters: Ex: polyhydroxy alkanoils.

- Others: Ex: lignin, shaellac, natural rubber.
- Synthesized biodegradable polymers: the polymers which are derived from petrochemical or biological source are biodegradable. The following are synthetic resins produced
- Polyalkaline esters.
- Polyacetic acid and its copolymers
- Polyamide esters
- Polyvinyl esters
- Polyvinyl alcohol
- Poly anhydrides

10.5.2. Bio-degradable polymers

In recent times the usage of synthetic polymers has been at assumingly high levels. With these polymers the recycling of the starting materials for their production has not been done as is the case with natural polymers. This is due to the inert nature of the synthetic polymers for biodegradation even after a long time. It is for this very reason that management of the polymers, waste has become so difficult that use of polymers has created acute environmental problems.

On the other hand, biopolymers degrade quickly in living systems by enzymatic chemical reactions like oxidation or hydrolysis. In view of the disposed problem of the polymer wastes and the necessity for developing such polymers for safe usage by human beings, the bio-degradable synthetic polymers have been developed. These polymers have functional groups that are mostly present in biopolymers and lipids.

One class of polymers, that are potentially commercial biomaterials, are aliphatic polyesters. For these polymers a few examples are described briefly in the following paragraphs.

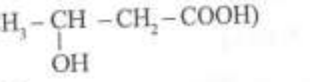
The condensation reaction between carboxylic acids and alcohols form esters. This principle was first utilized by Carothers to prepare polyesters and polyamides. When a dicarboxylic acid reacts with a dialcohol or a diol an ester is formed. The propagation of the esterification reaction results in a macromolecule known as polyester as shown below.

$$HOOC-R-COOH + HO-R'-OH \longrightarrow HOOC-R-COO-R'-OH + H_2O$$

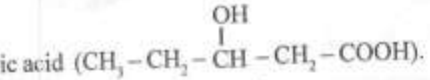
$$HOOC-R-COO-R'-OH + HOOC-R-COOH \longrightarrow$$
$$HOOC-R-COO-R'-OOC-R-COOH$$

Example : Dacron : Terelyne etc.

a. Poly β - hydroxybutyrate – Co – β – hydroxy valerate (PHBV)

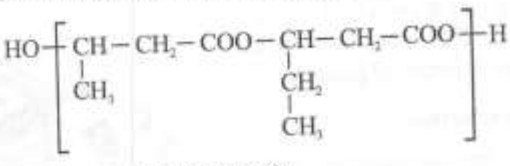


It is a copolymer of 3 - hydroxybutanoic acid $(CH_3-\underset{OH}{CH}-CH_2-COOH)$



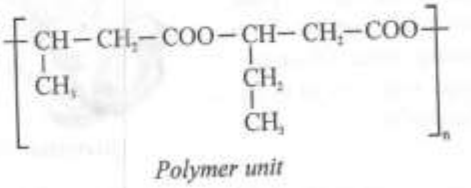
and 3 - hydroxy pentanoic acid $(CH_3-CH_2-\overset{OH}{CH}-CH_2-COOH)$.

The ester formed from these acids can be represented as



$$HO-\left[\underset{CH_3}{CH}-CH_2-COO-\underset{\underset{CH_3}{CH_2}}{CH}-CH_2-COO\right]-H \quad \text{and}$$

Monomer unit



$$\left[\underset{CH_3}{CH}-CH_2-COO-\underset{\underset{CH_3}{CH_2}}{CH}-CH_2-COO\right]_n$$

Polymer unit