MODULE – 1

Macromolecules for Engineering Applications

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Macromolecules for Engineering Applications

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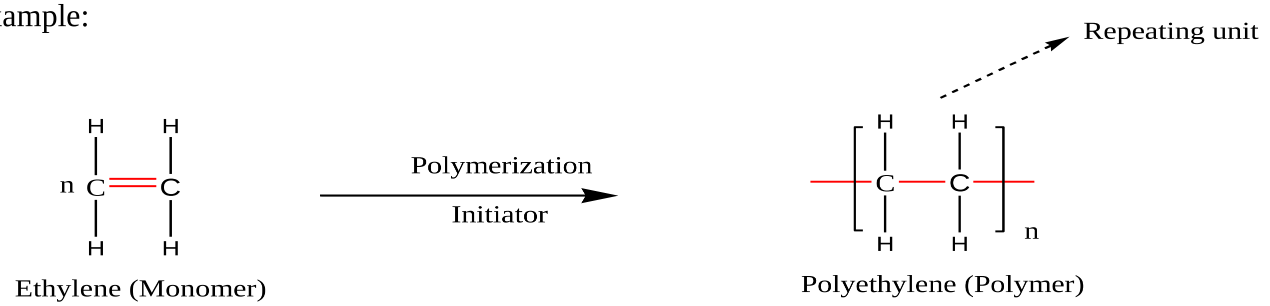
10 hours

Macromolecules for Engineering Applications

Macromolecules are very large molecules that are formed by the polymerization of smaller molecules called monomers.” Macromolecules are also termed as polymers.

The word polymer is derived from the Greek word: “poly” means ‘many’ and “mers” means ‘units/parts. Thus, polymer is a large molecule formed by repeated linking of small molecules called monomers.

Example:

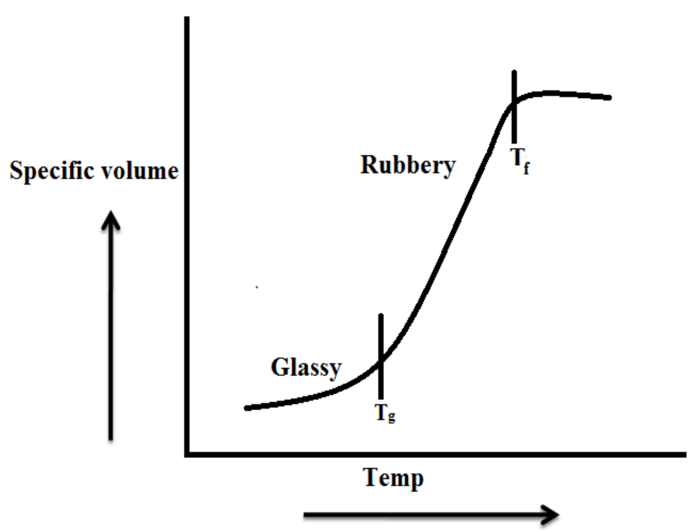


*The number of repeating units (n) present in chain is known as the “**Degree of polymerization**”.

[There may be thousands to lakhs of molecules (10^4 to 10^6)].

Glass transition temperature

All amorphous polymers, when cooled below a certain temperature become stiff, hard, brittle and glassy but above this temperature, they become soft, flexible, and rubbery. This transition temperature of a polymer is called glass transition temperature. It is denoted by Tg. The hard, brittle state is known as glassy state and the soft, flexible state as rubbery state.

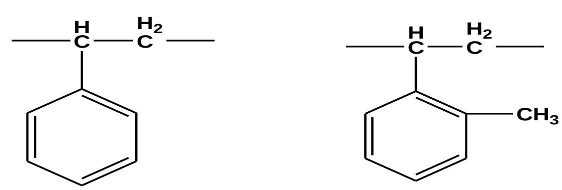


Factors influencing the Tg value

1. Crystallinity: The Tg value of a polymer largely depends on the degree of the crystallinity. Higher the crystallinity larger is the Tg value of a polymer. In crystalline polymer chains are lined up parallel to each other and are held by strong cohesive forces. This leads to a high Tg value of the polymer [Tg value for poly ethylene is -125^{0}C due to absence of cohesive force. On the other hand, Nylon-6 having similar structure has higher Tg value (50^{0}C). This is due to presence of strong cohesive forces].

2. Molecular weight: The Tg value of a polymer is also influenced by its molecular weight. The Tg value of all polymers, in general increases with molecular weight up to 20000 and beyond which the effect is negligible.

3.Effects of side groups: Poly methyl styrene has higher Tg value (170^{0}C) while polystyrene has lower Tg value (100^{0}C). The observed higher Tg value of poly methyl styrene is due to the presence of effective methyl side groups. This hinders the free rotation of the carbon-carbon bond of chain backbone and restricts the chain mobility and thereby increasing its Tg value.



Polystyrene Poly methyl styrene

Importance/Significances of Tg value

- Tg value is a measure of flexibility of polymers.
- The use of any polymer at any temperature is decided by its Tg value.
- Tg value along with Tm (polymer melting point) helps in choosing the right temperature for processing the polymer by different techniques.

Resins and plastics

Resins: Resins are linear, low molecular weight, soluble and fusible polymers. They are also called as pre-polymers or binding materials. The resins can be molded into products called plastics. Therefore plastics contain other ingredients along with resins

Example: Urea-formaldehyde resins, Phenolic resins, epoxy resins, etc.

Plastics: Plastics are high polymers which can be molded into any shape by the application of heat and pressure in the presence of catalyst. Example: Polyethylene, polystyrene, PVC, nylons etc.,

Compounding of resins to plastics

The process of mixing various additives into the polymer is called compounding of resins to plastic. The additives get incorporated into the polymer to give homogeneous mixture.

The functions of additives are as follows:

- To modify the properties of the polymer.
- To introduce new properties.
- To assist polymer processing.
- To make the polymer products more pleasing and colorful.

Compounding materials:

1. **Resins**
   The basic component of plastic is resin. It is a binder which holds different constituents together. Examples: Urea-formaldehyde resins, Phenolic resins, epoxy resins, etc.

2. **Fillers**
   These are added during the process of compounding for 2 reasons

I. To impart specific properties like tensile strength, thermal stability, electrical resistance, etc.
   Quartz and mica are added to provide extra hardness to the plastic.
   Asbestos is added to improve the thermal stability

II. Fillers are also added to reduce the final cost of the product. Examples: cotton, paper pulp, chain clay, sawdust, graphite, gypsum, waste fabric materials, etc. are added to reduce the cost of the product.

3. Plasticizers

These are added to the reaction mixture to increase the flexibility and plasticity of the product. The commercially used plasticizers are vegetable oil, non-edible oil, esters of stearic acid, phosphates, etc.

4. Stabilizers

These are added to improve thermal stability during processing. They avoid decoloring and decomposition. Examples: metallic anhydride, lead silicates, etc.

5. Accelerators- The polymerization reaction is very slow since it's a stepwise polymerization. In order to speed up the condensation polymerization reaction, Accelerators like ZnO_2, hydrogen peroxide, benzyl peroxide, etc are added

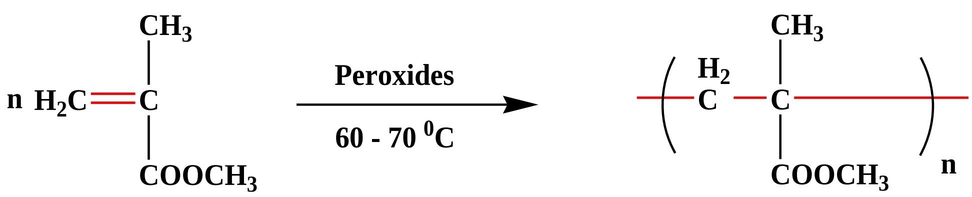
6. Colorant- The coloring agents are added to provide decorative color to the plastics.

Colour	**Compounds**
White	Barium sulfate, TiO_2
Black	Carbon black
Blue	Potassium ferrocyanide
Red	Fe_2O_3

Preparation, Properties and applications of some Synthetic polymers

PMMA (Poly **M**ethyl**M**eth **A**crylate**) or Plexi glass** (trade name)

PMMA is obtained by polymerization of methyl methacrylate in presence of peroxides.



Methyl methacrylate (MMA)

Poly methyl methacrylate (PMMA)

Properties:

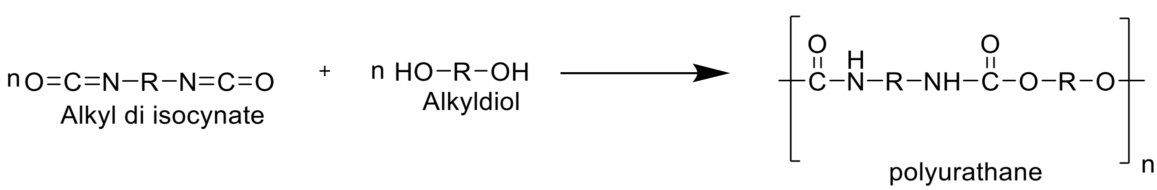
- PMMA is a white transparent thermo plastic.
- It is amorphous in nature due to bulky groups.
- It has excellent **optical clarity** which is not affected by sun light
- It has poor scratch resistant.
- It has low chemical resistance to hot acids and alkalis.

Uses:

It is used for making lenses, air craft windows, light fixtures, artificial eyes, artificial teeth, wind screens and used as paints, adhesives etc.,

POLYURETHANES (PU)

These are obtained by poly addition reaction between di-iso cyanate and diol.



Properties

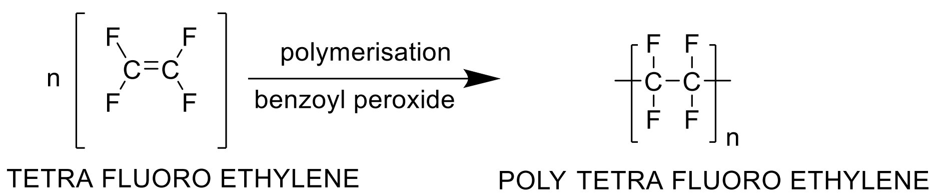
- It's a very **good flexible polymer**
- It is resistant to acids, alkalis, and many corrosive chemicals.
- They are flexible, resistant to oil and water

Uses

- It is used to coat the floor mats of the gymnasium.
- It is used to make tyres tubes, soles of slippers, shoes, etc.
- It is used in the manufacture of swimming suits.
- PU is used in cushion seats of furnishers, cars, etc

TEFLON (PTFE) POLY TETRA FLUORO ETHYLENE

Teflon is prepared by the polymerization of tetra fluoro ethylene in presence of benzoyl peroxide as a catalyst.



Properties

- Due to the presence of high electronegative fluorine atom they have very strong attraction between the different chains, this strong attraction force gives **extreme toughness**, high melting point (350 ^{0}C), and high chemical resistance towards all chemicals.
- Teflon has high thermal stability, mechanical strength, and excellent electrical insulating property.
- Teflon is insoluble in all most all solvents.

USES

- Teflon is used for insulation of motors, generators, transformers, cables, wires, capacitors, etc
- Teflon is used for making gaskets, pump parts, tank linings, chemical carrying pipes, household articles, etc,
- Teflon is an ideal lubricant because it stays slippery over a wide range of temperature (350 ^{0}C).

COMPOSITES

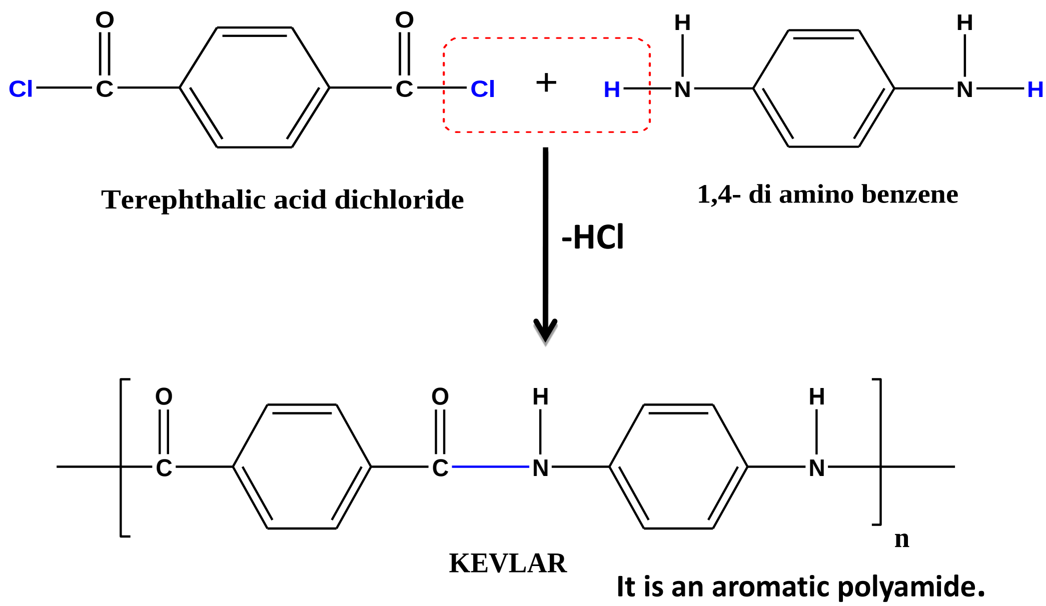
Composites: the combination of 2 or more distinct compounds to form a new class of material suitable for structural application is referred to as composite materials.

Generally made of two components, fiber is embedded in the matrix in order to make the matrix stronger

Fibers: fibers are those polymers whose chains are held by strong intermolecular forces like hydrogen bonding. They are crystalline in nature and have high tensile strength, due to strong intermolecular forces. Examples: Kevlar, polyesters, nylon, etc

KEVLAR

It is prepared by poly condensation between terephthalic acid dichloride and 1,4- di amino benzene.



Properties

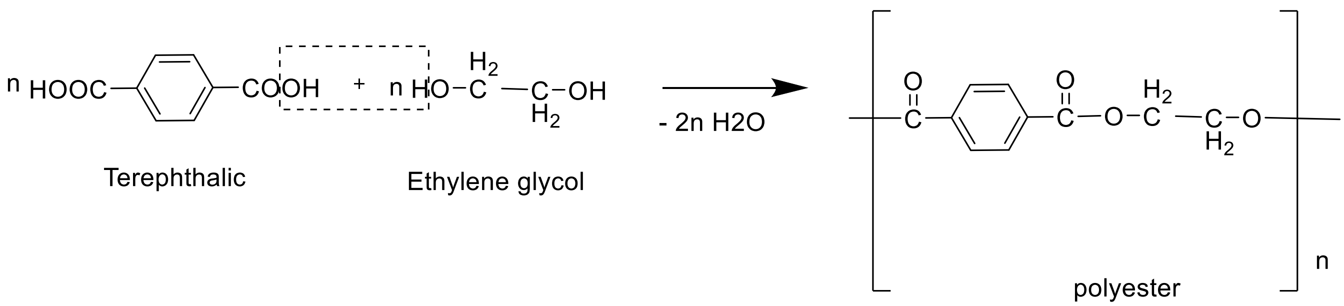
- Kevlar is 5 times stronger than steel.
- It is extremely lightweight.
- It does not undergo corrosion with acid and alkali.
- It absorbs vibration.
- It possesses the highest tensile strength.
- It has good resistance to high temperature, fire, and chemical attacks.

Uses

- It is used for making bulletproof jackets.
- Used for industrial cables.
- It is used in the construction of aircraft and spaces vehicles.
- Used in the manufacture of marine current turbines and wind turbines.
- It is used to make the tyres of race cars.

Polyester (Terelene)

Polyesters are prepared from the condensation of terephthalic acid and ethylene glycol



Properties

- Polyesters are a good fiber-forming material this is due to the presence of numerous polar groups, such fibers have high stretch resistance.
- PET (polyethylene terephthalate) is high resistance to minerals and alkalis.
- Easy recyclable.
- Abrasion resistance.
- Hydrophobic in nature

Uses

- By blending with wool to provide better wrinkle resistance.
- It is used as glass reinforcement material in safety helmets battery boxes etc.
- Used for making good insulators.
- Used in making air crafts and automobile parts.

ADHESIVES

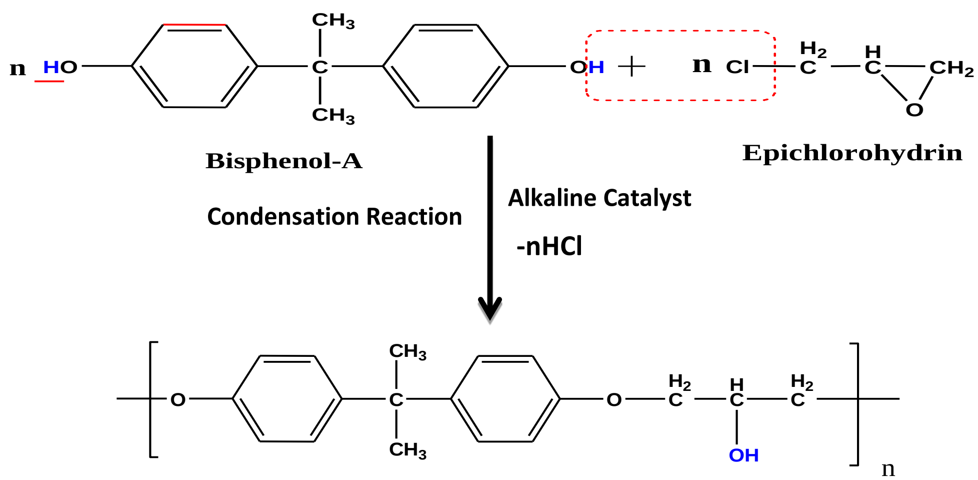
Adhesive is a non-metallic compound, which can hold firmly two materials together by surface attachment.

Ex: 1) Natural– Gum, glue, starch etc.

2) Synthetic – Phenol-formaldehyde, urea-formaldehyde, epoxy resins, silicones, etc.

SYNTHESIS, PROPERTIES AND APPLICATIONS OF EPOXY RESINS (ARALDITE)

Epoxy resins are prepared by the condensation of Bisphenols & epichlorohydrin excess in presence of alkaline catalyst.



Epoxy resin

Properties

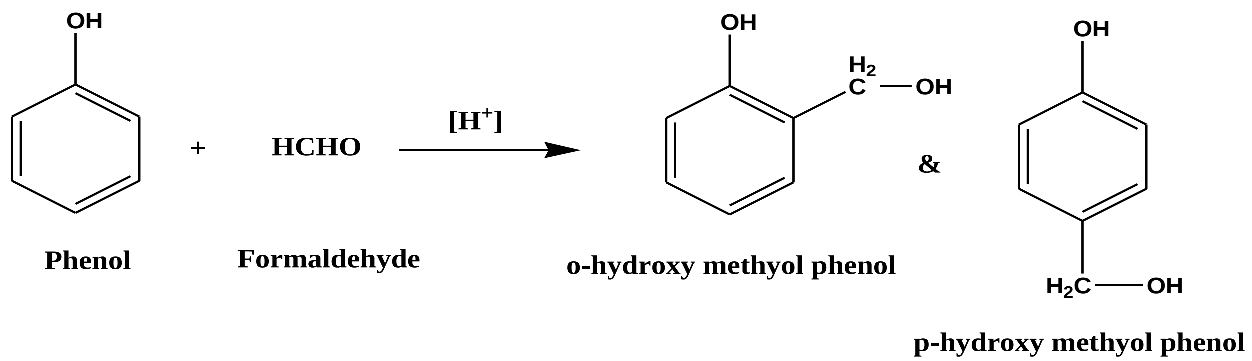
- They possess excellent adhesive property
- They have good abrasion resistance.
- It has excellent chemical resistance
- It also possess good electrical insulating property.

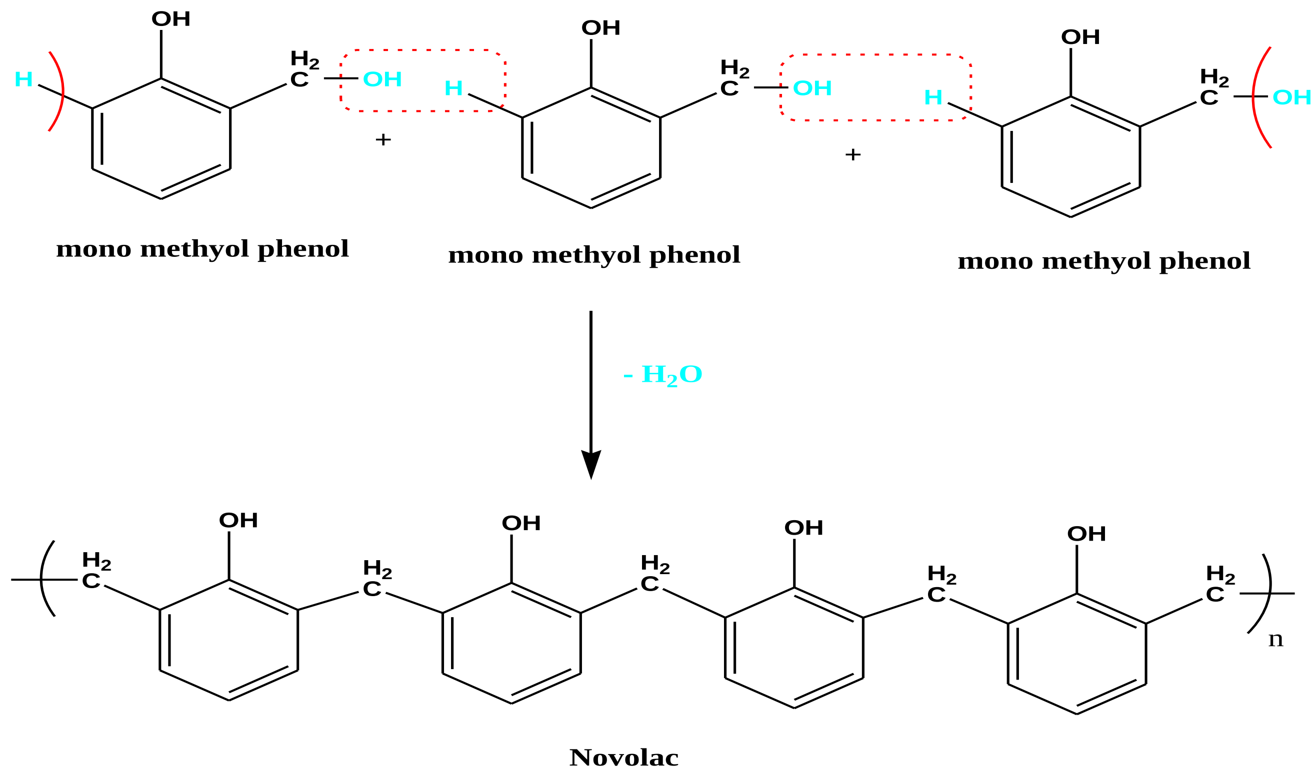
Applications

- They are used for laminating materials.
- They are widely used as structural adhesives.
- They are used in paint and varnishes.
- They are used in the preparation of decorative furniture.

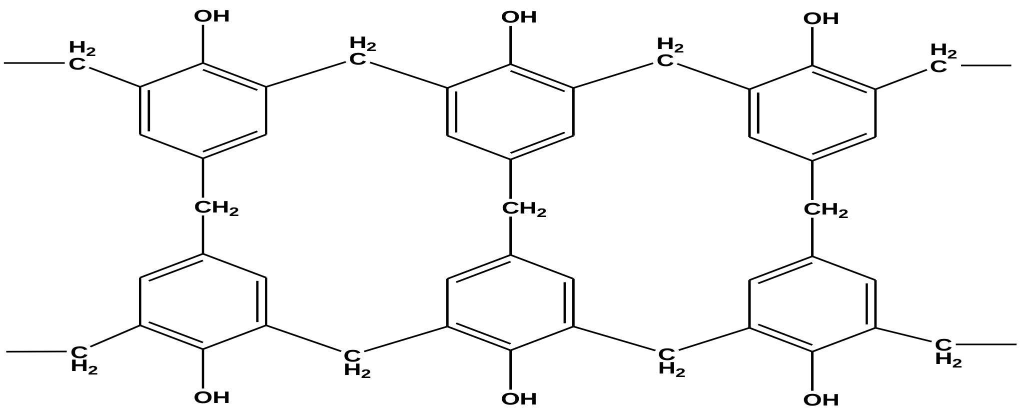
Phenol – Formaldehyde Resins (Bakelite)

P-F resin is prepared by condensing Phenol and Formaldehyde in presence of Acidic/alkaline catalyst. The initial reaction results in the formation of o- & p- hydroxy methylol phenol, which reacts to form linear low molecular weight prepolymer called **Novolac** .





Novolac are soft, fusible, and soluble in organic solvents. Further polymerisation converts soluble and fusible Novolac into rigid, hard, infusible, insoluble solids of cross-linked polymer called **Bakelite**.



Cross linked polymer Bakelite

PROPERTIES

Phenolic resin (Bakelite) set to rigid, hard, scratch resistant, infusible, water resistant, insoluble solids, which are resistant to acids, salts & many organic solvents, but attacked by alkalis because of the presence of free hydroxyl group in their structure. They possess excellent electrical insulating character.

USES

It is used for making electric insulator parts like-

- It is used for making electric insulator parts like switches, plugs, switch boards, heater handles etc.
- It is also used in making of telephone parts, cabinets for TV, radio and mobile.
- It is used as adhesives (binder) for grinding wheels and making bearings etc.
- They are used in paints and varnishes.

ELASTOMERS (RUBBERS)

Elastomers are high polymers which undergo very large elongation (300-1000%) under stress and regain original shape and size fully on release of stress (force). This property of elastomers is called elasticity. This arises due to coiled structure of elastomers. Example: - Rubber band.

Types of rubber:

There are two types of rubber.

1. Natural rubber 2. Synthetic rubber

Natural rubber

Natural rubber consists of basic material latex, which is dispersion of isoprene. During the treatment, these isoprene molecules polymerize to form long coiled chains of cis-polyisoprene.

PREPARATION OF NATURAL RUBBER FROM LATEX

The latex is collected by making small cuts or trapping in the trees in such a manner so as to allow the latex (milky liquid or sap) to accumulate in small cups. The percentage of rubber in it is 25-35%. The average composition of the latex is water 60%, rubber 35%, proteins, enzymes and nucleic acid is 3%, fatty acids and esters is 1% and inorganic salts is 0.5%, (In these trees the rubber is formed from polymerization of isoprene to produce poly-isoprene by a biochemical reaction in which a particular type of enzyme acts as catalyst).

The latex is first sieved (filter) to remove the impurities such as leaves, barks, dirt, etc. present in it. It is then diluted from 25-35% rubber content to 15-20% of rubber content. The rubber is then separate from the latex by the process of coagulation. The acetic acid or formic acid is added as coagulants and the rubber is coagulated to soft white mass. This coagulated mass is called crude rubber and it contains about 90-95% rubber, 2-4% proteins and 1-2% resins. The crude rubber is washed and treated for producing smoked rubber, crepe rubber etc.

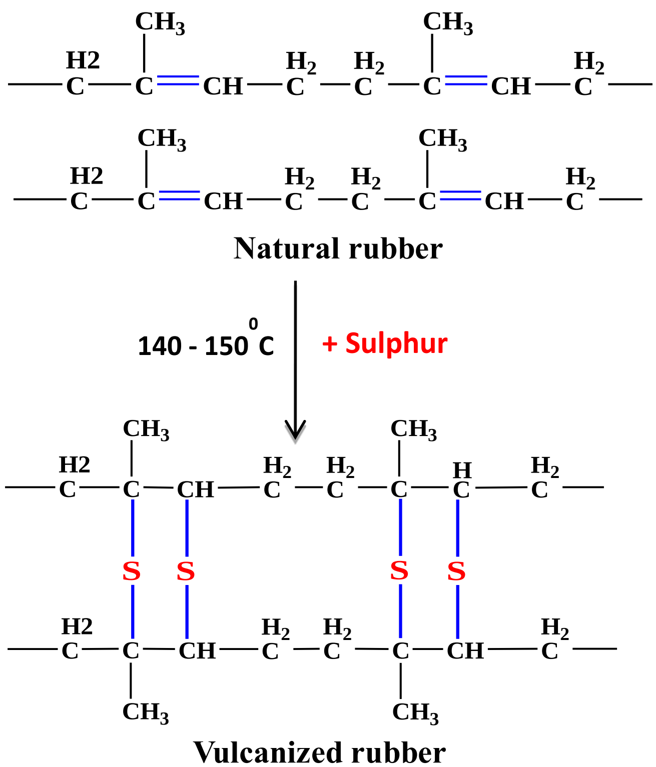
Deficiencies of natural rubber

The origin rubber is as useless as 24 carat gold. As such it has virtually no practical utility value. It is mainly because of its many inherent deficiencies.

1. It is hard and brittle at low temperature and soft and sticky at high temperature.
2. It has poor keeping qualities as it develops unpleasant odour on storage.
3. It is soft and soluble in many hydrocarbon solvents.
4. It has high water absorption power.
5. It is a sticky substance rather difficult to handle
6. It is readily attacked by acids and alkalies.
7. It has low tensile strength.
8. It has poor abrasion resistant.
9. It is sensitive to oxidative degradation.

Vulcanization of rubber: - (Good year in 1839)

Vulcanization is a process of heating natural rubber with sulphur and other compounding agents like Zinc oxide, hydrogen sulphide, benzoyl chloride, etc. at 140-150^{0}C temperature to improve the hardness and other mechanical properties like tensile strength, elasticity and resistance to swelling etc. is called vulcanization. The extent of stiffness of vulcanized rubber depends on the amount of sulphur added. For soft vulcanized rubber 1-5% of sulphur is used while for hard vulcanized rubber it is about 40%



The added Sulphur combines chemically at the double bonds of different layers (spring) of rubber molecules.

SYNTHETIC RUBBER (OR) ARTIFICIAL RUBBER

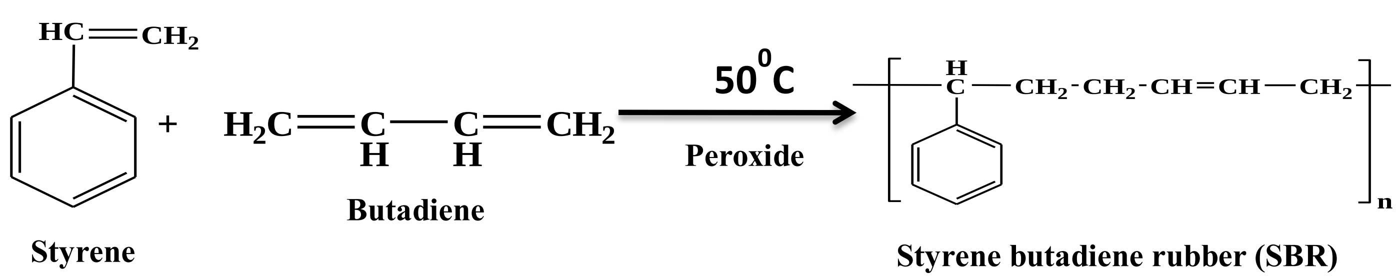
Synthetic rubber is a man-made rubber like polymer that can be stretched to at least twice its length, but it returns to its original shape and dimension as soon as stretching force is released.

Advantages of synthetic rubber over natural rubber

1. They are produced from petrochemical raw materials in abundant amounts
2. Their production cost is less.
3. They are not only replacement, but are superior to natural rubber in certain cases.
4. They have diverse applications.
5. They have high abrasion resistance and high tensile strength.
6. Certain elastomers like silicones have low temperature (-80^{0}C) flexibility and high temperature (250^{0}C) stability.

SBR rubber or Buna 'S'

Styrene-butadiene rubber (SBR) is the first commercially made synthetic rubber. It is produced by co-polymerization of butadiene (75%) and styrene (25%) in presence of peroxide.



Properties

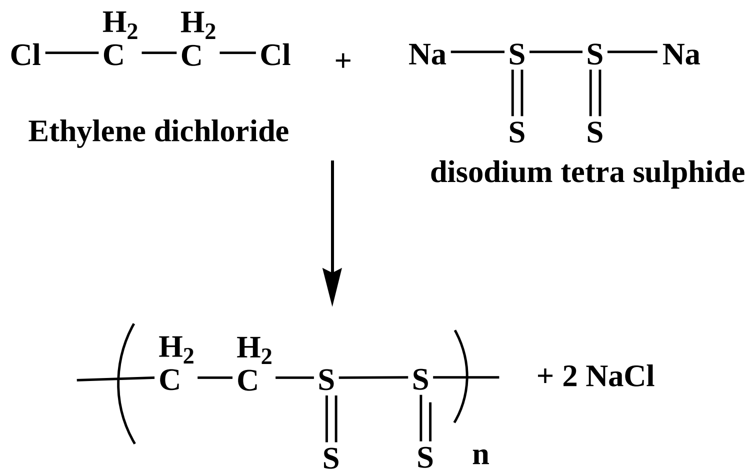
- SBR possesses high abrasion and high load bearing capacity.
- The weather ability of SBR is better than that of natural rubber.
- SBR easily oxidizes in the presence of trace amounts of ozone in the atmosphere.
- It undergoes swelling in presence of oils and solvents.

Applications

SBR rubber is mainly used for making light duty tyres, conveyor belts, shoe soles, floor tyres, gaskets, wires and cable insulation, adhesives, tank linings, carpet baking etc.

THIOKOL RUBBER (POLY SULPHIDE RUBBER)

Thiokol is the condensation polymer, which is obtained by the reaction between disodium tetra sulphide and ethylene dichloride.



Properties

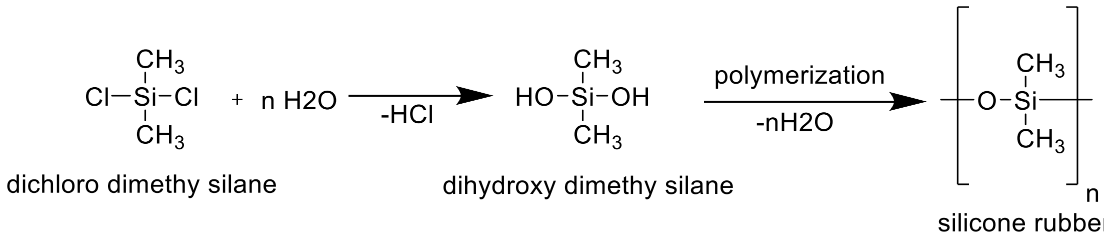
- Vulcanization of the Thiokol is not carried with Sulphur because polymer chain is not unsaturated (Sulphur will not react with the polymer). Hence it is not a hard rubber.
- Thiokol's are chemically resistant to most oil and solvent, practically unaffected by gasoline, kerosene, etc.
- They have good resistant to oxygen, ozone, and sunlight, because of low gas permeability.
- They are advantages in balloon fabrics.

Applications

Thiokol's are used for seals, gaskets, cable insulations, oil tank linings, etc. It is also used as a solid propellant fuel for rocket motors.

SILICONE RUBBER

Silicone rubber is prepared by treating water with dichloro dimethyl silane resulting in dihydroxy dimethyl silane intermediate, which condenses to form silicone rubber.



Properties

They possess exceptional resistance to prolonged exposure to sunlight, weathering, most common oils, dilute acids and alkalies. They remain flexible in a wide range of temperatures (-90 to 250^{0}C) and hence, find use in making tyres of fighter air craft’s since they prevent damage in landing. Ordinary rubber tyre becomes brittle and hence disintegrates.

Uses

1. As a sealing material in aircraft engines.
2. For manufacture of tyres for fighter aircraft’s.
3. For insulating the electrical wiring in ships.
4. It is used as artificial human body parts.

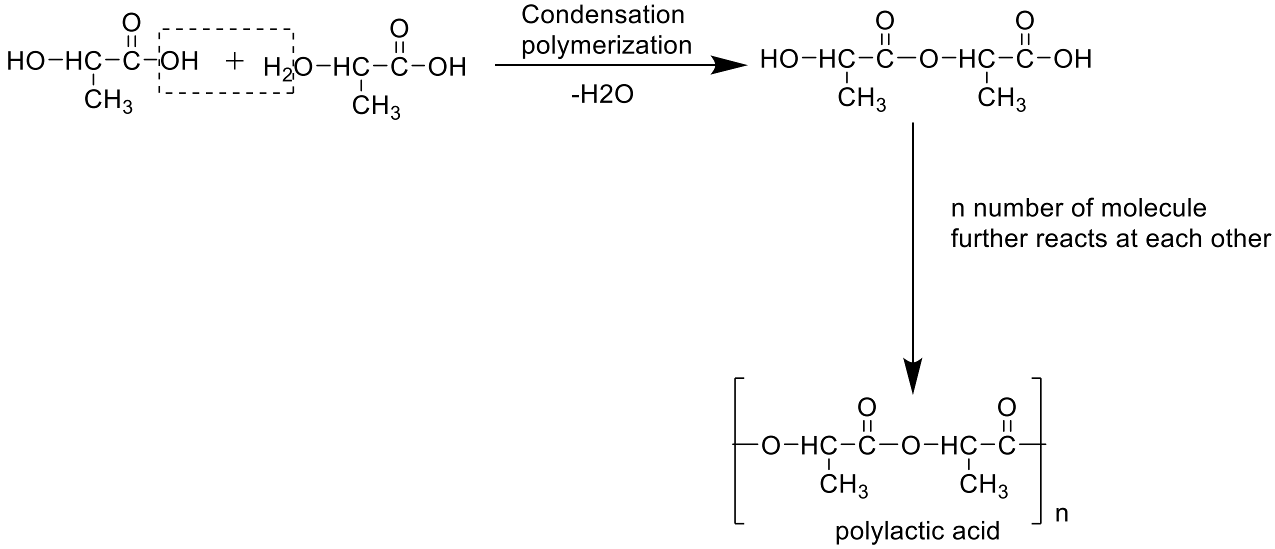
Biodegradable Polymers

The polymers which can be decomposed by bacteria or microorganism to produce harmless by products are known as biodegradable polymers.

Biodegradable polymers mainly consist of ester, ether, and amide functional groups.

Preparation, properties, and application of polylactic acid (PLA)

Polylactic acid is obtained by the condensation polymerization of lactic acid, with the removal of water as a byproduct.



Properties of PLA

- It is derived from natural sources or renewable source such as corn starch, sugarcane, etc.
- PLA is a biodegradable thermoplastic polymer.
- PLA is aliphatic polyester.
- PLA is nontoxic polymers.
- The glass transition temperature of PLA is 60-65 ^{0}C.
- PLA has a melting point of about 130-180 ^{0}C
- PLA is soluble in chlorinated solvent, hot benzene, etc,

Application

- PLA is used in n large Variety of consumer products such as disposable tableware includes disposable cups plates, paper napkins, table clothes, garments, etc.
- PLA can be used food-packing king polymer.
- These are used for stitching wounds after an operation or surgery.
- These are used in agricultural materials such as films as seed coatings.
- PLA has mostly used plastic filament materials in 3D printing.
- It is used for automotive parts like floor mats, panels, and covers.

TEXT BOOKS

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.3. Text Book of Polymer Science by V. R. Gowarikar, N.V. Viswanathan and J. Sreedhar, Wiley-Eastern Ltd (2006 edition).