

MODULE – 3

Macromolecules for Engineering Applications

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Macromolecules for Engineering Applications

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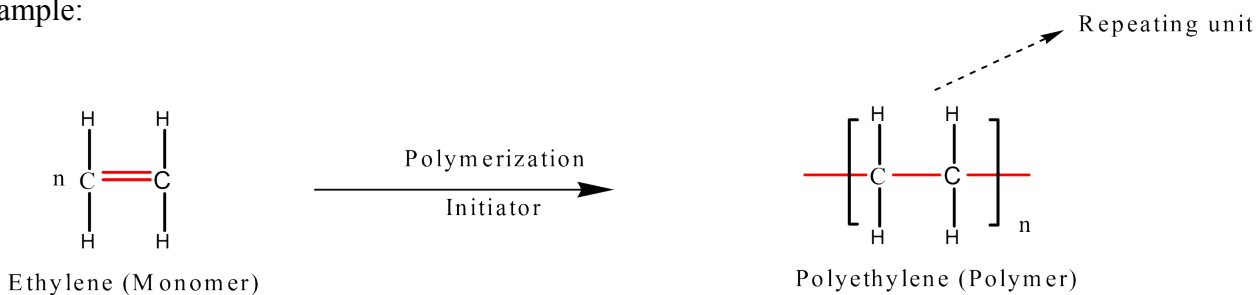
Synthetic rubbers- Preparation, properties and industrial applications of SBR rubber, Thiokol, and Silicon rubber.

10 hours

HIGH 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) in chain formed in a polymer is known as the “**Degree of polymerization**”.

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

*The polymers with identical monomers are called **Homo polymers** and the polymers with different monomers are called **co-polymers**.

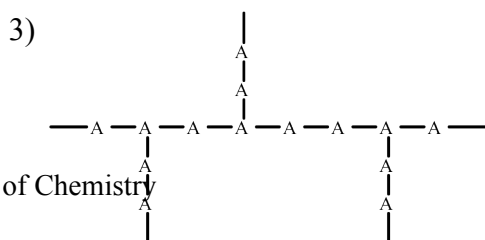
Example: (a) Homo polymer — A — A — A — A — A —

(b) Co-polymer — A — B — A — B — A — B —

*The monomeric units in a polymer may be present in linear, branched or cross linked (Three dimensions).

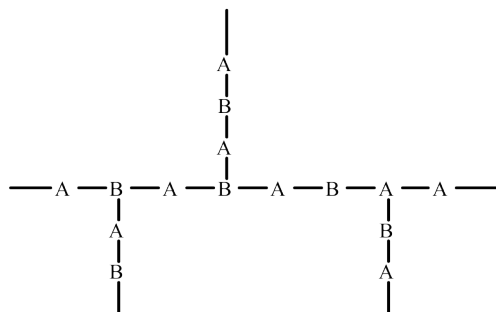
Example: 1) — A — A — A — A — A — Linear homo polymer

2) — A — B — A — B — A — B — Linear copolymer



Branched chain homo polymer

4)

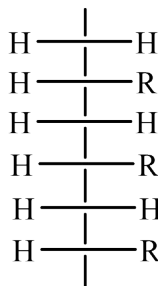


Branched chain copolymer

*The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain.

If the group lies on the same side of the chain then it is called an Isotactic polymer.

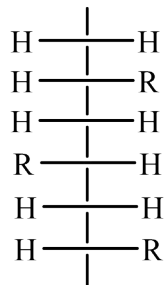
Example:



Natural rubber (cis-arrangements)

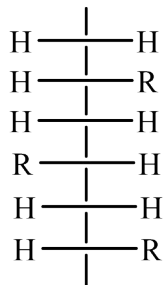
If the monomers have entered the chain in a random fashion, it is called an atactic polymer.

Example: Poly propylene



If the arrangement of side groups is in alternating fashion, it is called a syndiotactic polymer.

Example: Gutta percha



Classification

On the basis of their chemical structures, physical properties, mechanical behavior, thermal characteristics, stereochemistry, polymers can be classified into different types.

1. Natural and synthetic polymers.

Ex: Silk, wool, rubber etc., for natural polymers

Poly ethylene, PVC, Nylon etc., for synthetic polymers.

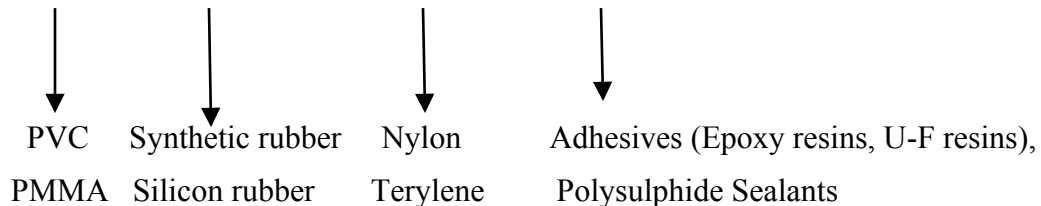
2. Thermo plastic and Thermo setting polymers.

Ex: Polythene, PVC, Plexiglass for thermoplastic

Phenol formaldehyde, epoxy resin, urea formaldehyde for thermosetting polymers

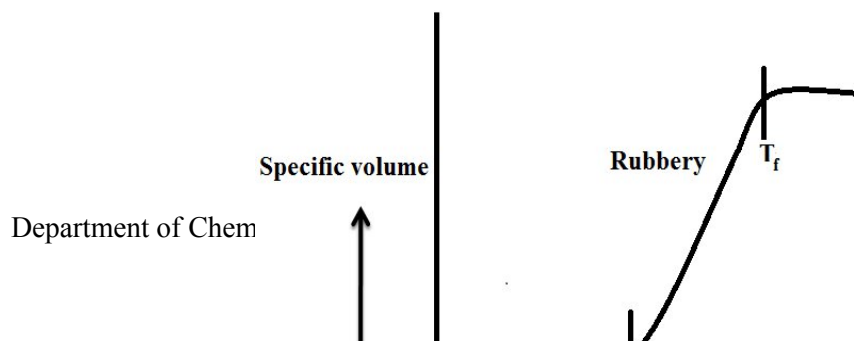
3. Plastics Elastomers Fibres and Liquid resins

Ex; |



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 T_g . The hard, brittle state is known as glassy state and the soft, flexible state as rubbery state.

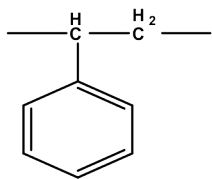


Factors influencing the Tg value

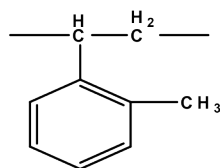
1. Crystallinity: The Tg value of a polymer largely depends on the degree of the crystallinity. Higher the crystallinity larger is the Tg value of a polymer. In crystalline polymer the linear or stereo regular chains are lined up parallel to each other and are held by strong cohesive forces. This leads to a high Tg value of the polymer [Tg value for poly ethylene is -125°C due to absence of cohesive force. On the other hand, Nylon-6 having similar structure has higher Tg value (50°C). This is due to presence of large polar groups in polymer chains. The chains are held together by strong cohesive forces through inter chain hydrogen bonding].

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°C) while polystyrene has lower Tg value (100°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 about 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

The Tg value is an important parameter of polymer. The polymer above their Tg value are soft and flexible while below Tg, they are hard and brittle. Thus, 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. These pre-polymers during curing undergo further polymerization or extensive cross linking, resulting in hard and rigid three-dimensional network.

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

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

Differences between Thermoplastics and Thermosetting plastics

No.	THERMOPLASTICS	THERMOSETTING PLASTICS
1	They are formed by addition polymerization.	They are formed by condensation polymerization.
2	They consists of long chain linear polymer	They have three-dimensional network structure, joined by strong covalent bond.
3	They soften on heating and hard on cooling.	They are fusible on initial heating, but become permanently hard, rigid and infusible product on further heating.

4	They can be reshaped by heat cycle.	They cannot be reshaped by heat cycle.
5	They are soluble in organic solvents.	They are insoluble in organic solvents (due to strong bond and cross linking)
6	They are soft and flexible.	They are hard, rigid and infusible.
7	They can be reclaimed from wastes	They cannot be reclaimed from wastes.
	Example: Polyethylene, polypropylene, polystyrene, PVC, Plexi glass etc	Example: Phenol-formaldehyde resin, urea-formaldehyderesin, epoxy resins,etc,.

Compounding of resins and plastics

The process of mixing various additives to the polymer is called compounding of plastic and resins. 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 into the fabricated article.
- To assist polymer processing.
- To make the polymer products more pleasing and colorful.

Compounding materials:

1. Fillers
2. Plasticizers
3. Stabilizers
4. Accelerators
5. Colorants
6. Flame retarders

1. Fillers

Filler is an organic or inorganic compound added into polymer to transform a non-serviceable polymer into a serviceable one. The main functions of the fillers are:

- To reduce the cost of the fabricated plastic articles.
- To impart certain specific properties to the product.

There are two types of fillers used in the compounding of plastics, they are,

(a) Particulate fillers

(b) Fibrous fillers

(a) Particulate fillers:

The important fillers are wood flour, asbestos, mica, limestone, clay, silica, talc, etc. These are all inert fillers and are added as diluents, mainly to reduce the cost of the product. They also impart hardness and dimensional stability, but do not improve tensile strength.

(b) Fibrous fillers:

The most commonly used fillers are cotton flocks, fabric scraps, nylons, polyesters, glass fibres, carbon black, etc. These fillers are called reinforcing fillers. They greatly enhance the tensile strength, impart resistance and abrasion resistance.

(2) Plasticizers

A plasticizer is a substance incorporated into plastic to increase its workability and flexibility. The added plasticizer lowers the polymer melt viscosity and glass transition temperature. This helps in converting a hard, brittle, glass and difficult to process polymer into a soft, flexible and tough material. Thus, the process ability of polymer is greatly enhanced by plasticizers. The main requirements of a good plasticizers are---

- It should be miscible with the polymer.

- It should be inert.
- It should be high molecular weight, high B.P. and non-volatile substance.

Example: Phosphate esters (Tri crystal phosphate, Tri phenyl phosphate), phthalicesters (Di-Octyl Phthalates), fatty acid esters (natural), etc.

3. Stabilizers

Many polymers in service or during processing undergo degradation by the action of air, UV-rays and heat. This can be avoided by incorporating the polymer with certain compounds. A stabilizer is a compound incorporated onto the polymer to retard degradation of polymers.

Example:

(1) Elastomers have a tendency to undergo degradation by air and light. This can be prevented by adding anti- oxidants like alkyl phenols and naphthols.

(2)The polymers such as polystyrene, PVC, polyesters, polypropylene are easily undergone degradation by UV light. This can be prevented by adding phenyl salicylate.

4. Colourant

A substance incorporated into a polymer to give a specific color to the product is called a colorant. Most of commercial plastic products come in highly attractive and more pleasing colours. Thus, the colourants are mainly used for decorative purpose. They do not influence the properties of polymer product.

There are two types of pigments.

1. Organic pigments
2. Inorganic pigments.

The color imparted to the product depends upon the nature of the pigments used. The organic colors are brighter, less dense and more transparent. But the color imparted by the inorganic pigments is less bright and more opaque.

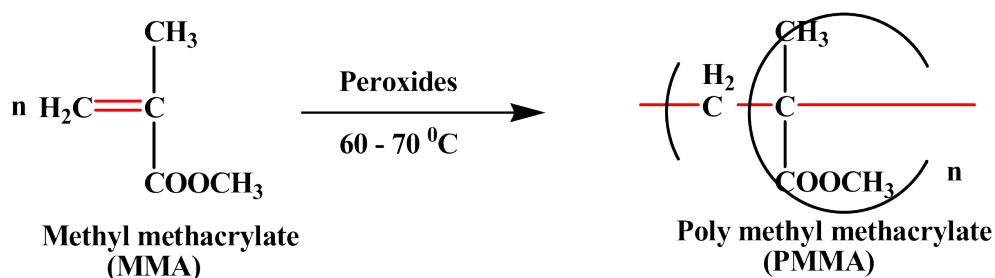
Ex: Organic pigments: carbon black, Azo dye stuff, anthraquinones, etc.

Ex: Inorganic pigments: Titanium oxide, Barium sulphate, lead chromate, Zinc chromate, Iron oxide, etc.

Preparation, Properties and applications of some Synthetic polymers

PMMA (Poly MethylMeth Acrylate) or Plexi glass (trade name)

PMMA is obtained by polymerization of methyl methacrylate (ester of methyl acrylic acid) in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer.

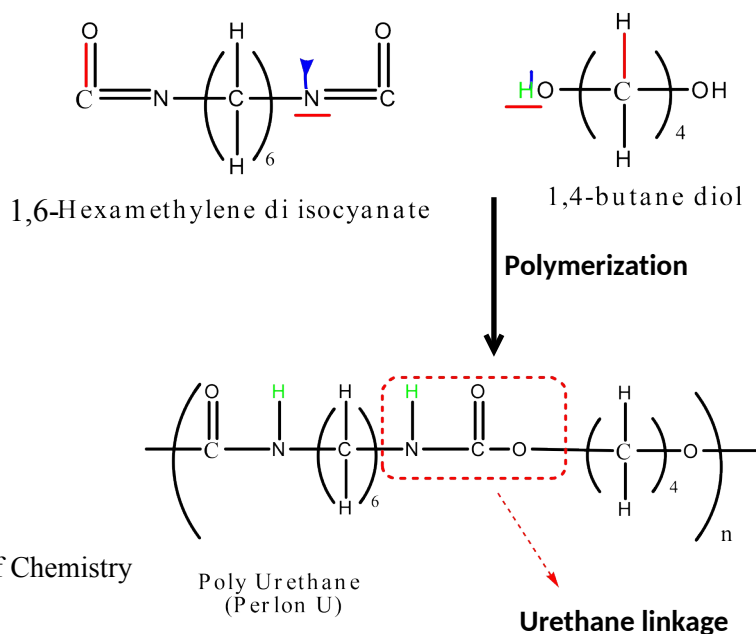


Properties: PMMA is a white transparent thermo plastic. It is amorphous in nature due to bulky groups. It has excellent optical clarity which is not affected by sun light but poor scratch resistant. It has low chemical resistance to hot acids and alkalis.

Uses: It is used for making lenses, air craft windows, light fixtures, artificial eyes, dentures (set of 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

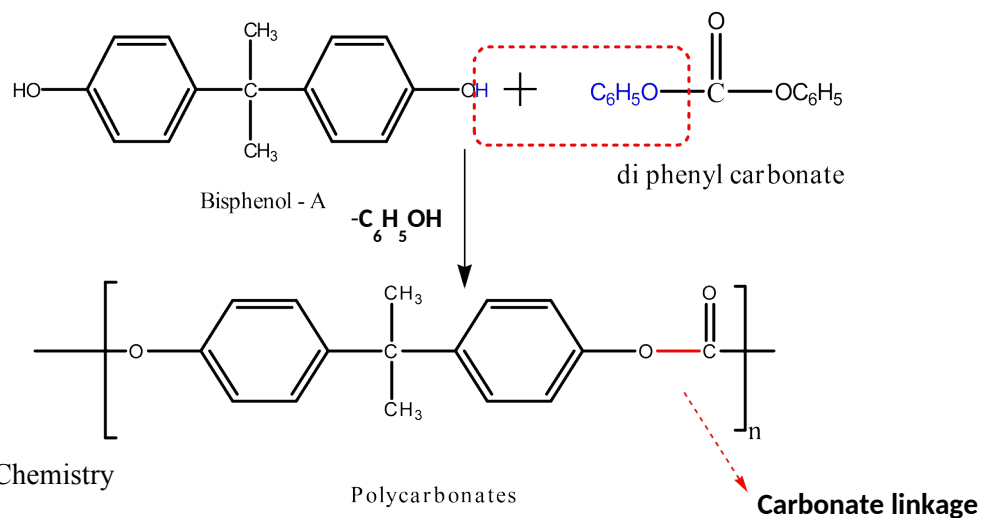
The presence of additional oxygen in the chain increases its flexibility. This is the cause for its much lower melting point than polyamides. (Polyurethane m.p. = 150°C and nylon-6 (polyamide) m.p.=250°C) (Less stable at high temperature). They resist abrasion and chemical attack.

Uses

Polyurethanes are very light. Therefore, they are used in light weight garments and swimming suits (due to stretching). They are used as coatings (floor), films, foams, adhesives ,etc. (Cushions for furniture and automobiles).

POLY CARBONATES

Poly carbonates are prepared by interaction of bisphenol-A with di phenyl carbonate



Properties

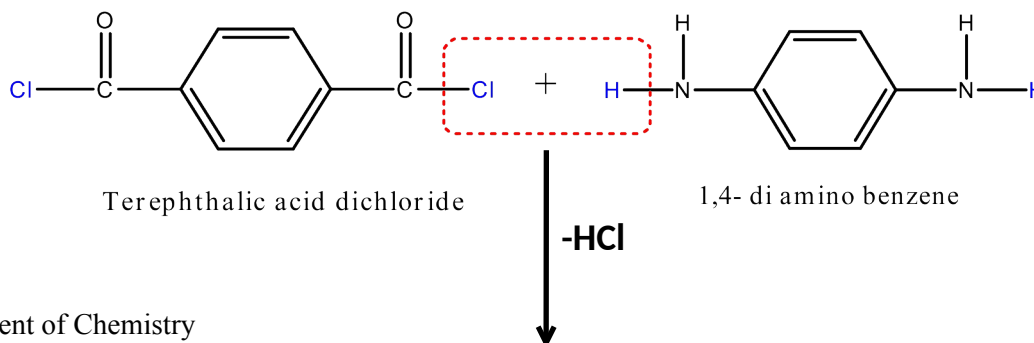
Polycarbonates melt at about 265°C and are characterized by high impact and tensile strength over a wide range of temperature. They are also resistant to water and many other organic compounds, but they are soluble in organic solvents and alkalies.

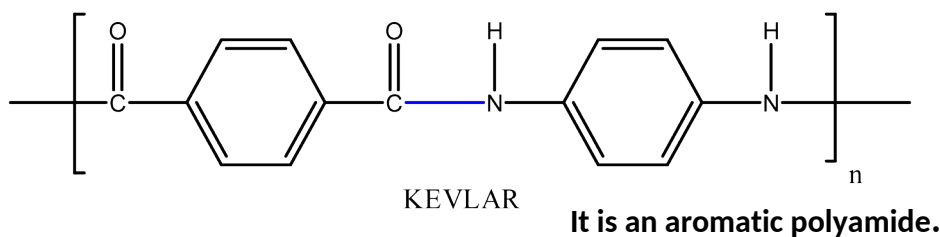
Uses

It is mainly used for preparing moulded domestic wares, housing for apparatus and electrical insulator in electronics and electrical industries. Polycarbonate is a white transparent plastic, hence they are used in sun glass lenses, automotive heat lamp lenses, C.D., DVDs, and also they can be laminated to make bullet-proof glass.

KEVLAR

Kevlar is an aromatic polyamide similar to nylons, but with benzene rings rather than aliphatic chains linked to the amide groups $-\text{CONH}-$. It is prepared by poly condensation between aromatic dichloride and aromatic di amines.





Properties

Kevlar is exceptionally strong (5times stronger than steel and 10times stronger than aluminum). It has high heat stability and flexibility. The unique properties to Kevlar are due to the delocalized bonding which causes the benzene rings to be inflexible. Therefore, Kevlar is for more rigid than nylons. The high electron density in the chains of Kevlar also results in relatively stronger Vander walls inter molecular forces between neighboring polymer molecules.

Uses

Kevlar is used extensively in the aerospace and air craft industries, car parts(brakes, clutch,linings, etc) ropes, cables, protective clothing's, bullet proof vests, motor cycle helmets and other high-performance materials.

ADHESIVES

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

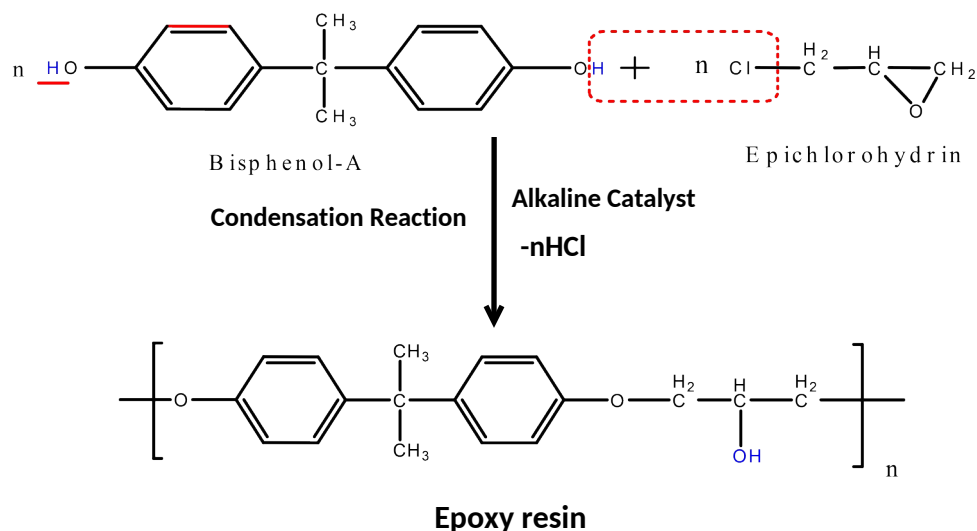
Ex: 1) Natural– Gum, glue, starch etc.

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

SYNTHESIS, PROPERTIES AND APPLICATIONS OF SOME POLYMER

EPOXY RESINS (ARALDITE)

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



Properties

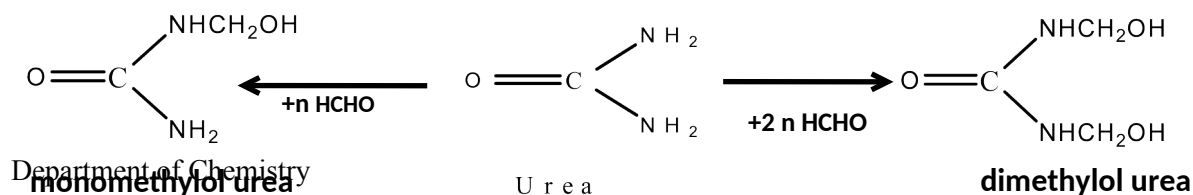
Epoxy resin is a linear, low molecular weight polymer. It is insoluble in organic solvents. During curing, they form cross linking with diamines, dicarboxylic acid, etc. After adhesion, they are highly resistant to water, solvents, acids, alkalies and weather.

Applications

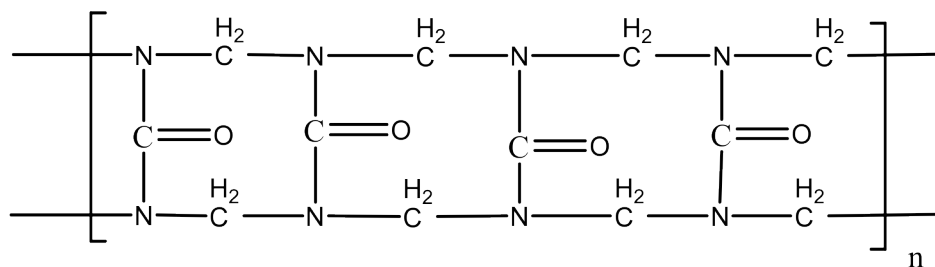
1. They are used for laminating materials.
2. As surface coatings
3. Adhesives like araldite (for joining glass, metals, etc.)
4. Epoxy resins are applied over cotton, rayon and bleached fabrics to impart grease resistance and shrinkage control.

UREA- FORMALDEHYDE RESIN

Urea formaldehyde is prepared by the reaction between two parts of urea and one part of formaldehyde in basic medium in stainless steel vessel at about 50°C. The primary products formed are mono and dimethylolurea.



For moulding the methylol derivatives are compounded (with fillers, plasticizers, pigments and catalyst) and then cured (by applying heat and pressure). During curing long $-C-N-C-N$ bonds chains are formed.



Cross link U-F resin

Properties

Urea formaldehyde resin is a clear white product of good tensile strength, good electrical insulation, good chemical resistance, great hardness, great light stability and good abrasion resistance.

Uses

1. For bonding grinding wheels.
2. For bonding glass fibers, rock wool etc.
3. For binding foundry cores.
4. For bonding plywood.
5. Used in cat-ion exchanger
6. Used in electrical insulation.
7. Used for decorative articles like plates, drinking glasses, dishes etc.

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 and
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% dry rubber content of the latex to about 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.

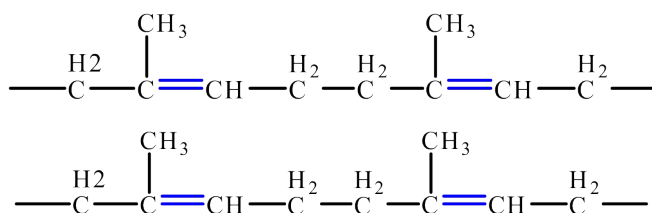
1. It is hard and brittle at low temperature and soft and sticky at high temperature.
2. It has poor keeping qualities as it develops obnoxious odour on storage.
3. It is soft and soluble in many hydrocarbon solvents and carbon disulphide.
4. It has high water absorption power.
5. It is a sticky substance 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.

Compounding

The process of mixing various ingredients or chemicals such as fillers, plasticizers, stabilizers, colorants, vulcanizing agents etc. in to the rubber is known as compounding of the rubber.

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°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%



Natural rubber



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

SYNTHETIC RUBBER (OR) ARTIFICIAL RUBBER

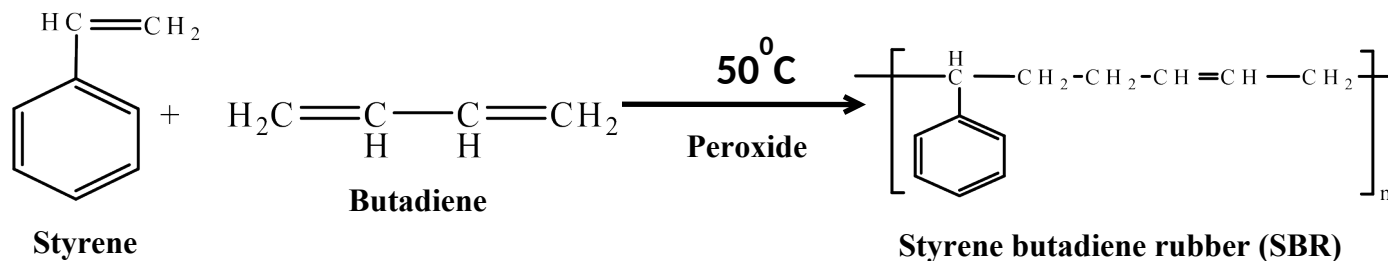
Synthetic rubber is a vulcanizable man made rubber like polymer which can be stretched to at least twice its length, but it returns to its original shape and dimension as soon as stretching force is released.

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 are tailor made elastomers with diverse applications.
5. They have high abrasion resistance and high tensile strength.
6. Certain elastomers like silicones have low temperature (-80°C) flexibility and high temperature (250°C) stability.
7. They are used for the manufacture of motor tyres, floor tiles, shoe soles, foot wear components, wire and cable insulations, tank linings etc.

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 (cold polymerization take place at 5°C and hot polymerization is carried out 50°C temperature).



Properties

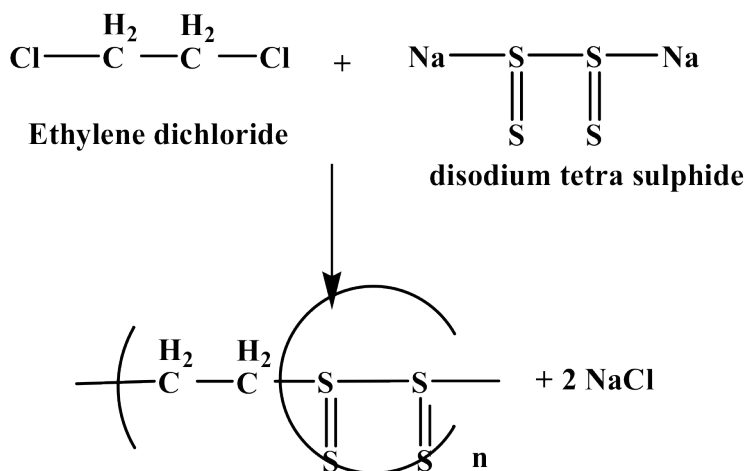
SBR possesses high abrasion and high load bearing capacity. The weather ability of SBR is better than that of natural rubber. SBR gets easily oxidized in presence of traces of ozone present in atmosphere and also it undergoes swelling in presence of oils and solvents.

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 backing etc.

THIOL RUBBER (POLY SULPHIDE RUBBER)

Thiokol is the condensation polymer, which is obtained by the reaction between disodium tetra sulphide and ethylene dichloride. This reaction results in a bond being formed between the Sulphur and carbon atoms and a long chain molecule is formed.

**Properties**

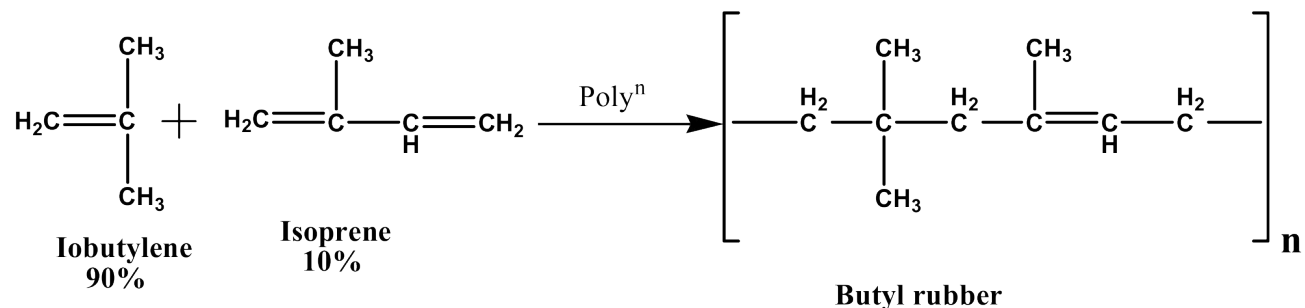
Vulcanization of the Thiokol is not carried with Sulphur because polymer chain is not unsaturated (Sulphur will not react with the polymer). Hence it is not a hard rubber. For vulcanization active metal oxides like ZnO are used. (Sulphur has the ability to react with ZnO and as a result interlinks the chains in to a network). Thiokol's are chemically most oil resistant and solvent resistant and 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.

BUTYL RUBBER

Butyl rubber is prepared by co-polymerization of isobutene (90%) in presence of small amounts of isoprene (5-10%).

**Properties**

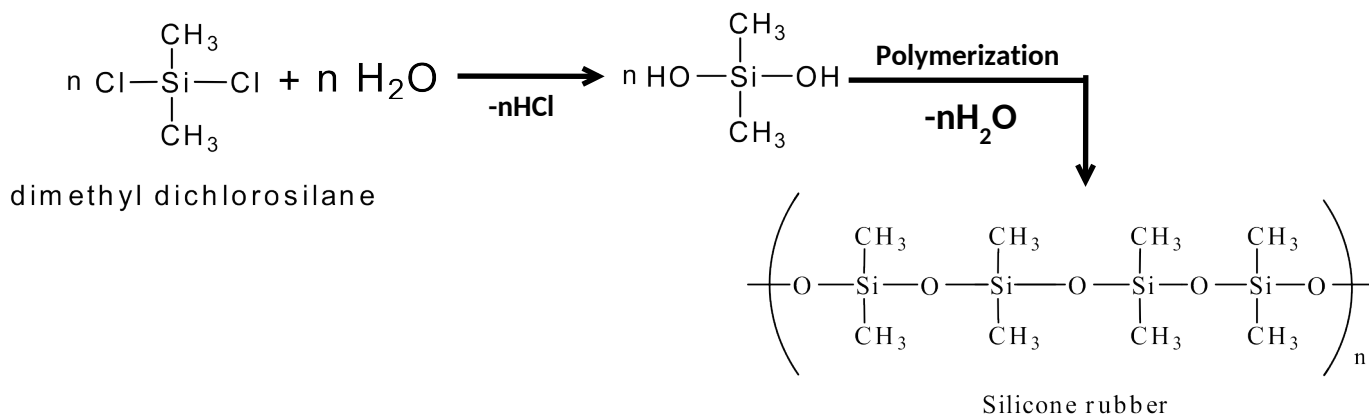
It has excellent resistance to heat, abrasion, chemicals, (H_2SO_4 , HNO_3 , HCl , HF) and polar solvents (alcohol, acetone) but is soluble in hydrocarbon solvents like benzene. It has high resistance to ozone and good electrical insulating properties. It can be vulcanized, but it cannot be hardened much, due to very low unsaturation.

Uses

For making cycle and automobile tubes, automobile parts, hoses, tank linings, insulation for high voltage wires and cables etc.

SILICONE RUBBER

Silicone rubbers are prepared by mixing high molecular weight linear di methyl silicone polymers with fillers [like finely divided silicon dioxide (SiO_2)] and a peroxide as curing agent. Peroxide helps to form bridges (cross-link) between methyl groups of adjacent chains.

**Properties**

They possess exceptional resistance to prolonged exposure to sunlight, weathering, most common oils, dilute acids and alkalies. They remain flexible in the wide range of temperature ($90\text{--}250^\circ\text{C}$) 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 air craft engines.
2. For manufacture of tyres for fighter air craft's.
3. For insulating the electrical wiring in ships.

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