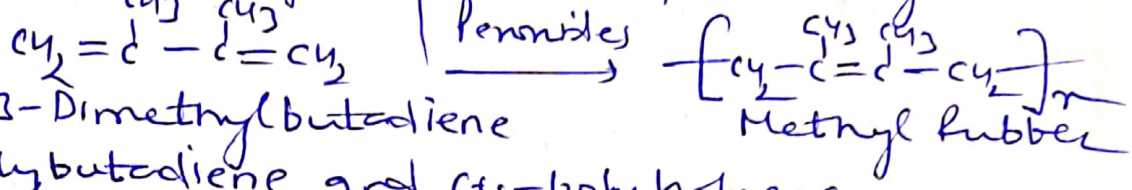
Synthetic Rubbers

To improve the qualities of natural rubber and to meet the ever lasting demands of mankind, a number of synthetic rubbers have been prepared. Majority of them are derived from butadiene derivatives & contains (C=C) double bonds so that it can be vulcanized.

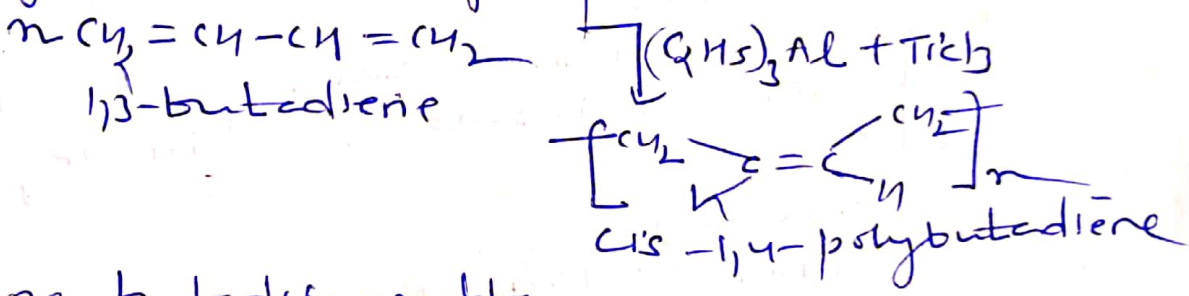
① Methyl Rubber

First commercial synthetic rubber by Germany. It involves polymerization of 2,3-dimethyl butadiene



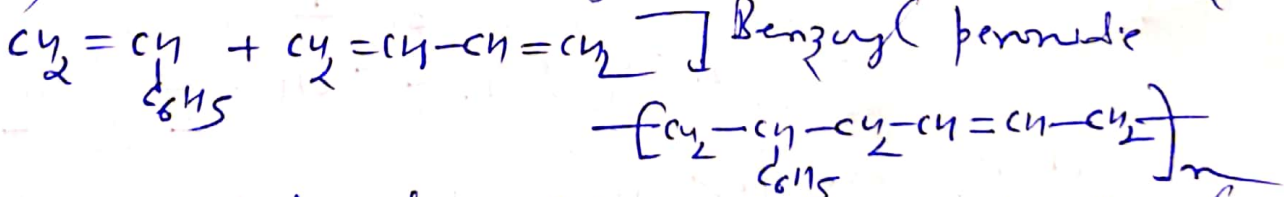
② Cis-Polybutadiene and cis-polyisoprene

Polymerization of 1,3-butadiene in presence of Ziegler-Natta catalyst gives cis-polybutadiene. Similarly all cis-polyisoprene can be prepared by Ziegler-Natta polymerization.



③ Styrene-butadiene rubber (Buna-S)

It is a copolymer of butadiene (75%) and styrene (25%) and is produced by free radical polymerization



→ It is very tough and is a good substitute of natural rubber. It has high abrasion resistance, high load bearing capacity, used for auto tyres, footwear components, Bubble gum etc.

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(4) Buna-N

It is a copolymer of 1,3-butadiene and acrylonitrile and is prepared by free radical polymerization

$$n\,CH_2=CH-CH=CH_2 + n\,CH_2=\underset{\underset{CN}{|}}{CH} \xrightarrow[\text{Peroxide}]{\text{Heat}} -\left[CH_2-CH=CH-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2\right]_n$$

Buna-N

→ It is used for making oil seals, manufacturing of tank linings etc.

(5) Neoprene

It is a polymer of chloroprene i.e. 2-chloro-1,3-butadiene

$$CH_2=\underset{\underset{Cl}{|}}{C}H-CH=CH_2 \xrightarrow{\text{Peroxide}} -\left[CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2\right]_n$$

chloroprene → Neoprene

→ Neoprene is inferior to natural rubber in some properties but superior in its stability to aerial oxidation and in its resistance to oils & solvents

→ It is used in manufacture of shoe heels, stoppers, an insulator, printing rollers etc

(6) Butyl rubber

Copolymer of 95% (Isobutylene) & 5% Isoprene

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH_2 \longrightarrow -\left[CH_2-\underset{\underset{CH_3}{|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-\underset{\underset{CH_3}{|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{C}\right]_n$$

→ It is used for making automobile inner tubes & tyre liners.

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Polymer additives

Polymers are found to degrade or change their properties in presence of air, light and at elevated temperature. To avoid this change, it is to introduce some properties, additives are added.

Some additives

Plasticizers- A plasticizer is a substance or material incorporated generally into plastic or elastomers to increase its workability, flexibility

classification of Plasticizers

Primary and secondary plasticizers

Primary

These are active solvents for resin i.e. there are force of attraction b/w plasticizer molecules the resin. They maintain the solution of the resin.

Secondary

Secondary plasticizers are non-solvents and must always be blended with active plasticizer to give satisfactory performance.

Eg:- butyl, acetyl ricinolate is a primary plasticizer for nitrocellulose, but a secondary plasticizer for vinyl chloride

Simple and resinous plasticizers

Simple plasticizers are low mwt liquids of low viscosity (viscid). Can always be poured. A few simple plasticizer are also crystalline solid like camphor.

Some of these plasticizer are fluid & these fluid low mwt polymers are termed as resinous plasticizers.

Inert and convertible Plasticizers

Inert plasticizers do not undergo any change after their incorporation in the plastic composition. A convertible plasticizer reacts to increase its mwt during processing.

→ In general, plasticizer is a stable chemical material, the mixing of a plasticizer with a polymer is like the mixing of two liquids. First of all, the plasticizer wets the surface of the polymer and then enters the

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microscopic cracks.

General role of Plasticizer – Plasticizer molecule leads to a type of lubrication of the chain comprising polymer structure. The plasticizer acts as a lubricant b/w the polymer molecule rendering the flow process easier, decrease the elasticity of the melt, increases the extensibility, improve the resistance to impact and reduce the flow temperature

Mechanism of Plasticizer action

There are four theories that have been given
a) lubricity theory b) gel theory
c) mechanistic theory d) free volume theory

a) lubricity Theory

The plasticizer acts as a lubricant to facilitate the movements of macromolecules over each other & provide internal lubricity

b) Gel Theory

The theory assumes the formation of an internal 3-D honey comb structure or gel.
Plasticizer attached to the resin macromolecule by force of different magnitude but none of them are bound permanently. There is continuous exchange of plasticizer molecule.

c) Mechanistic Theory

Mechanistic theory assumes that solution brings about aggregation of molecules, while dissolution brings about disaggregation of molecule. The continious aggregation and disaggregation is done by plasticizers

d) free Volume Theory

free volume theory assumes that there is free space b/w molecules. This free vol. increases with temperature and with the increased molecular motion. The addition of flexible side chain by ext group plasticization increases the free volume. By providing enough free volume, freedom of movement is increased & polymer chain moves more readily

Properties of Plasticizers

A good plasticizer exhibits following properties

1) low vapour pressure
2) chemical stability
3) miscibility with polymer
4) insolubility in water or hydrocarbon
5) Non-toxicity
6) Non-inflammability
7) Absence of colour
8) Good electrical insulating value.

further classifications of Copolymer

A Copolymer has got two or more different monomer units and the polymerisation reaction is called Copolymerisation. Copolymers can be classified based on how these units are arranged along the chain

1. Random Copolymer - It has a random arrangement of different monomers in the chain. The Copolymer has got atactic arrangement
2. Alternating Copolymer - The Copolymer may have an orderly arrangement completely alternated. The Copolymer may have syndiotactic
3. Block polymers - A block Copolymer comprises two or more homopolymer subunits linked by covalent bonds. A block of several units of 'A' followed by several units of 'B' followed by A & so on.

Block Copolymers with two or more three distinct blocks are called diblock Copolymers and triblock Copolymers respectively.

Block Copolymers are made up of blocks of different polymerised monomers. Eg —

Polystyrene-Poly(methyl methacrylate)

Copolymer is usually made by first polymerising

styrene & then subsequently polymerising MMA from the reactive end of the polystyrene chains. This polymer is obtained as diblock copolymer

Eg2 ABS rubber is a triblock copolymer, which has three blocks of acrylonitrile, butadiene & styrene.

Eg Graft copolymers

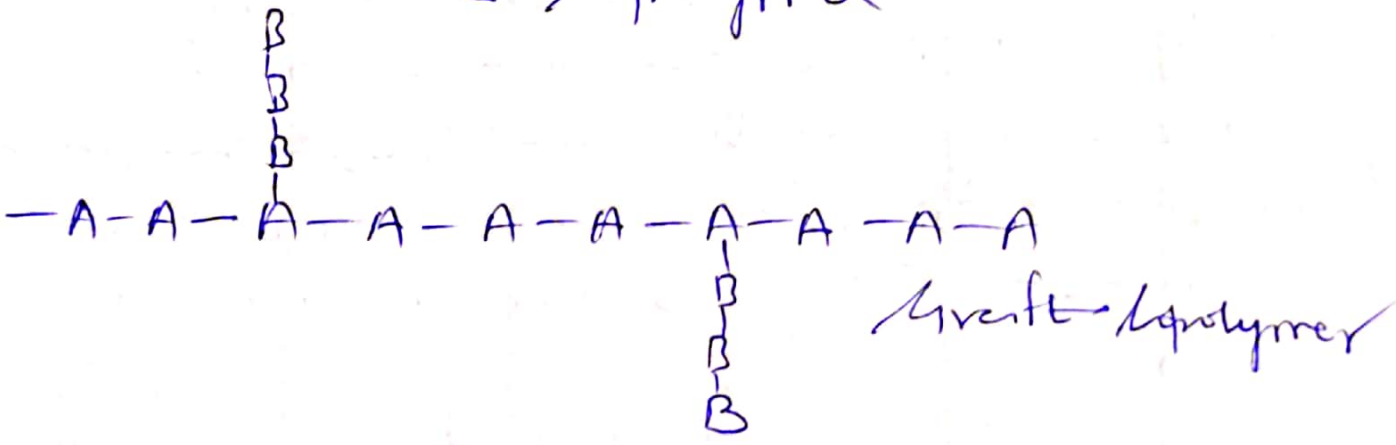
A special type of branched copolymers in which the side chains are structurally different from the main chain.

Copolymers (monomer units represented by 'A' & 'B')

—A—A—B—A—A—B—A—B—A—A—B
Atactic copolymer

—A—B—A—B—A—B—A—B—A—B—A—B
Syndiotactic copolymer

—A—A—A—B—B—B—A—A—A—B—B—B—A—A—A
Block copolymer



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