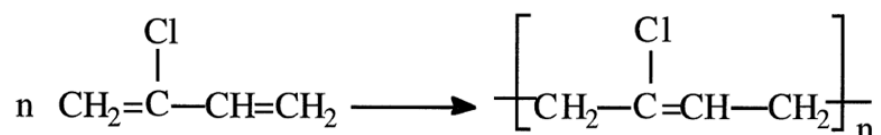


## POLYCHLOROPRENE (Neoprene Rubber)

Polychloroprene is the oldest synthetic rubber. It is produced by the polymerization of 2-chloro-1,3-butadiene in a water emulsion with potassium sulfate as a catalyst:



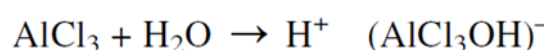
The product is a random polymer that is vulcanized with sulfur or with metal oxides (zinc oxide, magnesium oxide etc.). Vulcanization with sulfur is very slow, and an accelerator is usually required.

Neoprene vulcanizates have a high tensile strength, excellent oil resistance (better than natural rubber), and heat resistance.

Neoprene rubber could be used for tire production, but it is expensive. Major uses include cable coatings, mechanical goods, gaskets, conveyor belts, and cables.

## BUTYL RUBBER

Butyl rubber is a copolymer of isobutylene (97.5%) and isoprene (2.5%). The polymerization is carried out at low temperature (below 95°C) using  $\text{AlCl}_3$  cocatalyzed with a small amount of water. The cocatalyst furnishes the protons needed for the cationic polymerization:



The product is a linear random copolymer that can be cured to a thermosetting polymer. This is made possible through the presence of some unsaturation from isoprene.

Butyl rubber vulcanizates have tensile strengths up to 2,000 psi, and are characterized by low permeability to air and a high resistance to many chemicals and to oxidation. These properties make it a suitable rubber for the production of tire inner tubes and inner liners of tubeless tires. The major use of butyl rubber is for inner tubes. Other uses include wire and cable insulation, steam hoses, mechanical goods, and adhesives. Chlorinated butyl is a low molecular weight polymer used as an adhesive and a sealant.

## **ETHYLENE-PROPYLENE RUBBER**

Ethylene-propylene rubber (EPR) is a stereoregular copolymer of ethylene and propylene. Elastomers of this type do not possess the double bonds necessary for crosslinking. A third monomer, usually a monoconjugated diene, is used to provide the residual double bonds needed for cross linking. 1,4-Hexadiene and ethylidene norbornene are examples of these dienes. The main polymer chain is completely saturated while the unsaturated part is pending from the main chain. The product elastomer, termed ethylene-propylene terepolymer (EPT), can be crosslinked using sulfur. Crosslinking EPR is also possible without using a third component (a diene). This can be done with peroxides.

Important properties of vulcanized EPR and EPT include resistance to abrasion, oxidation, and heat and ozone; but they are susceptible to hydrocarbons.

The main use of ethylene-propylene rubber is to produce automotive parts such as gaskets, mechanical goods, wire, and cable coating. It may also be used to produce tires.

## **THERMOPLASTIC ELASTOMERS**

Thermoplastic elastomers (TPES), as the name indicates, are plastic polymers with the physical properties of rubbers. They are soft, flexible, and possess the resilience needed of rubbers. However, they are processed like thermoplastics by extrusion and injection molding. TPE's are more economical to produce than traditional thermoset materials because fewer steps are required to manufacture them than to manufacture and vulcanize thermoset rubber. An important property of these polymers is that they are recyclable.

Thermoplastic elastomers are multiphase composites, in which the phases are intimately depressed. In many cases, the phases are chemically bonded by block or graft copolymerization. At least one of the phases consists of a material that is hard at room temperature.

Currently, important TPE's include blends of semicrystalline thermoplastic polyolefins such as propylene copolymers, with ethylene-propylene terepolymer elastomer. Block copolymers of styrene with other monomers such as butadiene, isoprene, and ethylene or ethylene/propylene are the most widely used TPE's. Styrene-butadiene-styrene (SBS) accounted for 70% of global styrene block copolymers (SBC).

However, they are noted for their flexibility, strength, toughness, and abrasion and chemical resistance. Blends of polyvinyl chloride with elastomers such as butyl are widely used in Japan.

Important properties of TPE's are their flexibility, softness, and resilience. However, compared to vulcanizable rubbers, they are inferior in resistance to deformation and solvents.

Important markets for TPE's include shoe soles, pressure sensitive adhesives, insulation, and recyclable bumpers.

## SYNTHETIC FIBERS

Fibers are solid materials characterized by a high ratio of length to diameter. They can be manufactured from a natural origin such as silk, wool, and cotton, or derived from a natural fiber such as rayon. They may also be synthesized from certain monomers by polymerization (synthetic fibers). In general, polymers with high melting points, high crystallinity, and moderate thermal stability and tensile strengths are suitable for fiber production. Man-made fibers include, in addition to synthetic fibers, those derived from cellulose (cotton, wood) but modified by chemical treatment such as rayon, cellophane, and cellulose acetate. These are sometimes termed "regenerated cellulose fibers." Rayon and cellophane have shorter chains than the original cellulose due to degradation by alkaline treatment. Cellulose acetates produced by reacting cellulose with acetic acid and modified or regenerated fibers are excluded from this book because they are derived from a plant source. Fibers produced by drawing metals or glass ( $\text{SiO}_2$ ) such as glass wool are also excluded. Major fiber-making polymers are those of polyesters, polyamides (nylons), polyacrylics, and polyolefins. Polyesters and polyamides are produced by step polymerization reactions, while polyacrylics and polyolefins are synthesized by chain-addition polymerization.

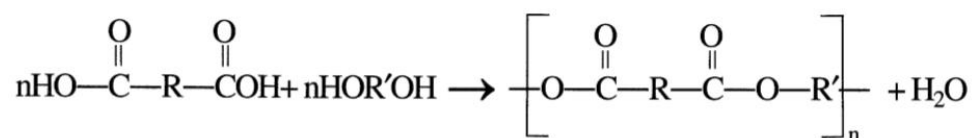
### POLYESTER FIBERS

Polyesters are the most important class of synthetic fibers. In general, polyesters are produced by an esterification reaction of a diol and a diacid. Carothers (1930) was the first to try to synthesize a polyester fiber by reacting an aliphatic diacid with a diol. The polymers were not suitable because of their low melting points. However, he was successful in preparing the first synthetic fiber (nylon

66). In 1946, Whinfield and Dickson prepared the first polyester polymer by using terephthalic acid (an aromatic diacid) and ethylene glycol.

## Synthetic Petroleum-Based Polymers

Polyesters can be produced by an esterification of a dicarboxylic acid and a diol, a transesterification of an ester of a dicarboxylic acid and a diol, or by the reaction between an acid dichloride and a diol. The polymerization reaction could be generally represented by the esterification of a dicarboxylic acid and a diol as:



Less important methods are the self-condensation of w-hydroxy acid and the ring opening of lactones and cyclic esters. In self condensation of w-hydroxy acids, cyclization might compete seriously with linear polymerization, especially when the hydroxyl group is in a position to give five or six membered lactones.

## References

1. Uttam Ray Chaudhuri "Fundamentals of Petroleum and Petrochemical Engineering." University of Calcutta Calcutta, India, 2011.
2. Matar S., Hatch L.F, "Chemistry of PETROCHEMICAL PROCESSES ", 2nd Edition, Gulf Publishing Company, (1994).