Polychloroprene, Chloroprene Rubber (CR)

APPLICATIONS

Among the speciality elastomers polychloroprene [poly(2-chloro-1,3-butadiene)] is one of the most important with an annual consumption of nearly 300 000 tons worldwide. First production was in 1932 by DuPont ("Duprene", later "Neoprene") and since then CR has an outstanding position due to its favourable combination of technical properties.

CR is used in different technical areas, mainly in the rubber industry (ca.61%), but is also important as a raw material for adhesives (solvent and water based, ca.33%) and has different latex applications (ca.6%) such as dipped articles (e.g. gloves), molded foam and improvement of bitumen.

The typical delivery form of CR is "chips", a consequence of the special production process (see below). Application areas in the elastomer field are widely spread, such as molded goods, cables, transmission belts, conveyor belts, profiles etc.

Picture 1:
Typical polychloroprene "chips"

Picture 2 :
Rubber applications
(belts, hoses)

RUBBER PROPERTIES

CR is not characterized by one outstanding property, but its balance of properties is unique among the synthetic elastomers.
It has:

- Good mechanical strength
- High ozone and weather resistance
- Good aging resistance
- Low flammability
- Good resistance toward chemicals
- Moderate oil and fuel resistance
- Adhesion to many substrates

Polychloroprene can be vulcanized by using various accelerator systems over a wide temperature range.

Chemistry and Manufacture

From the beginning until the 1960s, chloroprene was produced by the older "acetylene process". This process has the disadvantages of being very energy-intensive and having high investment costs. The modern chloroprene process, which is now used by nearly all producers, is based on butadiene, which is readily available. Butadiene is converted into the monomer 2-chlorobutadiene-1,3 (chloroprene) via 3,4-dichlorobutene-1.

In principle it is possible to polymerize chloroprene by anionic, cationic and Ziegler-Natta catalysis techniques. However, because of product properties and economic considerations, free radical emulsion polymerization is used exclusively today.It is carried out in a commercial scale using both batch and continuous processes.

A production flow diagram is shown in Figure 1.

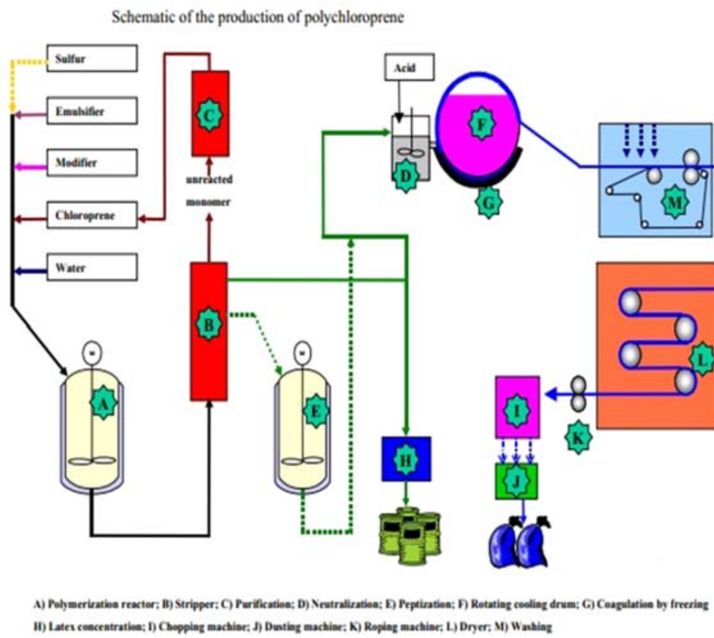

Figure 1 Production Scheme

With the aid of radical initiators, chloroprene in the form of an aqueous emulsion is converted into homopolymers or, in the presence of comonomers into copolymers. The polymerization is stopped at the desired conversion by the addition of a short stopping agent. The latex is freeze-coagulated on large, refrigerated revolving drums, from which it is drawn as a thin sheet. After washing and drying, the sheet is formed into a rope and then chopped to form the familiar chips or granules.

STRUCTURE AND STRUCTURAL UNITS

The basic polymerization scheme leads to incorporation of the monomer into a polymer consisting of different structural units
(Figure 2):

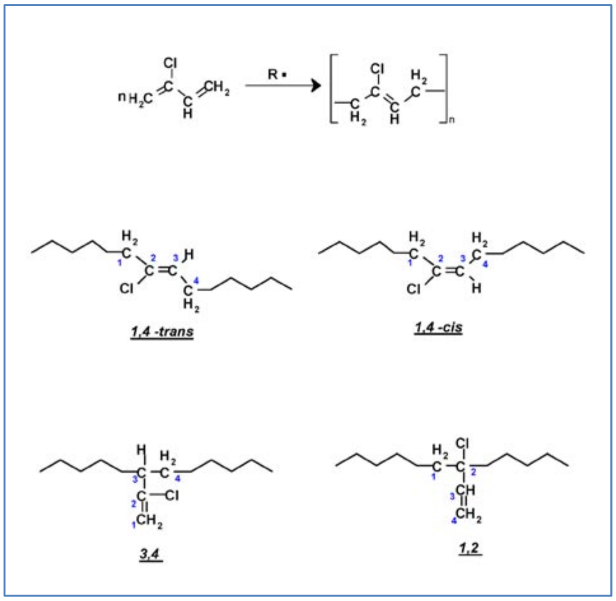

Figure 2- Basic polymerization scheme

The physical, chemical and rheological properties of the different grades of commercial polychloroprene are dependent on the ability to change the molecular structure by changing polymerization conditions, e.g. polymerization temperature or monomer conversion, polymerization aids (comonomers, type and amount of molecular weight modifier and emulsifier) and conditions during finishing.

The high amount of trans-1, 4-units in the polymer (about 90 % at standard polymerization conditions) leads to synthetic rubber, which has crystallization as an inherent property.

Types of Polychloroprene: Structure and properties of elastomers

Normal linear grades (general-purpose grades):

General-purpose grades are mostly produced with n-dodecyl mercaptan as the chain transfer agent and occasionally with xanthogen disulfides. If xanthogen disulfides are used, the elastomers are more readily processible and give vulcanizates with improved mechanical properties.

Precrosslinked grades:

Precrosslinked grades consist of a blend of soluble polychloroprene and crosslinked polychloroprene. They show less swelling after extrusion (die swell) and better calenderability. Precrosslinked grades are particularly suitable for the extrusion of profiled parts.

Sulfur-modified grades:

Sulfur-modified grades are copolymers of chloroprene and elemental sulfur. The viscosity is adjusted – in contrast to general-purpose grades - mostly after polymerization by "peptization" of the polysulfide bonds by e.g. thiuramdisulfides as peptization agents. Sulfur modification improves the breakdown of the rubber during mastication (lowering of viscosity). Sulfur-modified grades are used in particular for parts exposed to dynamic stress, such as driving belts, timing belts or conveyor belts because of their excellent mechanical properties. But the polymers are less stable during storage and the vulcanizates less resistant to aging.

Slow crystallizing grades:

Slow crystallizing grades are polymerized with 2,3-dichloro-1,3-butadiene as a comonomer. This comonomer reduces the degree of crystallization by introducing irregularities into the polymer chain. High polymerization temperatures also make structural irregularities, if this comonomer is not available. Crystallization resistant grades are used to produce rubber articles, which have to retain their rubbery properties at very low temperatures.

CONCLUSION

Polychloroprene will continue to be one of the most important synthetic speciality elastomers because its balance of properties is unique.