

INTRODUCTION

Part of this chapter has been published in J. Macromol.
Sci. - Rev. Macromol. Chem. C 21(2), 313 - 332 (1982).

Rubbers are long-chain molecules which are plastic in nature in raw or unvulcanized state. Vulcanization is an irreversible process by which the predominantly plastic rubber is converted to predominantly elastic and three-dimensional network structure through the anchoring between two polymer chains. Chemically, this is done by an intermolecular cross-linking reaction. Cross-linking increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force. These links between polymer chains may be chains of sulfur atom or atoms, carbon-carbon bonds, polyvalent metal ions, etc., depending on the nature of the vulcanizing system. Properties of elastomers depend on how efficiently this cross-linking has been achieved and also which types of cross-linking agents are used. For example, the retractive force resisting a deformation is proportional to the number of network supporting polymer chains per unit volume of

elastomers [1]. Again the strength of elastomers depends on the stress relaxation mechanism in the cross-linked material [2]. The modulus of a vulcanizate is proportional to the number of cross-links formed, while the tensile strength normally passes through a maximum with increase in the number of cross-links. The resilience, heat buildup and fatigue properties depend on the chemical nature of the cross-links and on the chemical structure of the base polymer [3]. Different types of cross-links have both advantages and disadvantages in respect to technical properties. To cite one example, a sulfur cross-linking system produces good tensile strength, but poor ageing properties. On the other hand, carbon-carbon cross-links produce good ageing properties, but poor tensile properties. Thus there are reasons for using a mixed cross-linking system in order to obtain the right compromise.

What is meant by mixed crosslinks ? By the term 'mixed cross-linking' we mean formation of network of rubber vulcanizate with different types of cross-links, for example, cross-linking by peroxide and sulfur in the same mix. Cross-linking by one vulcanizing agent (for instance sulfur alone) yielding cross-links of different sulfur ranks (monosulfidic/polysulfidic) is not considered as mixed cross-linking. Covulcanization of the rubber blend system, also is not considered as mixed cross-linking.

The property of the vulcanizates depends mainly on the base polymer and also on the vulcanizing systems which affect

the chemical nature of the links and flexibility of the chains. The chemical nature is dependent to some extent on the bond energies of the links. Bond energies of some cross-links are given below.

<u>Type of linkage</u>	<u>Bond energy, KCal/mole</u>
-C-S _x -C-	< 64
-C-S ₂ -C-	64
-C-S-C-	68
-C-C-	84
-Se-Se-	73
-Te-Te-	54

Methods by which rubber chains can be anchored by mixed cross-linkages, are divided broadly into two parts.

- (1) Modification of the base polymer
- (2) Manipulations of different vulcanizing agents.

One method of polymer modification is the introduction of active groups in the polymer chain. A well-known method is the synthesis of telechelic polymer, i.e., a polymer molecule having an active group at the chain end [4]. Various functional groups like carboxyl, hydroxyl, amino, silane etc. are introduced at the chain ends. Main object of synthesising end active groups in polymer chains is to study the effect of the contribution of the free chain ends on the physical properties. Most of the

telechelic polymers are liquid in nature and they are used mostly in adhesives and paints.

Next attempt was made to synthesize rubber as a terpolymer containing co-monomer units with pendent active groups. One successful attempt is the synthesis of carboxylated rubbers. This rubber is unique in that it can be vulcanized by reactions of the carboxylic group as well as normal sulfur type vulcanization. Since sulfur-curing system contains metal oxide (as activator) the vulcanizate is likely to consist of mixed (metallo carboxylate and sulfur-sulfur) type cross-links. Hence the modification of the polymer gives rise to mixed cross-link vulcanizates during the process of sulfur vulcanization. Carboxylated nitrile rubber is one such example. A short review on this rubber is given in the following section.

A. CARBOXYLATED NITRILE RUBBER

Introduction : The ever increasing way of modification of special purpose rubber for specific use has stimulated the introduction of new polymers to cover a wide range of end-use property. One of such advancements in the field of nitrile rubber technology is the emergence of carboxylated nitrile rubber which has been found to be useful as an oil resistant polymer. The acrylonitrile-butadiene-methacrylic acid terpolymer may be most concisely described as the speciality rubbers with the conventional technology. Carboxylated nitrile rubber has established

a reputation for providing harder, tougher vulcanizates with higher abrasion resistance, modulus, tensile strength and tear strength than conventional nitrile rubbers.

Historical : The first preparation of a carboxylic elastomer was recorded in 1933 in a French patent [5] and this described the co-polymerization of butadiene and acrylic acid in an acid emulsion at 60°C. But only in 1946 the terpolymers such as carboxylated butadiene acrylonitrile were reported in the patent literature [6]. At that time, the preparation of terpolymers of butadiene/acrylonitrile with acrylic acid and methacrylic acid in emulsion polymerization were described, and it was claimed that the resultant polymers showed greater solvent resistance than analogous non-carboxylated polymers.

In retrospect, this was, of course, an obvious claim. It is a well known fact that the solvent resistance of polymers is dependent upon their polarity. If, therefore, carboxyl groups, which are highly polar are added to the polar acrylonitrile contained in nitrile rubber, the resultant terpolymer will have greater solvent resistance.

The literature prior to 1950 only reported the preparation and evaluation of carboxylated rubbers as polar elastomers, and no one appeared to have taken advantage of the fact that the carboxyl groups could, because of their high chemical reactivity, be made to participate in cross-linking reactions. Later Brown [7] reviewed the cross-linking process of carboxylated elastomers. The involvement of carboxyl groups in cross-