

To Study the Effect of Various Additives on Vulcanized Rubber – A Review

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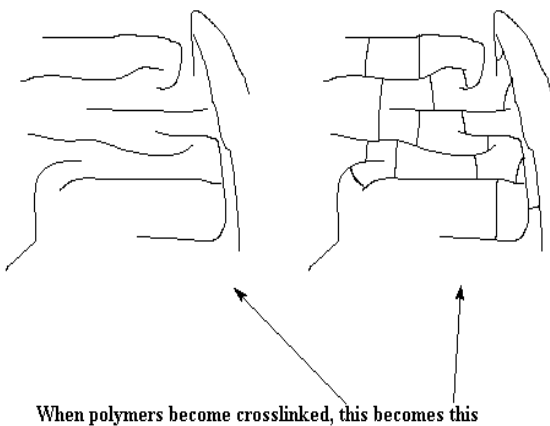
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Abstract

Vulcanization is a chemical process discovered by Charles Good Year in 1839. Using this process, mechanical and physical properties of natural rubber or synthetic rubber are improved. There are different types of vulcanization processes like sulphur vulcanization, urethane cross – linkers vulcanization, etc. There are also different methods of vulcanization such as press vulcanization, open vulcanization, continuous vulcanization and cold vulcanization. The objective of the present work is to review literature related to vulcanization of natural rubber or rubber blend to know about the effect of various additives used in vulcanization process on the properties of the rubber vulcanized.

1. Introduction

Vulcanization is a chemical process employed to enhance the properties of natural rubber or its blend. Natural rubber is soft, sticky and thermoplastic. In order to enhance its properties, it is vulcanized. There are different types of vulcanization processes based on curative used like sulphur vulcanization, urethanes cross-linkers vulcanization, metallic oxide vulcanization, duece vulcanization and acetoxysilane vulcanization. Sulphur vulcanization process is the most commonly used vulcanization process in which sulphur as curative is used. Vulcanization process consists of heating a compound containing various additives and curative. The curative used provides the cross linking between the long chain polymers of natural rubber which can otherwise move independently as shown in figure 1. The cross linking restricts the movement of these long chain polymers and hence rubber so obtained after vulcanization has more strength and a lot of commercial applications.



When polymers become crosslinked, this becomes this
Fig. 1. (a) Before Cross linking; (b) After Cross linking

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Apart from curative, various types of additives like reinforcing fillers, accelerators, activators, anti-degradants, inhibitors, extenders, softeners, etc. are added to make the rubber process economical, efficient and to improve properties of final product. Table 1.1 shows the general process flow chart of vulcanization process.

2. Literature Review

Loo (1974) investigated the influence of curing temperature on (i) the chemical crosslink density, (ii) the distribution of crosslink types, (iii) the extent of sulphidic main-chain modifications, and (iv) the zinc sulphide formation in natural rubber (NR) gum mix with a conventional N-cyclohexyl-2-benzothiazylsulphenamide (CBS) accelerated sulphur system. The ratio of the CBS/S was 0.5: 2.5 and vulcanization temperatures varied from

Table 1. Process flow chart of vulcanization

S. No	Vulcanization process
1	Weighing – weighing the ingredients as per required composition.
2	Blending – mixing of natural and synthetic rubber
3	Mastication – adding additives except curative and spreading them throughout the rubber matrix.
4	Maturation – giving enough time to all the ingredients for reacting with one another.
5	Compounding – adding accelerators and curative.
6	Shaping – giving required shape to the compound by extrusion or any other method.
7	Curing – cross linking between the long chain molecules of rubber compound by the curative.

140°C to 200°C. Results show that elevated cure temperatures produce a network with a lower crosslink density, in particular a lower polysulphidic crosslink density. The formation of intramolecular sulphidic groups and zinc sulphide increases with increasing temperatures.

(Kok 1986) determined the effect of zinc oxide on the vulcanization enthalpy of various sulphur vulcanization systems. The plots between enthalpy and zinc oxide represent minima in the natural rubber-sulphur un-accelerated system as well as in the synthetic polyisoprene-sulphur un-accelerated system, which contains extracts of natural rubber impurities. However, this complex behavior is not observed in accelerated sulphur vulcanizing systems for the two rubbers and is also absent from unaccelerated sulphur vulcanization of styrene butadiene rubber. Therefore, it is clear that non-rubber impurities play an important role in producing these minima in the enthalpy-zinc oxide plots.

(Kok 1987) studied the effect of compounding ingredients on the reversion of accelerated sulphur vulcanization of natural rubber (NR). It is observed that the more severe reversion is caused by the accelerators normally providing fast cure than that of the slower ones. MgCO₃, CaCO₃, silica and China clay all increase reversion but the severity depends on the accelerated system employed. Antidegradants increase reversion in general. But, the effect is more prominent with 2-mercaptobenzimidazole.

(Kuriakose and Rajendran 1995) proposed the use of raw rice bran oil in the vulcanization of carbon black and silica filled systems in NR compounding in place of process oil, antioxidant and fatty acid and came to a conclusion that the cure characteristics of the mixes and physical properties of the vulcanizates. Furthermore, it not only has a low cost but also saves energy during mixing. The added advantage of this non-edible natural oil in the rubber product manufacturing industry is that it is non-toxic in nature and has high free fatty acid content.

(Haque et al. 1996) used radiation dose to optimize the vulcanization of natural rubber latex. Various sensitizers were used to enhance the crosslinking. Among the sensitizers, n-butyl acrylate (n-BA) alone was found to be the best one. The effects of concentration of n-Ba, mixing and standing time of latex with n-BA on the tensile properties of latex film were examined. Results show that 12 kGy radiation dose, 5 phr n-BA and 30–40 min of mixing time were the optimum conditions for irradiation.

(Ismail and Chia 1998) investigated the concentration effects of multifunctional additive (MFA) and vulcanization systems on silica filled epoxidized natural rubber (ENR 25) in the concentration range 0–7.5 phr. Three vulcanization systems were used; conventional vulcanization (CV), semi-efficient vulcanization (semi-EV) and efficient vulcanization (EV). With the increase of MFA concentration, the cure time and scorch time of all vulcanization systems decrease. Results reveal that EV system has a shortest cure time and scorch time whereas the mechanical properties increase with the addition of MFA. At a similar MFA concentration, semi-EV systems gives better tensile and tear strengths followed by EV and CV systems.

(M.A Ansarifar et al. 2003) investigated the effect of bifunctional oranosilane on the joint strength of some natural rubber compounds to nylon 6,6. The compound contains 60 parts per hundred of rubber (P.H.R) by weight precipitated amorphous white silica to nylon 6.6. The compound also contained 3 and 7 P.H.R bis L3 triethoxysilylpropyl tetrasulphane (TESPT). The joint strength of the compound was measured by means of constant rate peel tests and constant load peel tests. These tests were performed at an angle of 90 in air. At constant rate, peeling energies up to 17 KJ/m² were measured. Under constant load, joint failure occurred in a time-dependence manner, and was cohesive in the rubber and in the primer, as well as at the primer/nylon interface. The results show that the joint strength of sulphur cored natural rubber compound containing 60 P.H.R. precipitated amorphous white silica and 3 or 7 P.H.R. TESPT when joined to nylon 6,6 and peeled off at constant rate under constant load was independent of the rate of peeling and of the loading of TESPT. Under constant load, joint failure occurred in a time-dependent manner.

(Maya Jacob et al. 2004) studied effects of concentration and modification of fiber surface in sisal/Palm hybrid fiber reinforced rubber composites. Sisal fibers of lengths 10mm and Palm fibers of lengths 6 mm were chopped. They were treated for 1 h with sodium hydroxide solutions of varying concentration viz., 0.5, 1, 2, 4 and 10% at room temperature. The fibers were added at the end of mixing process. Results show that the mechanical properties of the composites in the longitudinal direction superior to those in the transverse direction. Addition of sisal and oil palm fibers lead to increase of tensile and tear strength. The extent of adhesion between fiber and rubber matrix increases on alkali treatment of fibers. The alkali treated fibers exhibit better tensile properties than untreated composites.

(A. Ansarifar et al. 2006) studied the effect of synthetic precipitated amorphous white silica Nano filler on the properties of natural rubber. Coupsil 8113 is precipitated amorphous white Silica-type Ultrasil VN3, surfaces of which have been pretreated with bis (3-triethoxysilylpropyl) tetrasulphane (TESPT). TESPT helps adhere silica to rubber and also prevent it from interfering with the reaction mechanism of sulphur-cure. It has 20-54 mm particle size. The compounds were cured in a compression mould at 140° C with a pressure of 11 Mpa for measuring the mechanical properties of the rubber. The hardness, compression set, tensile strength and stored energy density at break were increased, but tearing energy, strain at break and cyclic fatigue life deteriorated when Silica was added to the rubber.

(Enver Demirhan et al. 2007) investigated the effect of carbon blacks on the mechanical and rheological properties of SBR 1502 styrene butadiene rubber. For this experimental work, 36 compounds were prepared with SBR 1502 and different furnace blacks by changing ratio in the compound formulation. Compounding ratios of carbon black were taken as 20,40,60,80 and 100 phr while rubber and other ingredients were kept constant. All samples were vulcanized at 145° C. results show that carbon black type and loading ratio changed the rheological and mechanical properties. Maximum tensile strength values are obtained in 60 phr carbon black loading for N 220, N 330 and N 347, in

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80 phr for N 326 and N 550 and in 100 phr for N 660 grade. The modulus values increase proportionally till 60 phr and then decrease with loading ratio of all types.

3. Conclusion

From literature review the following conclusions can be drawn:

1. Cross link density decreases with increase in cure temperature.
2. Accelerators providing fast cure such as MgCO₃, CaCO₃ affects more severely on reversion. Anti-degradants also increase reversion.

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