S.K. De Self-Vulcanisable Rubber Blends*

Mill-mixed blends of rubbers with appropriate reactive groups, when moulded at higher temperatures (140 °C-190 °C) for a long time (approx. 60 min.), get vulcanized even in the absence of crosslinking agents. This type of rubber blends where crosslinking occurs in the absence of any vulcanising agent has been designated as "Self-vulcanisable rubber blends". Several pairs of such unique rubber blends have been studied.

For example, epoxidised natural rubber (ENR) has been found to form self-vulcanisable rubber blend with carboxylated nitrile rubber (XNBR), when moulded at 150 °C for 60 min. Epoxy group of ENR reacts with –COOH group of XNBR. Such self-vulcanisable rubber blends can be reinforced by fillers and behave like conventional sulfur vulcanisable rubbers. The degree of crosslinking can be controlled by varying the blend ratio, moulding time or moulding temperature.

ENR also forms self-vulcanisable blend with polychloroprene rubber (neoprene). This blend is abbreviated as N-E. Miscibility here depends on both blend ratio and epoxy content of ENR.

ENR forms self-crosslinkable rubber blend with chlorosulfonated polyethylene (Hypalon). Miscibility in this system, abbreviated as H-E, depends on the expoxy content of ENR.

Hypalon forms self-vulcanisable blend also with carboxylated nitrile rubber (XNBR). This blend, abbreviated as H-X, is miscible in all blend ratios when moulded for 60 minutes at 180 °C. The blend can be reinforced by ISAF carbon black.

XNBR and neoprene forms self-vulcanisable rubber blend (N-X system) which is immiscible in all proportions when moulded at 180 °C for 60 min. Addition of ENR to the binary N-X system results in the formation of the ternary blend (E-N-X), which is also self-vulcanisable. Miscibility of the ternary system (E-N-X) depends on blend composition.

This principle of self-vulcanisation in rubber blends was extended to self-crosslinkable rubber-plastic blend. For example, mill-mixed blend of polyvinyl chloride (PVC) and ENR forms self-crosslinkable blend when moulded for 30 to 60 min. between 160 °C-180 °C. The blend shows extraordinarily high degree of processing safety at processing conditions. Such blends were found to exhibit good oil resistance, high abrasion resistance, high modulus, but low resilience with moderate tensile and tear strength. Similarly, PVC-XNBR system forms a self-crosslinkable rubber-plastic blend. The degree of crosslinking and physical properties depend on blend ratio and moulding time and temperature. The blends are partially miscible and the extent of miscibility depends on blend ratio.

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Living Carbocationic Polymerisation: New Functional Polymers Blocks and Thermoplastic Elastomers*

J.P. Kennedy

Rapid recent advances in the understanding of the mechanism of carbocationic polymerizations led to the discovery of living carbocationic polymerizations which in turn gave rise to a variety of promising new rubbery materials, specifically new polyisobutylene-based telechelics, blocks and thermoplastic elastomers.

The seminal discovery concerned new initiating systems of Friedel-Crafts acids in combination with tert-esters or ethers i.e., nucleophilic reagents that heretofore were regarded as severe poisons of these polymerizations. Specifically, it has been

demonstrated that systems such as cumyl acetate/BCl₃ or cumyl methyl ether/TiCl₄, are efficient initiating combinations for the living polymerization of isobutylene and other olefins. Further discoveries have shown that tert-chlorides in the presence of Friedel-Crafts acids (BCl₃, TiCl₄) and esters, amines, pyridine, dimethyl sulfoxide, etc, in other words strong purposefully added nucleophiles, also lead to living polymerizations and give polyisobutylenes of predetermined molecular weights and narrow molecular weight distribution (M_w/M_n) = 1.1-1.3). Justification for interest in living polymerization, however, is due not so much