

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 epoxy 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/ BCl_3 or cumyl methyl ether/ TiCl_4 , 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 (BCl_3 , TiCl_4) 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

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to molecular weight and molecular weight distribution control, but more so to the possibility of the preparation of terminally functional liquid or rubbery prepolymers (telechelics, macromonomers), and of thermoplastic elastomeric block copolymers by sequential monomer addition. This presentation will focus on developments in the latter areas. In the realm of terminally functional prepolymers, the recent one-post synthesis of a unique allyl-terminated polyisobutylene (PIB) is of particular interest.

In the field of thermoplastic elastomers (TPE) the synthesis of several linear and three-arm star TPE with the general microarchitectures, where glassy denotes high Tg glasses, will be described and discussed. These developments were mainly inspired by Shell's highly successful Kraton materials. Kratons are linear triblocks comprising polystyrene (PS) glassy outer segments and polybutadiene or polyisoprene or hydrogenated polybutadiene (i.e., poly(ethylene-co-1-butene) rubbery inner segments.

The synthesis of PS-PIB-PS or PS-(PIB-PS)-PS has been accomplished by the living carbocationic polymerization of isobutylene initiated by appropriate two (or three) functional

initiating systems followed by the addition of styrene. The product was a TPE with promising mechanical properties.

The strength of TPE is strongly affected by the Tg of the outer glassy segment. With this information in mind, TPE's have been prepared containing relatively high Tg glassy domains.

The copolymerization of styrene derivatives yielding relatively high Tg polymers leads to products whose Tg can be controlled by controlling the overall composition of the copolymer.

The Tg of the glassy segment of the TPE can also be controlled. The synthesis of a representative TPE with random p-tert-butylstyrene/indene copolymer glassy domain will be outlined.

P-Chlorostyrene and p-fluorostyrene, i.e., monomers that heretofore could not be satisfactorily polymerized by other (i.e., anionic) living techniques; have been readily polymerized by living carbocationic methods to high molecular weight products with predictable molecular weights. Subsequently, TPE containing the poly(p-chlorostyrene) is of interest on account of its relatively high Tg (127 °C) and flame resistance.

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Optimized Reinforcing Systems*

The direction of requirements concerning the performance of an article is pre-determined by its desired functionality and service life. These demands are complicated even further by economic, ecological, and toxicological aspects.

The car industry, for instance, requires tires with a long service life, a high degree of driving safety, and low fuel consumption, i.e. tires giving low treadwear, excellent traction on wet and dry surfaces, and low rolling resistance, and if possible all at the same time.

While striving to achieve such goals by changing the compound composition, it is necessary to re-investigate the state of the art with a view to decoupling vulcanizate properties which have so far been considered as being intricately linked. This can be done either by using conventional products or by developing new ones. This applies both to polymers and fillers as the constituents of reinforcing systems.

The only fillers suitable for use in tire treads are active blacks and silicas. This investigation therefore attempts to determine in how far these fillers are able to help solve the above problem.

The major difference between the two filler groups lies in their reinforcing mechanism. The question therefore arises as to whether a combination of different reinforcing mechanism could optimize vulcanizate properties, in particular E*, tan δ , and treadwear, and produce the desired effect.

The reinforcing effect of furnace blacks is caused above all by the adsorption (hardly any covalent bonds) of the polymer on the

accessible surface of the carbon black aggregates and agglomerates. The latter is characterized by 24M4-DBP absorption and CTAB adsorption. Only by including the dispersive component of surface energy γ_s^d is it possible to describe more accurately and for all furnace blacks the dependence of E* and tan δ on carbon black properties, including treadwear.

Silicas are governed by a different reinforcement mechanism.

The low value of the dispersive component of surface energy γ_s^d and the higher value for TEA absorption in the case of the silica are of considerable importance: the lower γ_s^d is responsible for the low abrasion resistance of silica vulcanizates. E* and tan δ , on the other hand, are determined by the presence of a silica network within the rubber matrix, as indicated by the high TEA absorption.

The modification of silicas with bis (3-triethoxysilylpropyl)-tetrasulfane changes their reinforcing mechanism in such a way that the adsorptive rubber bonds at their surface are replaced by covalent rubber-to-filler bonds.

This raises abrasion resistance to the level of N 220, whereas the, for silicas, typically low tan δ -value is maintained or reduced even further.

The right choice of suitable active blacks and silicas, of the blend ratio and the degree of silanization permits the different reinforcing mechanisms to be matched in such a way that E*, tan δ , and treadwear are to a large extent decoupled and can finally be tailored to suit the particular application.

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