Binary Accelerator Systems in Rubber Vulcanization

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SYNOPSIS

The increasing use of binary accelerator systems in the vulcanization of elastomers and their blends is due to several factors including the aim to optimize the end use properties, better cure properties etc. Even though there has been wider use of binary accelerators in elastomer vulcanization, the combined / synergic action of accelerators is not fully understood. It is known that sulfur containing nucleophiles like thiourea improves the activity of conventional activators like CBS, TMTD etc. at lower temperatures.

In part I of the present work, efforts have been made to synthesize and characterize novel secondary accelerator N-benzylimine aminothioformamide (BIAT) and also to investigate the effect of BIAT binary accelerator system on cure and physico-mechanical properties of NR, SBR, NR / SBR blend microcomposites. Considerable reduction in cure time and remarkable enhancement in physico-mechanical properties of these vulcanizates compared to the reference mixes cured with primary accelerator alone shows the nucleophilic character of BIAT and the synergism between it and the primary accelerator used. Though scorch safety was poor, it is remedied by further studies, i.e., by capping of zinc oxide. Based on the cure and other properties, optimum dosage of BIAT has also been suggested.

In part II of the work, attempts have been made to study the effect of BIAT binary accelerator system on cure and physico-mechanical properties of NR / NBR nanocomposites. Surface-modified nano zinc oxides like BIAT-capped zinc oxide (ZOB), stearic acid-coated-BIAT-capped zinc oxide (ZOBS), and stearic acid-coated zinc oxid (ZOS) have been synthesized by sol-gel process. Nano modified form of BIAT, surface modified fillers like PEO-coated calcium silicate (PCS) and silicate-coated calcium carbonate (SCC) have also been prepared by the sol-gel process. These particles were characterized by FTIR spectroscopy, XRD, SEM and TEM images. The nano ingredients were effective in improving the cure and technological properties of NR mixes compared to the microcomposites. The capping process

was an effective technique for improving scorch safety. The enhancement of various properties of NR nanocomposites is due to better dispersion of the nanoparticles in the NR matrix, which was evidenced by the electron microscopy images of the resultant vulcanizates.

In the later section of the part II of the work, emphasis has been given to the preparation of NBR / NR blend (80 / 20) and its nanocomposites using PCS , SCC and carboxylated multiwalled carbon nanotubes (MWCNT). A detailed comparative study has been conducted with special reference to cure properties, tensile properties, tear resistance, compression set, abrasion resistance, hardness, bound rubber content, crosslink density, transport and electrical properties.

The carboxylated CNT-filled NBR / NR blend mixes showed improved cure properties when cured with nano modified BIAT and micro CBS binary system. Cure time decreased with increase in concentration of CNT. The delta torque values of the CNT-filled mixes also showed increase with increase in concentration of CNT. This improved cure properties is due to the better dispersion of CNT by increasing the filler-polymer interaction leading to intercalation of polymer matrix, as compared to silicate-coated calcium carbonate and PEO-coated calcium silicate. The polar groups on CNT could enhance the NBR-NR compatibilization. The XRD curves, TG-DTG-DSC curves and microscopic images provided support for the better mixing of CNT compared to silicate-coated calcium carbonate and PEO-coated calcium silicate. The improved mixing has lead to the enhancement of the physico-mechanical properties like tensile strength, modulus, elongation at break % values, tear strength, abrasion resistance, bound rubber content and hardness. The enhanced crosslink density values are in agreement with other physico-mechanical properties. The elongation at break % values increased with increase in dosage of CNT because of the sliding effect caused by the intercalated CNT. The CNT-filled vulcanizates exhibited reduced vapor permeability and improved solvent resistance, compared to the vulcanizates containing inorganic fillers. This is due to the improved barrier property imparted by the better dispersed CNT. Tortuous paths were created in presence of CNTs. However, the resistance to low molecular weight and polar solvents was lower for the vulcanizates as compared to the non polar and high molecular weight solvents. The polar-polar interaction between the polar part of NBR and the polar solvent molecules has accelerated swelling and permeation. As molecular size increases, it becomes more difficult for them to pass through the tortuous paths. The intercalation process has improved the electrical properties of the CNT-filled NBR / NR vulcanizates, compared to inorganic-filled

vulcanizates. The polar groups on the CNTs have also increased the conductivity of the NBR / NR vulcanizates. The increased filler-polymer interaction caused an increase in the thermal stability of CNT-filled NBR / NR mixes compared to other inorganic filled mixes like SCC-filled mix. Thus when the overall performance in various technological properties are considered, CNTs show superiority over other inorganic fillers like silicate-coated calcium carbonate and PEO-coated calcium silicate for the use in NBR / NR blends.

The present investigation also shows that nano rubber ingredients are better for the enhancement of overall properties of various elastomers and their blends due to the possibility of attainment of better and efficient dispersion in polymer matrices. The investigations further show that BIAT is an effective accelerator when used in binary accelerator systems for advantageously vulcanizing elastomers, compared with the use of conventional single accelerators.

Application of binary accelerators remains a better and efficient method for improving technological properties of elastomers like NR, SBR, NR / SBR blends, and NR / NBR blends. Since the nanocomposites have superior properties to the microcomposites, studies can be extended even to ternary blends using binary accelerators and compound fillers like mixture of nanosilica and CNT, nanoclay and CNT etc.

Solid state NMR is highly useful for the determination of crosslink density of the composites. The detailed mechanism of vulcanization can be derived from solid state C^{13} NMR. This can serve as a powerful tool for the investigation of structural changes upon vulcanization especially in presence of fillers. Since the magnetic field near filler particle is different from the rest of the sample, the elastomer chains near filler particle will experience a different frequency, which will result a shift in NMR spectrum. So, studies can be extended in this direction in future.

Due to the high dielectric constants of the CNT-filled NBR / NR vulcanizates, high performance capacitors can be developed using these compounds. Also, owing to the high oil and solvent resistance, products like automobile parts, oil and fuel hoses, washers of various appliances etc. can be developed by future researchers.