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Influence of network structure on the viscoelastic properties of dynamically vulcanized rubber/plastic blends: An alternative approach to understand the microstructure evolution

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ABSTRACT

The formation of finely dispersed micron-sized cross-linked rubber agglomerates in the thermoplastic matrix during dynamic vulcanization is now a well accepted theory to explicate the final properties of thermoplastic vulcanizates (TPVs). Based on our previous results, we have investigated further in the present work on the most influential and essential parameters which controls the ultimate properties of the TPVs. Three TPVs based on poly[styrene-b-(ethylene-co-butylene)-b-styrene] triblock copolymer (S-EB-S) and solution polymerized styrene butadiene rubber (S-SBR) have been prepared containing different proportions of rubber fraction. A semi-efficient (SEV) sulphur based curing system has been adopted to cross-link the rubber phase and advanced microscopic techniques viz. transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) have been used for the microstructure analysis. Thereafter, dynamic experiments have been performed to correlate the morphological observations with viscoelastic properties. The experimental results and the morphological images confirm that the network structure formation during dynamic vulcanization and its integrity is the most influential parameter to cause the utmost properties of the TPVs. The finely dispersed cross-linked rubber particles obtained during dynamic vulcanization are actually the disintegrated and agglomerated rubber nano-particles having average particle size between 80 and 85 nm. It has also been confirmed that the integrated rubber network structure has an inverse relationship with the proportion of rubber fraction present in the TPVs. Mechanical properties, melt rheology and dynamic viscoelastic measurements also support the network structure disruption and disintegration observed in the morphological images and thus, nullifies the supremacy of dispersed phase morphology theory behind the superior properties obtained from the TPVs. This work elucidates the necessity and importance of integrated network structure formation over the morphology evolution during dynamic vulcanization and leads to a new avenue to understand morphology–mechanical–rheological–viscoelastic property correlation in TPVs.

1. Introduction

Thermoplastic vulcanizate (TPV) is a specific group of elastomeric alloy (EA) [1] where the rubber phase is selectively cross-linked upon dynamic vulcanization and dispersed in presence of a molten thermoplastic phase during intensive mixing [2]. It exhibits rubber-like properties: such as lower compression set, lower stiffness, greater resistance to fatigue, better resistance to heat and chemicals etc. [3,4] apart from imparting melt-processibility like thermoplastics. These phenomenal qualities led them as a potential competitor to the fast growing rubber market [5,6] for last two decades and still gaining considerable momentum from various industries such as automotives, electronics, construction and so on.

S-EB-S is a hydrogenated styrenic triblock copolymer which is primarily used as a compatibilizer for various binary blend systems [7]. However, several researchers have reported a blend of S-EB-S with polypropylene (PP) to prepare the TPEs [8,9]. Sengupta et al. carried out a comparative study of the oil extended S-EB-S/PP blend with PP/EPDM TPV [10,11]. Sengers et al. investigated the

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rheological properties of PP/S-EB-S blends [12,13]. Subsequently, Ahmad et al. achieved a highly transparent TPE from isotactic PP and S-EB-S triblock copolymer [14]. Picchioni et al. studied the mechanical and thermal behavior of polystyrene (PS)/S-EB-S blend [15]. Therefore, to the best of our knowledge, there is no literature available which in-detail investigates the controlling factors responsible for the ultimate properties of the sulphur cured S-EB-S/S-SBR TPVs as a potential competitor of PP/EPDM or PP/EOC TPVs (dynamically cured by peroxide) for automobile applications. The solubility parameters of both S-EB-S and S-SBR are rather comparable and thus it is presumed that the dynamic vulcanization would result in a TPV that can meet the growing demand of the industries.

Dynamic vulcanization is an easy process but a complicated technique, as it involves the breakup and cross-linking of the rubber phase simultaneously leading to phase inversion of the rubber phase in the thermoplastic matrix [5,16]. It has been reported that the cross-linking and breakup of the rubber phase is the primary factor responsible for the phase inversion of TPVs during dynamic vulcanization [17–20]. Several prior studies have been reported earlier describing the morphological evolution of the rubber phase in the TPVs during dynamic vulcanization [4,21–24]. Some studies reported the effect of cross-linking and rapid increase in the viscosity on the morphology evolution [4,21] and some other reported the consequences of early stage cross-linking during in situ vulcanization and its induced effect on surface tension of the rubber phase leading to the breakdown of rubber agglomerates and dispersion of same in the thermoplastic matrix through the occurrence of phase inversion [23,24]. Irrespective of the route of morphological evolution almost all studies reported the dispersion of micron-sized rubber particles (0.5–3.0 μm) in the thermoplastic matrix [4,21,23,24] which led to an improved mechanical and dynamic mechanical properties in terms of ultimate tensile strength and elastic recovery through hydrodynamic effect by acting as a soft filler in the thermoplastic matrix [22,25].

In a previous communication the authors have found that the cross-link density and elastic modulus of the rubber phase do have more relevance over the final morphology formation (dispersed or continuous) to describe the mechanical and dynamic properties of S-EB-S/S-SBR TPVs [26]. In the subsequent study, regarding the reprocessibility of aforesaid systems, the major influence of cross-link density (over the final morphology formation) was reconfirmed while discussing the final properties of the respective TPVs [27]. These facts have motivated us to understand whether the dispersed phase morphology with micron-sized rubber particles in TPVs are really the influential and deciding parameter to describe the ultimate properties of the S-EB-S/S-SBR TPVs or there is something else behind it!

In this present work, S-EB-S/S-SBR TPVs at various proportion of rubber are prepared to impart different phase morphology for the respective TPVs keeping a consistent degree of cross-linking. Their melt rheology, dynamic viscoelasticity, physico-mechanical properties and phase morphologies have been studied and results are reported.

2. Experimental

2.1. Materials

S-EB-S (trade name Kraton® G1657) is a clear, linear tri-block copolymer (consists of 30% di-block) based on styrene and ethylene/butylene having a polystyrene content of 13%. Density of S-EB-S is 0.90 g/cc and the melt flow index is 22 g/10 min. at 230 °C/5 kg. The supply came from Kraton Polymer of Belgium in the physical form of dusted pellet. S-SBR (trade name SPRINTAN™ SLR 4601) is procured from Styron, India having a styrene content of 21%, density of 0.93 g/cc and Mooney viscosity of 50 MU (ASTM D1646). It consists of 63% vinyl content and the volatile matter and ash content have been reported as 0.3% and 0.2%, respectively. The chemical structures of S-EB-S and S-SBR are given in Fig. 1(a) and (b). The solvent toluene was obtained from Merck Specialities Private Ltd., India. Accelerator activators, i.e. Zinc oxide (Zinc content 82%) and stearic acid (max. ash content 0.1%) were procured from Sunrise Overseas, India. Antioxidant, TDQ (2,2,4-trimethyl-1, 2-dihydroquinoline (Polymerized)) possessing softening point of 88–95 °C and ash content below 0.3% was procured from NOCIL Limited, India. Accelerator TBBS (N-tert.butyl-benzothiazyl sulfenamide) was obtained from Lanxess Rubber Chemicals, India, having a melting point of 110 °C as well as ash content below 3%. Finally, the cross-linking agent sulphur powder (max. ash content 0.2%) was procured from Triveni Chemicals, India.

2.2. Compositions of various TPVs

TPVs were prepared using different S-EB-S/S-SBR blend ratios as shown in Table 1. The amount of antioxidant, accelerator activators, accelerator and sulphur were kept constant relative to the amount of S-SBR. In a compounding recipe containing highly unsaturated di-ene rubber (S-SBR), antioxidants are generally used to protect it from thermal oxidation and help to extend the useful service life of products made with this kind of rubbers. The addition of 1% of antioxidants with respect to the total quantity of rubber is the minimum requirement to prevent it from oxidative degradation [28]. Zinc oxide (ZnO) is well known as cure activator during sulphur vulcanization. In the development of maximum cure state, the initial cross-link structure, which may be high in polysulfides, goes through a rearrangement process in which the Zn-accelerator complexes, which promote curing, extrude sulfur from the initial cross-links and reutilize the extruded sulfur to form additional cross-links. Stearic acid, on the other hand, is used along with ZnO in many compounds as a cure activator and in addition may serve as a processing agent to improve mill and processing equipment release properties. The standard requirements of ZnO and stearic acid in a conventional rubber compounding recipes are 3–5 phr. and 1–3 phr. respectively with respect to 100 phr. of rubber [28]. Finally, the accelerator and sulphur used in the compounding recipe, together form vulcanization system. Vulcanization is a chemical process where sulfur forms cross-links in the rubber and thereby improves the polymer's mechanical properties. The compositions in terms of the weight percentage of components for TPVs are presented in Table 1. It comprises different blends ratios viz. S-EB-S/S-SBR (70/30 wt%) to S-EB-S/S-SBR (30/70 wt%) with 10% increment in S-SBR content and a semi-efficient sulphur vulcanization system (SEV) has been adopted to cure the rubber phase.

2.3. Preparation of TPVs

TPVs, based on S-EB-S/S-SBR in the proportion of 50/50 wt%, were prepared by using a Brabender Plastograph EC (Digital 3.8 KW motor, a torque measuring range of 200 Nm and a speed range from 0.2 to 150 min^{-1}). All the mixing was carried out at 160 °C at a rotor speed of 60 rpm. To make the TPVs, S-EB-S was first loaded into the chamber and allowed to melt for 2 min, then S-SBR was added and melt-blended for another 1 min. Thereafter, zinc oxide and stearic acid were added and mixed for another minute. Finally the sequence ended up with the addition of sulphur and accelerator and the mixing was continued till the torque reached the plateau. The resulting TPVs were then quickly removed from the chamber and passed through a two-roll mill having a close nip-gap at room temperature to sheet it out.