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Physico-mechanical properties and thermal stability of thermoset nanocomposites based on styrene-butadiene rubber/phenolic resin blend

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ABSTRACT

Effect of organoclay (OC) on the performance of styrene-butadiene rubber (SBR)/phenolic resin (PH) blend prepared by two-roll mill was investigated. The influence of OC content ranging between 2.5 and 30 phr on the performance of SBR/PH was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), interfacial energy analysis, tensile, dynamic mechanical, swelling, cure rheometry and thermogravimetric analysis (TGA). It was found that the OC is mainly localized in the SBR phase of SBR/PH blend through the kinetically favored mechanism relevant to rubber chains. The results also demonstrated the positive role of PH on the dispersion of OC. Both PH and OC showed accelerating role on the cure rate of SBR and increased the crosslinking density of the rubber phase. Additionally, the mechanical and dynamic mechanical properties of SBR were influenced by incorporation of both PH and OC. TGA showed that the OC improves thermal stability of SBR vulcanizate, while it exhibits a catalytic role in presence of PH.

1. Introduction

Incorporation of organoclay (OC), i.e. layered silicate mineral modified with organic surfactants, with polymers leads to substantial improvement in the properties even at low filler content, namely less than 10 wt% [1–5]. This is known to be due to the extremely large interfacial area between the polymer matrix and platelets of the OC because of its nanometric thickness, namely 1 nm for an individual platelet, as well as large aspect ratio of silicate layers [1,2]. Thus, it can be anticipated that such unexpected properties are closely related to the quality of dispersion of OC in the polymer matrix.

The use of carbon black, serving as nanofiller [2], in the rubber compound is not new and it has been the primary filler in the rubber industry for a long time. As a growing demand in rubber industry to use the nonblack fillers, the OC can then be a promising alternative for such applications [6]. Consequently, a great deal of researches has been devoted recently to characterize the performance of rubber/OC nanocomposites and to analyze structure–property relationship in such systems [7–14].

Albeit many rubber/OC nanocomposites have been studied by researchers, little work has been performed on nanocomposites based on rubber two-phase blend [15,16]. The available literature in this area is mostly limited to thermoplastic matrices. One of the important aspects of OC is its influence on the phase morphology of the immiscible polymer blends. It has been observed in many cases that the domain size of the dispersed phase greatly decreases upon addition of OC [17–20]. Moreover, OC may be localized in one of the phases preferentially or dispersed in both phases or even at the interface of two phases [18–24]. The uneven distribution of nanofiller in polymer blends has been known to be due to the dominant thermodynamic interaction between the OC and the host polymer [25].

In some applications such as railroad brake shoes, the mixture of phenolic resin (PH) and a synthetic rubber can be utilized as a polymeric binder [26–28]. PH shows several desirable properties such as outstanding mechanical performance, thermal resistance, dimensional stability as well as high resistance against water, acids and other chemicals [29]. However, the rigid aromatic units tightly held by the short methylene linkages make the PH brittle. Incorporation of PH into rubber matrix enables one to obtain a polymeric binder with balanced properties of flexible rubber and the thermosetting resin. One of the most widely used general purpose synthetic rubber for such application is styrene-butadiene rubber (SBR). It is known that the mixture of SBR and PH, at excess amount of PH namely greater than 10 phr, leads to a two-phase blend [30,31]. In such blend the PH forms dispersed phase within the rubber matrix.

Open literature shows many publications, addressing the morphological [13,32], rheological [33], flammability [34], thermal [35], barrier [14] and mechanical and dynamic mechanical [13,14,32,35,36] characteristics of SBR/OC nanocomposites. However, the nanocomposite of SBR/PH blend filled with OC has not been addressed yet. This blend is comprised of two different

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thermosetting polymers having different glass transition temperatures (T_g). The lowest T_g belongs to SBR, i.e. ∼−40 °C [31], while that of PH is approximately 140 °C [31]. Structural characteristics of OC in such a blend produced by melt mixing with traditional open two-roll mill, which is operated at moderated temperature, i.e. around 50 °C, could be interesting. Because this processing temperature, which is much higher than T_g of SBR but lower than that of PH, is thought to dominate the dispersion state of OC in the SBR/PH blend.

In our earlier works, the performance characteristics of nitril-butadiene rubber (NBR)/PH nanocomposites filled with nanoalumina and OC have been reported [37,38]. The objective of the present work was to examine the capability of the OC in enhancing the properties and thermal stability of the SBR/PH blend. As the widespread usage of rubber based friction materials, i.e. like SBR/PH, is restricted by the lower thermal stability of rubber phase [31], such investigation is important to characterize the influence of OC on the performance of rubber/PH blends. Simple model systems, i.e. the nanocomposites with simpler morphologies, have been successfully employed to obtain a better understanding concerning the structure–property correlation in multicomponent nanocomposites [23,39]. In this study, nanocomposites of SBR and OC can be a suitable candidate for acting as model system. Therefore, SBR/OC nanocomposites were examined to obtain a basis for analyzing the ternary hybrid of SBR/PH/OC.

2. Experimental

2.1. Materials

Styrene-butadiene rubber (SBR1502, styrene content of 23%, density of 0.97 g/cm^3) was supplied by BIPC Co., Iran. Phenolic resin (Novolac IP502, hexamethylenetetramine content 10 wt% and density of 1.28 g/cm^3) was supplied by Rezitan Co., Iran. The rubber additives, namely mercaptobenzthiazyl disulfide (MBTS), zinc oxide (ZnO) and stearic acid, are all obtained from the laboratory of the Machinlent-Tehran Co., Iran. The OC used in this study was Nanolin DK1, which is montmorillonite modified with a quaternary ammonium salt (high purified smectic, CEC of 110–120 mequiv./100 g, d_{001} spacing of 2.16 nm) produced by Zhejiang Fenghong Clay Chemicals Co. Ltd., China.

2.2. Sample preparation

All the compounds were prepared via melt mixing in a laboratory scale two-roll mill with roll diameter of 0.3 m. Prior to the mixing process, the SBR was first subjected to a mastication process at temperature around 50 °C. Then the other components including PH (if applicable), OC and rubber curing additives were incorporated sequentially into the masticated SBR so that the total mixing time including mastication was kept to be 30 min for all compounds. Table 1 summarizes the recipes of all compounds and their abbreviation used in this article. In all of them, the rubber curing-agents were retained as sulfur 5 phr, MBTS 2 phr, zinc oxide 5 phr, acid stearic 2 phr. Moreover, the proportion of PH in SBR/PH blend was always kept to be 25 phr. It should be kept in mind that the sulfur content used in this study, i.e. conventional sulfur curing system, is higher than those reported in the literature for many rubber/OC nanocomposites investigated. To investigate the role of order of mixing on the microstructure, the mixture SP/OC-5 (MS) is adopted. In SP/OC-5 (MS) the blending sequence was as SBR + OC + PH + curing-agents in which the OC was first added to the rubber and then PH was incorporated into the compound.

All compounds were compression molded into rectangular sheets with dimensions of 15 mm × 15 mm × 2 mm at molding temperature of 145 °C for 1 h under a pressure of 3.5 MPa. Then the sheets were post-cured for additional 2 h in the same molding temperature. The required samples for mechanical and physical tests were cut from the vulcanized rubber sheets.

Table 1
Recipe of compounds used in this study.

Designation	Composition and mixing condition
S0	SBR + 0 phr PH + 0 phr OC
S/OC-2.5	SBR + 0 phr PH + 2.5 phr OC
S/OC-5	SBR + 0 phr PH + 5 phr OC
S/OC-7.5	SBR + 0 phr PH + 7.5 phr OC
S/OC-15	SBR + 0 phr PH + 15 phr OC
S/OC-30	SBR + 0 phr PH + 30 phr OC
SP0	SBR + 25 phr PH + 0 phr OC
SP/OC-2.5	SBR + 25 phr PH + 2.5 phr OC
SP/OC-5	SBR + 25 phr PH + 5 phr OC
SP/OC-7.5	SBR + 25 phr PH + 7.5 phr OC
SP/OC-15	SBR + 25 phr PH + 15 phr OC
SP/OC-30	SBR + 25 phr PH + 30 phr OC
SP/OC-5 (MS)	The same as SP/OC-5 but with different mixing sequence [mixing sequence: SBR + 5 phr OC + 25 phr PH]

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a Philips diffractometer (40 kV, 40 mA, λ = 15.4 nm, Netherlands) within the 2θ angles of 2–10° at a scanning rate of 0.02°/s.

Scanning electron microscopy (SEM, LEO 1455VP, UK) was used to characterize the morphology of the blends. An image analyzing software (Clemex vision, professional edition, version 3.5, Clemex technologies Inc., Canada) was used to measure the resin particle size based on the microphotographs obtained by SEM. The dispersion of the OC platelets in the nanocomposite was also investigated by means of transmission electron microscopy (TEM, Philips CM-200) operating with an acceleration voltage of 200 kV. Firstly, ultra thin section of the cured sample was prepared using an OmU3 microtom (C. Reichert, Austria) equipped with a diamond knife with the aid of liquid nitrogen.

Curing behavior of compounds was determined using the oscillating disk rheometer (ODR GT7070-S2, Gotech, Taiwan). Torque–time curves produced by ODR were used to extract the scorch time (t_5) and optimum curing time (t_{90}). The cure rate is also expressed in terms of cure rate index (CRI) which is defined as CRI = 100/($t_{90} - t_5$) [8]. Thermogravimetric analysis (TGA, Pyris Diamond TG/DTA PerkinElmer, Japan) was performed under nitrogen from room temperature up to 500 °C at the heating rate of 20 °C/min.

The surface free energy of the pure samples, i.e. SBR, PH and OC, was determined by the Owens and Wendt procedure based on contact angle measurement [40]. According to this procedure, dispersive and polar components of the surface energy can be determined for a given solid surface. Contact angle measurements were performed at room temperature using OCA15 plus (data physics instruments, Germany). Test liquids were distilled water, formamide, ethylene glycol and Diiode methane. OC in the form of pressed disk was used in wettability measurements.

Tensile testing was performed on a Hounsfield model H10KS, UK, operated at crosshead speed of 60 mm/min. Storage modulus (E') and loss tangent (tan δ) were recorded as a function of temperature by dynamic mechanical thermal analyzer (DMTA-PL, Triton, Tritic Technology, England) at a frequency of 1 Hz with a heating rate of 3 °C/min. The DMTA experiments were performed in an extension mode with the deformation of 0.02%.

The parameters ν (crosslinking density) and M_c (the number average molecular weight between two crosslinks per primary rubber chains) of rubber phase were estimated by the Flory–Rehner