



Research paper

Morphology and rheology of (styrene-butadiene rubber/acrylonitrile-butadiene rubber) blends filled with organoclay: The effect of nanoparticle localization

Alireza Monfared^{a,b}, Azam. Jalali-Arani^{a,*}^a Department of Polymer Engineering & Color Technology, Amirkabir University of Technology, P.O. Bo, 15875-4413, Tehran, Iran^b Lorestan Petrochemical Co., Building No. 1286, 5th Floor, North Kargar St., Tehran, Iran

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ABSTRACT

In this study, immiscible acrylonitrile butadiene rubber/styrene butadiene rubber (NBR/SBR) blends and their nanocomposites with cloisite 15A (C15A) and cloisite 30B (C30B) nanoparticles were prepared via a melt mixing method. The structure and morphology of the prepared samples were investigated by theoretical methods and by using equipment including X-Ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The experimental results proved that the C30B, the more hydrophilic organoclay (OC) tended to confine in the NBR, the more polar rubber phase, and in the interface whereas C15A, the less hydrophilic one was located at the SBR and interface. This was in agreement with the results obtained by the calculation of the wetting parameter. The EDS results showed that the average area of the NBR droplets in the SBR/NBR (80/20) blend decreased from 1.13 to 0.8 and 0.76 μm^2 in the presence of C30B and C15A, respectively. The use of epoxidized natural rubber (ENR) in conjunction with the OC caused more reduction of the NBR droplet size. Rheo-mechanical spectroscopy displayed the significant effect of OC localization on viscoelastic properties of the blends. Meanwhile, the rheological behavior of the blends was quantitatively similar to that predicted by Palierne's model extended to filled immiscible blends. This model was applied to obtain morphological and interfacial information for the SBR/NBR nanocomposite.

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1. Introduction

The blending of polymers is an attractive way to develop new materials; however, most polymer blends are thermodynamically immiscible which results in phase separation upon blending and weak properties. Therefore, the control of phase morphology during blend processing is a key issue for the production of a new blend with improved properties compared with the constitutive immiscible polymers. One of the classical methods to reduce the interfacial tension between the phases is the use of a compatibilizer. By the use of this method, a finer and more stable morphology, better adhesion between the phases and consequently better mechanical properties of the final product can be achieved (Grace, 1982; Huitric et al., 2009).

In a blend with droplet-matrix morphology, the dispersed droplet size is affected by a competition between shear forces, which tend to deform the droplets, and interfacial tension forces, which resists the deformation. Therefore, it can be said that during mixing, the shape and size of the droplets are controlled by the competition between break-up and the coalescence mechanism (Grace, 1982; Huitric et al., 2009). It is known that by the use of a compatibilizer, the morphology

of immiscible blends can be stabilized through suppressing coalescence and enhancing interfacial adhesion which results in a finer droplet size (Huitric et al., 2009). During the last decades, block, graft or random copolymers have been used as the compatibilizers for immiscible polymer blends to prevent phase separation (Ramesan and Rosamma, 2001; Botros et al., 2006; Khalf et al., 2010; Noriman et al., 2010); however in recent years, using inorganic nanoparticles, as the compatibilizer have attracted particular attention (Wang et al., 2001; Steinmann et al., 2002; Gu et al., 2004; Elias et al., 2007). For instance, Elias et al. (2007) investigated the effect of hydrophilic and hydrophobic silica on morphology and rheology of the polypropylene/polystyrene (PP/PS) and also PP/ethylene vinyl acetate (EVA) blends and reported a significant reduction of the dispersed phase droplets size in the presence of only 3 wt.% of both types of silica. In this context, clay mineral, a naturally occurring material composed primarily of fine-grained minerals (Bergaya et al., 2011; Bergaya and Lagaly, 2013), was also used in the polymer blends as a compatibilizer. To improve the clay mineral compatibility with the hydrocarbon matrices, the hydrophilic clay mineral are modified with various alkylammonium salts to expand the interlayer space and also reduce the surface energy of the layers (Bergaya et al., 2011). Wang et al. (2001) used montmorillonite (Mt) particles organically modified with octadecylammonium in a blend composed of Nylon6 (PA-6)/PP and showed the significant effect of using organically

* Corresponding author. Tel.: +98 21 64542435; fax: +98 21 66468243.
E-mail address: ajalali@aut.ac.ir (A. Jalali-Arani).

modified clay mineral (OC) nanoparticles on the reduction of the dispersed phase size and enhancement of the tensile modulus and strength. Huitric et al. (2009) reported the reduction of the dispersed phase size with increasing the OC content in the immiscible blends based on polyethylene/polyamide (PE/PA).

The solid particles are well known to distribute unevenly in the phases of an immiscible polymer blend (Ren et al., 2000; Galgali et al., 2001; Elias and Fenouillot, 2008; Fenouillot et al., 2009), however in the domain of high viscosity immiscible polymer blends, it was less studied (Fenouillot et al., 2009). The first study in this context concerned essentially elastomer blends with carbon black as the reinforcing filler (Elias and Fenouillot, 2008). In the field of nanoparticles, Elias et al. (2007, 2008) in their research on using silica nanoparticles in the PP/PS and PP/EVA blends proved that the hydrophilic silica tended to confine in the more polar PS or EVA phase. This is while the hydrophobic silica was located at the PP/PS interface and in the PP phase. Wang et al. (2001) reported a good affinity of Mt particles organically modified with octadecyl ammonium toward the polar polymer in the PA-6/PP blend.

Different methods such as electron microscopy, X-ray scattering, dynamic mechanical analysis, mechanical and rheological testing have been used to investigate the compatibilizing effect of nanoparticles. In this view point, recently much attention has been paid to measuring rheological properties as indicative of the melt-processing behavior and structure, particle size, shape, and surface characteristics of the dispersed phase. Evaluation of rheological behavior has also been used as a tool to assess the state of nanoparticles dispersion in polymer nanocomposites at the melt state (Michael et al., 2001; Starr and Douglas 2003; Gu et al., 2004). Since applying small strains while measuring the rheological behavior of the blends provides conditions in which the spherical droplets remain nearly unchanged, so the linear oscillatory flow can be used to study the morphology of the blends with droplet-matrix morphology (Vinckier et al., 1996; Lipatov et al., 2002). In this regard, many researchers have tried to find a relation between melt linear viscoelastic behavior and morphology of the blends (Scholz et al., 1989; Graebing and Muller, 1990; Gramespacher and Meissner, 1992; Graebing et al., 1993). As an example, for a narrow distribution of droplet diameters and constant interfacial tension, Paliarne expressed the following equations to determine the complex modulus of the blends (Bosmina, 1999).

$$G^* = G_m^* \frac{1 + 3 \sum_i \phi_i H_i}{1 - 2 \sum_i \phi_i H_i} \quad (1)$$

$$H_i = \frac{4 \left(\frac{\gamma}{R_v} \right) (2G_m^* + 5G_d^*) + (G_d^* - G_m^*) (16G_m^* + 19G_d^*)}{40 \left(\frac{\gamma}{R_v} \right) (G_m^* + G_d^*) + (2C_d^* + 3C_m^*) (16G_m^* + 19G_d^*)} \quad (2)$$

Where G^* , G_m^* and G_d^* are a complex modulus of the blend, matrix, and dispersed phase, respectively, ϕ is the volume fraction of the dispersed phase, γ is the interfacial tension between the components of the blend and R_v is the volume average radius of the dispersed phase (Paliarne, 1990; Graebing et al., 1993; Vinckier et al., 1996; Charles et al., 2002).

The SBR/NBR blend is known as an immiscible blend with poor mechanical properties due to unfavorable interaction between SBR and NBR. Many researchers have tried to make this blend compatible. In our previous work, the effects of epoxidized natural rubber (ENR) and two different kinds of OC on compatibilization of this blend was explained (Monfared et al., 2014). In this study by means of X-ray diffraction (XRD) analysis, field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), energy dispersive X-ray spectroscopy (EDS) and measuring melt linear viscoelastic properties in conjunction with theoretical analysis, the morphology of the blend and also localization of the used nanoparticles were investigated in

the SBR/NBR blends containing cloisite 30B (C30B) or cloisite 15A (C15A). The obtained experimental results were compared with those predicted by the theoretical models.

2. Experimental

2.1. Materials

Acrylonitrile butadiene rubber (NBR6240, LG Chem. Korea) with 34% acrylonitrile bound content, and Mooney viscosity of: ML (1 + 4, 100 °C) = 41, styrene butadiene rubber (SBR1502, Bandar Emam Petrochemical Co. Iran) with 23.5% styrene content, and Mooney viscosity of: ML (1 + 4, 100 °C) = 55, epoxidized natural rubber (ENR-50, Dynathai, Thailand), dicumyl peroxide (Shenyang Chemical Co. Ltd., China) and organo-modified layered nanosilicates included C30B a methyl-tallow-bis(hydroxyethyl)-ammonium treated Mt (modifier concentration: 90 meq/100 g); and C15A a dimethyl-dihydrogenated tallow-ammonium treated Mt (modifier concentration: 125 meq/100 g); made by Southern Clay (USA) were used to prepare the samples. The polarity of C30B is greater than that of C15A.

2.2. Preparation of the samples

Compounds containing different ratios of SBR/NBR (100/0, 80/20, 20/80 and 0/100) with and without OC as well as ENR were prepared by using a melt mixing method. The formulation of the compounds (Table 1) is given by the name X/Y/Z in which X shows the SBR (phr) amount, Y shows the kind and used amount of cloisite (for example Y = A5 indicates 5phr C15A and Y = B5 indicates 5phr C30B) and Z shows the amount of ENR in terms of phr. As an example, 80/A5/5 indicates the 80/20 ratio of a SBR/NBR blend containing 5phr of C15A and 5phr of ENR. To prepare the compounds; in the first stage, mixing of the OC with rubber was carried out in an internal mixer (Brabender Plasticorder, Germany) at a temperature of 90 °C and a rotor speed of 60 rpm for 20 min, and then the curing agent was added on a laboratory two roll mill at a temperature of 50 °C. The samples were cured at a temperature of 160 °C with respect to their cure times (t_{90}) obtained by the rheometric characterization technique as described in our previous work (Monfared et al., 2014). The ASTM D3182 “standard laboratory mold” was used for the preparation of vulcanized sheets.

3. Theoretical and experimental characterization

3.1. Theoretical characterization

Controlling the location of nanoparticles in the polymer matrices is known as a fundamental challenge in the preparation of polymer nanocomposites and depends on the polymer-polymer, polymer-filler and filler-filler interactions.

Table 1
Formulation of the samples.

Sample code	SBR/NBR	C15A (phr)	C30B (phr)	ENR (phr)
100/B5/0	100/0	0	5	0
0/B5/0	0/100	0	5	0
100/A5/0	100/0	5	0	0
0/A5/0	0/100	5	0	0
80/B5/0	80/20	0	5	0
80/A5/0	80/20	5	0	0
20/B5/0	20/80	0	5	0
20/A5/0	20/80	5	0	0
80/B5/5	80/20	0	5	5
80/B5/10	80/20	0	5	10

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