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Enhanced compatibility and mechanical properties of carboxylated acrylonitrile butadiene rubber/styrene butadiene rubber by using graphene oxide as reinforcing filler

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ABSTRACT

This work reports a novel compatibilizer and reinforcing filler, graphene oxide (GO), which significantly improved the thermal and mechanical properties of immiscible carboxylated acrylonitrile butadiene rubber (XNBR) and styrene butadiene rubber (SBR) blends. The observed glass transition temperature shift of XNBR/SBR blends demonstrated the improved compatibility of XNBR and SBR. The analysis by Fourier transform infrared spectra and Raman spectroscopy indicated that GO could form both hydrogen bonding with XNBR and π-π conjugation with SBR, which favored the compatibility of XNBR and SBR components in the blends. This unique amphiphilic character of GO enabled it interact with both polar and non-polar components and significantly improve the mechanical properties of the system. With incorporation of only 0.3 phr (parts per hundred rubber) GO, the tensile strength and tear strength of XNBR/SBR blend increased by 71% and 94%, respectively. The temperature of the maximal rate of degradation process improved by 10 °C, and a higher resistance to swelling in toluene was obtained as well. This work suggests the GO has the potential to be a suitable reinforcing filler and compatibilizer in the immiscible XNBR/SBR blends.

1. Introduction

Blending of two or more rubber components is considered as an economical method to take advantage of each individual rubber, through varying the compositions and the types of rubber components, the properties of rubber blends can be finely tuned to meet specific requirements [1,2]. However, simple rubber blends may not always deliver desired performances, blends of two incompatible rubbers, particularly with large unfavorable enthalpy of mixing, leads to unwanted phase separation, e.g., two-phase morphology, narrow interphase zone, poor physical and chemical interaction across the phase boundaries [3]. Therefore, the development of suitable compatibilizers or interfacial additives is always one of the key topics in rubber blends research to achieve advanced rubber properties [4–6].

Graphene oxide (GO) has attracted great interest in academic and industry, due to its excellent thermal, mechanical, barrier properties, the large specific surface, cost-effective and easy processing. It is well known that GO has been proven to be amphiphilic with a largely hydrophobic basal plane and hydrophilic edges [2,7]. This amphiphilic property enables it have strong interactions with both polar and nonpolar polymers, and act as a compatibilizer in polymer blends [8–10]. For instance, Cao et al. [2] used GO to compatibilize immiscible polyamide/polyphenylene oxide (PA/PPO, 90/10) blends, and found that the droplet diameter of the dispersed minor phase (PPO) was dramatically reduced by more than 1 order of magnitude, indicating a largely improved compatibility in the polymer blends. With the incorporation of 1.0 wt% GO, the tensile strength and the temperature for 10% weight loss of PA/PPO/GO increased by 87% and 50 °C, respectively, compared with neat PA/

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PPO. Yan et al. [11] found that the addition of GO to the natural rubber/high density polyethylene (NR/HDPE, 60/40) blends reduced the NR domain size and improved the miscibility and interfacial adhesion between the binary phases. When the content of GO was 1.5 phr (parts per hundred rubber), the tensile strength and tensile modulus at 300% strain (M_{300}) of NR/HDPE blend were increased by 27% and 24%, respectively. Chen et al. [10] showed that the addition of 0.5 wt% GO increased the tensile strength and elongation at the break by more than 50% and 30%, respectively, in the ethylene-propylene-diene rubber/petroleum resin (EPDM/PR, 40/60).

Styrene butadiene rubber (SBR), a non-polar elastomer, is widely used in automotive tire tread where low rolling resistance and high wet grip are required. Carboxylated acrylonitrile butadiene rubber (XNBR) is a polar elastomer with a superior resistance to oil and oxidation [12]. The blends of XNBR and SBR are of the special interest to utilize both advantages. However, XNBR and SBR are usually physically incompatible at some composition, where suitable compatibilizer is necessary to overcome this difficulty. In this work, GO was adopted, for the first time, to improve the compatibility of the immiscible XNBR/SBR blends. The effects of the GO on the static and dynamic mechanical properties, thermal stability as well as solvent resistance of the samples were investigated thoroughly and the results are presented in following sections.

2. Experimental

2.1. Materials

Carboxylated acrylonitrile butadiene rubber latex (XNBR 6721, solid content: 43 wt%, M_L (1 + 4) 100 °C = 90) was received from Zhenjiang Nantex Industry Co. Ltd., Zhenjiang, China. Styrene butadiene rubber latex (SBR 1712, solid content: 22 wt%, M_L (1 + 4) 100 °C = 49) was received from YPC-GPRO Rubber Co. Ltd., Nanjing, China. Natural graphite powder (particle size $\leq$ 30 μm, purity $\geq$ 99.85%), sulfuric acid (H_2SO_4, 98%), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%), and sodium chloride (NaCl) with analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Curing agents including, *N*-isopropyl-*N*'-phenyl-*p*-phenylenediamine (4010NA), zinc oxide (ZnO), stearic acid (SA), *N*-cyclohexyl-2-benzothiazole sulfenamide (CZ) and sulfur with industry grade were kindly provided by Nanjing Jinsanli Rubber Plastic Co. Ltd., China.

2.2. Preparation of GO compatibilized XNBR/SBR blends

GO aqueous suspension with a concentration of 1 mg mL^{-1} was prepared through 1 h ultrasonic treatment of graphite oxide according to Hummers' method [13]. The GO aqueous suspension was added to the mixture of XNBR and SBR latex with magnetic stirring for 1.5 h. After that, the mixture was co-coagulated by adding NaCl aqueous solution (8 wt%), washed with deionized water several times and dried at 50 °C until a constant weight compound was formed. Then the dried compound was mixed with rubber ingredients on an open two-roll mill (LN-120, Lina Industrial Co. Ltd., China) with a friction ratio of 1:1.2 at room temperature. The curing formula was as follows: XNBR 75 phr, SBR 25 phr, 4010NA 2 phr, ZnO 2 phr, SA 2.4 phr, CZ 2.2 phr, S 1.5 phr, and GO, variable. A series of GO compatibilized XNBR/SBR blends containing 0, 0.1, 0.2, and 0.3 phr GO were prepared by compression molding at 160 °C and 15 MPa for the optimal curing time. These blends were abbreviated as “GO-*i*” below. The *i* denoted original GO loading (phr) in the blends.

2.3. Characterization and tests

Atomic force microscope (AFM) images was taken by a Nanoscope III D Multimode scanning probe microscope (Bruker Corporation, Switzerland) in a tapping mode. The GO dispersion was spin-coated onto a freshly exfoliated mica substrate at 2000 rpm and dried at room temperature.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a Phi Quantera II XPS (Ulvac-Phi Co. Ltd., Japan).

Thermogravimetric analysis (TGA) was carried out using a DTG-60 differential thermogravimetric (Shimadzu Corporation, Japan) by heating from 25 to 600 °C at a rate of 20 °C min^{-1} under nitrogen atmosphere.

The differential scanning calorimetry (DSC) analyses were performed on a 200F3 DSC (Netzsch Corporation, Germany) at a heating rate of 10 °C min^{-1} from −70 to 20 °C under a nitrogen atmosphere.

Fourier transform infrared spectra (FTIR) were collected on a FTIR-8400S spectrometer (Shimadzu Corporation, Japan) in a transmission mode of KBr pellets with wavenumber range from 400 to 4000 cm^{-1} at a scanning resolution of 4 cm^{-1}.

Raman spectra were recorded with an inVia-H31894 Raman spectrometer (Renishaw Corporation, Britain) by an argon-ion laser at an excitation wavelength of 514.5 nm and a resolution of 1 cm^{-1}.

The dispersion morphology of GO in XNBR/SBR the blends was observed by Tecnai G2 F30 S-TWIN transmission electron microscope (TEM) (FEI Corporation, USA) operated at an acceleration voltage of 200 kV. The ultrathin sections of samples were cut by the help of ultra-thin microtome instrument equipped with a diamond knife at −100 °C.

The tensile and tear tests were measured on a universal testing machine (Shenzhen SANS Co. Ltd., China) at ambient temperature with a cross-head speed of 500 mm min^{-1} according to ASTM D-412 and ASTM D-624, respectively. The results were averaged based on five measurements.

The dynamic mechanical properties were measured with a Q800 dynamic mechanical analyzer (DMA) (TA Co. Ltd., USA) under a nitrogen atmosphere at a heating rate of 3 °C min^{-1} from −70 to 50 °C and a tensile mode at 1 Hz. The results were averaged based on three measurements.

The swelling behavior of the sample was tested in toluene at room temperature according to ASTM D 471. The sample was weighed before immersion to obtain m_1. After immersion, the soaked sample at swollen equilibrium with stable weight was wiped and weighed to obtain m_2. The sample was dried in vacuum at 50 °C and then weighed to obtain m_3. The swelling rate (Q) was calculated by eq. (1). The results were averaged based on five measurements.

$$Q = (m_2 - m_1)/m_1 \tag{1}$$

Crosslinking density (ν_e) was determined according to the Flory-Rehner equation:

$$\nu_e = -\frac{\ln(1-\nu_r) + \nu_r + \chi_1 \nu_r^2}{V\left(\nu_r^{\frac{1}{3}} - \nu_r/2\right)} \tag{2}$$

where χ_1 is the Flory-Huggins polymer-solvent interaction parameter (0.446). V is the solvent molar volume (106.5 $cm^3 \cdot mol^{-1}$ for toluene); ν_r is the volume fraction of rubber and the value of ν_r is obtained according to:

$$\nu_r = \frac{m_3/\rho_r}{(m_2 - m_3)/\rho_s + m_3/\rho_r} \tag{3}$$

where ρ_r and ρ_s are the densities of the polymer and the solvent