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Morphological and mechanical properties of styrene butadiene rubber/nano copper nanocomposites

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ABSTRACT

In this research, rubber based nanocomposites with presence of nanoparticle has been studied. Styrene butadiene rubber (SBR)/nanocopper (NC) composites were prepared using two-roll mill method. Transmission electron microscope (TEM) and scanning electron microscope (SEM) images showed proper dispersion of NC in the SBR matrix without substantial agglomeration of nanoparticles. To evaluate the curing properties of nanocomposite samples, swelling and cure rheometric tests were conducted. Moreover, the rheological studies were carried out over a range of shear rates. The effect of NC particles was examined on the thermal behavior of the SBR using thermal gravimetric analysis (TGA). Furthermore, tensile tests were employed to investigate the capability of nanoparticles to enhance mechanical behavior of the compounds. The results showed enhancement in tensile properties with incorporation of NC to SBR matrix. Moreover, addition of NC increased shear viscosity and curing time of SBR composites.

Introduction

In recent years, polymer nanocomposites have become the center of interest due to their appropriate properties. The use of nanomaterials in polymers is dramatically increased in recent years. The presence of nanofillers in polymer matrix results in improvement of mechanical [1–4], thermal [5,6], electrical [7,8] and rheological properties [9] of polymers. Among polymeric materials, rubbers are famous for their easy processing, crack resistance and high flexibility. With regard to these advantages, researchers have widely studied the preparation and performance of rubber nanocomposites [10,11]. Styrene butadiene rubber (SBR) is one of the synthetic rubbers that can be used as commercial matrix for rubber nanocomposites fabrication. Moreover, some researchers have focused on preparation and characterization of ternary SBR blends. SBR is a non-polar rubber and has good mechanical properties. Great demands of SBR motivates researchers to investigate on their nanocomposites [12–19].

Recently, copper/polymer composites are considered as promising materials due to their enhanced characteristics [20–23]. In this research, nanocopper (NC) particles are used to improve the mechanical and physical properties of SBR for the first time. A two-roll mill method is employed for mixing ingredients in SBR. This mixing method is attractive for commercial and industrial applications [24,25]. To the best of author's knowledge, the characteristics of SBR/NC nanocomposites have not been systematically addressed in the literature. Therefore, the influence of NC on curing behavior, swelling characteristics, rheology, thermal degradation, tensile performance and tear strength of SBR is explored.

Experimental

Materials

Styrene butadiene rubber (SBR 1502) as the matrix was supplied from Bandar Imam Petrochemical Co. (Iran). The density and the styrene content of SBR were 0.98 g/cm^3 and 23%, respectively. The curing system consisted of sulfur (S), zinc oxide (ZnO), stearic acid were supplied from Iran Petrochemical Co. (Iran). Tetramethyl thiuram disulphide (TMTD) and mercaptobenzothiazole disulphide (MBTS) were used as accelerator agents. Nanocopper was supplied from US Research Nanomaterials, Inc. with

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average particle size (APS) of 70 nm and specific surface area 6–8 m^2/g. The shape of NC particles was spherical and their density and purity were 8.9 g/cm^3 and 99.9% respectively. Industrial grades of toluene and acetone were used as solvents in extraction and swelling experiments.

Preparation of nanocomposites

A laboratory scale two-roll mill was used for blending the compounds. First, SBR was masticated for 3 min, then NC particles were added to SBR (at 2, 4 and 6 parts per hundred rubber (PHR)) and mixed for additional 10 min. Next, the curing agents (see Table 1 which summarizes the compositions) were added to the compound. The compounds were then mixed for another 10 min to achieve appropriate dispersion of the ingredients in the rubbery matrix. Afterwards, the compositions were cured for 60 min at 150 °C in compression molding process. The cure time was selected slightly higher than t_{95} (time to 95% cure) to ensure complete curing (100% cure) of the compounds. The value of t_{95} was determined by measuring the increase of the torque values of the none-vulcanized rubber compounds at 150 °C. After curing, test samples were cut from the obtained sheets.

Observation techniques

Dispersion of nanoparticles in the matrix was evaluated using transmission electron microscopy. The apparatus was Philips CM-200 TEM used at accelerating voltage of 200 kV. Ultra-thin section of samples was cut with OmU3 ultramicrotom (Reichert, Austria).

The fractured surface of tensile test sample was analyzed by scanning electron microscope (LEO, 1455VP, UK). The fractured surfaces were coated by a thin gold layer and SEM images were taken from the coated surfaces.

Characterization techniques

The cure characteristics of the compounds were measured via oscillating disk rheometer (ODR GT7070-S2, GOTECH, Taiwan) operated at 150 °C at a 1° arc and a frequency of 1.66 Hz based on ASTM D5289. The scorch time (t_s) and curing time (t_{95}) were obtained from torque difference. The cure rate index (CRI) was extracted from rheometric data via the following relation:

$$CRI = \frac{100}{t_{95} - t_s} \quad (1)$$

Swelling ratio of samples was determined by placing a piece of sample in toluene for 48 h. at room temperature. Regarding to size of the samples (1 cm × 1 cm with thickness of 2 mm), this time (48 h) is adequate for complete solvent diffusion into the samples. The swelling ratio was calculated with the following equation:

$$\text{Swelling Ratio} = \frac{x - y}{y} \quad (2)$$

where x and y are the weights of the sample after and before swelling, respectively. For calculating the average molecular weight between two crosslinks, M_c, Flory-Rehner relation was used as:

$$M_C = \frac{\rho_r V_S \left(\frac{v_r}{2} - v_r^{1/3}\right)}{\ln(1 - v_r) + v_r + \chi v_r^2} \quad (3)$$

where M_c is the average molecular weight between two crosslinks, ρ_r is the density of rubber, V_S is the molar volume of solvent (V_S = 106.3 cm^3/mol for toluene), χ is the polymer-solvent interaction parameter (0.378 for SBR-toluene [26]) and v_r is the volume fraction of the rubber in swollen rubber (measured from the swelling experiment).

Melt flow behavior of compounds was investigated using capillary rheometer CEAST 1000 (Italy), with capillary die diameter (d) of 1 mm and length (l) of 40 mm. The rheological test was carried out at 150 °C over a range of shear rates i.e. 10–1000 s^{-1}. The apparent viscosity (η) was measured as the ratio of shear stress (τ) to shear rate ($\dot{\gamma}$). The shear stress was measured as $\tau = (\Delta P \times d)/4l$ and shear rate was calculated by $\dot{\gamma} = 32Q/(\pi d^3)$, where ΔP and Q are pressure drop and flow rate of compound, respectively.

Thermogravimetric analysis was conducted from room temperature to 500 °C at the heating rate 20 °C/min using Perkin-Elmer Diamond TG/DTA thermal analyzer. The analysis was carried out at a nitrogen atmosphere to prevent the oxidation of the samples. From the TGA results, temperature at 5 and 50% mass degradation (T_5, T_{50}) and temperature at maximum rate of mass loss (T_{max}) were obtained.

Tensile characteristics of compounds were measured using Hounsfield H10Ks testing machine at crosshead speed of 50 mm/min. Test samples were cut from vulcanized sheets of SBR compounds. For each compound at least five mechanical tests were performed.

Results and discussion

Morphology

Due to the high surface energy, nanoparticles incline to form agglomerates [27], hence, achieving good dispersion and distribution of nanofiller in matrix is still a critical issue in nanoparticle/rubber composites. Low and high magnification TEM images of SN6 sample are presented in Fig. 1a and b, respectively. As seen, most nanoparticles have been uniformly dispersed in the SBR matrix. However, some agglomerations can be seen in these images which consist of several NC particles that formed aggregates with size of 100–250 nm. Tendency of nanoparticles to form agglomerates in rubber matrix has been reported by some researchers [28,29].

Similar trend can be observed by SEM images (Fig. 1c and d) from fractured surfaces of SN6 sample. As seen, homogenous dispersion and distribution of NC particles are shown through the SBR matrix (Fig. 1c). It seems that NC particles have good interaction with SBR and there are no clear detachment of particles. Moreover, some separated NC particles is evidently observed in Fig. 1d which indicates proper de-agglomeration of nanoparticles in the polymer. Overall, one can conclude that NC particles are rather well dispersed and distributed in the rubber matrix. It implies that

Table 1
Formulations of compounds (all in PHR).

Sample	SBR	NC	Sulfur	ZnO	Stearic acid	MBTS	TMTD
S	100	0	3	5	1.5	1	0.2
SN2	100	2	3	5	1.5	1	0.2
SN4	100	4	3	5	1.5	1	0.2
SN6	100	6	3	5	1.5	1	0.2

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