



Research paper

Structure and properties of organo-montmorillonite/nitrile butadiene rubber nanocomposites prepared from latex dispersions

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ABSTRACT

The organo-montmorillonite (OMt)/nitrile butadiene rubber (NBR) nanocomposites were prepared by emulsion intercalation method. The TEM images of the nanocomposites showed uniform dispersions of the OMt particles in NBR and the XRD patterns confirmed an effective intercalation of NBR in the interlayer space of the OMt. The nanocomposites demonstrated excellent mechanical properties and solvent resistance comparing to those of pure NBR. The TGA curves showed that the temperature of maximum decomposition rate (T_{max}) of the nanocomposites (30 wt.%) had increased by 10 °C in comparison with that of pure NBR, which indicated that the nanocomposites had excellent thermal stability. The vulcanized curves showed that the OMt could accelerate the vulcanization process. The glass transition temperature, storage modulus, and loss modulus of the nanocomposites have increased, but the $\tan\delta$ has decreased compared with pure NBR.

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1. Introduction

Clay polymer nanocomposites (CPN) have attracted great interest of researchers in the fields of both industry and science, since this kind of nanocomposites has exhibited excellent properties when compared with their pure polymers or conventional filled polymers due to the fine phase dimensions and special phase structure involved (Wang et al., 2005). CPN with a relatively low loading of the filler possess unique properties such as stiffness, strength, thermal stability, flame retardancy and gas barrier actions due to the nanometer scale dispersion of clay mineral in the polymer matrix (Gao et al., 2008). The CPN are generally classified into three groups according to their structures, i.e., nanocomposites with intercalated, exfoliated or both of intercalated and exfoliated structure. The completely exfoliated nanocomposites are desired due to the fact that the exfoliated layers exhibit the greatest reinforcement (Wu et al., 2005).

The clay mineral used as filler for nanocomposites, usually needs to be organically modified. This aims to improve the compatibility of polymer and organoclay layers, and which would enlarge the interlayer space which becomes more accessible to the intercalation of polymer chains (Li et al., 2008). The sodium ions are usually ion-exchanged with an organic ammonium or phosphonium salt to convert this material into

a hydrophobic ammonium or phosphonium treated clay mineral (Kong et al., 2008).

The CPN can be prepared by several intercalation methods, including in situ polymerization, solution, melt and emulsion intercalation. In situ polymerization needs special monomers and clay mineral treatment, which limits its application in other polymers. The solution method needs a compatible polymer-solution system and organo-modified clay minerals. Its disadvantage is that the solvent must be de-absorbed. Melt intercalation can be applied to most polymers, especially plastic, but it needs a polymer that has good process properties in the molten state (Wang et al., 2000). Comparing with other methods, the emulsion intercalation is a promising method for industrialization due to the simplicity of preparation process, low cost and superior performance ratio. Thus, in this study, the organo-montmorillonite (OMt)/nitrile butadiene rubber (NBR) nanocomposites were prepared by emulsion intercalation. The structures and properties of the nanocomposites were investigated.

2. Experimental

2.1. Materials

The bentonite was obtained from the clay mine in Shandong Province of China, which has the cation exchange capacity (CEC) of 119 meq/100 g. The NBR latex (45 wt.%) was obtained from Lanzhou Petrochemical Company (China). Other materials are commercial products (AR grade).

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2.1.1. Preparation of organo-montmorillonite (OMt)

The bentonite was wetted with water, and then purified by sedimentation and washing, finally the refined bentonite was montmorillonite (Mt). The dried Mt (50 g) was dispersed into 5000 mL of distilled water at 65 °C under vigorous stirring. A mixture of 40 g dimethyl ditallow-ammonium, 200 g distilled water and 6 mL 98.0% concentrated sulfuric acid were prepared at 65 °C and then slowly added into the dispersion of Mt. The reaction was maintained for 4 h. The sediment was collected by filtration and washed for ten times using hot water, and then dried at 90 °C in vacuum, grounded and sieved to 30 μm.

2.2. Preparation of OMt/NBR nanocomposites

The OMt was dispersed in the water. Then, the aqueous dispersion (10 wt.%) was added into the NBR latex. The mixture was then vigorously stirred for 15 min at 60 °C. The amounts of OMt added were 0, 5, 10, 15, 20, 25 and 30 wt.% of rubber. The mixture was co-coagulated with 10% calcium carbonate solution, washed with water and dried at 60 °C. The OMt/NBR nanocomposites were mixed further on a two-roll mill with other ingredients at ambient temperature for about 15 min. The charging order is ZnO (Zinc Oxide), SA (Stearic Acid), M (2-mercaptobenzothiazole) and sulfur one by one. Finally, the compounds were compression-molded at 143 °C under 15 MPa for the optimum cure time (T_{90}) to yield vulcanizates.

Recipes of OMt/NBR nanocomposites: NBR 100 phr, ZnO 5 phr, SA 1.5 phr, M 1.5 phr, Sulfur 2 phr; phr is the abbreviation of weight parts per 100 weight parts of rubber.

2.3. Characterization

TEM observation was performed on ultra-thin films prepared by cryoultramicrotomy using a JEM-1200EX (JOEL, Japan) at an acceleration voltage of 80 kV.

XRD experiments were performed with a D/max-RB diffractometer (Rigaku, Japan), graphite monochromator, and Cu K α radiation. The samples were scanned with 5°/min between 2 θ of 3°–10°.

Tensile and tear tests were measured on a DXLL-50000 (Dings Company, China) universal testing machine at a crosshead speed of 500 mm/min. Measurements of mechanical properties of all specimens were conducted at 25 ± 2 °C according to relevant ISO standards (ISO 37 and ISO 7619). Five samples were tested and the average of the values was taken.

The curing behavior was investigated at 143 °C using rotorless rheometer MDR2000 (D and G Company, China) according to ISO 6502-1999 with frequency of 1.66 Hz.

Thermo-gravimetric analysis (TGA) of the samples was performed using a thermo-gravimetric analyzer (TGA/STDA851, Mettler Toledo, Shanghai, China) attached to an automatic programmer from ambient temperature to 700 °C at a heating rate of 10 °C/min in an air atmosphere. A sample weight of approximately 15 mg was used for the measurement. The temperature reproducibility of the TGA instrument is ± 3 °C and on run for each sample.

The samples of 20 × 10 × 2 mm³ were used to determine the swelling behavior of vulcanized rubber according to ISO1817-198. The initial weight of the samples was taken, and then they were put into ASTM 1# oil. The samples were periodically removed from the test bottles, the adhering solvent was cleaned from the surface, and the samples were weighed immediately. The weight–swelling ratio (Q_t), was also determined from the weight of the sample in the unswollen and swollen states. The equation is as follows:

$$Q_t = (W_1 - W_0) / W_0 \times 100\%$$

where Q_t is the weight–swelling ratio, W_1 is the weight of the sample in the swollen states, and W_0 is the initial weight of the samples. Three samples were tested and the average of the values was taken.

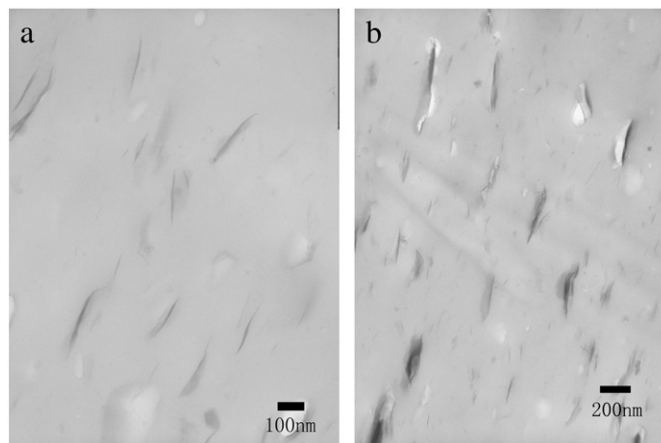


Fig. 1. TEM microphotographs of OMt/NBR nanocomposites.

Dynamic mechanical properties were measured with a TA 2980 DMA dynamic mechanical analyzer with a multifrequency–film–tension module. The specimens (1.5 mm × 4.5 mm × 20 mm) were cut from the center of the samples. A temperature sweep of 5 K/min was used, and the amplitude of the vibration was 10 nm with a frequency of 1 Hz.

3. Results and discussion

3.1. Morphology and structure of OMt/NBR nanocomposites

The black lines and area were OMt particles, and the white region was the rubber matrix (Fig. 1). Low-magnification TEM photographs clearly displayed that clay particles were homogeneously dispersed in the NBR matrix, and in some areas of the polymer matrix, the intercalated silicate particles were locally stacked up to hundreds of nanometers in thickness. The high-magnification TEM images revealed that there were some single exfoliated clay particles in the rubber matrix besides intercalated clay particles (Liang et al., 2008). The thickness of most clay mineral particles was in the range of 10–40 nm and the length was about 100–200 nm.

The Mt showed a basal spacing of the montmorillonite of 1.55 nm, the OMt a spacing of 1.92 nm (Fig. 2). The reflection (001) of OMt/NBR (10 wt.%) showed a spacing of 2.40 nm, indicating that the NBR chains were between the OMt layers. Both TEM and XRD results indicated that the intercalated nanocomposites had formed.

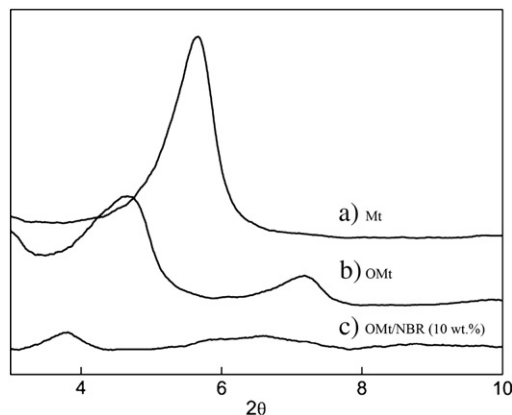


Fig. 2. XRD curves of OMt/NBR nanocomposites.

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