Preparation and properties of organo-montmorillonite/cis-1,4-polybutadiene rubber nanocomposites by solution intercalation

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ABSTRACT

Organo-montmorillonite (OMMT)/cis-1,4-polybutadiene rubber (BR) nanocomposites were prepared by solution intercalation. The microstructure of these composites was characterized by TEM and XRD. The effect of OMMT on mechanical properties, thermal stability and swelling behavior of the nanocomposites was investigated. TEM and XRD confirmed the intercalated structure of OMMT/BR nanocomposites. When the OMMT content was <12 mass%, the nanocomposites showed excellent tensile properties, which was attributed to the nanometer scale dispersion and stronger interactions between OMMT and BR chains. The introduction of a small amount of OMMT greatly improved the thermal stability and swelling behavior, which was attributed to the good barrier properties of OMMT layers.

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1. Introduction

Polymer clay mineral nanocomposites have attracted great interest both in industry and in science (Usuki et al., 1993). This kind of nanocomposites exhibit improved properties compared to their micron or macro-composites due to the fine phase dimensions and special phase structure involved (Wang et al., 2005a,b). In general, this kind of nanocomposites have superior mechanical properties, thermal stability, flame retardancy and gas barrier properties (Yen and James, 2001; Alexander et al., 2002; Changwoon et al., 2002; Jin-tae et al., 2004).

Cis-1,4-polybutadiene rubber (BR) is widely used in the tire industry due to its superior dynamic mechanical properties, abrasion resistance, elasticity, and flex crack resistance (S.Z. Xie, 1989). However, the tensile strength of BR is much lower than that of other rubber; BR must be reinforced by filler to obtain adequate strength. Polymer/clay nanocomposites can be prepared by many methods, including in situ polymerization intercalation, solution intercalation, melt intercalation and co-coagulating of rubber latex and aqueous clay dispersions (Li et al., 2004). The OMMT/BR nanocomposites have been prepared by direct blending (Wang et al., 2005a,b) and polymerization intercalation (Liao et al., 2006).

In this study, we aimed at developing a clay/cis-1,4-polybutadiene rubber (BR) nanocomposite using organo-montmorillonite (OMMT). The OMMT/BR nanocomposites were prepared by solution intercalation.

2. Experimental

2.1. Materials

The bentonite was obtained from the clay mine in Shandong Province of China, the montmorillonite (MMT) of the bentonite had the cation exchange capacity (CEC) of 1.19 meq/g. The montmorillonite was modified with dimethyl ditallow-ammonium. BR solution (mass fraction of total solid 23 mass%) and 6# solvent oil (contain 74 mass% n-hexane and 16 mass% cyclo-hexane) were obtained by Qilu Petrochemical Company (China). Other materials were commercial products.

2.2. Preparation of OMMT/BR nanocomposites

OMMT was dispersed in the solvent oil, then added to the BR solution. The mixture was vigorously stirred for 30 min at 60 °C. The amounts of OMMT added to BR were 0, 3, 6, 9, 12 and 15 mass% related to the rubber. After the solvent evaporation, vulcanization agents were added in an open two-roll mill. The specimens were cured at 155 °C in an electrically heated hydraulic press for 30 min.

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Fig. 1. XRD patterns of MMT and OMMT.

2.2.1. Recipes of OMMT/BR compounds

BR 100 phr; ZnO (zinc oxide) 4 phr; SA (stearic acid) 1 phr; 4010NA (N-isopropyl-N'-phenylenediamine) 1 phr; CZ (N-cyclohexylbenzothiazole-2-sulphenamide) 0.7 phr; Sulfur 1.5 phr.

2.3. Measurements

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

The basal spacing of the montmorillonite was derived from the XRD patterns between 3° and 40° (Rigaku 2500PC, Japan, 40 kV, 200 mA Cu K α radiation) at room temperature.

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 $\pm$ 2 °C according to relevant ISO standards (ISO 37, and ISO 7619).

Thermo-gravimetric analysis (TGA) was performed with a thermo-gravimetric analyzer (TGA/STDA851, Mettler Toledo, Shanghai, China) connected to an automatic programmer from ambient temperature to 600 °C at a heating rate of 10 °C/min in an air atmosphere. A sample mass of about 15 mg was used for the measurements.

Samples of 20 $\times$ 10 $\times$ 2 mm³ were used to determine the swelling behavior of vulcanized rubber according to ISO1817-198. The samples were periodically removed from the test bottles, the adhering solvent was cleaned from the surface, and the samples were weighed

Fig. 2. XRD patterns of OMMT/BR nanocomposites with different OMMT contents.

Fig. 3. TEM of OMMT/BR nanocomposites with 3 mass% of OMMT, a_1 : 50 K magnification. TEM of OMMT/BR nanocomposites with 3 mass% of OMMT, a_2 : 25 K magnification.

immediately and then placed into toluene again. The mass-swelling ratio (Q_t), was also determined from the mass of the sample in the unswollen and swollen states:

$$Q_t = ((M_t - M_0) / M_0) \times 100\%$$

where M_0 and M_t are the mass of the sample before and after swelling.

3. Results and discussion

3.1. Morphology and structure of OMMT/BR nanocomposites

The original MMT showed a (001) reflection at $2\theta = 5.68^\circ$, corresponding to the basal spacing of 1.55 nm. After organic modification with dimethyl ditallow-ammonium, the basal spacing was increased to 1.89 nm (Fig. 1).

Basal spacing increased to 3.63 nm for OMMT indicates that the BR chains were intercalated (Fig. 2). At higher montmorillonite content the basal reflection shifted to slightly higher angles indicating the presence of some interlayer spaces free of BR chains.

XRD may not reveal the real microstructures due to weak diffraction intensity, bias toward the surface region, and poor peak resolution for those nanocomposites with low clay content as well as overlapping of diffraction patterns of exfoliated and intercalated structures (Galgali et al., 2001). In contrast to XRD, TEM can provide information on the morphology and spatial distribution of various phases. Fig. 3 shows the TEM photographs of OMMT/BR nanocomposites with 3 mass% OMMT. The dark lines and areas are OMMT layers and aggregates, and the light

Fig. 4. TGA curves of OMMT/BR nanocomposites with different OMMT contents.

areas always add space to the rubber matrix. The thickness of most clay particles was 20–30 nm and the length about 100–250 nm. Low magnification TEM clearly displayed the homogeneous dispersion of the OMMT layers in the BR matrix. High magnification TEM revealed some single exfoliated particles in the BR matrix. Combined with XRD results, the intercalated microstructure formed.

3.2. Thermal properties of OMMT/BR nanocomposites

The TGA curves of OMMT/BR nanocomposites are shown in Fig. 4. Fig. 5 shows the differentiated curves used to find out the temperature of maximum decomposition rate ($T_{\max}$) (Peiyao et al., 2008). The marked temperature ($T_{\max}$) is the fastest mass loss temperature that represents the heat resistance of the nanocomposites.

Overall, the thermal stability of OMMT/BR nanocomposites was better than of pure BR. The onset temperature and the $T_{\max}$ of the nanocomposites were higher than those of pure BR. At the loading of 6 and 12 mass% of OMMT, $T_{\max}$ was 458 and 465 °C, respectively, 10 and 17 °C higher than of pure BR. This is mainly attributed to the good gas barrier action of OMMT. The well dispersed OMMT layers not only hindered the evaporation of decomposition products but more effectively hindered the access of oxygen to the polymer, reducing the rate of initiation of polymer chain scission to produce volatile small products (Zanetti et al., 2001). The high decomposition temperature indicates the improved thermal stability of the nanocomposites.

Fig. 5. The differentiated data of TGA curves of OMMT/BR nanocomposites.

Fig. 6. Mechanical properties of OMMT/BR nanocomposites with different OMMT contents.

3.3. Mechanical properties of OMMT/BR nanocomposites

The tensile strength and tear strength of OMMT/BR nanocomposites increased with the OMMT content, when the OMMT content was <12 mass% (Fig. 6). At 12 mass%, the nanocomposite showed the highest tensile strength, 8.06 MPa, which was about five times higher than that of pure BR. Highest tear strength was 21.23 kN/m, which was 2.33 times higher than that of pure BR. The improvement of the mechanical properties is attributed to two facts: (1) Nano-dispersed OMMT with high aspect ratio possesses a higher stress bearing capability and efficiency; (2) Stronger interactions between OMMT and BR chains associated with the larger contact surface result in more effective constraint of the motion of rubber chains (Kojima et al., 1993).

Further addition of OMMT decreased the mechanical properties. As OMMT content increased, some OMMT layers aggregated (Shi and Gan, 2008). The formation of OMMT aggregates reduces the interface area between polymer and OMMT layers, which decreases the mechanical properties.

3.4. Swelling behavior of OMMT/BR nanocomposites

Solvent absorption decreased with increasing OMMT contents (Fig. 7) due to good dispersion of OMMT and the strong interactions between OMMT and BR. The presence of nano-dispersed impermeable OMMT layers with excellent barrier properties decreased the rate of

Fig. 7. Swelling behavior of OMMT/BR nanocomposites in toluene at 25 °C.

transportation by lengthening the average diffusion path length in BR matrix (Konstantinos et al., 2005).

4. Conclusion

OMMT/BR nanocomposites were prepared by solution intercalation. TEM and XRD analysis indicated that the BR chains were intercalated.

The introduction of OMMT greatly improved the mechanical properties of OMMT/BR nanocomposites. The nanocomposite with 12 mass% OMMT showed the highest tensile strength, 8.06 MPa, which was about five times higher than that of pure BR.

The OMMT/BR nanocomposites exhibited excellent thermal stability and swelling behavior, which is attributed to the improvement of the barrier properties of nanocomposites.

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