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The properties of organo-montmorillonite/cis-1,4-polybutadiene rubber nanocomposites and the effect of recovered solvent on the conversion of butadiene polymerization

Guojun Song, Zheng Gu *, Peiyao Li, Li Wang, Li Gao

Institute of Polymer Materials, Qingdao University, Qingdao 266071, China

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ABSTRACT

The organo-montmorillonite (OMt)/cis-1,4-polybutadiene rubber (BR) nanocomposites were prepared by solution intercalation. The structure and properties of the nanocomposites were investigated. The effect of recovered solvent on the conversion of butadiene polymerization was investigated. The results of the XRD and TEM showed that the molecular chains of BR were intercalated into the OMt particles. Compared with the pure BR, the tensile strength of OMt/BR nanocomposites (6 wt.%) increased by 172%. The conversion of butadiene polymerization was higher than 90% by using recovered solvent. The OMt/BR nanocomposites (2 wt.%) had the maximum crosslink density. And the nanocomposites exhibited a higher glass transition temperature and lower tanδ peak value.

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1. Introduction

Since the cis-1,4-polybutadiene rubber (BR) was widely used in the tire industry due to its superior dynamic mechanical properties, abrasion resistance, elasticity, and flex crack resistance (Xie, 1989). But the BR could not form crystals at room temperature unless it was sufficiently stretched (stress-induced crystallization). Moreover, the stress-induced crystallization of BR was obviously less than that of natural rubber (NR). That was why the tensile strength of BR was much lower than that of NR. Therefore, the BR must be reinforced by filler in order to obtain adequate strength. Carbon black was an effective reinforcing filler for rubber, but the carbon black reinforced rubber was always black in color, which limits its applications in medical, sports and domestic products (Shaohui et al., 2005a).

Since the clay polymer nanocomposites (CPN) were invented, polymer layered silicate nanocomposites had attracted great interest of researchers in the world both in industry and in science. This kind of nanocomposites exhibited excellent properties when compared with their micron or macro-composites due to the fine phase dimensions and special phase structure involved (Usuki et al., 1993; Yiqing et al., 2005). In general, clay polymer nanocomposites with a relatively low loading of the filler had superior mechanical properties, thermal stability, flame retardancy and gas barrier properties (Gao Jianming et al., 2008). These improvements of the properties were the result of the nanometer scale dispersion of clay particles in the polymer matrix.

Liao et al. prepared exfoliated BR/clay nanocomposites through in situ anionic intercalation polymerization (Mingyi et al., 2005) while Wang et al. prepared intercalated BR/clay nanocomposites via direct melt mixing of BR, sodium clay, and DDAC without the usual pretreatment of the sodium clay (Shaohui et al., 2005b). This process was called in situ organic modification. The results showed that the tensile strength, elongation at break, and tear strength of the BR/clay/DDAC vulcanizates were greatly improved in comparison with those of the gum BR and BR/pristine clay vulcanizates, but were somewhat lower than those of BR/organo-clay vulcanizate (Chaoying et al., 2008). In this study, the organo-montmorillonite (OMt)/cis-1,4-polybutadiene rubber (BR) nanocomposites were prepared by solution intercalation. The structure and properties of OMt/BR nanocomposites were investigated. The effect of recovered solvent on the conversion of butadiene polymerization was also investigated.

2. Experimental

2.1. Materials

The montmorillonite (Mt) was obtained from the clay mine in Shandong Province of China, which 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 wt.%) and 6# solvent oil (contain 74 wt.% n-hexane and

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* Corresponding author. Tel./fax: +86 532 85950691.
E-mail address: guzheng596@163.com (Z. Gu).

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16 wt.% cyclo-hexane) were obtained by Qilu Petrochemical Company (China). Other materials were commercial products.

2.2. Preparation of OMt/BR nanocomposites

OMt was dispersed in 6# solvent oil, then the OMt suspension was added into the BR solution and the mixture was vigorously stirred for 30 min at 60 °C. After the solvent was evaporated, the compounds of OMt/BR were obtained. Incorporation of the curatives and other ingredients took place on a two roll mixing mill with a nip clearance of 1 mm and friction ratio 1.3 (22/17 rpm). Mixing was performed at room temperature for about 14 min. The specimens were cured through plate vulcanization machine at 145 °C for the respective curing time (T_{90}) derived from measurements on a rotorless curometer (MDR2000). Table 1 is the recipes of OMt/BR compounds.

2.3. Recovery of the solvent by distillation

Firstly, the mixture of the OMt and BR solution was stirred about 15 min. After mixing, the solvent was decompression distilled off by injection stream from the bottom of the reactor. Then, after standing for 24 h, remove the free water of the fraction and dewater it using 5A molecular sieve, marked it as 1# solvent; secondly, remove the oxygen by heating and blowing nitrogen to 1# solvent, then reserve it under the nitrogen protection, marked it as 2# solvent; thirdly, rectify the 1# solvent on glass rectification tower. Under the nitrogen protection, reserve the fractions which have removed the light components, marked it as 3# solvent.

2.4. 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 Kα radiation) at room temperature.

Tensile and tear tests were measured on a DXLL-50000 (Dirs 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).

A GC-17A gas chromatograph (Shimadzu, Japan) and hydrogen flame ionization detector was used for detecting the composition of recovered solvent after distillation. As the carrier gas, N_2 was used. For the GC separation, OV-101 capillary column ($25\ \text{m} \times 0.25\ \text{mm}$ i.d., $d_f = 0.33\ \mu\text{m}$) was employed with an appropriated preconditioning before the use.

The crosslink densities of the vulcanizates from both methods were determined using a toluene-swelling method, as prescribed in ASTM D6814-02. The vulcanizate samples were cut into squares (1 cm wide and 3–5 mm thick) and weighed before being swollen in toluene until equilibrium swelling, which normally took 72 h. The crosslink density was calculated by using the *Flory–Rehner* equation (Youping et al., 2005):

$$V_e = -\left[\ln(1-V_r) + V_r + \chi_1 V_r^2\right] \Big/ \left[V_1\left({V_r}^{1/3} - V_r/2\right)\right]$$

where V_e is the network chain density (mol/cm^3), V_r is a volume fraction of rubber in a swollen network, V_1 is the molar volume of toluene (106.3 cm^3/mol), and V_r is the *Flory–Huggins* interaction parameter between toluene and polymer (0.391) (Yiqing et al., 2005):

$$V_r = [(m_d - m_f)/\rho_d]/[\,(m_d - m_f)/\rho_d + m_s/\rho_s]$$

where m_d and m_s are the weight of dry rubber and the weight of solvent adsorbed by the sample, respectively, m_f is the weight of the filler in the sample, ρ_d is the density of the rubber compound, and ρ_s is the density of toluene (0.867 g/cm^3).

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 μm with a frequency of 1 Hz.

Table 1
Recipes of OMt/BR compounds.

Materials	Sample 1 (phr)	Sample 2 (phr)	Sample 3 (phr)	Sample 4 (phr)
BR9000	100	100	100	100
OMt	0	2–10	0	6
CB(carbon black)	0	0	60	54
ZnO	4	4	0	0
SA	2	2	2	2
4010NA	1	1	0	0
CZ	0.7	0.7	0	0
TBBS	0	0	0.9	0.9
ASTM103# oil	0	0	15	15
S	1.5	1.5	1.5	1.5

3. Results and discussion

3.1. Morphology and structure of OMt/BR nanocomposites

The Mt showed a (001) reflection at 2θ = 5.68°, corresponding to the basal spacing of 1.55 nm. After organic modification using dimethyl ditallow-ammonium, the OMt showed a (001) reflection at 2θ = 4.66°, corresponding to a larger basal spacing of 1.89 nm. The reflection (001) of OMt/BR nanocomposites (6 wt.%) appeared at 2θ = 3.50°, corresponding to a larger basal spacing of 2.52 nm (Fig. 1). This indicated that the BR chains were intercalated into the clay particles.

The TEM provided information in real space on morphology and spatial distribution of various phases. The light color areas were BR matrix, the dark lines and areas were OMt particles and their aggregates (Fig. 2). The TEM photograph indicated that the OMt particles were homogeneously dispersed in the BR matrix. The intercalated and partially

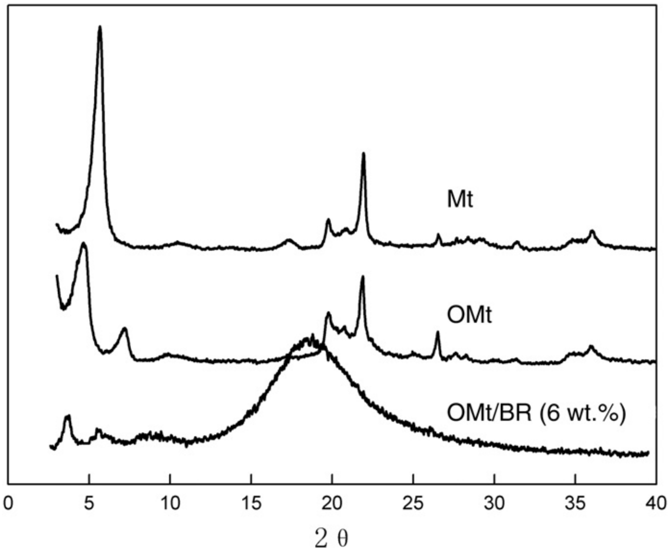

Fig. 1. XRD patterns of (a) Mt (b) OMt (c) OMt/BR (6 wt.%).

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