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STRUCTURE AND PROPERTIES OF ISOBUTYLENE-ISOPRENE RUBBER/SWOLLEN ORGANOCLAY NANOCOMPOSITES PREPARED BY SHEAR MIXING*

Ying-jie Tan[a, b], Yu-rong Liang[b**], Guo-sheng Hu[a], Yi-qing Wang[c], Yong-lai Lu[c] and Li-qun Zhang[c**]

[a] *The Institute of Materials Science and Engineering, North University of China, Taiyuan 030051, China*
[b] *The Institute of Materials Engineering, Taiyuan Institute of Technology, Taiyuan 030008, China*
[c] *Key Lab for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China*

Abstract A new approach was developed to prepare high-performance isobutylene-isoprene rubber/swollen organoclay nanocomposites by shear mixing. Compared with traditional melt compounding method, better dispersion of nanoclay layers in rubber matrix was verified through transmission electron microscopy (TEM) and X-ray diffraction (XRD). The nanocomposites also exhibit significantly improved mechanical properties and gas barrier property. As a mechanism, the molecules of organic swelling agent play a vital role in accelerating the diffusion and intercalation of the matrix molecules.

Keywords: Isobutylene-Isoprene rubber; Clay; Nanocomposites; Shear mixing.

INTRODUCTION

As it is an effective way to overcome some shortcomings of conventional composites, polymer/clay nanocomposites have attracted a great deal of interest in academia and industry since the last decade of 20th century[1–6]. Based on the different arrangements of the silicate layers in polymer matrix, two types of morphology can be achieved in nanocomposites: intercalated or exfoliated. Compared with the intercalated structure, the exfoliated structure is well recognized as a better morphology for getting higher performance or reducing clay loading. Therefore, how to achieve the ideal dispersion state of clay layers (*i.e.*, exfoliate) in rubber matrix is a key issue for rubber/clay nanocomposites, and it is important to explore both the scientific meaning and potential industrial application of polymer/clay nanocomposites.

To date, a series of rubber/clay nanocomposites have been prepared by various methods, including *in situ* polymerization intercalation[7], solution intercalation[8, 9], melt intercalation[10–13] and co-coagulating of rubber latex and clay aqueous suspension[14–18]. Among them, the latex method has advantages over the *in situ* polymerization intercalation and solution intercalation methods because of its environmental friendliness and simple procedure because pristine clay can be directly used. But it is promising for polymers having a latex

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** Corresponding author: Yu-rong Liang (梁玉蓉), E-mail: tl980913@sohu.com
Li-qun Zhang (张立群), E-mail: zhanglq@mail.buct.edu.cn
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form. The latex of isobutylene-isoprene rubber (IIR) is not commercially available. Melt compounding, a conventional processing method, is more convenient (Solution intercalation is environmentally unfriendly because large quantities of organic solvent are needed, although the properties of nanocomposites prepared by solution intercalation are somewhat superior to those of nanocomposites by melt intercalation[19]). But exfoliated structure is difficult to achieve by melt intercalation[20–22].

Up to now, to authors' knowledge, there was little concern on the processing method. In this research, a new approach was developed to prepare high-performance rubber/organoclay nanocomposites. IIR/orgnomontmorillonite (OMMT) nanocomposites were prepared by shear mixing swollen OMMT and IIR on a two roll mill, and exfoliation was achieved. The properties, such as Shore A hardness, tensile strength, air-tightness and so on, of nanocomposites prepared by the new method were superior to those of nanocomposites obtained by the traditional melt intercalation method with non-swollen organoclay. Therefore the new approach is promising for industrialization due to simplicity of the preparation process and superior performance, and it is applicable to the other rubber materials reinforced by clay.

EXPERIMENTAL

Materials and Formulation

Isobutylene-isoprene rubber (IIR, Polysar301) was provided by the North Special Rubber Corporation of Hengshui (Hebei Province, China). The organoclay, using *N*-allyl-*N,N*-dimethyl-octadecylammonium chloride as the modifier, was supplied by the Applied Chemistry Laboratory at Beijing University of Chemical Technology (Beijing, China). Its chemical formula is $(CH_3CH{=}CH)(C_{18}H_{37})(CH_3)_2N^+Cl^-$. Other materials and reagents used in this work were commercial products. Table 1 illustrates an IIR compound.

Table 1. IIR compound

Ingredients	Contents (phr[a])
IIR	100.0
S-OMMT	5.0
Zinc oxide (ZnO)	5.0
Stearic acid (SA)	2.0
Tetramethyl thiuram disulfide (accelerator TMTD)	1.0
2-Mercapto benzothiazole (accelerator M)	0.5
N-phenyl-α-naphthylamine (antioxidant A)	1.0
Sulfur	1.8

[a] Phr is the abbreviation of parts per hundred rubber.

Preparation of IIR/Clay Nanocomposites

The nanocompound was made based on two steps: First, the swollen OMMT (S-OMMT) was prepared by intercalating the small organic and innocuous swelling agent, such as butyl alcohol, oleic acid and castor oil. In this study, we used butyl alcohol as the swelling agent. OMMT and organic swelling agent were mixed in proportion to one gram/one milliliter under the frictional function of a muller for 30 min. After that, S-OMMT was dried at room temperature for 48 h. Then the swollen organoclay and IIR were compounded for *ca*. 15 min using a two roll mill, and the additives, ZnO, stearic acid, sulfur, accelerators and antioxidant were gradually mixed with the compound.

As a contrast, we prepared IIR/OMMT nanocompounds by direct mixing OMMT with IIR on a two roll mill for 15 min, the vulcanization additives and other additives were mixed with the nanocompounds according to the recipe listed in Table 1.

The nanocompounds were vulcanized in a standard mold at 160°C with 15 MPa pressure for their optimum cure times (t_{90}), which were determined using a disc oscillating rheometer (P355B2, Beijing Huanfeng Chemical Technology and Experimental Machine Plant, China).

Characterization

X-ray diffraction (XRD) measurements were carried out by using a diffractometer (D/Max-III C, Rigaku, Japan)

with a Cu Kα radiation, operating at 40 kV and 200 mA. Basal spacing between silicate layers was observed from 0.5° to 10° (2θ) at a scanning rate of 1 (°)/min.

Transmission electron microscopy (TEM) observations were performed on an H-800-1 transmission electron microscope (Hitachi Co., Japan) with an accelerating voltage of 200 kV. The ultra-thin sections of rubber/clay nanocompounds for TEM were cut using a liquid nitrogen cooled microtome at about –100°C and collected on a copper grid.

Measurements of mechanical properties of all specimens were conducted at (25 ± 2)°C according to ISO 37 and ISO 7619. For tensile tests a CTM 4104 tensile tester was used at a crosshead rate of 500 mm/min.

The permeation of nitrogen was carried out with a gas permeability measuring apparatus according to ISO 2782. The pressure was maintained at 0.57 MPa on one side of the specimen sheet (about l mm in thickness and 8 cm in diameter) and initially zeroed on the other side. The nitrogen permeability was calculated from the rate of transmission through the sheet at 40°C, which was determined by gas chromatography.

RESULTS AND DISCUSSION

Micro-structural and Morphological Analyses

XRD patterns supply useful information of the gallery of the hybrids by monitoring the basal (001) *d*-spacing. Generally intense reflections in the range of 2° ≤ 2θ ≤ 10° indicate an intercalated structure.

In Fig. 1(b), XRD pattern of the organoclay shows a diffraction peak at about 2.2° for an interlayer spacing of 3.9 nm. After being swollen by the organic swelling agent, the diffraction peak of S-OMMT obviously shifts to lower 2θ values, corresponding to a basal spacing of 4.4 nm (d_{001}). This expansion of gallery height is attributed to the intercalation of small organic molecules by the diffusion and adsorption reaction. Furthermore, XRD patterns of OMMT and S-OMMT shearing mixed with IIR before curing show that all peaks have almost disappeared. This means that isobutyl-isoprene rubber macromolecules are fully embedded in the clay layer spacing, and the dispersion structure is extremely disordered and closes to exfoliated structure.

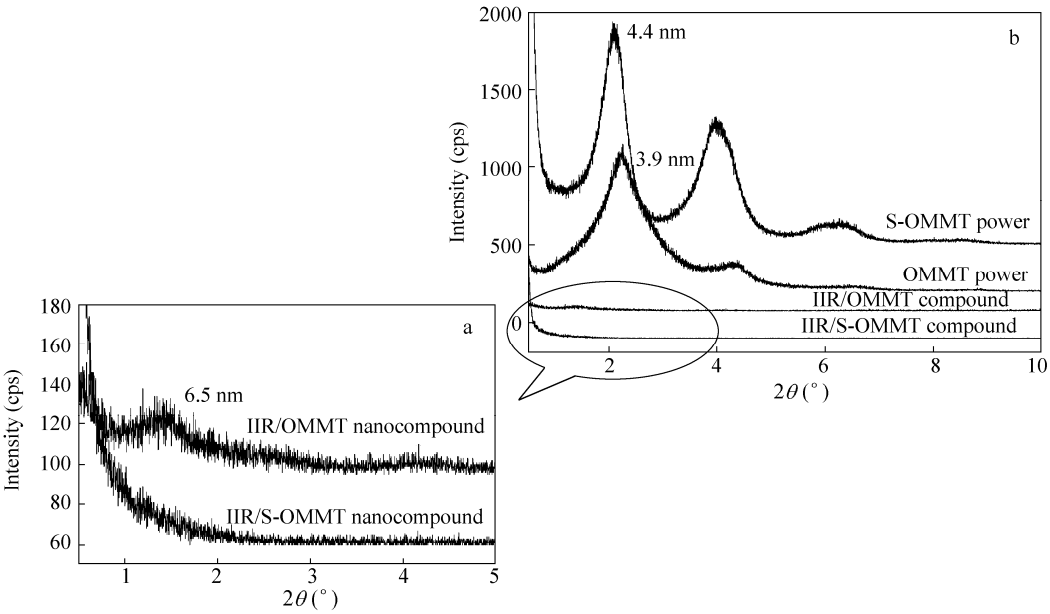

Fig. 1 XRD patterns of OMMT, S-OMMT, IIR/OMMT (100/5) nanocompound and IIR/S-OMMT (100/5) nanocompound

For sake of clarity, XRD patterns of the two nanocompounds are plotted again by reducing the ordinate height shown in Fig. 1(a).

A weak peak appears in the XRD curve corresponding to the (001) plane reflections of OMMT in the IIR/OMMT nanocompounds, and the basal spacing of OMMT is about 6.5 nm. After shear mixing with IIR, the diffraction peak of OMMT shifts to lower 2θ values compared with that of OMMT, the intensity of the diffraction pattern decreases significantly, and this indicates that rubber molecules intercalate into the interlayer spacing and disperse uniformly. Therefore both exfoliated and intercalated nanoclay layers co-exist in IIR/OMMT nanocompounds. This is possibly due to the high shear stress acts on the clay layers and results in the peeling off of the layers, because of the extremely high viscosities of rubber during melt compounding[23].

On the other hand, the intensity of the (001) reflection for IIR/S-OMMT nanocompounds decreases dramatically compared with corresponding IIR/OMMT nanocompounds, no obvious XRD peak is found for IIR/S-OMMT nanocompounds, demonstrating that OMMT in IIR/S-OMMT nanocompounds is disorderly exfoliated.

Why the two nanocompounds possess a little different structure? What is the driving force for the transformation of structures from intercalated (IIR/OMMT nanocompounds) to exfoliated (IIR/S-OMMT nanocompounds)?

It should be essentially on the exfoliation of substantial OMMT and the decrease of amount of intercalated structures due to the effect of organic solvent. As was expected，swollen organoclay has better dispersion in IIR than organoclay. When organic swelling agent is used to pre-swell the organoclay, the interlayer spacing of OMMT is expanded and the layer-layer interaction is weakened. As a result, IIR macromolecules more easily intercalate into layer gallery, and layers exfoliation more easily takes place.

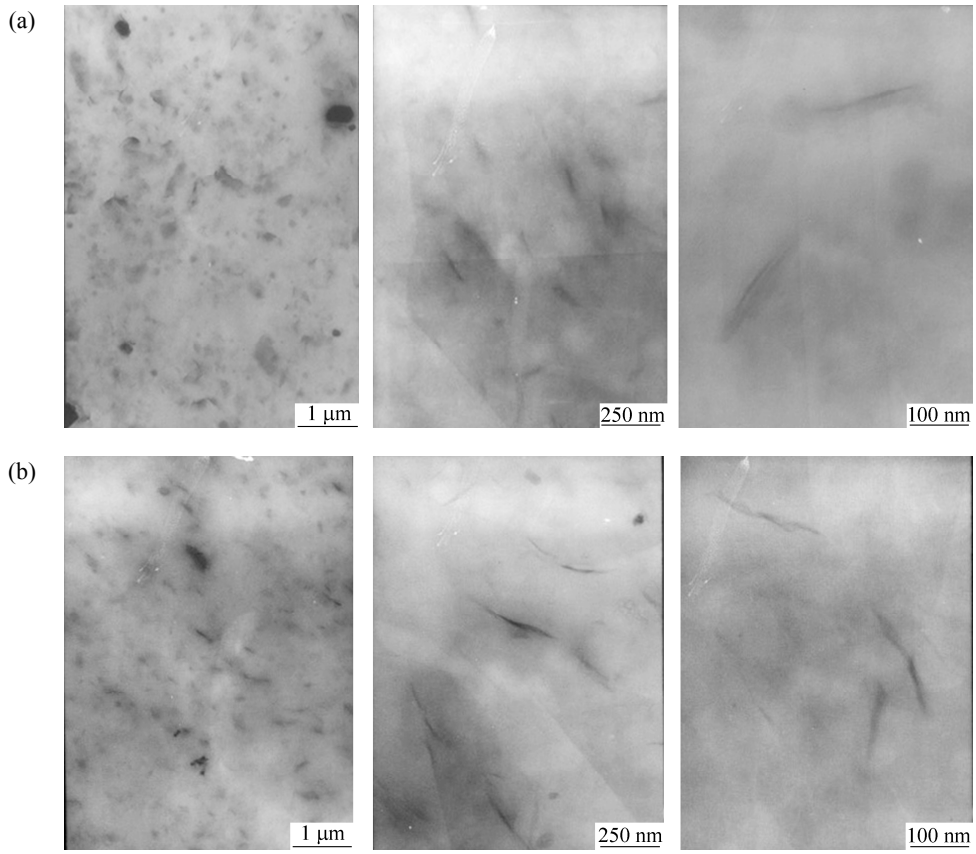

Fig. 2 TEM micrographs of IIR/OMMT (100/5) nanocompounds (a) and IIR/S-OMMT (100/5) nanocompounds (b)

To further confirm the dispersion states of OMMT and S-OMMT in the IIR matrix, TEM studies were carried out. Figures 2(a) and 2(b) present TEM photographs of the two nanocompounds respectively, in which the darker phase represents the organoclay dispersion particles.

From Fig. 2(a), it can be seen that the dispersion of organoclay particles is quite fine, and their dispersion state is homogeneous in IIR/OMMT nanocompounds. In low magnification TEM micrograph exfoliated nanolayers are observed, some aggregates (several hundred nanometers) are also found, which might be comprised of exfoliated layers or intercalated layers. The higher magnification TEM images of them reveal that many OMMT layers exist in aggregate form with 10−50 nm thickness. In the highest magnification TEM micrograph, there are some single exfoliated clay layers in IIR matrix besides intercalated clay layers. This means that IIR macromolecules does not completely diffuse into all clay galleries during the melting process, however, each layer of clay nearly disperses homogeneously in the rubber matrix. Therefore, IIR/OMMT nanocomposites exhibits well dispersed structures of intercalated (scarcely) and exfoliated (mostly) organoclay. Furthermore, as can be observed in Fig. 2(b), S-OMMT more uniformly disperses within the IIR matrix than OMMT, whether the low magnification or the high magnification. As a consequence, it is deemed that the small organic molecule is effective on improving the dispersion homogeneity of silicate layers in IIR/S-OMMT nanocompounds. Therefore the new method can promote the exfoliation of silicate layers and improve the distribution homogeneity of silicate particles in IIR matrix.

The TEM observation is consistent with the XRD results, and the combination of them provides overall information about the disorderly exfoliated structure of nanocompounds prepared by the new approach.

Mechanical Properties

The variation in the degree of intercalation of organoclay in the IIR vulcanizates should manifest itself in the mechanical properties of the rubber nanocomposites. The mechanical properties of IIR/OMMT nanocomposites and IIR/S-OMMT nanocomposites are shown in Table 2.

Table 2. Mechanical properties of neat IIR, IIR/OMMT (100/5) nanocomposites and IIR/S-OMMT (100/5) nanocomposites

Sample	Shore A hardness	Stress at 100%/300% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)
Pure IIR	32	0.4/0.6	5.3	587	11.8
IIR/OMMT	35	0.4/0.8	6.7	649	13.1
IIR/S-OMMT	38	0.5/1.0	9.3	676	15.1

The improving of the mechanical properties, including hardness, stress at 100% and 300% elongation, tensile strength, elongation at break and tear strength, of the IIR/OMMT and IIR/S-OMMT nanocomposites is remarkable compared with those of the corresponding pure IIR. The tensile strength of IIR/S-OMMT nanocomposites is about 75% higher than that of the neat IIR. All these can be attributed to the high aspect ratio and the nanometer dispersion of organoclay layers which act as the intensifier in the rubber matrix. On the other hand, clay was modified by $(CH_3CH{=}CH)(C_{18}H_{37})(CH_3)_2N^+Cl^-$. The double bond of the modifier is located in the molecule, and makes it possible to react in the sulfur curing system, which consequently forms a strong interaction between the matrix and the clay interface.

More important, the properties of nanocomposites prepared by the new method are superior to those of nanocomposites by melt intercalation, which can be ascribed to the better dispersion of swollen organoclay in IIR than organoclay. In IIR/S-OMMT nanocomposites, the molecules of organic swelling agent play an important role in accelerating the diffusion and intercalation of the matrix molecules. Swelling organoclay through suitable small organic molecules benefits to further expand the layer space and weak the layer-layer interaction, both of which benefit the rubber macromolecules intercalation and exfoliation in the view of thermodynamic and dynamic aspects. Therefore this simple method is applicable to the other rubber materials reinforced by clay.

Gas Barrier Properties

Figure 3 shows the gas barrier property of IIR/OMMT and IIR/S-OMMT nanocomposites.

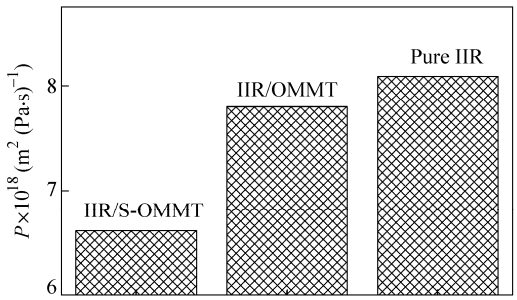

Fig. 3 Comparison of the gas barrier property of pure IIR, IIR/OMMT (100/5) nanocomposites and IIR/S-OMMT (100/5) nanocomposites

Compared with pure IIR, the permeability of IIR/S-OMMT (100/5) and IIR/OMMT (100/5) nanocomposites decreases by about 18% and 4%, respectively.

In general, there are two reasons causing the enhancement of gas barrier property for polymer/clay nanocomposites. First, gas-impermeable nanoclay layers disperse in polymer matrix forming a tortuous pathway. Secondly, exfoliated clay layers and intercalated clay layer bundles strongly restrict the motion of polymer chains, and probably reduce the diffusion coefficient of the gas molecules in the composites.

Moreover, IIR/S-OMMT nanocomposites made by the novel approach have better gas barrier property than the IIR/OMMT counterparts. It further proves that the new method can promote organoclay with high level dispersion in rubber matrix.

Therefore, pre-swell the organoclay and then shear mix it with IIR are a favorable method for reducing the gas permeability of IIR matrix, which makes it possible for IIR to be used as some products which require high gas barrier property.

CONCLUSIONS

A novel method has been proposed to prepare high-performance IIR/clay nanocomposites by shear mixing swollen organoclay with IIR. Compared with nanocomposites obtained by direct melt blending, the dispersion structure is extremely disordered and close to exfoliated structure by using this new approach, and is verified by XRD and TEM analyses. As a result of the good dispersion of clays, a significant improvement in the mechanical and gas barrier properties was observed. It can be attributed to the effect of organic swelling agent which plays a vital role in accelerating the diffusion and intercalation of the rubber macromolecules.

Therefore, the new method can promote the exfoliation of silicate layers and improve the distribution homogeneity of silicate particles in rubber matrix. Moreover, this new method is also promising for industrialization due to simplicity of the preparation process and environmental friendliness.

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