

Preparation, Structure, and Properties of a Novel Rectorite/Styrene–Butadiene Copolymer Nanocomposite

Yiqing Wang,¹ Huifeng Zhang,¹ Youping Wu,¹ Jun Yang,² Liqun Zhang^{1,3}

¹The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing, 100029, China

²Zhuzhou Times New Materials Science and Technology Corporation Limited, Hunan Zhuzhou 412007, China

³Key Laboratory for Nanomaterials, Ministry of Educational, Beijing 100029, China

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ABSTRACT: Rectorite/styrene–butadiene copolymer (SBR) nanocomposite was prepared by cocoagulating SBR latex and rectorite/water suspension. Transmission electron microscopy showed that the layers of rectorite were well dispersed in the SBR matrix and the aspect ratio (width/thickness) of it was higher than that of montmorillonite (MMT). X-ray diffraction indicated that the nanocomposite produced by this method was of neither intercalated type nor exfoliated type. The gas barrier proper-

ties and mechanical properties of the novel nanocomposites were excellent. The nanocomposites are expected to be candidates for tire tube or inner materials. Rectorite appears to be a promising filler for the nanocomposite. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 324–328, 2005

Key words: clay; rubber; nanocomposites; gas permeability

INTRODUCTION

Recently, polymer–clay nanocomposites have attracted considerable attention due to their unique physical and other properties, such as excellent gas barrier, improved heat resistance, and enhanced fire retardance.^{1–9} For the majority of polymers, owing to their hydrophobic character, the clay must be modified to enhance the compatibility between the polymer and the organically modified clay. However, it is a useful process from an industrial standpoint to produce nanocomposites utilizing original clay. Cocoagulating polymer latex and layered silicate/water suspension method developed by author's research group is a simple, effective, and low cost technique of preparing rubber–clay nanocomposites. Studies originated from this method are described in our previous work.^{10–15}

Sodium montmorillonite (MMT) is the most commonly used clay to construct the nanodispersion phase by intercalation or/and exfoliation method. In this study another layered silicate different from MMT in structure, namely rectorite, is used. Rectorite is defined as a 1 : 1 type of layer structure arranged regularly with an alternating dioctahedral mica layer and dioctahedral smectite layer.¹⁶ The general chemi-

cal formulae of the mica layer and the smectite layer are $(\text{Ca}_{0.55}\text{Na}_{0.02}\text{K}_{0.01}\text{Mg}_{0.03})_{0.61}(\text{Al}_{4.1}\text{Fe}^{2+}_{0.09}\text{Mg}_{0.07})_{4.26}(\text{Si}_{6.46}\text{Al}_{1.54})_8\text{O}_{22}$ and $(\text{Na}_{0.79}\text{K}_{0.39}\text{Ca}_{0.26})_{1.44}\text{Al}_4[\text{Si}_6\text{Al}_2]_8\text{O}_{22}$, respectively. The interlayer cations of smectite structure can be replaced easily by either organic or inorganic cations, which make it possible to separate rectorite layers to prepare polymeric nanocomposites. The thickness of a single sheet of rectorite is the sum of the thickness of the smectite layer and the thickness of the mica layer. Additionally, the original rectorite single sheet is about 40 μm in length and 5 μm in width whereas MMT is about 1 μm in length as well as in width. As a result, the separable layer thickness and layer aspect ratio (width/thickness) of rectorite are larger than those of regular MMT. Therefore, the incorporation of rectorite in rubber will improve the modulus and the gas barrier property of the rubber. In addition, the layered silicate layers become short on high shear force exerted by polymer melting during processing.¹⁴ Since rectorite layers are thick, they may endure the shear force and hence keep the high aspect ratio after processing.

Styrene–butadiene rubber (SBR) is an important and widely used rubber. In this paper, rectorite/SBR nanocomposites are prepared, and the mechanical properties and permeability are investigated. Results of this study reveal that rectorite can be a new excellent precursor to prepare clay/polymer nanocomposites in the future.

Correspondence to: L. Zhang (zhangliqunghp@yahoo.com).

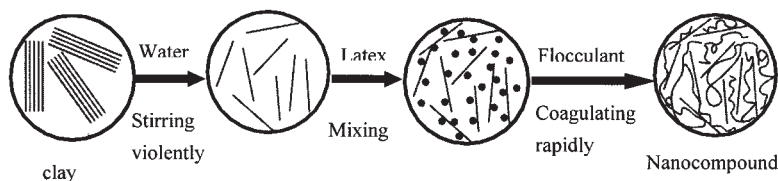


Figure 1 Schematic of processing of clay/rubber nanocomposites.

EXPERIMENTAL PROCEDURES

Materials

Rectorite (from HuBei Celebrities Rectorite Technology Co. Ltd., HuBei Province, China), SBR1502 latex (from Qilu Rubber Co. Ltd., ShanDong Province, China) are used in this study.

Preparation of nanocomposites

First, natural rectorite was dispersed in water with vigorous stirring for 5 h and an aqueous suspension of silicate was achieved. To purify natural rectorite, the aqueous suspension was kept at room temperature for 24 h and the deposition was rejected. The interfacial agent ($C_4H_9N^+(CH_2CH_2OH)_3Br^-$, 0.1 mol/100 g) and the SBR latex then were added into the aqueous suspension and stirred for 20 min. Finally, the mixture was coagulated by a cation-type coagulating agent (dilute sulfuric acid, 2%), washed with water several times until its pH was about 7, and then dried at 70°C for 24 h.

The process of the technique was illustrated in Figure 1. First, rectorite layers combined together were divided into separated layers in water as a result of its hydrophilic property. Subsequently the latex were mixed with rectorite aqueous suspension. Rubber latex didn't cause the aggregation of rectorite layers because both of them were hydrophilic, and a uniform and stable mixture was obtained. The third step was cocoagulating of the mixture by the addition of a flocculant. At this step, the flocculant coagulated both the rubber latex and the silicate layers. Because of the presence of a great deal of rubber latex particles, the rectorite layers were "separated," which caused the layers dispersed uniformly in the rubber. Then, the rectorite/SBR nanocompound was formed.

Compounding and processing of composites

The rectorite/SBR nanocompound was mixed with various necessary ingredients shown in the recipes in Table I in a 6-in. mixing roll; the compounds then were vulcanized at 150°C by a hot press. The curing time was determined by a rheometer from the Beijing Huan Feng Mechanical Factory.

Compounds filled with carbon black (N330) or calcium carbonate were prepared by directly adding the filler into SBR in a two-roll mill and mixing for 10 min, then adding ingredients listed in Table I and mixing for 5 min. After those steps, the resultant compounds were vulcanized at 150°C to obtain vulcanizates.

Characterization

X-ray diffraction studies were performed with a Rigaku RINT by using $CuK\alpha$ radiation. TEM observations were carried out with an H-800 TEM by using an acceleration voltage of 200 kV.

Shore A hardness was measured according to ISO 48-1994. Tensile tests were performed on dumbbell-shaped specimens according to ISO 37-1994. Tear strength was carried out according to ISO 34-1 1994. Five samples were tested and the average of the values was taken.

The specimens for gas barrier property measurement had a diameter of 8 cm and thickness of about 1 mm and the test was taken at $40 \pm 0.5^\circ C$, 0.57 MPa pressure. A 99.5% nitrogen was used as the test gas and 99.9% hydrogen as the carrier gas. Prior to testing, specimens were conditioned by H_2 inside the unit for over 24 h to remove traces of atmospheric nitrogen and oxygen.

RESULTS AND DISCUSSION

Morphology and structure of nanocomposites

The TEM micrograph of rectorite/SBR nanocomposite is shown in Fig. 2(a). To compare the differences of

TABLE I
Recipe of SBR Matrix Composites (phr)

	SBR	100
Filler		Variable
Zinc oxide		5.0
Stearic acid		2.0
Dibenzothiazole disulfide(DM)		0.5
Diphenyl guanidine(D)		0.5
Tetramethyl thiuram disulfide(TMTD)		0.2
Sulfur (S)		2.0
<i>N</i> -isopropyl- <i>N'</i> -phenyl- <i>p</i> -phenylene dianime (Antioxidant 4010NA)		1.0

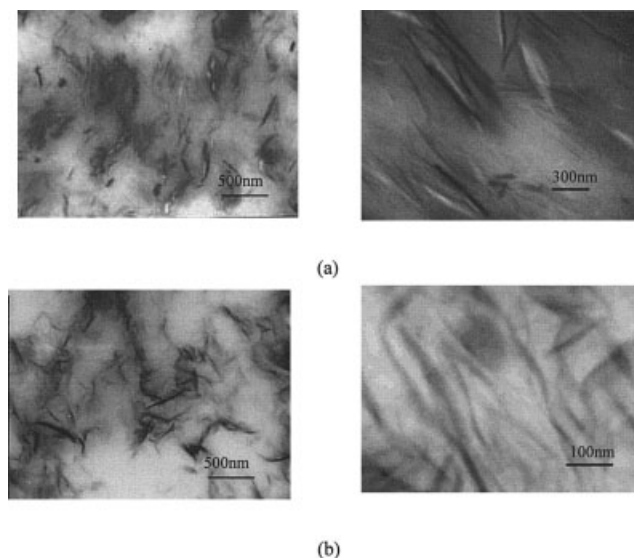


Figure 2 TEM micrographs of (a) rectorite/SBR and (b) MMT/SBR nanocomposites.

structure, the TEM micrograph of the MMT/SBR nanocomposite is also shown [Figure 2(b)] (filler 20 phr). The thick dark lines are clay sheets, viewed as the edge of the clay, therefore the thickness of dispersed clay can be obtained from the width of the line. The micrographs clearly indicate that the silicate layers are dispersed into SBR at a nanometer scale (i.e., thickness of layers < 100 nm). There are some individual sheets and some stacking sheets. The latter may be caused by the aggregation of silicate layers during flocculation. The thickness of rectorite layers dispersed in SBR is about 30 ~ 50 nm and the length is about 1 μm as shown in Fig. 2(a), while that of MMT is about 10 ~ 20 and 200 ~ 300 nm as shown in Fig. 2(b), which reveals that the aspect ratio of the dispersion unit of rectorite/SBR nanocomposite is higher than that of the MMT/SBR nanocomposite, just as expected. Considering the original lengths of the layers of these two silicates, it is believed that rubber processing results in serious breakage of nanodispersed silicate layers due to the higher viscosity of rubber than that of plastic, as has been reported.¹⁴ The processing shortens the difference of aspect ratios of these two kinds of silicates dispersed in rubber. To obtain a high gas barrier property, keeping the high original aspect ratio of rectorite in rubber is important.

The X-ray diffraction pattern of rectorite powder and the rectorite/SBR nanocomposites with various rectorite contents are shown in Figure 3. The rectorite powder shows the primary harmonic at $2\theta = 4.116$, corresponding to 2.15 nm, the characteristic of the succession of rectorite unit. Interestingly, the XRD patterns of rectorite/SBR nanocomposites display that there are still remnants of the original spacing of rectorite. Peak just shifts from 2.15 to 2.4 nm, implying no

macromolecules intercalated into the space between rectorite layers, although dispersed layers of rectorite are small enough. The slight change of space may be caused by some ion exchange of flocculant. Therefore, the nanocomposites prepared by this method are neither of an intercalated type nor of a completely exfoliated type. The nanocomposites contain some single silicate layers and some stacking layers without macromolecules intercalated therein.

Mechanical properties of nanocomposites

The mechanical properties of rectorite/SBR are illustrated in Table II. The introduction of rectorite into SBR leads to a great increase of mechanical properties of SBR. The rectorite/SBR nanocomposite with 20 phr rectorite exhibits a tensile strength of 12.7 MPa, which is 6.3 times that of pure SBR. It is also observed that the mechanical properties of the nanocomposites increase with the increase of filler content. Compared with carbon black(N330)/SBR and calcium carbonate/SBR composites (see Table III), rectorite/SBR nanocomposites possess the higher stress (at 300% strain), tensile strength, and tear strength. This substantial enhancement of mechanical properties is ascribed to the nanoscale dispersion of rectorite in SBR matrix and the strong interaction between SBR and dispersed phase.

In short, the results of mechanical properties indicate that rectorite can be a promising filler in the rubber industry. If the advantage of the high original aspect ratio of rectorite unit could be kept, the mechanical properties relating to aspect ratio, such as hardness, stress at certain strain, tear strength, etc., would be much higher.

Gas barrier properties of nanocomposites

Compared with carbon black, calcium carbonate, and micron MMT, the MMT/rubber nanocomposites

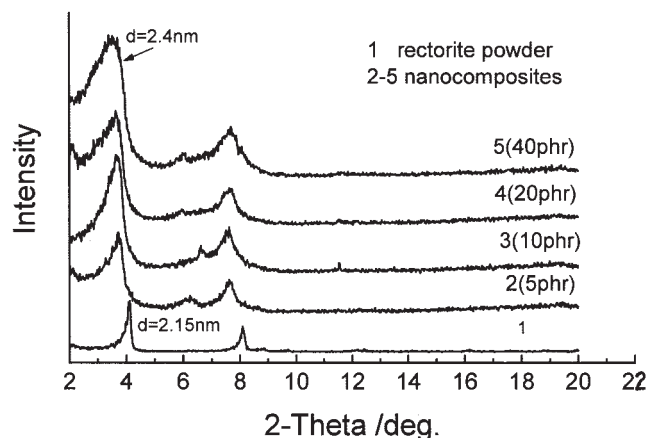


Figure 3 X-ray diffraction patterns of rectorite/SBR nanocomposites.

TABLE II
Mechanical Properties of Rectorite/SBR Nanocomposites

Properties	Filler/phr					
	0	5	10	20	30	40
Stress at 300% strain (MPa)	1.9	3.3	4.3	8.6	11.4	13.5
Tensile strength (MPa)	2.0	4.9	8.3	12.7	13.6	16.4
Elongation at break (%)	368	440	524	456	380	400
Permanent set (%)	2	8	16	28	36	—
Tear strength (KN · m ⁻¹)	15.2	25.8	33.7	51.6	58.9	—
Shore A hardness	46	54	60	68	76	80

made in our previous work exhibit excellent gas barrier property due to the higher aspect ratio of nanoscale MMT.¹⁵ Rectorite/SBR nanocomposites demonstrate the similar behavior in gas barrier property in this study.

Figure 4(a) shows that the permeability of the rectorite/SBR nanocomposites and carbon black/SBR composites are gradually reduced with the increase of filler content. Due to the effectiveness of the high aspect ratio of rectorite/SBR nanocomposites, their permeabilities are much lower than those of carbon black (N330) filled SBR composites.

Changes in diffusivity, D , express the same trend as that of permeability [Fig. 4(b)], however, it seems that the aspect ratio exerts a stronger effect on D than on P . The presence of filler reduces the diffusivity by increasing the tortuosity of the transport path, which can be described by Nielsen approximation,¹⁷ as shown in eq. (1). This model describes diffusivity D in a system filled with dispersed particles of aspect ratio α .

$$D = D_0 \left(\frac{1 - \phi_f}{1 + \frac{\alpha}{2} \phi_f} \right) \quad (1)$$

where D_0 is the diffusivity of the amorphous polymer and Φ_f is the volume fraction of filler.

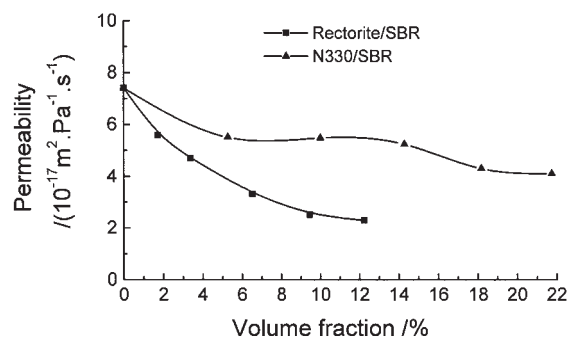
As can be seen from this model, the higher the aspect ratio α of filler is, the lower the diffusivity D of composite. The experiment results are fitted to the equation with an aspect ratio of about 20 for the rec-

TABLE III
Comparison of Mechanical Properties of Different Filled SBR Composites (the Amount of Fillers Is 20 phr)

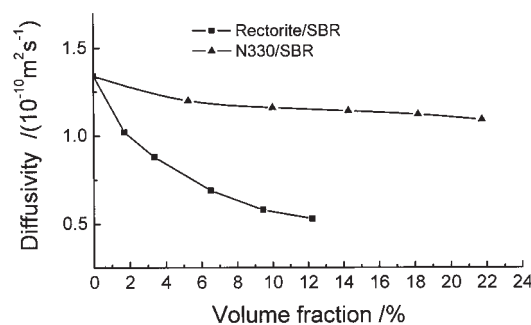
Properties	Filler type		
	Rectorite	N330	Calcium carbonate
Stress at 300% strain (MPa)	8.6	5.6	2.2
Tensile strength (MPa)	12.7	10.1	2.4
Elongation at break (%)	456	420	336
Tear strength (KN · m ⁻¹)	51.6	25.9	18.4

torite/SBR system and 1 for the carbon black/SBR system. Therefore, designating and forming fillers with high aspect ratio in polymer matrix are a promising and practical way to make polymer materials with a high gas barrier property.

Butyl rubber and halogenated butyl rubber are the main and popular rubbers for inner tubes and liners of tires. However, they are difficult to process and hard to cocrosslink with body rubbers, which are generally natural rubber, butadiene rubber, and SBR, due to the significant difference in saturation degree. Rectorite/SBR nanocomposites made in the study with high mechanical properties and excellent gas barrier property are expected to be candidates for tires in the cases of butyl rubber and halogenated butyl rubber.



(a)



(b)

Figure 4 Transport properties of rectorite/SBR nanocomposites and SBR filled with N330: (a) permeability; (b) diffusivity.

CONCLUSION

Rectorite/SBR nanocomposite is prepared by cocoagulating SBR latex and rectorite water suspension. The layers of rectorite are dispersed into SBR at a nanometer scale and the aspect ratio (width/thickness) of dispersed rectorite unit is higher than that of MMT. The mechanical properties of SBR are greatly enhanced by introduction of the nanodispersed rectorite. The gas barrier property of rectorite/SBR nanocomposite is excellent and higher than that of N330/SBR composite due to the higher aspect ratio of dispersed unit. Rectorite appears to be a promising filler in the preparation of nanocomposites. Rectorite/SBR nanocomposites are expected to be good candidates for tire tube or inner materials.

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