Preparation, Structure, and Properties of a Novel Rectorite/Nitrile Butadiene Rubber (NBR) Nanocomposites

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ABSTRACT: Rectorite/nitrile butadiene rubber (NBR) nanocomposite was firstly prepared by co-coagulating NBR latex and rectorite water suspension. The microstructure of the resulted nanocomposite was characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results indicated that the rectorite layers were dispersed in the NBR matrix in form of single layers and nano-meter stacking layers. Moreover, the nano-sized stacking layers were not intercalated. Compared with silica or carbon black, the incorporation of rectorite in NBR leads to stronger filler network in the compound and further results in higher storage modulus of the vulcanizate. The mechanical properties and the gas barrier property of rectorite/NBR vulcanizate were remarkably improved by introduction of nano-dispersed rectorite. [DOI 10.1295/polymj.37.154]

KEY WORDS Preparation / Properties / Rectorite / Rubber Nanocomposites / Structure /

Since Toyota Central Research and Development Laboratories invented layered silicates/polyamide nanocomposites,¹ polymer layered silicate (PLS) nanocomposites have attracted great interest of researchers around the world of both in industry and in science, because this kind of novel nanocomposites exhibit new and improved properties compared to their microcomposite counterparts due to the ultra fine phase dimensions and special phase structure involved.^{2–9} The nano-concept is of significant importance for rubber composites, and nano-reinforcement has been proved to be an extremely effective and necessary way for rubber applications.^{10–12} Up to now, carbon black and silica, which have been applied in rubber industry for many years, are two main kinds of nano-fillers for rubber reinforcement due to their huge specific surface area, nano-size and a certain of reactive groups on the surface.

Commercial clay, however, has also been used as cheap and non-reinforcing filler in rubber industry for many years. Success of PLS nanocomposites based on plastics matrixes greatly promotes and impels the study of PLS based on rubber matrixes. A few clay/rubber nanocomposites with excellent properties and unique phase structure have been prepared by different methods, such as nitrile butadiene rubber (NBR),^{13–16} polyurethane (PU),¹⁷ Ethylene–Propylene–Diene Monomer (EPDM),^{18,19} natural rubber (NR),²⁰ butadiene rubber (BR) and styrene-butadiene

rubber (SBR).^{21,22} These methods for the preparation of rubber-clay nanocomposites include *in situ* polymerization, solution and melt intercalation, wherein organic modified clay must be employed. In contrast, co-coagulating rubber latex and layered silicate aqueous suspension is a promising method for preparing layered silicate/rubber nanocomposites wherein pristine clay is utilized instead of organic clay.^{23–26}

Layered silicates commonly used for preparation of polymer matrix nanocomposites are montmorillonite and hectorite. In this study, a novel layered silicate, *i.e.* rectorite, is used as the precursor of nano-phase. Rectorite is an interstratification layered silica mineral consisting of a regular stacking of mica-like layers and montmorillonite-like layers (1:1).²⁷ The interlayer cations of montmorillonite-like layers can be exchanged easily by either organic or inorganic cations, and therefore, rectorite has the similar water swelling property to montmorillonite, which makes it possible to prepare rectorite/rubber nanocomposites by co-coagulation technique. The thickness of a single rectorite layer is about 2 nm, thicker than that of montmorillonite layer 1 nm. The width and length vary from a micron to several microns, larger than that of montmorillonite layer. Such structural characteristics can be expected to confer improved barrier property, fire-resistance, modulus, heat-resistance of rectorite/polymer nanocomposite in comparison with montmorillonite.

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Table I. Details of the rectorite clay

Rectorite	Total contents mass wt %		Atom ratio		Mica	Smectite
SiO ₂	51.88		Si	12.46	6	6.46
Al ₂ O ₃	41.18		Al	11.64	6	5.64
FeO	0.46		Fe ²⁺	0.09	0	0.09
MgO	Exchangeable	0.18	Mg	0.07	0	0.07
	Un-exchangeable	0.08		0.03	0	0.03
CaO	Exchangeable	1.08	Ca	0.26	0.26	0
	Un-exchangeable	2.07		0.55	0	0.55
Na ₂ O	Exchangeable	1.72	Na	0.79	0.79	0
	Un-exchangeable	0.04		0.02	0	0.02
K ₂ O	Exchangeable	1.27	K	0.39	0.39	0
	Un-exchangeable	0.03		0.01	0	0.01

Table II. Recipe of the NBR compounds

Samples	NBR/rectorite nanocomposites	NBR/N330 composite	NBR/silica composite
Ingredients (phr)			
NBR	100	100	100
Clay	Variable	—	—
N330	—	Variable	—
Precipitated silica	—	—	Variable
Zinc oxide	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
Dibenzothiazole disulfide (DM)	1.5	1.5	1.5
Tetramethyl thiuram disulfide (TMTD)	0.75	0.75	0.75
Sulfur	2.0	2.0	2.0
<i>N</i> -Isopropyl- <i>N'</i> -phenyl- <i>p</i> -phenylene dianime	2.0	2.0	2.0

Since NBR is an important and widely used rubber, in this paper, the preparation, structures and properties of rectorite/NBR nanocomposites will be discussed in detail.

EXPERIMENTAL

Materials

Sodium rectorite (70 wt %) was kindly provided by Hubei Celebrities Rectorite Technology Co., Ltd., China. Details of the layered silicate were given in Table I. NBR-26 latex (AN 26%) was from Lanzhou Petrochemical Company, China. Precipitated silica was purchased from Hydrated Silica Factory of Jiangsu Nanji Co., Ltd., China; carbon Black (N330) was from Tianjing Dolphin Carbon Black Co., Ltd., China.

Preparation of Nanocomposites

Natural Na⁺-rectorite was dispersed in deionized water with vigorous stirring at a concentration of 3% and an aqueous suspension of silicate was obtained. Then a given amount of NBR latex was added into the aqueous suspension and stirred for 20 min.

After that, the mixture was co-coagulated by CaCl₂ solution (2 wt %), washed with water several times until the Cl⁻ was removed completely (no Cl⁻ detected by X-ray energy dispersive spectroscopy), and dried at 70 °C for 24 h. Thus, the rectorite/NBR nanocompounds were obtained.

To obtain vulcanizates, nanocompounds were mixed with ingredients according to the recipes in Table II with a 6-in. two-roll mill, and vulcanized at 160 °C in a hot press for the optimum cure time (*t*₉₀) determined by a rheometer (Beijing Huanfeng Mechanical Factory, China.).

Compounds filled with carbon black (N330) or silica were prepared by directly adding the filler into NBR in a two-roll mill and mixing for 10 min, then adding ingredients listed in Table II and mixing for another 5 min. After these steps, the resulted compounds were vulcanized at 160 °C for *t*₉₀ to obtain vulcanizates.

Characterization of Structure and Test of Properties

Transmission electron microscopy (TEM) micrographs were taken from ultrathin sections of nano-

composites produced under freezing condition of liquid nitrogen using an ultramicrotome with an H-800 TEM, using an acceleration voltage of 200 kV. The contrast of pictures arises from differences in atomic number within the materials, *i.e.*, rectorite regions containing Si with high atomic number appear dark, while rubber regions of low atomic number appear light. Scanning Electron Microscopy (SEM, S-250-III) was used to observe the morphology of rectorite powder as received. SEM photomicrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV, and the surface of sample was coated with gold layer. X-Ray diffraction (XRD) analysis was performed using a Rigaku D/max 2500 VB2+/PC. An acceleration voltage of 40 kV and 200 mA were applied using Cu K α radiation.

Strain sweep experiments at the strain range from 1 to 400% were performed on compounds using a RPA 2000 Rubber Process Analyzer of Alpha Technologies at 60 °C, 1 Hz. Frequency sweep experiments were performed on vulcanizates at 60 °C, 1% strain.

The specimens for gas barrier property measurement had a diameter of 8 cm and thickness of about 1 mm. The test was carried out with gas permeability-measuring apparatus. The pressure on one face of a sample was kept at 0.57 MPa and the other face at zero pressure initially, and the nitrogen permeated through the sample. The rate of transmission of nitrogen at 40 °C was obtained by gas chromatography and the nitrogen permeability was calculated from it.

Shore A hardness was measured according to ISO 48-1994. Tensile tests were performed on dumb-bell shaped specimens according to the ISO 37-1994. Tear strength was carried out according to ISO 34-1 1994.

RESULTS AND DISCUSSION

Morphology and Structure of Nanocomposites

The SEM morphology of rectorite powder is presented in Figure 1. Clearly, the dimensions of the original rectorite layers are on the order of micron, about 4 μ m. TEM micrographs of the rectorite/NBR nanocomposite with various clay contents are shown in Figure 2. The dark lines or areas are the intersections of the dispersed rectorite layers. The rectorite layers were dispersed in NBR as individual layers and stacking layers. Clearly, at all loadings of rectorite, the thickness range of stacked rectorite layers is less than 30 nm, and it is on nano-meter level. This result is direct evidence that the rectorite/NBR nanocomposites have formed. In addition, the number of stacking rectorite layer aggregates increases with the loading increasing from 5 to 20 phr.

TEM allows a qualitative understanding of the

Figure 1. SEM of rectorite as received.

structure of nanocomposites through direct observation. On the other hand, XRD is a conventional method to determine the interlayer spacing of clay layers in the original clay and in the polymer/clay nanocomposites. The XRD patterns of the NBR/rectorite nanocomposites and rectorite powder are presented in Figure 3. From Figure 3, the measured d_{001} basal spacing of sodium rectorite is 2.2 nm, whereas the nanocomposites are 2.5 nm; the d_{002} basal spacing of the rectorite layers also increases from 1.1 nm of original rectorite powder to 1.25 nm of nanocomposites. With the rectorite content increasing from 5 to 20 phr, NBR/rectorite nanocomposites show almost the same diffraction peak except for the increase of intensity. The d_{001} basal spacing of the nanocomposites increased only by 0.3 nm, which are comparable to the lateral dimension of rubber molecule chains and would be too small for intercalation of rubber molecules into the space of rectorite. In order to make sure of this point, we prepared Ca²⁺-rectorite by flocculating Na⁺-rectorite water suspension using calcium chloride. Ca²⁺-rectorite shows the same XRD peaks as that of nanocomposites. Therefore, the slight increase of the d_{001} and d_{002} basal spacings should be mainly assigned to the cations of flocculant (Ca²⁺) intercalated into the intergallery of rectorite through a cation exchange reaction during the process of coagulating. This nano-dispersed structure without macromolecules intercalated into intergallery is apparently due to the unique preparation method. This will be explained in the later section.

Additionally, the XRD peak intensities increase with rectorite loading increasing from 5 to 20 phr, which is mainly related to the increase in the number of stacking rectorite layer aggregates. This is in good agreement with the TEM observation. Simultaneously, it is believed that the exfoliated individual layers also increase with the content of rectorite.

Figure 2. TEM micrographs of rectorite/NBR nanocomposites: (a) 5 phr; (b) 10 phr; (c) 20 phr.

Figure 3. XRD patterns of rectorite/NBR nanocomposites with different loading of rectorite: (a) rectorite powder; (b) 5 phr; (c) 10 phr; (d) 20 phr, (e) flocculated rectorite by Ca^{2+} .

Mechanism of Preparing Rectorite/NBR Nanocomposites

Based on the above results, the rectorite layers were dispersed in the NBR matrix in form of single layers and nano-meter stacking layers, and the nano-sized stacking layers were not intercalated. To explain the formation mechanism of this special dispersion structure and explore the potential possibility of further exfoliating, the water swelling ability of rectorite were

Figure 4. XRD patterns of rectorite with different water contents.

investigated, and the preparation process is also described as follows.

The change of the space of rectorite layers in rectorite water suspension with the various water contents is described in Figure 4. It is shown that with the water content increasing, the d_{001} diffraction peaks of rectorite gradually shift to small angles, which means the in-

Figure 5. Schematic of the co-coagulating process.

terlayer space is gradually enlarged by the introduction of water. When the water content is more than 90%, no diffraction peak appears, indicating that rectorite can be separated into the individual layers in the dilute aqueous solution. This result is consistent with that reported by other researchers.²⁸

The preparation process is summarized in Figure 5. As shown in Figure 5, in the first step, the rectorite is dispersed in water. In the presence of water, the cations existing in the space of montmorillonite-like layers have a strong tendency to hydrate, thereby forcing the layers apart.

The second step is to mix the NBR latex with the dilute rectorite aqueous suspension. Since both the surface of rubber latex particles and rectorite layers are negatively charged, the introduction of rubber latex does not cause the aggregation of silicate layers. Moreover, in our experiment, the mixture of NBR latex and dilute rectorite aqueous suspension did not show any XRD diffraction peak of rectorite between 2 and 10°, which also indicated that the mixture is stable.

The third step is to co-coagulate mixture by the addition of a flocculant. After adding a flocculant, the flocculant coagulated the rubber latex and the silicate layers simultaneously, but the rubber macromolecules did not intercalate into the galleries of clay. This mainly resulted from the competition between separation of rubber latex particles and re-aggregation of single rectorite layers upon addition of flocculant. Since rubber latex particles are composed of several rubber macromolecules, the existence of latex particles between the galleries of rectorite layers in the water medium should result in a completely exfoliated

structure. However, cations in flocculant probably cause the separated rectorite layers to re-aggregate so that the rubber latex particles between the rectorite layers may be expelled. As a result, there are some non-exfoliated (stacking) layers in the nanocomposites. In the meantime, due to the fact that the amount of latex is more than that of rectorite layers and the latex particles agglomerate rapidly, the re-aggregation of rectorite layers is evidently obstructed to some extent by the agglomerated latex particles around the rectorite layers. Consequently, the size of aggregates of rectorite layers is on nano-meter level, and the thus obtained nanocomposites contain both the exfoliated layers and non-exfoliated (not intercalated) aggregates of nanometer thickness in the rubber matrix.

The last step is drying the NBR/rectorite nanocompound.

From the above description, the mechanism for forming nanocomposite structure by co-coagulation is totally different from that by melt compounding. During the process of melt compounding, rubber molecules first intercalate into the intergallery of organoclay, leading to the decreased interaction between layers, and then the intercalated organoclay is exfoliated under the shear force or during vulcanization processes.¹⁸ Consequently, the nanocomposites prepared by melt compounding method bear both intercalated and exfoliated silicate layers simultaneously, even completely exfoliated structure. In contrast, the non-exfoliated layer aggregates in rubber-clay nanocomposites prepared by co-coagulation are formed by the re-aggregation of exfoliated clay layers during the co-coagulating process. There are following factors suggested to affect the final dispersion level of

nanocomposites prepared by co-coagulation: (1) the ratio of rubber latex to rectorite; (2) the size of rubber latex particles; (3) the compatibility between the rectorite layers and rubber molecules; although NBR is polar, the compatibility between matrix and rectorite is still insufficient; (4) the speed of co-coagulating. It can be expected that the more latex content, the smaller latex particles will provide nanocomposites with fewer stacking rectorite layer aggregates. If the NBR latex and rectorite layers were rapidly co-coagulated by a flocculant or sufficient compatibility between the NBR and the rectorite was rendered before co-coagulating, even completely exfoliated nanocomposites will be obtained.

Analysis Results by RPA

RPA can provide important information on the viscoelasticity of uncured and cured rubber. The storage moduli (G') as a function of strain for three different compounds with 20 phr fillers are shown in Figure 6. This strong strain dependence of dynamic modulus is well known as the Payne effect, reflecting disruption-formation process of the filler network produced by the interaction of the filler-filler and filler-rubber in the compound.²⁹ In Figure 6, the storage modulus of the rectorite/NBR nanocompound is the highest among the three compounds, whereas no significant difference in G' is observed for NBR compounds filled with carbon black and silica, implying stronger filler network in the rectorite/NBR nanocompound. This network can be mainly attributed to the high aspect ratio of nano-dispersed rectorites, which benefits the formation of filler network. Combined with the morphology presented in Figure 2, the above RPA results also reflect that the stacking rectorite layers can withstand the strong stress applied by rubber melt with high viscosity during processing and still maintain

Figure 6. Strain dependence of G' for NBR filled with different fillers (60 °C, 1 Hz, 20 phr filler).

Figure 7. Frequency dependence of storage modulus for NBR filled with different fillers (60 °C, strain 1%, filler 20 phr).

the high aspect ratio after a obvious breakage of layers occurred. The high aspect ratio is significant to improve the efficiency of reinforcement of nano-scale layers, in particular, enhance the gas barrier property of nanocomposite.

Figure 7 shows the frequency dependence of the storage modulus for rectorite/NBR nanocomposites and NBR filled with carbon black or silica. Compared with NBR filled with carbon black or silica, the incorporation of rectorite in NBR markedly increases the storage modulus in the studied frequency range. This behavior also reflects the strong filler network in the nanocomposites.

Gas Barrier Properties of Nanocomposites

The permeability of the rectorite/NBR nanocomposites and NBR composites filled with carbon black or silica are plotted as a function of the filler volume fraction in Figure 8. The permeability for the three

Figure 8. Plots of permeability versus filler content for NBR filled with different fillers.

Figure 9. Experimental permeability data and the fit to eq 1.

types of composites all gradually decreases with increasing filler content, because the impermeable fillers decrease the amount of permeable amorphous matrix. However, compared with NBR filled with carbon black or silica, rectorite/NBR nanocomposites exhibit much higher gas barrier property at the studied filler contents. Relative to the gum NBR vulcanizate, the nitrogen permeability of rectorite/NBR nanocomposites with 10 vol% rectorite reduces by 75%, while just 48% for MMT/NBR with the same filler content in our previous work.¹⁶ The mechanism for the remarkable improvement is attributed to the increase in the tortuosity of the diffusive path for a penetrant molecule, which can be explained using the Nielsen model.³⁰ The model describes permeability P in a polymer filled with particles with an aspect ratio α

$$P = P_0 \left(\frac{1 - \phi_f}{1 + \frac{\alpha}{2}\phi_f} \right) \quad (1)$$

Where P_0 is the permeability of the amorphous polymer. The fit of eq 1 to the data of the rectorite/NBR nanocomposite is presented in Figure 9. As seen from Figure 9, the fit resulted in an aspect ratio of 25–50, almost the same value estimated by TEM. The aspect ratio is larger than the fit result of eq 1 to the permeability data of the MMT/NBR nanocomposites, in which an aspect ratio of 15 was obtained.¹⁶ Therefore, it is the higher aspect ratio of rectorite than that of MMT in NBR rubber matrix that leads to the better gas barrier properties of rectorite/NBR nanocomposites.

In addition, the permeability obtained from eq 1 with $\alpha = 1$ is close to those of NBR filled with silica or carbon black. The increasing in α will result in decreasing in P when ϕ_f keeps the same. The results can explain the best gas barrier properties of rectorite/NBR nanocomposites.

Table III. Mechanical properties of NBR with different fillers

Content of filler/phr		5	10	20
Shore A hardness	Rectorite	58	63	76
	N330	56	58	65
	Silica	55	58	61
Stress at 300%/MPa	Rectorite	4.8	7.6	10.9
	N330	2.5	3.1	5.1
	Silica	2.1	2.2	3.0
Tensile strength/MPa	Rectorite	6.9	11.4	13.2
	N330	5.8	9.1	14.5
	Silica	3.4	6.2	8.9
Elongation at break/%	Rectorite	312	320	312
	N330	444	456	508
	Silica	392	460	484
Tear strength/(KN m ⁻¹)	Rectorite	31.1	41.1	53.6
	N330	22.9	30.7	39.2
	Silica	17.8	19.3	24.1

Mechanical Properties of Nanocomposites

Comparisons of mechanical properties of NBR with different fillers are listed in Table III. It is observed that the mechanical properties of composites increase with the increase of filler content. Among the three types of NBR composites, rectorite/NBR nanocomposites exhibit the highest hardness, stress at 300% strain and tear strength. These substantial enhancements of mechanical properties are still ascribed to the nano-dispersed structure and its high aspect ratio. However, the tensile strength of the rectorite/NBR nanocomposite at higher rectorite content (20 phr) is slightly lower than that of carbon black filled NBR. This behavior may be attributed to the existence of filler network that is actually an inhomogeneous microstructure, and higher stress concentration exists in nanocomposites caused by high aspect ratio rectorite layers. Accompanied with above results of the tensile strength, it is noticed that the elongation at break of rectorite/NBR nanocomposites are lower than that of carbon black or silica filled NBR.

CONCLUSIONS

Rectorite/NBR nanocomposite has been prepared by co-coagulating NBR latex and rectorite water suspension. The dispersed rectorite in the NBR matrix contains both single layers and nano-meter stacking layers, which easily result in strong filler network in the compound and substantially increase the storage modulus of the vulcanizate compared with silica or carbon black. The mechanical properties and the gas barrier property of NBR were also remarkably improved by introduction of nano-dispersed rectorite. Compared with the gum NBR vulcanizate, the nitro-

gen permeability of rectorite/NBR nanocomposites with 10 vol % rectorite reduces by 75%.

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