

Effect of the organo–rectorite content on the mechanical properties of hydrogenated nitrile rubber (HNBR)/organo–rectorite nanocomposites

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The HNBR/organo-rectorite nanocomposites were prepared by the melt blending method. The mechanical properties, akron abrasion and the crude oil medium ageing-resistant of HNBR nanocomposites were examined as a function of the organo-rectorite content in the matrix of polymer. The effect of sulfur vulcanization on the dispersion of organo-rectorite in the HNBR matrix was also investigated. The results of XRD indicated that the nanocomposites belong to exfoliated and intercalation structure. The test results show remarkable improvement in the tensile strength, tear strength and ageing-resistant of HNBR/organo-rectorite nanocomposites. It's obviously that the 8 phr of rectorite filled nanocomposites has far better mechanical properties than that of other phr and unfilled HNBR.

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1. Introduction

In recent years Polymer/Layered Silicate (PLS) nanocomposites has attracted a great interest both for the industrial and scientific applications [1, 2]. This kind of novel nanocomposites as a new class of materials in which organic particles with nanoscale dimensions are dispersed in the polymer matrix and special phase structure involved compared to their micron- or macro- composites has already exhibit new and improved properties [3-6].

As for the Polymer/Layered Silicate's high performance materials and the first commercial applications are introduced to the market. Several developments and investigations were performed for elastomer/clay systems [7-15], which have been proved to be an extremely effective and necessary way in the rubber application.

The properties of the rubber/layered silicate nanocomposites are mostly controlled by the silicate dispersion in the rubber compounds [13, 15-17]. Commercial clay has also been used as cheap and non-reinforcing filler in rubber industry for many years. Commonly, the clay used for preparation of polymer matrix nanocomposites is montmorillonite [11-13, 15-17].

In this study a novel layered silicate, namely rectorite, is used as the nanophase. Rectorite is a kind of rare clay minerals, which structure and characteristics are much similar to the MMT. Rectorite is an interstratification

layered silicate mineral consisting of a regular stacking of mica-like layers and montmorillonite-like layers (1:1). The thickness of a single rectorite layer is about 2 nm and the width and length vary from a micron to several microns. The image of rectorite shows as Fig. 1 [18].

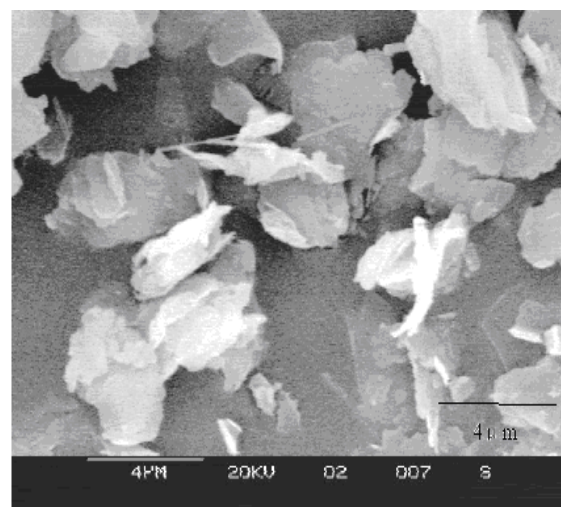


Fig. 1. The SEM image of rectorite powder [18].

In this article, the HNBR/organo-rectorite nanocomposites were prepared by the melt blending method. In order to measure the change of gallery distance and the dispersion of organo-rectorite after mixing with HNBR matrix, the X-ray diffraction (XRD) was carried out. The mechanical properties and the crude oil medium ageing-resistant of HNBR nanocomposites were examined as a function of the rectorite content in the matrix of polymer. The results show remarkable improvement in the HNBR/organo-rectorite nanocomposites.

2. Experiments

2.1 Materials

Fully hydrogenated acrylonitrile butadiene rubber (HNBR) (Therban A-4367) having 43 % acrylonitrile content and 5.5 % residual double bonds was provided by Bayer AG. This rubber exhibits a Mooney viscosity $ML_{1+4} 100\text{ }^{\circ}\text{C} = 60$. The type of organo-clay, organo-rectorite (JZ-b), modified with octadecylammonium salt was provided by Wuhan Mingliu Company.

Polymer/Organo-rectorite nanocomposites were prepared by the melt blending method [15]. For compounding and curing, the additives listed in Table 1 were purchase in the vicinal Market. The mixing procedure and curing for preparing the HNBR/organo-rectorite nanocomposites are reported elsewhere [15].

Table 1. The formation for the HNBR/Rectorite nanocomposites.

Therban4367(HNBR)	100
Organo-rectorite	Variable
MgO	2
ZnO	2
TP795	8
Zinc methylmercaptobenzimidazole (ZMMBI)	1.5
Diphenylamine (445)	1.5
Cyclohexyl-2-benzothiazole sulfenamide (CBS),	0.5
Tetramethyl thiuram disulfide (TMTD)	2
Sulfur	1

2.2 Characterization of HNBR/rectorite nanocomposites

X-ray diffraction (XRD) was carried out by using Phillips X'Pert X-ray generator with CuK α radiation at 40

KV and 40 mA. The diffractograms were scanned in 2 θ range from 1 to 10 $^{\circ}$ at a rate of 2.4 $^{\circ}$ /min.

The tensile measuring test was carried out with universal tensile tester (Model DCS-5000, Shimadzu Co.) at 25 $^{\circ}\text{C}$, the head speed was 500 mm/min, according to ASTM D412 specifications. Akron abrasion was measured by using Inserts Flexing Resistance Tester (GOTECH Testing Machine, China). Fix the center part of the insert with clamping plates, and use a pair of gripping bars to clamp the specimen at a distance of 70 mm (toward the fore part) from the clamping plate, and then flex it repeatedly.

3. Results and discussion

3.1. Organo-rectorite dispersion

Fig. 2 showed the XRD patterns of composites of HNBR with different organo-rectorite content. It was clear that the organo-rectorite was shifted to lower angles after mixing with all the additives. This was caused by the shear-induced diffusion of polymer chains into the agglomerates and the diffusion of polymer chains with in the silicate galleries [15]. For some nanocomposites with low organo-rectorite content such as 6 phr, 8 phr, the weak peak of the organo-rectorite almost disappeared, while the peak of the composite with 10 phr, 12 phr was evidence. This can be attributed to inevitable aggregation of the clay in high organo-rectorite content. The results indicated that the exfoliation and interlayer structures were all exist in the nanocomposites.

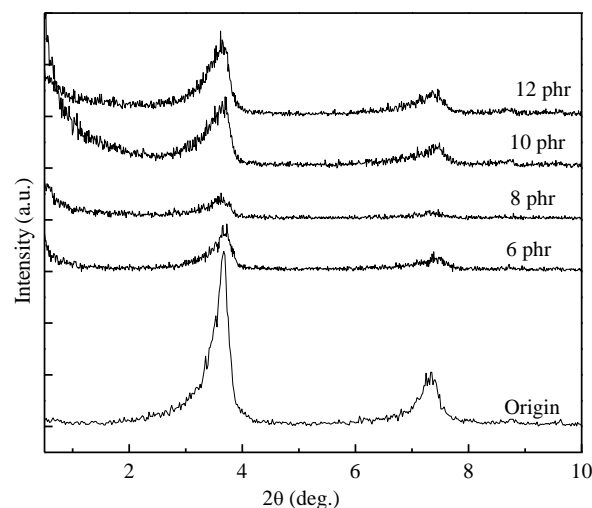


Fig. 2. XRD patterns of samples with different content of organo-rectorite.

The relationship between structure and property of the nanocomposites by the sulfur curing was studied, shown

as Fig. 3. Exfoliated structure was obtained as verified by the absence of any distinct diffraction peak before the vulcanization. After the vulcanization, the distinct diffraction peak of the composites was appeared. The vulcanization greatly changed the dispersion of organo-rectorite in HNBR matrix.

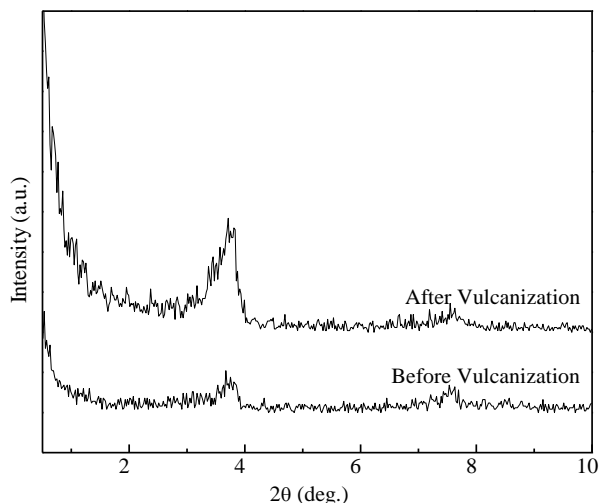


Fig. 3. XRD patterns of HNBR/organo-rectorite nanocomposites before and after vulcanization process.

3.2 Mechanical properties and ageing performance

Addition of inorganic fillers to a polymer matrix has been demonstrated to be an effective method to achieve reinforcement of the polymer. The effect of different organo-rectorite content load on the tensile strength before and after ageing experiment was shown as Fig. 4.

Before the ageing resistance, the tensile strength of HNBR/organo-rectorite nanocomposites substantially increased with increasing organo-rectorite content, which can be attributed to the more uniformly dispersion of the organo-rectorite in the polymer matrix. The shape of layered silicates is usually expressed in its aspect ratio. This is the ratio between the diameter and the thickness of a platelet. Dispersion of layered silicates has resulted in reproducible enhancement of mechanical properties of the nanocomposites at unexpectedly small inorganic contents. But the little tensile strength increase above 8 phr organo-rectorite for the inevitable aggregation of the silicate layers in high organo-rectorite content.

After the ageing resistance, the tensile strength of HNBR/organo-rectorite nanocomposites substantially decreased. The tensile strength of the unfilled composite decreased as high as 87 %. Additional organo-rectorite to the HNBR matrix shows excellent barrier properties. Dispersed platelets of the silicate sheet block the shortest path of gas molecules and force them to take a roundabout way [15].

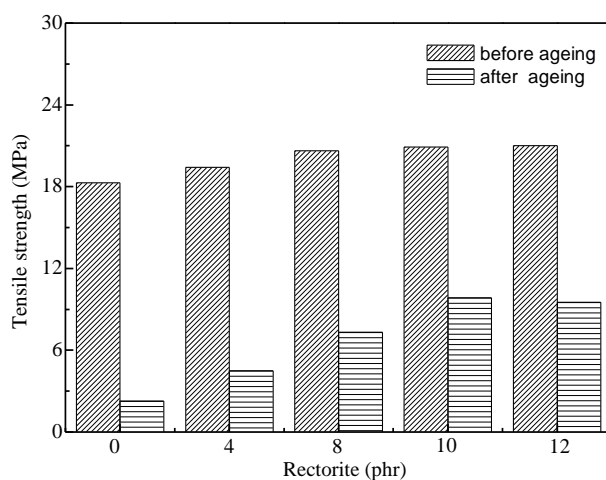


Fig. 4. Tensile strength of HNBR/organo-rectorite nanocomposites before and after crude oil ageing resistance.

The effect of different organo-rectorite content on the elongation at break of HNBR/organo-rectorite nanocomposites before and after ageing experiment was shown in the Fig. 5. The elongation at break of HNBR/organo-rectorite nanocomposite decreases with the clay content increasing. This may be attributed to the fact that ductility decreases when stiffness is increased by reinforcement. But the elongation at break approached to a flat after 8 phr rectorite in the HNBR matrix, which can attribute to inevitable aggregation of the silicate layers in high organo-rectorite content. The aggregation of the silicate layers in the rubber matrix lead to each laminar distance reduces which can bring about interface force between organo-rectorite and rubber decrease.

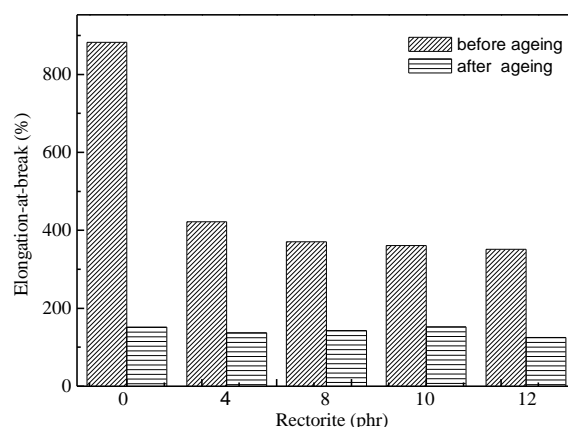


Fig. 5. Elongation at break of HNBR/organo-rectorite nanocomposites before and after crude oil ageing resistance.

The results of tear strength of HNBR/organo-rectorite nanocomposites with different organo-rectorite content before and after ageing experiment were shown in Fig. 6.

Before the ageing experiment, the tensile strength of HNBR/organo-rectorite nanocomposites substantially increased with increasing organo-rectorite content. A little tensile strength increased above 8 phr organo-rectorite additional to the HNBR matrix. After the ageing resistance, the tear strength of HNBR/organo-rectorite nanocomposites decreased.

The high decrease of the mechanical properties of the nanocomposite after ageing experiment can attributed to higher separate out of the accelerant TMTD which were added to the compounding. In the 90 °C crude oil, TMTD can be very easily separated out, thereby the performance sharply decline.

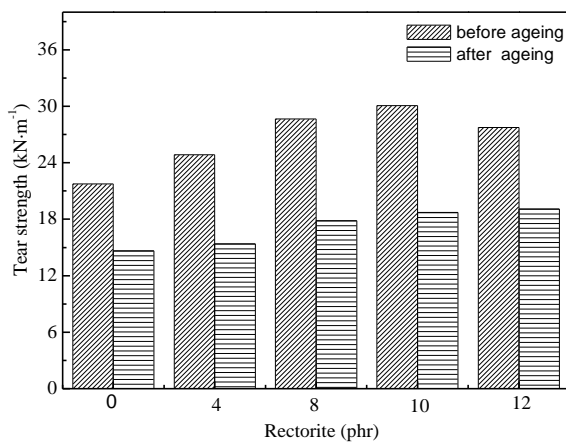


Fig. 6. Tear strength of HNBR/organo-rectorite nanocomposites before and after crude oil ageing resistance.

3.3 Density and wear resistance

The effect of different clay content on density was

Table 3. Akron abrasion of HNBR-4367/organo-rectorite nanocomposites.

Akron abrasion (cm ³ ·1.61km)	Content/phr				
	0	6	8	10	12
HNBR-4367/organo-rectorite	0.06950	0.06615	0.06925	0.08701	0.08955

4. Conclusion

The polymer, Hydrogenated Nitrile-Butadiene Rubber (HNBR) was mechanically mixed with organo-rectorite via melt blending method.

(1) The results of XRD indicated that the nanocomposites belong to the exfoliated and interlayer structure respectively. The sulfur vulcanization changed the dispersion of organo-rectorite in polymer matrix greatly and its basal spacing is decreased after vulcanization.

also studied, as shown in Table 2. The density was increased with the organo-rectorite content increasing. Rectorite is an interstratification layered silicate mineral consisting of a regular stacking of mica-like layers and montmorillonite-like layers (1:1), which differs from the montmorillonite. The thickness of a single rectorite layer is about 2 nm and the width and length vary from a micron to several microns, and also it includes the mica sheet. Therefore, the density difference is increasing large with the content of organo-rectorite increasing.

Table 2. Density of HNBR-4367/organo-rectorite nanocomposites.

Density (g·cm ³)	Content/phr				
	0	6	8	10	12
HNBR-4367/organo	1.0	1.1	1.1	1.1	1.1
-rectorite	20	27	57	77	95

The effect of different organo-rectorite content loading on wear resistance was also studied. Addition of inorganic fillers to a polymer matrix has been demonstrated to be decreased the wear resistance of the polymer. Table 3 shows the results of different clay content loading on wear resistance. First, the wear resistance decreased with the rectorite content increasing, then with the organo-rectorite content increasing, the wear resistance increased, which can be attributed to inevitable aggregation of the silicate layers in rubber matrix.

(2) The mechanical properties, density, akron abrasion and the crude oil medium ageing-resistant of HNBR nanocomposites were examined as a function of the organo-rectorite content in the matrix of polymer. The results of the test show remarkable improvement in tensile strength, tear strength and ageing resistance of HNBR nanocomposites than that of unfilled HNBR. It is obviously that the 8 phr of organo-rectorite filled nanocomposites have far better properties than that of other phr and unfilled HNBR.

Additional rectorite to the HNBR matrix has been

demonstrated to be an effective method to change the mechanical properties, gas permeability resistance and crude oil aging-resistance. The remarkable improvement can help the applications of HNBR in the automotive and industry screw pump, etc.

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Reference

- [1] N. T. McManus, G. L. Rempel, *Polymer Reviews*, **35**, 239 (1995).
- [2] Suprakas Sinha Ray, Masami Okamoto, *Progress in Polymer Science*, **28**, 1539 (2003).
- [3] Myoung Whan Noh, Dong Choo Lee, *Polymer Bulletin*, **42**, 619 (1999).
- [4] Guillermo Jimenez, Nobuo Ogata, Hidekazu Kawai, Takashi Ogihara, *Journal of Applied Polymer Science*, **64**, 2211 (1997).
- [5] X. Koynmann, H. Lindberg, L. A. Berglund, *Polymer*, **42**, 1303 (2001).
- [6] X. H. Liu, Q. J. Wu, L. A. Berglund, *Polymer*, **43**, 4967 (2002).
- [7] Sunil P. Lonkar, A. Pratheep Kumar, Raj Pal Singh, *Polymers for Advanced Technologies*, **18**, 891 (2007).
- [8] J. T. Kim, T. S. Oh, D. H. Lee, *Polymer International*, **52**, 1058 (2003).
- [9] J. T. Kim, D. Y. Lee, T. S. Oh, D. H. Lee, *Journal of Applied Polymer Science*, **89**, 2633 (2003).
- [10] J. T. Kim, T. S. Oh, D. H. Lee, *Polymer International*, **53**, 406 (2004).
- [11] Z. Gu, G. J. Song, W. S. Liu, B. J. Wang, J. Li, *Applied Clay Science*, **45**, 50 (2009).
- [12] Wolfram Herrmann, Claudia Uhl, Gert Heinrich, Dieter Jehnichen, *Polymer Bulletin*, **57**, 395 (2006).
- [13] K. G. Gatos, L. Szazdi, B. Pukanszky, J. Karger-Kocsis, *Macromolecular Rapid Communications*, **7**, 915 (2005).
- [14] Y. L. Lu, Y. R. Liang, Y. P. Wu, L. Q. Zhang, *Macromolecular Materials and Engineer*, **291**, 27 (2005).
- [15] R. L. Zhang, L. Liu, Y. D. Huang, Y. R. Tang, T. C. Zhang, S. Z. Zhan, *Journal of Applied Polymer Science*, **117**, 2870 (2010).
- [16] K. G. Gatos, N. S. Sawanis, A. A. Apostolov, R. Thomann, J. Karger-Kocsis, *Macromolecular Materials and Engineering*, **289**, 1079 (2004).
- [17] K. G. Gatos, R. Thomann, J. Karger-Kocsis, *Polymer International*, **53**, 1191 (2004).
- [18] Y. Q. Wang, H. F. Zhang, Y. P. Wu, J. Yang, L. Q. Zhang, *European Polymer Journal*, **41**, 2776 (2005).

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