

Preparation, Characterization, and Application of NR/SBR/Organoclay Nanocomposites in the Tire Industry

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ABSTRACT: The natural rubber/styrene butadiene rubber/organoclay (NR/SBR/organoclay) nanocomposites were successfully prepared with different types of organoclay by direct compounding. The optimal type of organoclay was selected by the mechanical properties characterization of the NR/SBR/organoclay composites. The series of NR/SBR/organoclay (the optimal organoclay) nanocomposites were prepared with various organoclay contents loading from 1.0 to 7.0 parts per hundreds of rubber (phr). The nearly completely exfoliated organoclay nanocomposites with uniform dispersion were confirmed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results of mechanical properties measurement showed that the tensile strength, tensile modulus, and tear strength were improved significantly when the organoclay content was less than 5.0 phr. The tensile strength and the tear strength of the nanocomposite with only 3.0 phr organoclay were improved by

92.8% and 63.4%, respectively. It showed organoclay has excellent reinforcement effect with low content. The reduction of the score and cure times of the composites indicated that the organoclay acted as accelerator in the process of vulcanization. The incorporation of a small amount of organoclay greatly improved the swelling behavior and thermal stability, which was attributed to the good barrier properties of the dispersed organoclay layers. The outstanding performance of co-reinforcement system with organoclay in the tire formulation showed that the organoclay had a good application prospect in the tire industry, especially for the improvement of abrasion resistance and the reduction of production cost. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1185–1194, 2011

Key words: NR; SBR; organoclay; tire industrial application

INTRODUCTION

Polymer/layered silicate nanocomposites have attracted considerable interest for both scientific challenges and industrial applications due to their perfect properties in the past two decades.^{1–5} Because polymer chains can intercalate into silicate galleries, even make layers exfoliated, which combines polymers and inorganic layers in the nanorange, the polymer matrix is reinforced dramatically by uniformly dispersed inorganic particles at a lower clay concentration (usually 10 phr or less). The polymer/layered silicate nanocomposites are usually divided into three main types according to their structure: conventional or phase separated composite, intercalated nanocomposite, and exfoliated nanocomposite.⁶ The key objective in preparing polymer/clay nanocomposites is to achieve exfoliation and

intercalation of silicate nanoclays with uniform dispersion. Polymer/layered silicate nanocomposites exhibit perfect mechanical,⁷ thermal stability,^{8–10} rheological,¹¹ flame retardancy,¹² gas barrier,^{13,14} and chemical properties¹⁵ comparing to pure polymer or conventional composites. Those kinds of composites have been widely used in many fields, such as automobile industries, tire industries, construction fields, foot packaging fields, electrical fields, and so on.

The polymer blending is an effective method to alter the performance of polymer materials by simple blending to fulfill industry needs for a specific set of properties, especially in tire manufacture.¹⁶ An elastomer is mixed with another one can improve the inferior properties of the original material, such as mechanical properties, processibility, or reduce the cost.¹⁷ NR and SBR are conventional rubbers with wide use, especially the excellent stress strength of NR and higher abrasion resistance of SBR, but their deficiencies in some aspect limit the range of their application in practical industry. Several studies have already dealt with the blends of NR and SBR to obtain a series of good properties which one constituent alone can not supply.^{18–20} The incorporation of a small amount of SBR into NR can endow the

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product with higher abrasion resistance, wet skid resistance, oil resistance, and lower rolling resistance, so it is widely used on the surface of tires.

Scientists used to employ kaolin, nano-magnesium hydroxide, and nano-calcium carbonate to improve the properties of NR/SBR blends, but it needed too much content.^{21–23} Among the clay minerals, montmorillonite have been extensively used to prepare nanocomposites due to its specific structure and property. The high aspect ratio silicate clay layers in the nanocomposites greatly enhance chemical and fluid resistance and flame retardancy by hindering diffusion pathway.²⁴ Surface organic modification is always carried out through ion exchange reaction to lower the surface energy and improve the compatibility with the polymer. Besides, organoclay has the characteristics of low content and high reinforcement. Generally, the uniform dispersion of 3–5 phr of thin layered silicates exhibits the improvements in properties of the polymer matrix to the same extent as 30–50 wt % of micro-sized fillers.^{25,26}

According to other scientists and our previous studies, NR/organoclay and SBR/organoclay nanocomposites had superior performance.^{27–29} Gu et al. had discussed the characteristics of SBR/NR/organobentonite nanocomposites, and the nanocomposites exhibited perfect mechanical, thermal, and swelling properties,³⁰ but the industrial application of those nanocomposites was investigated only a few till now. In this study, we focused on the properties and morphology of NR/SBR/organoclay nanocomposites incorporating with small amount of organoclay and further studied the application prospect of organoclay in tire industry. First, several types of organoclay were incorporated into NR/SBR to select the optimal organoclay by mechanical properties measurements. Second, different contents of the optimal organoclay that affected the mechanical properties were investigated to find out the best percent. Third, the morphology of organoclay dispersed in NR/SBR matrix was characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The effect of organoclay on the cure characteristics, thermal stability, and swelling behavior was investigated and discussed. At last, the prospect of organoclay in tire industry was analyzed, and this experiment supplied a solid foundation for industrial application.

EXPERIMENTAL

Materials

The NR (Standard Ribbed Smoked Sheet NO.3(RSS3), Mooney viscosity, ML (1 + 4) 100°C 68) was purchased from Thailand and the SBR (synaprene 1502, styrene content 23.5%, Mooney viscosity, ML (1 + 4) 100°C 50) was supplied by Qilu Petro-

TABLE I
Recipes of the Model Rubber Compounds and the Industrial Rubber Compounds

Content (phr) ingredient	The model recipe	The industrial recipe
Rubber (NR/SBR = 70 : 30)	100	100
Organoclay	Various	3.0
Zinc oxide	5.0	4.0
Stearic acid	1.0	2.5
Sulfur	2.5	1.5
Antioxidant (NA4010)	1.5	3.5
Paraffin	–	1.5
Coupling agent A151	–	1.5
Accelerator M	0.8	–
Accelerator NOBS	–	0.8
Silica	–	8.0
Carbon black N330	–	53
Aromatic oil	–	6.5

chemical Company (China). Sodium montmorillonite with a cation exchange capacity (CEC) of 119 mequiv/100 g was obtained from the clay mine in Shandong Province of China. The organoclay named Nos. I, II, III, and IV was prepared as mentioned in the following page, which were produced in Institute of Polymer Materials of Qingdao University, China. High abrasion furnace carbon black (N330) and calcium carbonate were commercial products, which were made in China. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, antioxidant (NA4010), accelerator M, etc., were obtained from local manufacturer and commercial products. The recipes of the model rubber compounds and the industrial rubber compounds are presented in Table I.

Preparation of organoclay

The montmorillonite was dispersed in water and purified by sedimentation and washing. The dried montmorillonite (50 g) was dispersed into 5000 mL of distilled water at 80°C under vigorous stirring with a magnetic stirrer. A solution of 35 g dodecyl amine (or 50 g hexadecyl amine or 95 g didodecyl methyl amine or 60 g dimethyl ditallow-ammonium chloride), 200 g distilled water and 10 mL 98% concentrated sulfuric acid, prepared at 80°C was slowly added to the montmorillonite dispersion. The reaction was maintained for 2 h (4 or 7 or 4h). The sediment was collected by filtration and washed ten times with hot water to remove all excess modifier, dried at 90°C in an air oven and sieved to 30 μm. The organophilic clay was designated as organoclay I or II or III or IV.

Preparation of the nanocomposites

According to the conventional tire industrial recipe, the mass ratio of NR/SBR is 70 : 30. In this study,

the binary blends of NR/SBR were compounded with different types and various concentrations of organoclay or other fillers. The compounds were prepared in an open two-roll laboratory mill (SK-160B, Shanghai Light Industrial Mechanical company, China) with a nip clearance of 0.8 mm and friction ratio 1 : 3 (22/17 rpm), operated at room temperature, and in the order organoclay, ZnO, SA, antioxidant (NA4010), sulfur, and accelerator M. The duration of the mixing process was about 10 min for each specimen. Finally, the compounds were compression molded in clean polished molds at 143°C under a pressure of 15 MPa for the optimum cure time (T_{90}). The vulcanized sheets were placed at room temperature for 24 h, and then they were used to measure the performances.

Characterization

Transmission electron microscope

The structure and morphology of the nanocomposites was investigated using a JEM-1200EX (JOEL, Japan) at an acceleration voltage of 80 kV. The ultra-thin films were prepared by cryoultramicrotomy with a diamond knife.

X-ray diffraction pattern

XRD spectra were recorded to determine the inter-spatial distance within the clay platelets with a D/max-RB diffractometer (Rigaku, Japan) with a graphite monochromator, Cu K α radiation at a generator voltage of 40 kV, generator current of 40 mA, and wavelength of 0.154 nm at ambient temperature. The samples were scanned in a step mode at a scanning rate of 5°/min, and the data were collected for 2 θ from 1° to 30°.

Mechanical properties

Dumbbell and crescent shaped specimens for tensile and tear tests were cut from the molded slabs according to ISO 37-1994 and ISO 34-1: 1994, respectively. Tensile and tear tests were measured on a DXLL-50000 (Durs Company, China) universal testing machine at a crosshead speed of 500 mm/min. The measurements of mechanical properties were conducted at 25 \pm 2°C according to ISO standards (ISO 37 and ISO 7619). The test for hardness was carried out using a Shore-A durometer (XY-1, Shanghai Chemical Machinery Company, China) according to Chinese National Standard GB/T 531-92. The samples having a thickness of 6 mm were used. The reported values were the average of five measurements.

TG analysis

The thermal properties of the nanocomposites was measured by thermo-gravimetric analysis (TGA), and the samples were carried out using a thermo-gravimetric analyzer (TGA/STDA851, Mettler Toledo, Shanghai, China) attached to an automatic programmer from room temperature to 700°C at a heating rate of 10°C/min under dynamic nitrogen atmosphere at a flow rate of 50 mL/min. The weight of the samples was 10.0 \pm 0.5 mg to eliminate any sample size effects. The temperature reproducibility of the TGA instrument was \pm 3°C.

Swelling behavior

Swelling tests were performed on 20 \times 10 \times 2 mm³ samples using the remnants from the slabs after cutting the testing specimens for mechanical testing, by the gravimetric method to measure the swelling behavior of vulcanized rubber according to ISO1817-198 in standard oil No. 3 at room temperature for 9 h. The samples were periodically removed from the test bottles, and the surface of the samples were cleaned gently to remove the adhering solvents without any pressure using a paper towel, weighed immediately, and then placed into the solvent again. The experimental procedure was continued until the equilibrium swelling was attained. The value of swelling ratio of each vulcanizate was the average of two parallel specimens. The mass-swelling ratio was computed using the equation,

$$Q_t\% = \frac{M_t - M_0}{M_0} \times 100\%$$

where $Q_t\%$ is the mass-swelling ratio, M_0 and M_t are the mass of the test piece before and after swelling, respectively.

Curing characteristics

The curing characteristics of the compounds were studied in a rotorless rheometer MDR2000 (D and G Company, China) according to ISO 6502-1999 at 143°C with a frequency of 1.66 Hz.

Abrasion test

Abrasion test was performed with an Akron type abrasion tester (Tianfa Company, China) according to Chinese National Standard GB/T 1689-1998. The weight loss of the specimen was obtained after an abraded distance of 1610 m, and the volume of rubber loss per 3416 revolutions of the abrasive wheel was calculated according to the following equation: $V = (M_0 - M_1)/\rho$, where M_0 and M_1 were the mass

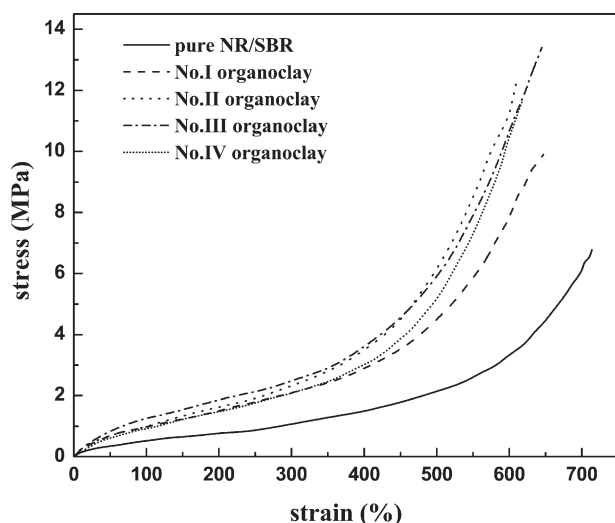


Figure 1 Stress-strain curves of pure NR/SBR and composites with 3.0 phr organoclay I, II, III, and IV.

of the test piece before and after abrasion, ρ was the density of the test piece.

RESULTS AND DISCUSSION

The selection of the optimal organoclay

The stress-strain characteristics of crosslinked pure NR/SBR and NR/SBR/organoclay composites samples with four types of organoclay of 3.0 phr were shown in Figure 1. It clearly showed that the tensile modulus increased, elongation at break decreased, and the tensile strength was enhanced in the presence of organoclay compared with pristine polymer. Among those composites, the tensile modulus of the composite with organoclay (III) was higher than that of pure NR/SBR and other composites. The composites containing organoclay (III) had the highest tensile strength. The mechanical properties of NR/SBR/organoclay composites with 3.0 phr different types of organoclay were presented in Table II. It was clear that the composites filled with organoclay I, II, III, and IV had better mechanical properties compared to the pure NR/SBR composites. Espe-

cially, the composites filled with organoclay (III) showed 92.8% increase in tensile strength, 63.4% increase in tear strength, and 111% increase in Modulus at 200% elongation. The elongation at break decreased slightly. The hardness (shore A) of the compounds was highly improved, and the organoclay (III) showed the highest hardness, which was 49. The increase in stiffness contributed to the immobilization of rubber phase as discussed by Eisenberg.³¹

The organoclay had a good reinforcement effect on the mechanical properties of NR/SBR composites. This was because the addition of organoclay restricted the movement of polymer segments near the filler surface, and resulting in an increase of mechanical properties of the matrix.³² The intercalation of organic modifier enlarged the distance of the clay layers, which facilitate the intercalation of a hydrophobic polymer into clay to form exfoliation and intercalation, and interfacial energy was improved. So the organoclay (III) had the best intercalation of modifier. Besides, the enhancement in the mechanical properties was due to the better dispersion of the organoclay layers with the high aspect ratio in the NR/SBR matrix and rubber-filler interaction, which would be discussed in the following XRD and TEM.³³

The organoclay (III) had the best reinforcement effect on NR/SBR composites, so the optimal organoclay of this study was the organoclay (III).

Morphology and structure of NR/SBR/organoclay (III) nanocomposites

Figure 2 displayed the XRD spectra for the pristine MMT, organoclay (III), and NR/SBR/organoclay (III) composites. The pristine MMT and organoclay (III) patterns showed a broad intense peak at around 2θ equaling to 5.65° and 2.65° , corresponding to a basal spacing (d_{001}) of 1.69 nm and 3.33 nm. The increase of basal spacing demonstrated that the positive effect of intercalation due to the surface organic modification. However, the XRD spectrum of NR/SBR/organoclay (III) nanocomposites showed the

TABLE II
Effects of Four Kinds of Organoclays on the Mechanical Properties of Pure NR/SBR and Composites with 3.0 phr Organoclay I, II, III and IV

Organoclay types (3.0phr)	Hardness (shore A)	Modulus at 200% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)
Pure NR/SBR	34	0.9	6.9	714	16.1
Organoclay I	40	1.3	9.9	650	19.2
Organoclay II	45	1.6	12.6	600	21.8
Organoclay III	49	1.9	13.3	641	26.3
Organoclay IV	43	1.5	11.2	618	22.7

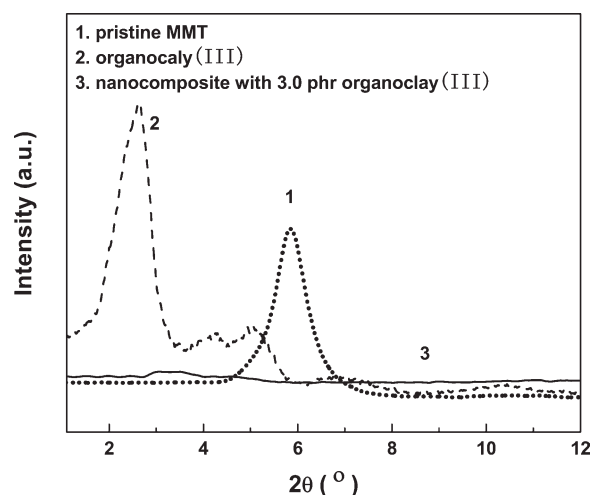


Figure 2 XRD patterns of pristine MMT, organoclay (III), and NR/SBR/organoclay composite [3.0 phr organoclay (III)].

disappearance of characteristic peak of organoclay corresponding to the interlayer basal spacing of organoclay, and indicated that the silicate layers of clay were nearly completely exfoliated in the NR/SBR matrix due to the insertion of the polymer chains into the galleries of the organophilic montmorillonite.

The TEM images for NR/SBR/organoclay (III) nanocomposites with 3.0 phr organoclay were depicted in Figure 3(A,B), which had been screened at high and low magnification. The black lines are organoclay layers, and white region indicates the rubber matrix. In the white region, it showed two

phases, and considering the weight ratio of NR/SBR was 70 : 30, it could be said that NR and SBR phases appeared in gray and bright white color, respectively. The TEM images showed that NR was the continuous phase, and SBR was the dispersed phase. Figure 3(A) showed the organoclay layers existed at the form of single layers and a little of nanoscale stacking with two or three sheets, and the thickness of nanoclay layer is in the range of 5–10 nm and its length is about 100–200 nm. This was in good agreement with the XRD patterns. The nanoclays were orderly oriented in the matrix and confirming the formation of exfoliation. Figure 3(B) in a large area showed the homogeneous dispersion of nanoclay platelets through out the NR/SBR matrix, and a high degree of exfoliation of clay layers nearly no aggregate existed. The TEM photographs revealed that the rubber chains were intercalated into the organoclay and most particles were exfoliated into single layers. So the nearly exfoliated NR/SBR/organoclay (III) nanocomposites were prepared successfully.

Cure characteristic of NR/SBR/organoclay (III) nanocomposites

The cure characteristics of the rubber compounds with different contents of organoclay (III) were shown in Table III and Figure 4. The maximum torque (F_{\max}) and the difference between the maximum and minimum torque (ΔF) increased with the addition of organoclay. As expected, the addition of organoclay resulted in a significant increase in the

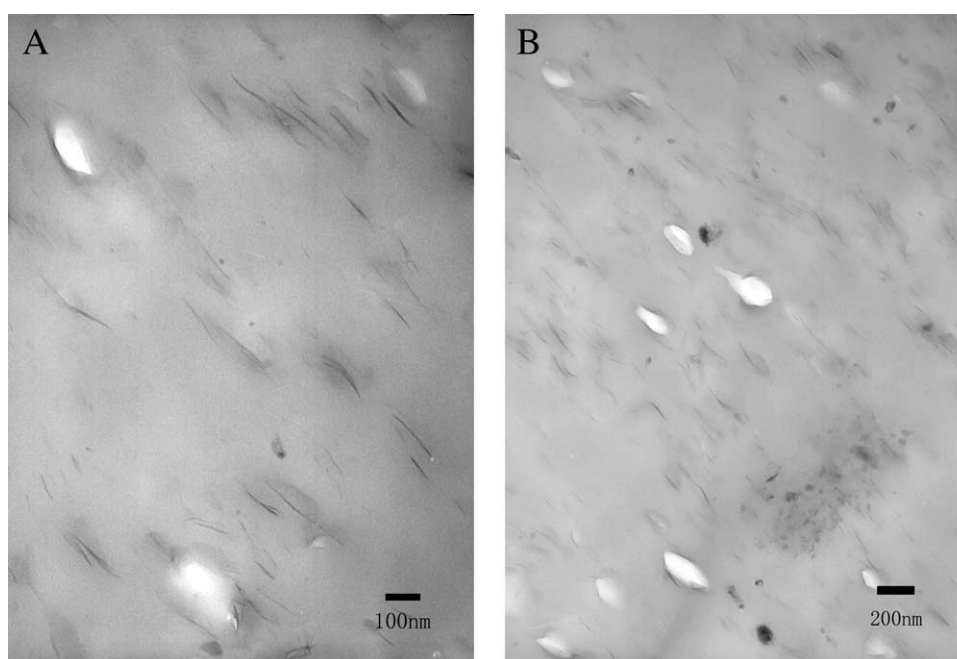


Figure 3 TEM of NR/SBR/organoclay nanocomposites with 3.0 phr of organoclay (III) at two magnifications (A: 100 nm) TEM of NR/SBR/organoclay nanocomposites with 3.0 phr of organoclay (III) at two magnifications (B: 200 nm).

TABLE III
Curing Characteristics of NR/SBR/Organoclay (III) with Various Organoclay Contents

Organoclay content (phr)	T_s (min)	T_{10} (min)	T_{90} (min)	F_{max} (nm)	F_{min} (nm)	ΔF (nm)	VC (min^{-1})
0	2.48	2.19	14.08	0.659	0.035	0.624	8.23
1	1.20	1.15	8.40	0.862	0.031	0.831	12.63
3	1.06	1.05	8.03	0.976	0.032	0.944	13.79
5	1.04	1.04	8.14	1.031	0.034	0.997	13.04
7	0.57	0.58	8.12	1.071	0.036	1.035	13.19

maximum torque, which was in agreement with a work reported by Sezna et al.³⁴ The compounds NR/SBR/organoclay (3.0 phr) and NR/SBR/organoclay (7.0 phr) depicted 48.1% and 62.5% increase in maximum torque value than that of pure NR/SBR blends. The maximum torque (F_{max}) and Torque difference (ΔF) mainly depended on both the extent of crosslinking and reinforcement by the exfoliation filler particles in the polymer matrix.³⁵ The increase of torque indicated that incorporation of organoclay enhanced the crosslink density of the rubber matrix, and the compounds containing low organoclay loading formed exfoliation in the NR/SBR matrix, which contributed for higher reinforcing efficiency of the nanofiller in the matrix.

The results also showed that scorch time (T_s) and optimum curing time (T_{90} , cure for 90%) decreased with increasing organoclay content, and T_{90} decreased slightly when organoclay content was more than 3.0 phr. But the scorch time (T_s) was too short when organoclay content was 7.0 phr, the specimen might scorching in compression molding and reduced the safety of manipulation in practical production. VC is the cure rate index, and it is proportional to the average slope of the cure curve ($100/T_{90} - T_s$) in the curing step region. It was obvious that the addition of organoclay accelerated the vulcanization process, and it acted as a vulcanizate accelerator. This effect was attributed to the

possible formation of a Zn complex in which sulfur and amine intercalated into the montmorillonite layers participate might facilitate for the increase of cure rate.³⁶ But when the addition of the organoclay content was more than 3.0 phr, the accelerating effect was not apparent. The reasons for this phenomenon had discussed in a work reported by Gu et al.³⁰ The decrease of T_{90} and the increase of VC would increase the productivity and reduced the energy consumption in the actual production process.

Mechanical properties of NR/SBR/organoclay (III) nanocomposites

The effect of organoclay (III) content on the mechanical properties of the nanocomposites was shown in Figures 5 and 6.

The tensile strength and the tear strength of NR/SBR/organoclay (III) nanocomposites increased with the addition of organoclay content and much higher than that of the pure NR/SBR blends. At 3.0 phr of organoclay, the nanocomposite showed the highest tensile strength, 13.4 MPa, which was about 92.8% higher than that of pure NR/SBR blends. Highest tear strength was 26.3 kN/m, which was 63.4% higher than that of pure NR/SBR blends. The improvement of the mechanical properties was

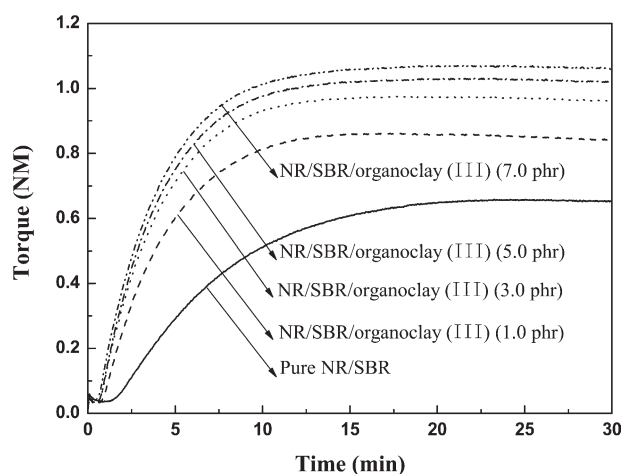


Figure 4 The curing characteristics of NR/SBR/organoclay (III) with various organoclay contents.

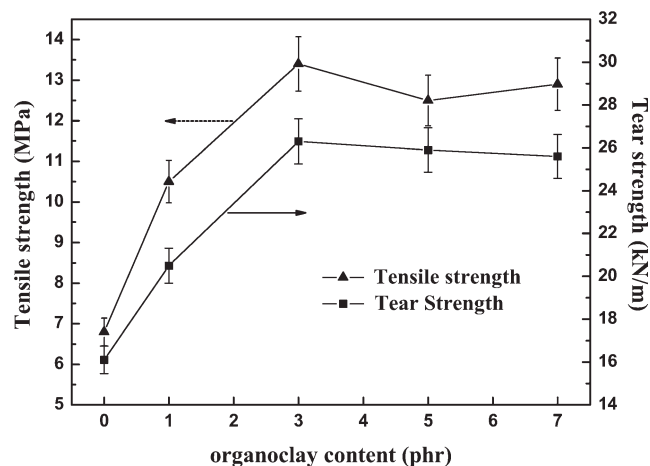


Figure 5 Curves of tensile strength and tear strength versus organoclay content (phr) of NR/SBR/organoclay (III) nanocomposites.

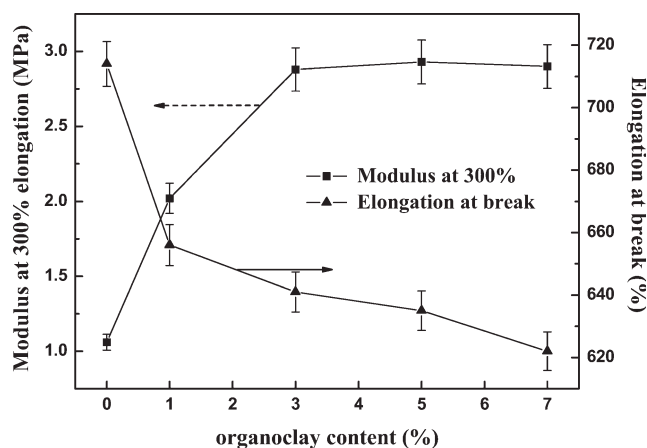


Figure 6 Curves of modulus at 300% and elongation at break versus organoclay content (phr) of NR/SBR/organoclay (III) nanocomposites.

attributed to two facts: (1) The dispersion of nearly completely exfoliated nanosilicate layers with high aspect ratio and platelet structure possessed a higher stress bearing capability and efficiency. (2) Stronger interactions between organoclay and rubber chains associated with the larger contact surface resulted in more effective constraint of the motion of rubber chains.^{37,38} But further addition of nanoclay beyond 3.0 phr, the mechanical properties of NR/SBR/organoclay (III) nanocomposites decreased a little or to be a plateau, which was due to the agglomeration of organoclay particles. The formation of organoclay aggregates led to produce weak points in the NR/SBR matrix and decreased the mechanical properties.³⁹

The 300% modulus and the elongation at break of NR/SBR/organoclay (III) nanocomposites with various organoclay contents were showed in Figure 6. It was seen that the 300% modulus increased with the organoclay content and then reached 2.93 MPa at 5.0 phr organoclay content, increased by 177% compared with pure NR/SBR blends which was 1.06 MPa. The remarkable enhancement of the modulus was due to the strong interaction, effectively constrained the motion of polymer chains. In reverse, the elongation at break of nanocomposites decreased slightly with the increase of organoclay content, but it did not influence the application of this material.

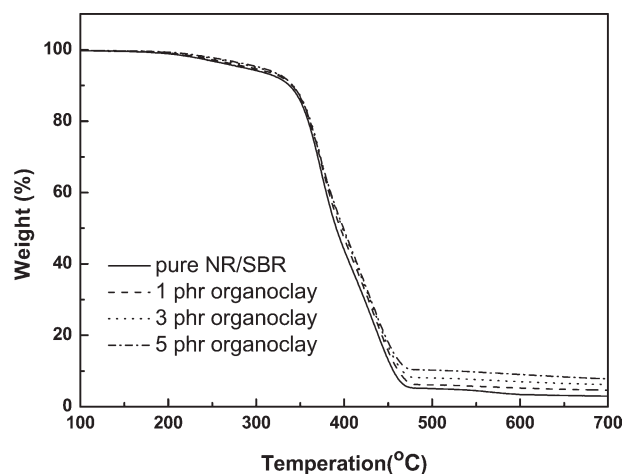


Figure 7 TGA curves of NR/SBR/organoclay (III) nanocomposites with different organoclay contents.

From the discussed above, it was obvious that the NR/SBR/organoclay (III) composites with only 3.0 phr organoclay (III) had the best mechanical properties, and it also showed organoclay has excellent reinforcement effect with low content.

Thermal properties of NR/SBR/organoclay (III) nanocomposites

Figure 7 demonstrated the TGA curves of pure NR/SBR and NR/SBR/organoclay (III) nanocomposites, and the initial thermal stability (T_i) was characterized by the temperatures at 5 and 10 wt % weight loss (T_{i-5} wt % and T_{i-10} wt %) in Table IV. The initial thermal stability (T_i) of NR/SBR/organoclay (III) nanocomposites increased remarkably with increasing the content of organoclay comparing with that of pure NR/SBR blends. But the thermal resistance of organoclay was not apparently with increasing organoclay content up to 5.0 phr. The temperature of maximum decomposition rate (T_{max}) of the nanocomposites increased slightly due to the low content of organoclay.⁴⁰ The first minimum peak T_{max1} at $\sim 374^\circ\text{C}$ indicated the temperature of maximum decomposition rate of NR, and the second minimum peak T_{max2} at $\sim 436^\circ\text{C}$ was characteristic of SBR, which had been confirmed by other articles.⁴¹ The nanocomposites remained the high amount of

TABLE IV
Temperatures of Weight Loss of Pure NR/SBR and NR/SBR/Organoclay(III) Nanocomposites

	T_{i-5} wt % ($^\circ\text{C}$)	T_{i-10} wt % ($^\circ\text{C}$)	T_{max1} ($^\circ\text{C}$)	T_{max2} ($^\circ\text{C}$)
Pure NR/SBR	286.1	337.1	373.8	432.3
NR/SBR/organoclay (1.0 phr)	294.6	340.5	374.0	436.5
NR/SBR/organoclay (3.0 phr)	302.1	342.3	374.1	435.8
NR/SBR/organoclay (5.0 phr)	305.6	342.4	373.9	435.8

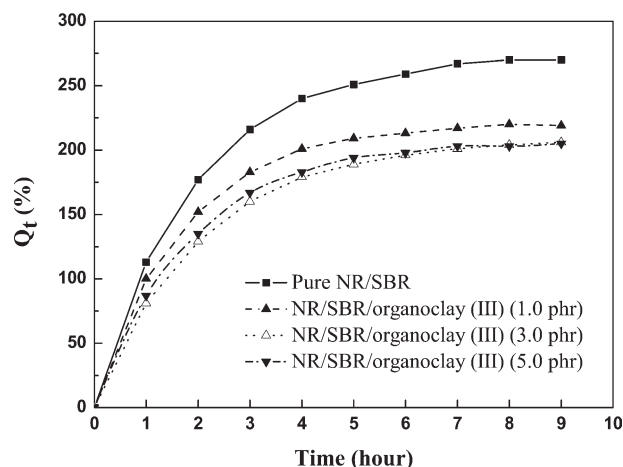


Figure 8 Swelling behavior of pure NR/SBR and NR/SBR/organoclay (III) nanocomposites in standard oil No. 3 at room temperature.

residue in Figure 7, and it indicated that the inorganic layers of clay were thermally stable and did not degrade much even at 700°C.

The results showed that the thermal stability of NR/SBR/organoclay nanocomposites at low organoclay content was better than of pure NR/SBR blends. It was mainly attributed to the good gas barrier action of organoclay layers and the strong interaction between the organoclay and polymer molecules, the nearly completely exfoliated nanosilicate layers dispersed homogeneously in NR/SBR matrix hindered the evaporation of decomposition products and the access of oxygen to restrict the continuous decomposition of the rubber matrix, which was named as “labyrinth effect” of dispersed organoclay.⁴² The addition of organoclay improved thermal stability of the NR/SBR/organoclay nanocomposites.

Swelling behaviors of NR/SBR/organoclay (III) nanocomposites

The changes of swelling ratio Q_t % of the nanocomposites filled with 1.0, 3.0, 5.0 phr organoclay (III) and pure NR/SBR blends versus time were shown in Figure 8. The results showed that the addition of

TABLE V
The mechanical properties of NR/SBR/organoclay nanocomposites according to industrial tire tread formula

Formula (g)	Modulus at 200% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)
0# 0/48/0	5.06	17.1	502	51.3
1# 0/45/3	5.65	19.0	537	60.4
2# 10/35/3	6.55	18.1	567	56.4
3# 20/25/3	4.26	16.5	586	43.2

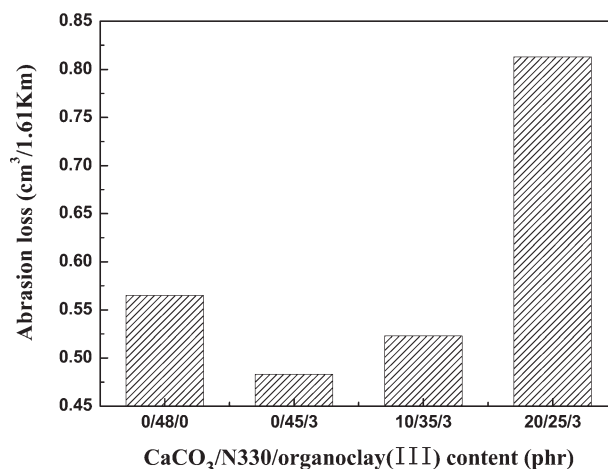


Figure 9 Abrasion resistance of CaCO₃/N330/organoclay(III) nanocomposites at various filler ratios.

organoclay decreased the swelling ratio with increasing the content of organoclay, the absorption of solvent was much less than that of pure NR/SBR composite. It was due to the presence of good dispersion and impermeable clay layers with excellent barrier properties decreased the rate of transportation by increasing the average diffusion path length in NR/SBR matrix.⁴³ Besides, the strong interaction between the clay layers and the NR/SBR matrix was another reason.⁴⁴

The applied analysis of organoclay in tire industry

According to the above discussion, organoclay (III) was used in industrial tire tread prescription for the advantage study of applied foreground of organoclay in industry. The mechanical properties and abrasion resistance of the composites filled with co-reinforcement according to Table I were shown in Table V and Figure 9. It was obvious that the mechanical properties of the composites were highly improved after the addition of only 3.0 phr organoclay (III) instead of identical content of carbon black N330 with the comparison of 0# and 1# samples, and it indicated that organoclay had excellent reinforcement effect at low content.

Among these properties, the abrasion resistance of the composites was improved obviously, the abrasion volume decreased from 0.565 cm³/1.61 Km to 0.483 cm³/1.61 Km. The abrasion resistance is a very important property for the application of tire and felt. Carbon black N330 was identical substituted by calcium carbonate in 2# sample, the abrasion resistance was also higher than that of 1# sample. The improvement of abrasion resistance was mainly due to higher modulus of the material and good dispersion of the fillers. A composite with good filler dispersion was claimed to have a better wear property

than that with poor filler dispersion.⁴⁵ So the improvement of abrasion resistance had a good practical prospect, especially for the application of tire tread rubber.

Besides, tear strength and tensile strength also increased to some extent, 17.8% increase in tear strength, and 11.1% increase in tensile strength according to the comparison of 0# and 1# samples. To reduce the cost, carbon black N330 was substituted partially by calcium carbonate and organoclay. The mechanical properties of the co-reinforcement system containing 10.0 phr calcium carbonate, 35.0 phr carbon black N330, and 3.0 phr organoclay, were higher than that of the composite only reinforced by identical content of carbon black N330. The cost could be reduced in a certain degree in practical industrial production, but the mechanical properties were not reduced. All of these excellent performances were due to good dispersion and strong interaction between organoclay and NR/SBR matrix. Thus, organoclay had a widely practical prospect of application in tire industry.

CONCLUSIONS

1. The nearly completely exfoliated NR/SBR/organoclay nanocomposites were successfully prepared by direct compounding and characterized by XRD and TEM. The optimal organoclay (III) was selected by the mechanical properties characterization of the NR/SBR/organoclay composites from four kinds of organoclay. TEM and XRD analysis indicated that exfoliated NR/SBR/organoclay (III) nanocomposites with good dispersion of organoclay layers were formed, and the compatibility of organoclay with the rubber matrix was improved.
2. Adding organoclay (III) in NR/SBR composites decreased the score time, optimum cure time, and increased VC, which would increase the productivity and reduce the energy consumption in the actual production process.
3. The addition of organoclay (III) greatly improved the mechanical properties of NR/SBR/organoclay nanocomposites due to the reinforcing effect of exfoliated organoclay and a high degree of organoclay dispersion. The nanocomposite with only 3.0 phr organoclay showed 92.8% increase in tensile strength, 63.4% increase in tear strength which was higher than that of pure NR/SBR blends. It also showed organoclay had excellent reinforcement effect with low content.
4. The NR/SBR/organoclay nanocomposites exhibited excellent swelling behavior and better thermal stability compared with pure NR/SBR

blends, which was attributed to the good gas barrier action of organoclay layers and strong interaction between the clay layers and the NR/SBR matrix.

5. When 3.0 phr of organoclay (III) was used in industrial tire tread prescription, the abrasion resistance and mechanical properties were improved greatly. In practical industrial production, the cost could be reduced in a certain degree. Its excellent performance indicated a good application prospect of organoclay in tire industry.

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