Prepared Hydrogenated Nitrile Rubber (HNBR)/Organo–Montmorillonite Nanocomposites by the Melt Intercalation Method

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ABSTRACT: The polymer, Hydrogenated Nitrile-Butadiene Rubber (HNBR) was melt compounded with organophilic montmorillonite (OMMT). The dispersion of the OMMT in the HNBR matrix was characterized by X-ray diffraction (XRD), which indicated that at the temperature of 100°C, the organoclay belong to the exfoliated and interlayer structure. The effect of sulfur on the dispersion of OMMT in the polymer matrix was also studied. The vulcanization changed the dispersion of OMMT in polymer matrix greatly and the basal spacing of clay layers is decreased after vulcanization. The mechanical properties, Akron abrasion and the crude oil medium aging-resistant of HNBR nanocomposites were examined as a function of the OMMT content in the matrix of polymer. The results of the test show remarkable improvement in tensile strength, tear strength, aging-resistant, and hardness of HNBR nanocomposites than that of unfilled HNBR. It is obvious that the 10 phr of OMMT filled nanocomposites have the best mechanical properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2870–2876, 2010

Key words: blending; organoclay; nanocomposites; hydrogenated nitrile rubber (HNBR)

INTRODUCTION

In recent years, Polymer/Layered Silicate (PLS) nanocomposites have attracted great interest both for industrial and scientific applications.[1,2] These systems appear as a new class of materials, in which inorganic particles with nanoscale dimensions are dispersed in the polymer matrix. Because of their nanoscale size, nanocomposites exhibit remarkable improvement in materials properties compared with conventional composites. These improvement include mechanical properties,[3–6] thermal stability,[7,8] gas permeability resistance,[9] and fire retardancy.[10–12] Additional inorganic fillers to a polymer matrix has been demonstrated to be an effective method to achieve reinforcement of the polymer.

Hydrogenated Nitrile-Butadiene Rubber (HNBR) is a highly oil resistant rubber, being applied in a wild temperature range, such as automotive industry and screw pump, etc. Especially for lip seals of ball bearings due to its moderate cost, excellent resistance to oils, fuels and greases, good resistance to swelling, resistance to chemically aggressive media, gas permeability resistance and thermal stability, and fire retardancy.[2,13–15]

To expand the range of HNBR application, many other materials were modified with HNBR. It's reported that PVC/HNBR has much higher hot air resistance and crude oil aging-resistance.[16] HNBR/PC has better processing performance and higher hot air resistance.[17] HNBR modified with EPDM can enhance its resistance to oils further.[18]

Several developments and investigations were performed for elastomer–clay systems. In polar elastomers like hydrogenated acrylonitrile butadiene rubber (HNBR) high reinforcement was observed. Huang et al.[19] studied that *in situ* and intercalation prepared Hydrogenated nitrile rubber/organo-montmorillonite nanocomposite. Herrmann et al.[20] investigated morphologies and dynamic mechanical properties of hydrogenated acrylonitrile butadiene rubber (HNBR) filled with organophilic layered silicates (OLS). Gatos et al.[21,22] observed HNBR nanocomposites for a strong reinforcing effect, which is caused by a strong matrix–filler interaction and they conclude a formation of a rubber shell in the vicinity of the silicate platelets and the effect of sulfur

vulcanization and peroxid vulcanization on the nanocomposite formation in rubber/clay systems. Therefore, compounding of HNBR with modified layered silicates by exploiting the latest findings on rubber/organoclay compounding[23,24] can result in further performance improvement, which may expand the range of HNBR applications.

There are essentially different approaches to prepare the rubber/organophilic montmorillonite (OMMT) nanocomposites. The melt intercalation technique has become the standard for the preparation of PLS nanocomposites, which process involves annealing a mixture of the polymer and OMMT above the softening point of the polymer, statically or under shear. This method has great advantages over either *in situ* intercalative polymerization or polymer solution intercalation. First, this method has avoided the use of organic solvent, and hence this is advantageous to the economy. Second, it is compatible with current industrial process, such as extrusion and injection molding.

To understand the effect of the temperature and mixed time on the dispersion of OMMT by the melt blending method, an experimental investigation has been carried out. The mechanical properties and solvent resistance of HNBR nanocomposites were examed as a function of the OMMT content in the matrix of polymer. The results of wear resistance test and mechanical properties tests show remarkable improvement in the HNBR nanocomposites.

EXPERIMENTAL

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°C = 60. This type of organoclays, organ montmorillonite(OMMT) (Nanomer I.44 P), MMT modified with dimethyl, dihydrogented tallow ammonium, was provided by Beijing East-West Chemical Technology LED.

For compounding and curing, the additives listed in Table I were purchased in the vicinal Market. This recipe contained primary and secondary accelerators suitable for nitrile rubber vulcanization, like tetramethyl thiuram disulfide (TMTD) and cyclohexyl-2-benzothiazole sulfenamide (CBS), respectively. Moreover additives, which offer heat stability and resistance to aging, like diphenylaminutee and zinc methylmercaptobenzimidazole (ZMMBI) were used. For a better processing of the HNBR, TP795 was introduced as plasticizer.

Investigation on the melt intercalation method

The melt intercalation methods were used to prepare HNBR/OMMT nanocomposites. The OMMT and

TABLE I
The Formation of HNBR Mixtures

HNBR 4307	Parts (phr)				
OMMT	0	6	8	10	12
Magnesia	2	2	2	2	2
Zinc oxide	2	2	2	2	2
TP795	8	8	8	8	8
ZMMBI(ZMB-2)	1.5	1.5	1.5	1.5	1.5
445	1.5	1.5	1.5	1.5	1.5
CZ	0.5	0.5	0.5	0.5	0.5
TMTD	2	2	2	2	2
S	1	1	1	1	1

HNBR were put into the Rheometer, model RM-200 (Harbin university of science and technology) for blending. The suitable experiment conditions were studied to get dispersed uniformly nanocomposites (such as temperature, rpm, and blend time). Set at 35 rpm, 10 min, and the temperature of 80, 90, 100, 110, and 120°C. The dispersion of the OMMT in HNBR matrix was studied by X-ray diffraction (XRD).

Preparation of HNBR/OMMT nanocomposites

Note that after the compounding, the additives were gradually added in the kneader. Incorporation of the curatives ZnO, MgO and TP795, ZMMBI, CBS, TMTD, and sulfur took place at room temperature on a two roll mixing mill, model SK-160B (Shanghai Liuling Instrument Factory) with a nip clearance of 1 mm and friction ratio 1.3 (22/17 rpm). Mixing was performed for about 15–20 min. The specimens were cured at 160°C in an electrically heated hydraulic press for 5 min. This cure time was sufficient to well crosslink HNBR compounds as verified by means of a M-2000 Moving die Rheometer.

Characterization of HNBR/OMMT nanocomposites

The tensile performance was tested with universal tensile tester (Model DCS-5000, Shimadzu Co.) at 25°C, the head speed was 500 mm/min, according to ASTM D412 specifications.

Hardness was measured by a Shore-A hardness instrument (LX-A, Shanghai Liuling Instrument Factory, China). All measurements were made several times and the result values were averaged.

Akron abrasion was measured by the Inserts Flexing Resistance Tester (Gotech Testing Machine, China). Fixing 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.

To measure the change of gallery distance and the dispersion of OMMT after mixing with HNBR
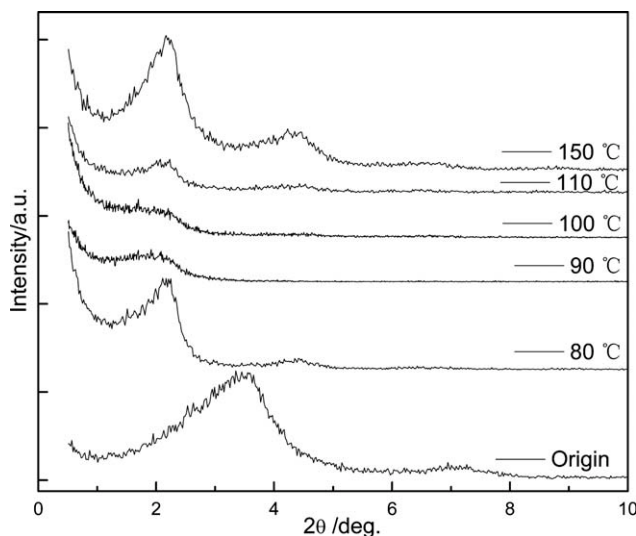
Figure 1 XRD patterns of HNBR/OMMT composites at different temperature conditions.

matrix, the basal spacing of the clay was studied. XRD was carried out by using Phillips X'Pert X-ray generator with CuKa radiation at 40 KV and 40 mA. The diffractograms were scanned in 2Θ range from $1°$ to $10°$ at a rate of $2.4°/$min.

RESULTS AND DISCUSSION

Study on the melt intercalation conditions

The OMMT blending process which is used, as well as the time of annealing after the nanocomposite prepared, have a significant influence on the structure, and the properties of the nanocomposite.

Figure 1 shows the XRD patterns of HNBR/ OMMT composites at different temperature. In the operation, the set temperature and the blend time were the critical factors, which affect the OMMT dispersion in the rubber matrix when the cubage and rotational speeds were invariability. So, the suitable experiment conditions were necessary for achieving a high degree of exfoliation structure in HNBR matrix. From the Figure 1, the peak for composite was shifted to lower angles compared to characteristic peak of OMMT.

From the Figure 1, at 80°C and 90°C, the rubber matrix wasn't melt that it can't provide with enough shear force, and also can't well wrap the OMMT, so the characteristic peak of the OMMT is exist at the low temperature. For higher temperature, at 150°C and 110°C, the characteristic peak is still exist resulted from that for the rubber may be disassemble. The characteristic peak for composite at 100°C was almost disappeared. Therefore, it can be concluded that the dispersibility of organoclay in the HNBR matrix at 100°C condition is better than others.

Figure 2 shows the melt intercalation patterns of composites of HNBR with OMMT at different temperature. The dispersion of the organoclay in the polymer depends on certainly shears force and mix time. The shear force plays an important role on the preparation of composite material. Too big shear force between the OMMT and polymer will lead to the degradation of polymers, which reduces the bulk properties of the materials, also waste of energy. The small shear force can't provide enough shear force between the MMT and polymer, so that the OMMT are not well dispersed, the material does not exert to its advantages. The appropriate shear force can provided better dispersion of organoclay. It had been proved that at the temperature 100°C, the OMMT layer basal spacing is lost, and the OMMT layers are more randomly distributed throughout the HNBR matrix, the system is described as an exfoliated nanocomposite, the torque was found around 22 N m. The blend time also can be got from Figure 2. It's clear that at 450 s, the line tend to be flat which means the OMMT disperse well in the HNBR matrix.

Effect of OMMT content on the dispersion of the OMMT in polymer matrix

Figure 3 shows the XRD patterns of composites of HNBR with different OMMT content. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers. It is clear that the dispersion of OMMT is shifted to lower angles with increase of clay content. For some nanocomposites with low OMMT content (6–10 phr), the peak of the OMMT nanocomposites almost disappeared, while the peak of the composite with 12% of organoclay is evidence. This is corroborated by the appearance of the XRD peaks representing correctly the higher order basal reflections (position and intensity ratio). 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. The composite with 12, 10, 8, and 6% of organoclay has characteristic peak at 2.07, 1.97, 1.97, and $1.99°$ in respect to their position or their relative intensities was produced with a basal spacing of 4.43, 4.48, 4.48, and 4.26 nm.

When basal spacing among the layers is maintained, the material is described as an intercalated material. When the basal spacing is lost, the OMMT layers are more randomly distributed throughout the polymer matrix, the system is described as an exfoliated or delaminuteated nanocomposite. The shape of layered silicates is usually expressed in its aspect ratio. During exfoliation, the layered silicates do not only become much smaller but simultaneously changes their shape from cubical blocks to flat
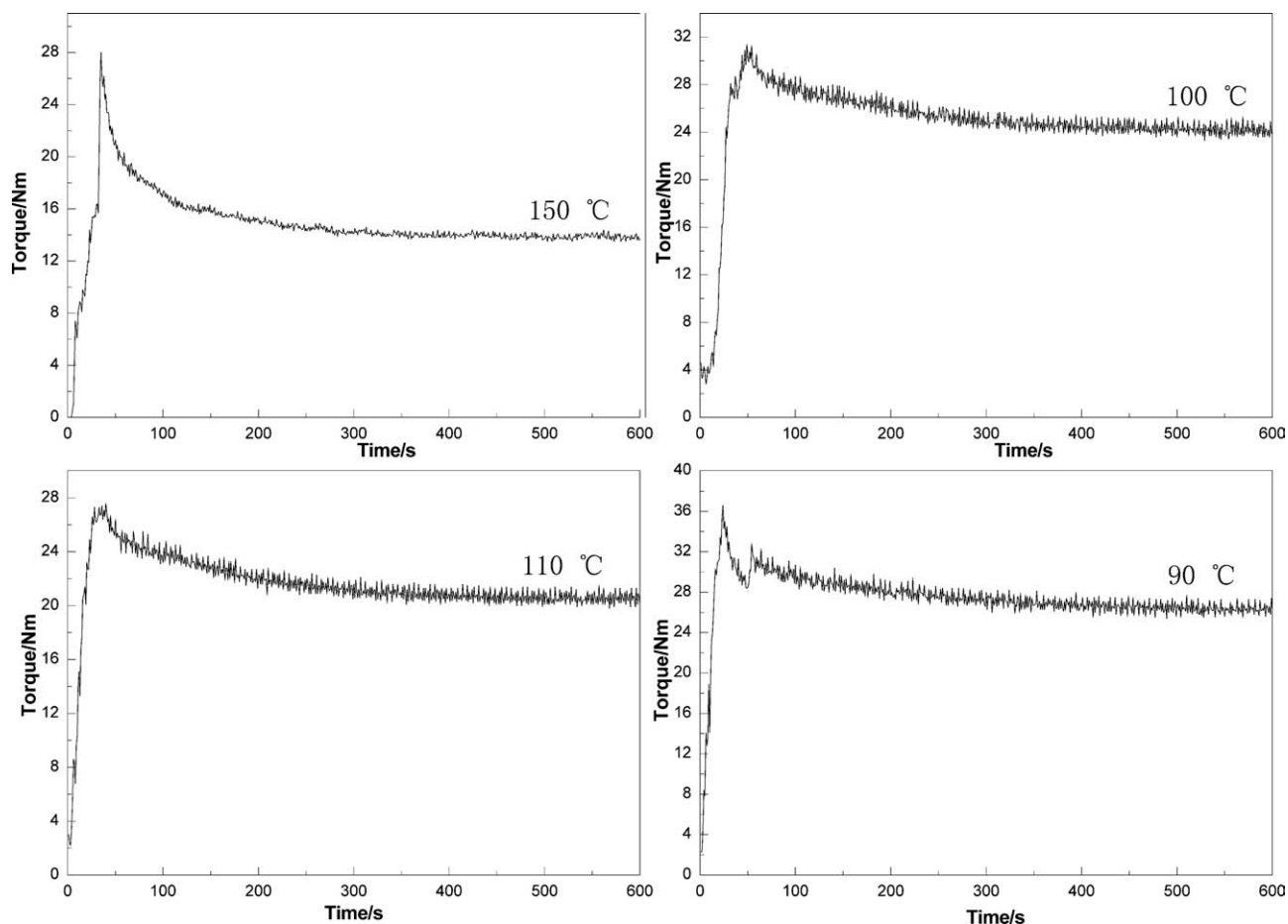
Figure 2   The melt intercalation patterns of HNBR/OMMT composites at different temperature.

platelets. The ratio between the diameter and the thickness of a platelet that can be whole hog to emphasized mechanical properties. Of course, if the OMMT is not dispersed, it is a simply filler and a nanocomposite is not formed. The high aspect

Figure 3   XRD patterns of HNBR/OMMT composites with different OMMT content.

ratio of OMMT and its good dispersion in HNBR should be reflected in an enhanced mechanical performance.

Effect of vulcanization on the dispersion of the OMMT in polymer matrix

The effect of the sulfur curing on the relationship between structure and property of the nanocomposite was studied, shown as Figure 4. Before vulcanization process for the nanocomposites with 10 phr clay content, exfoliated structure was obtained as verified by the absence of any distinct diffraction peak. It has a weak peak around 1.99° from Figure 4, where the spacing is 4.48 nm. But after vulcanization, the peak around 2.25° corresponding to a basal spacing of 3.92 nm. The vulcanization changed the dispersion of OMMT in polymer matrix greatly. The appearance, however, of a well-ordered highly intercalated structure after vulcanization supports the structure before curing consisted of disordered layers with a high basal spacing.

It has been recently shown that sulfur vulcanization strongly affects the nanocomposite formation in rubber/clay systems.[25–28] This phenomenon can be
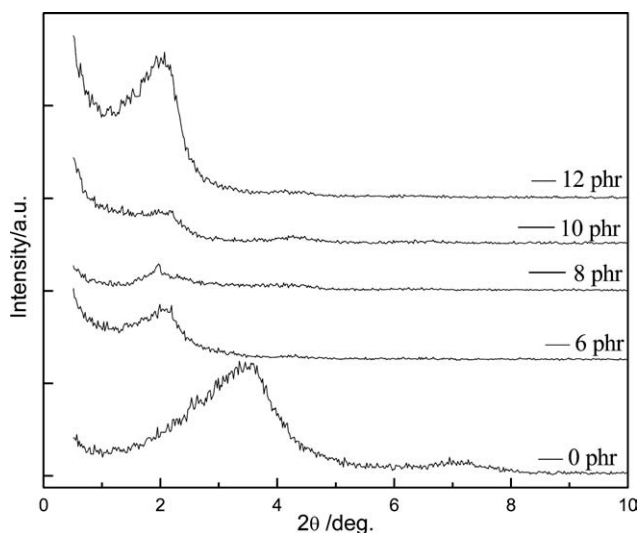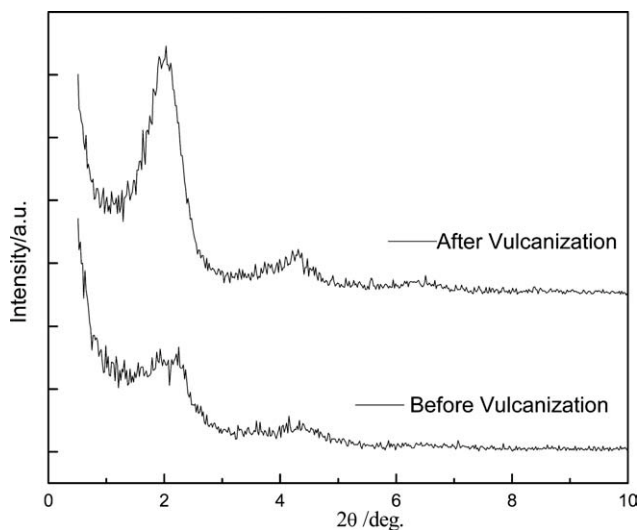
Figure 4 XRD patterns of HNBR/OMMT composites with 10 phr clay content before and after vulcanization process.

attributes to the formation of zinc complexes, in which both sulfur and primary aminutee intercalants of the organoclays participate. As the temperature raises, the dimethyl, dihydrogented tallow ammonium molecules are leaving the silicate surface and participate in the formation of vulcanization intermediates.[29]

Influence of OMMT dispersion on the HNBR/OMMT nanocomposite mechanical properties

Mechanical properties tests were performed on HNBR composites and HNBR/OMMT nanocomposites under different OMMT content and the results are shown in Table II. The tensile strength, tear strength, and hardness of HNBR/OMMT nanocomposite are substantially increased with increasing OMMT content, but the elongation at break and permanent transmogrification at break is decreased. This high reinforcement effect implies a strong interaction between the matrix and the clay interface that can be attributed to the nanoscale and uniform dispersion of silicate layers in the HNBR matrix. The effect of particle shape and particle size can be dis-

tinguished by comparing the properties of nanocomposites with those of microcomposites and unfilled polymer. The mechanisms developed for polymer/filler composites[30] were reported in other rubber compounds, which was attributed to the synergistic action of platelet orientation and chain slippage.

The elongation at break and permanent transmogrification at break of HNBR/OMMT nanocomposite decreases with increase in clay content. The lower tensile strength above 12 phr OMMT can be attributed to inevitable aggregation of the silicate layers in high OMMT content.

The obvious improvement in the mechanical properties can be attributed to the more uniform dispersion of the nanoparticals of the layered silicates in the matrix of the polymer. During exfoliation, the layered silicates do not only become much smaller but also simultaneously changes their shape from cubical blocks to flat platelets. Dispersion of layered silicates has resulted in reproducible enhancement of mechanical properties of the nanocomposites. It can be whole hog to emphasized mechanical properties. Addition of OMMT to the HNBR matrix has been demonstrated to be an effective method to achieve reinforcement of the HNBR matrix.

Influence of different OMMT content on the density and wear resistance of HNBR/OMMT nanocomposite

The effect of different content of OMMT on density and wear resistance of the HNBR/OMMT nanocomposite is also studied, shown as in the Table III. The nanocomposites exhibited not only superior mechanical properties but also exceptional low density was changed. The density changed slightly with the increase in OMMT content. A little higher than that of unfilled-HNBR composites. The density of HNBR nacocomposites filled with 10 phr OMMT only changed about 0.03 g/cm^3. It means the specific strength of this material will be greatly increased, which is the advantage of the materials.

The effect of different OMMT content on wear resistance is also shown in the Table III. Additional inorganic fillers to a polymer matrix has been

TABLE II
Effect of Different OMMT Content Loading on the HNBR/OMMT Nacocomposite Mechanical Properties

Properties/phr	100/0	100/6	100/8	100/10	100/12
Tensile strength (Mpa)	18.28	22.53	23.37	24.843	24.18
elongation at break (%)	882.28	642.12	524.9	497.64	415.4
Permanent transmogrifi-cation at break (%)	2.67	12	16	17.3	22.67
Tear strength (KN/M)	21.76	39.384	40.02	42.495	46.384
Hardness	53.1	61	63.7	65.9	69

TABLE III
Effect of Different OMMT Content Loading on Density and Wear Resistance

OMMT/phr	100/0	100/6	100/8	100/10	100/12
Density (g/cm^3)	1.02	1.04	1.046	1.05	1.055
Wear resistance(cm^3 1.61 km)	0.0695	0.074	0.083	0.1035	0.111

demonstrated to be decreased the wear resistance of the polymer. The wear resistance increased with the increase in OMMT content. The wear resistance of HNBR nacocomposites filled with 12 phr OMMT almost two times of the without OMMT HNBR composites. The wear resistance of HNBR composite is about 0.0695 cm^3 × 1.61 km, the 10 phr OMMT filled HNBR nanocomposite is 0.1035 cm^3 × 1.61 km. The wear resistance of the polymer decreased by 48.9%. Addition of OMMT to the HNBR matrix has been demonstrated to be decrease the HNBR matrix wear resistance.

Influence of different OMMT content on the crude oil medium aging-resistance

The nanocomposite has excellent barrier properties against oxygen, nitrogen, carbon dioxide, water vapor, gasoline, etc. Owing to the nanometer-size particles obtained by dispersion, these nanocomposites exhibit markedly improved gas barrier properties.[31–37] This effect is explained by the tortuous path principle (Fig. 5[38]). Dispersed platelets of the silicate sheet block the shortest path of gas molecules and force them to take a roundabout way. As a result, the permeation pathway is elongated, the application of the Nielsen's equation proved to be a reliable estimate for polymer/clay nanocomposite systems.[39,40]

The effect of different OMMT content loading on the crude oil medium aging-resistance of HNBR is also studied, is shown as Figures 6 and 7. The high decrease of the mechanical properties of the nano-
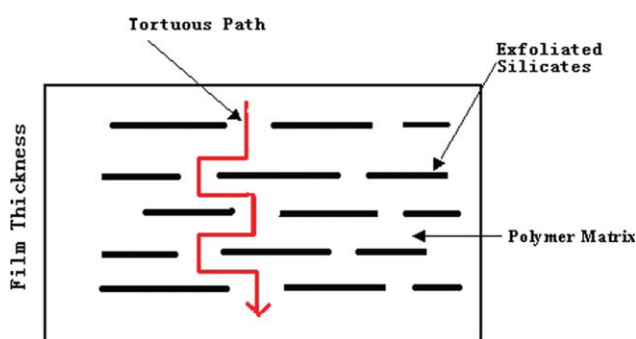
composite after aging experiment can be attributed to higher separate out of the accelerant TMTD which were added to the compounding. As one kind of highly effective vulcanizing accelerant, the number of TMTD influences the rubber properties greatly. In the 90°C crude oil, TMTD can be very easily separated out, thereby the performance decline sharply.

Addition of inorganic fillers to a polymer matrix has been not only exhibited superior mechanical properties but also exhibited exceptional crude oil aging-resistance, the aging-resistance increased with the increase in OMMT content due to the barrier properties of the OMMT. The performance of the nanocomposite which without the OMMT decreased as high as 80%, the HNBR/OMMT nanocomposite has shown excellent barrier properties. First, dispersed platelets of the silicate sheet block the shortest path of liquid molecules and force them to take a roundabout way. As a result, the permeation pathway is elongated, the crude oil not easily to permeate and exudate. Second, the layered silicate in the rubber with a bidimensional structure of space, and good dispersion characteristics, can be reinforced to enhance the materials.

CONCLUSIONS

Preparation of nanocomposites was studied, the uniformly dispersed nanocomposites was prepared at the temperature of 100°C, 10 min, 35 rpm. The sulfur
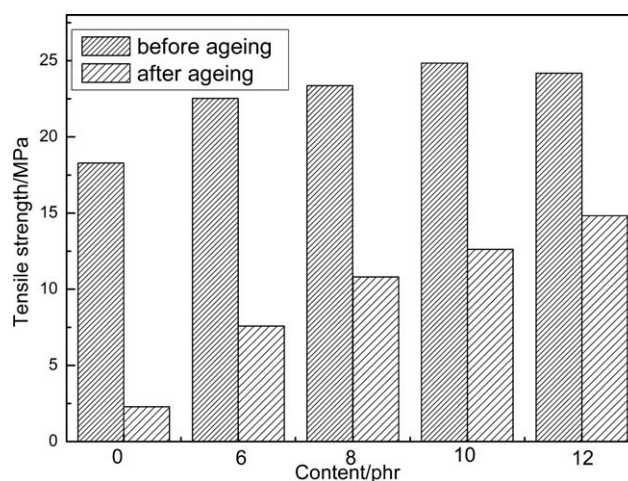

Figure 5 Illustration of Neilson's tortuous path model for barrier enhancement of nanocomposites.[38] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 Different OMMT content loading on the tensile strength before and after crude oil aging-resistance.
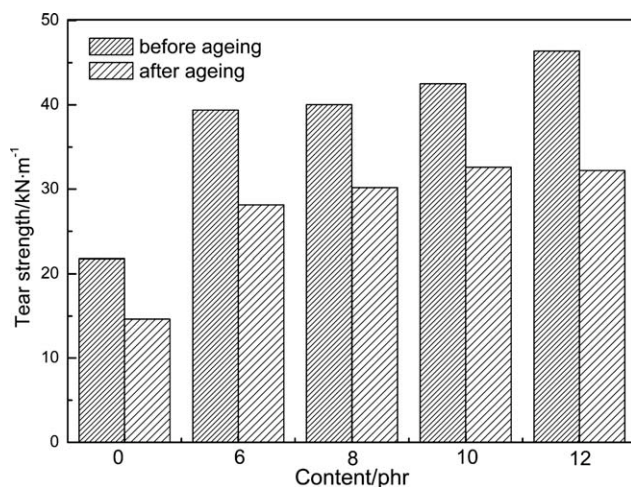
Figure 7 Different OMMT content loading on the tear strength before and after crude oil aging-resistance.

vulcanization affected on the dispersion of OMMT in the HNBR matrix. The vulcanization changed the dispersion of OMMT in polymer matrix greatly and the basal spacing of clay layers is decreased after vulcanization. The density changed slightly with the increase in OMMT content. The density of HNBR nacocomposites filled with 10 phr OMMT only changed about 0.03 g/cm^3. The results of the test show remarkable improvement in tensile strength, tear strength, hardness and the crude oil medium aging-resistance of HNBR nanocomposites than that of without OMMT HNBR composites. It is obvious that the 10 phr of OMMT filled nanocomposites have far better mechanical properties than that of other phr and unfilled HNBR.

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