Study of NBR/PVC/OMMT Nanocomposites Prepared by Mechanical Blending

Hanhua Li¹, Li Wang¹*, Guojun Song¹, Zheng Gu¹,², Peiyao Li¹, Changdong Zhang¹, and Li Gao¹

(1) Institute of Polymer Materials, Qingdao University, Qingdao 266071, PR China
(2) College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

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The effect of organo-montmorillonite (OMMT) on the properties of acrylonitrile butadiene rubber/polyvinyl chloride/OMMT (NBR/PVC/OMMT) nanocomposites is studied. Four different types of organo-modified OMMT were examined in NBR/PVC blend systems and an optimum type of OMMT (FMR11) was found by characterizing the mechanical properties of NBR/PVC/OMMT hybrids. Then, NBR/PVC/OMMT nanocomposites with various amounts of FMR11 were prepared by direct mechanical blending. The dispersion of OMMT layers and morphology of the nanocomposites were determined by X-ray diffraction (XRD) and transmission electron microscope (TEM). Mechanical properties, solvent resistance and thermal stability of nanocomposites were also investigated. TEM revealed that OMMT layers disperse uniformly in NBR/PVC matrix in nano-scale. XRD patterns revealed the intercalation of polymer chains inside the OMMT layer gallery. The tensile strength and tear strength of nanocomposites based on 6.0 phr OMMT improved by 50.0% and 36.9%, respectively compared to gum NBR/PVC hybrids. Solvent resistance properties of nanocomposites showed improvement with higher OMMT contents, which contribute to the excellent barrier effect of OMMT layers.

INTRODUCTION

Composites have been developed to meet several industrial requirements, such as the need for easier processing and broadening the range of properties, either by varying the type, relative content or the morphology of each component. These materials can be prepared so as, for example, to combine their high mechanical strength to a better dimensional stability and thermal resistance. Sometimes a higher stiffness is also attained with the use of fillers [1].

NBR/PVC is a miscible physical mixture of commercial importance. The elastomeric component, NBR, can act as a permanent plasticizer for PVC applications, as in electrical wires and cables coatings, wrapping films for the food industry, conveyor belts, domestic appliances, etc. The presence of PVC helps to improve
the ozone and ageing resistance of NBR, which enable the use of this blend in the automotive industry as gaskets, wires and cables, and in the manufacture of soles, footwear, artificial leather and others [2].

The clay for nanocomposites usually needs to be organically modified, aimed to improve the compatibility of polymer and organoclay layers, and which would enlarge the space of the layers in order to be more accessible to the intercalation of polymer chains [3]. After the introduction of polyamide 6 with montmorillonite [4,5], the works on organoclay as a reinforcing filler were continued in various polymer materials, such as for the plastics, nylon 6 [6], polypropylene [7,8], polystyrene [9], polycarbonate [10], poly(ethylene terephthalate) [11] and the rubbers, NBR [12], FKM [13], BR [14] and SBR [15].

The present investigation was aimed at developing an NBR/PVC/OMMT nanocomposites with high mechanical properties and oil-resistance with a low quantity of OMMT. The NBR/PVC/OMMT nanocomposites were prepared by a twin-roll mixing and characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). The effects of OMMT on the mechanical properties, thermal stability and swelling behaviour of the nanocomposites were also investigated.

EXPERIMENTAL

Materials
The acrylonitrile butadiene rubber (NBR) was supplied by Nancar Company, Zhenjiang, China. The PVC resins were obtained from Haijing Chemical Industry (commercial product). The bentonite was obtained from the clay mine in Shandong Province of China. The vulcanization curatives: stearic acid (SA), zinc oxide (ZnO), sulphur (S) and 2-mercaptobenzothiazole (M) were commercial products.

Recipes of NBR/PVC/OMMT compounds included: NBR/PVC 100 phr, ZnO 5.0 phr, SA 1.5 phr, M 0.75 phr and S 2.0 phr, and various organoclay.

Preparation of the Blends

Preparation of OMMT
The raw clay obtained from the bentonite mine was wetted with water, and then purified by sedimentation, washed and dried. The fine clay (50 g) was dispersed into 1000 mL of distilled water at 68°C under vigorous stirring. A mixture of 35 g octadecyl amine (or dodecyl amine or hexadecyl amine or didodecyl methyl amine), 10 mL 98% concentrated sulphuric acid was prepared at 65°C and then added into the montmorillonite dispersion. The reaction was maintained for 2 h. The sediment was collected by filtration and washed with water, and then dried in vacuum. After being ground and sieved, the organophilic clay was designated as organoclay FMR11 or FMR21 or FMR31 or FMR41.

Preparation of Nanocomposites
The mixing process took place on a twin-roll miller incorporating with NBR/PVC (70/30) organoclay and the other ingredients with a nip clearance of 0.6 mm and friction ratio 1.3 (22/17 rpm). Mixing was performed at room temperature for about 20 min. The specimens of approximately 2 mm thickness were vulcanized in plate vulcanization machine at 143°C and 20 MPa pressure for 45 min. The vulcanized sheets were laid aside at room temperature for 24 h, and then they were used to evaluate their performances.

Measurement

Mechanical Properties
Vulcanized composites sheets were cut into standard samples (five replicates from each sample) according to standard ISO37-1994 and ISO34-1:1994, respectively. The tensile properties and tear strength were determined on dumb-bell shaped and crescent-shaped specimens at a cross-head speed of 500 mm/min using an electronic universal testing machine. All measurements were made several times and the values were averaged.

X-Ray Diffraction
X-Ray diffraction patterns were taken with an X-ray diffractometer (Rigaku2500PC, Japan) at the wavelength Cu Ka = 0.154 nm with a generator voltage of 40 kV and a generator current of 100 mA. The diffractogram was scanned in the 2θ range from 1° to 30° at a rate of 5°/min.
**Transmission Electron Microscope**

TEM observation was performed on ultra-thin films prepared by cryoultramicrotomy using a JEM-1200EX (Joel, Japan) at an acceleration voltage of 80 kV.

**Swelling Behaviour**

The samples of 25×50×2 mm³ were used to determine the swelling behaviour of vulcanizates according to ISO1817:2005. The initial weights of the samples were taken and then they were put into standard oils No. 1 and machinery oil No. 32. The samples were removed from the test bottles each hour, then cleaned the adhering solvent from the surface and weighed immediately. The weight swelling ratio, \( Q_t \), was determined from the weight of the sample in the unswollen and swollen states. The equation is as follows:

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

where \( Q_t \) is the weight swelling ratio, \( M_t \) is the weight of the sample in the swell state and \( M_0 \) is the initial weight of the sample.

**Thermogravimetric Analysis**

Thermogravimetric analysis (TGA) of the samples was performed using a thermogravimetric analyzer (TGA/STDA851, Mettler Toledo, Switzerland) attached to an automatic programmer from ambient temperature to 600°C at a heating rate of 10°C/min in an air atmosphere. A sample weight of approximately 15 mg was used for the measurement.

**RESULTS AND DISCUSSION**

**The Selection of the Optimal Organoclay**

The effects of organoclay type on the tensile strength of the cross-linked NBR/PVC/OMMT composites are shown in Figure 1. The column graphs revealed that the tensile strength of the composites with organoclay FMR21 (15.4 MPa) or FMR31 (16.9 MPa) was higher than that of FMR41 (14.3 MPa), and moreover, organoclay FMR11 (17.8 MPa) endowed nano-composites the best tensile strength. We found that the reinforcing effect of organoclay increases gradually as the following sequence: FMR41 < FMR21 < FMR31 < FMR11, which is consistent with the molecular length of the organic modifier. That is to say, as the length of aliphatic group of organic modifier becomes longer, the reinforcing action of organoclay is improved. It can be interpreted that as the length of the organic modifier increases, the gap size of the organoclay becomes broader and the macrochains intercalate into the organoclay layers easier [16]. Thus, we selected organoclay FMR11 as the optimal organoclay to study NBR/PVC/OMMT nanocomposites.

**Characterization of Organoclay**

**XRD Analysis**

Figure 2 shows the X-ray diffraction curves for the cured NBR/PVC/OMMT nanocomposites with 3 phr OMMT (FMR11). The interlayer distance was determined from the diffraction peak position in the XRD diffractogram. OMMT shows a diffraction peak at \( 2\theta = 4.9^\circ \) which is assigned to the interlayer platelet spacing (001 diffraction peak) with a spacing of 1.80 nm. In the NBR/PVC/OMMT nanocomposites, a displacement of the peak to lower angles \( 2\theta = 2.6^\circ \) is observed. The interlayer distance has been increased to 3.40 nm. The enlarged basal spacing values indicate that the macromolecule chains were intercalated into the OMMT layers.
Figure 2. X-Ray diffraction patterns of OMMT and NBR/PVC/OMMT (FMR11).

TEM Micrographs of NBR/PVC/OMMT (FMR11) Nanocomposites
TEM photographs of NBR/PVC/OMMT nanocomposites are shown in Figure 3. The dark lines and areas were OMMT layers and its aggregates and the lighter areas were rubber matrix and the lightest areas were PVC in low magnification. TEM photograph clearly displayed that the OMMT layers were homogeneously dispersed in the NBR matrix and in the interface between NBR and PVC, which reveals that the OMMT has better compatibility with NBR. That may be interpreted that the long chain quaternary ammonium intercalated into the clay gallery, endows OMMT better affinity with the non-polar butadiene unit of NBR. While, the high magnification TEM photograph revealed that there were some single exfoliated clay layers in the NBR/PVC matrix besides aggregated clay layers. The thickness of most clay layer bundles was in the range of 20 and 30 nm and the length was about 100-250 nm. The typical sandwich microstructure consisted of parallel alternating clay layers and NBR/PVC matrix was observed in those TEM images. This indicated that the intercalated microstructure was formed.

Mechanical Properties of NBR/PVC/OMMT (FMR11) Nanocomposites
Figure 4 shows the stepwise increasing trend of tensile strength and tear strength of nanocomposites with increasing content of OMMT. It shows that the OMMT endowed NBR/PVC blends excellent mechanical properties. The tensile strength and tear strength of nanocomposites based on 6.0 phr loading
Figure 4. Curves of tensile strength and tear strength versus organoclay content (phr) of NBR/PVC/OMMT (FMR11) nanocomposites.

The sorption curves of filled nanocomposites within 12 h versus 2.0, 4.0, 6.0, 8.0 and 10.0 phr organoclay (FMR11) obtained by plotting $Q_t$ (weight swelling ratio) in standard oil No. 1 and machinery oil No. 32 at 120°C temperature are shown in Figures 6 and 7, respectively. Polymers absorb solvent and swell when it is immersed in oil, and at the same time some agents are separated out. The NBR has good resistance to oils and shows small swelling. On the other hand, some agents of the system separate out easily. So the weights of nanocomposites fall. This shows that with the increasing contents of clay less solvent leaves the

Swelling Behaviour of NBR/PVC/OMMT (FMR11) Nanocomposites

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The reasons may be found in the structure of the blends; the presence of the nano-dispersed impermeable clay layers and intercalated microstructure, which restricts the movement of molecular chains, and the special structure in lengthening the average diffusion path length in the blends. Above all, the rate of transportation is decreased and the swelling behaviour of NBR/PVC/OMMT nanocomposites is enhanced.

Thermal Stability of NBR/PVC/OMMT (FMR11) Nanocomposites

Clay layers have good barrier action, which can improve the thermal stability of polymer/clay nanocomposites. On the other hand, the alkyl-ammonium cations in the organoclay could suffer decomposition following the Hofmann elimination reaction [19] and its product would catalyze the degradation of polymer matrices [20]. Thirdly, the clay itself can also catalyze the degradation of polymer matrices [21,22]. The latter two actions would reduce the thermal stability of polymer/clay nanocomposites.

Figure 8 shows the TGA curves for NBR/PVC and NBR/PVC/OMMT (FMR11) nanocomposites based on 3.0 phr and 6.0 phr OMMT loadings. Figure 9 shows the differential calculus curves of TGA, which have been used to find the peak decomposition temperatures ($T_{\text{max}1}$, $T_{\text{max}2}$ and $T_{\text{max}3}$). The initial thermal stability ($T_i$) was characterized by the temperatures at 5 wt% and 10 wt% weight losses ($T_{i-5\text{ wt\%}}$ and $T_{i-10\text{ wt\%}}$), which are tabulated in Table 1. Before reaching 250°C, it is clearly evident that the $T_i$ of nanocomposites exhibits slight fall compared to pure NBR/PVC, because of the Hofmann elimination reaction and the clay catalyzed degradation. The decomposition of NBR occurs between 250°C and 450°C. We can clearly see that the onset degradation temperatures of the NBR and nanocomposites with 3.0 phr and 6.0 phr OMMT are 380°C, 397°C and 403°C, respectively. This may be...
explained by the fact that with more intercalated microstructure, there is stronger affinity between NBR and clays with higher OMMT content, and therefore it needs more energy to degrade. That is to say, the heat resistance of nanocomposites has been improved.

In summary, the organoclays have two opposing functions in the thermal stability of the NBR/PVC/OMMT nanocomposites. One is its barrier effect which should improve the thermal stability and the other is the catalytic effect towards the degradation of the polymer matrix which would decrease the thermal stability. When adding a low fraction of the clay into the polymer matrix, the clay layers should be well dispersed and the barrier effect is predominant, but with higher loading, the catalyzing effect rapidly rises and becomes dominant, so that the thermal stability of the nanocomposites is lowered.

CONCLUSION

The optimal OMMT (FMR11) was successfully selected by characterizing the mechanical properties of 3.0 phr clay-based NBR/PVC (70/30) nanocomposites. Then NBR/PVC/FMR11 nanocomposites with various amounts of FMR11 were prepared by direct mechanical blending. The intercalation of molecular chains into the organoclay was evident from XRD and was confirmed by TEM study. As a good dispersion of organoclay in the NBR/PVC matrix, a significant improvement in the solvent uptake and mechanical properties was observed. However, the amine intercalation into the MMT layers had a slight negative effect on the thermal stability of PVC, but by introduction of OMMT the thermal stability of NBR increased, which also contributed to the good dispersion of MMT layers.

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SYMBOLS AND ABBREVIATIONS

OMMT: Organo-montmorillonite
FMR11, FMR21, FMR31, FMR41: Organo-montmorillonite 11, 21, 31, 41.
NBR: Acrylonitrile butadiene rubber
PVC: Polyvinyl chloride
XRD: X-ray diffraction
TEM: Transmission electron microscope
FKM: Fluororubber
BR: Polybutadiene rubber
SBR: Styrene butadiene rubber
SA: Stearic acid
ZnO: Zinc oxide
S: Sulphur
M: 2-Mercaptobenzothiazole
TGA: Thermogravimetric analysis
\( T_{i-5\,\text{wt}\%} \): Temperatures at 5 wt% weight loss
\( T_{i-10\,\text{wt}\%} \): Temperatures at 10 wt% weight loss
\( T_{\text{max}} \): The peak decomposition temperature

REFERENCES


