

NBR/ORGANOMODIFIED BENTONITE INTERCALATED HYBRIDS AND THEIR EFFECTS ON THE TOUGHNESS OF PVC*

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Abstract Hybrids of intercalative nitrile-butadiene rubber/organomodified bentonite (NBR/OMB) were prepared by the latex intercalation technique. Investigation of their mechanical properties and the microstructure of NBR/OMB showed that the organomodified bentonite is an effective toughener for NBR. Transmission electronic microscopy (TEM) and X-ray diffraction (XRD) tests showed that the NBR macromolecule could be intercalated into the galleries of bentonite. Incorporation of NBR/OMB hybrids as tougheners into poly(vinyl chloride) (PVC) results in a substantial increase in the impact strength of PVC, but little decrease in its tensile strength and flexural strength, compared to the unmodified PVC.

Keywords Nitrile-butadiene rubber, Bentonite, Hybrids, Mechanical properties, Structure, Poly(vinyl chloride)

INTRODUCTION

Hybrids of intercalative polymer/clay are organic/inorganic nanocomposites with prospects of very important applications, because the properties of the hybrids are significantly improved, as compared with conventional macro- or micro-composites^[1]. In the earlier intercalative hybrids, most organic phases are plastics. Few investigations on rubber type organic/inorganic hybrids have been reported. The main preparation methods are melt intercalation, solution intercalation and monomer polymerization in situ intercalation. Latex intercalation as a simple and effective way to prepare rubber/clay hybrids has been developed in recent years^[2, 3]. Nitrile-butadiene rubber (NBR) has been used as toughening modifier for PVC, because the solubility parameters of NBR are similar to those of PVC. However, traditional methods of rubber toughening share a common shortcoming. They can increase the toughness, but not the strength, *i.e.* the tensile strength, modulus and heat resistance of the materials are obviously decreased when the methods are used to increase the toughness^[4–6].

In this paper, a suitable intercalating agent was used for bentonite intercalation modification, and then NBR/OMB hybrids were prepared by the latex technique. Their toughening effects on PVC were tested and compared with those of NBR.

EXPERIMENTAL

Materials

NBR latex (solid content: 40%) was obtained from Lanzhou Synthetic Rubbers Factory. Block NBR was obtained from Guangzhou Zhujiang Tire Company. PVC resin was supplied by Qilu Petroleum Chemical Company. OMB was prepared in our laboratory^[7].

* This work was supported by the National Natural Science Foundation of China (No.59933060)

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Received September 3, 2002; Revised January 9, 2003; Accepted January 13, 2003

Preparation of NBR/OMB Hybrids

An aqueous solution of OMB was mixed with NBR latex. The mixture was precipitated with 10% CaCl₂ aqueous solution and then dried in an oven. The dried hybrids were mixed with other compounds by a two-roller mill. The hybrids, so obtained, were pressed into sheets at 185 °C for 3 min. The samples were taken out after cooling to room temperature.

Formulation

PVC 100 phr, dibutyl (*o*-)phthalate 8.0 phr, tribasic lead sulfate 5.0 phr, zinc stearate 2.0 phr, lead stearate 1.0 phr, barium stearate 1.0 phr, stearic acid 0.5 phr.

Measurements

The impact strength of the material was tested by an X CJ-40 impact tester. Its tensile strength and flexural strength were measured according to “GB/T528-92 and GB-1042-92”, respectively. X-ray diffraction spectra were collected on a D/MAX-III type diffractometer equipped with CuK α radiation. TEM examination of the microtomed section of the hybrids was carried out on a JEM-100CX-II TEM with an acceleration voltage of 120 kV. The impact-fractured surfaces at room temperature were coated with gold and observed in a scanning electron microscope (JEOL TSM-T330).

RESULTS AND DISCUSSION

Mechanical Properties of NBR/OMB Hybrids

Tables 1, 2 and 3 show the effects of original bentonite, OMB and carbon black on the mechanical properties of NBR vulcanizates. The results indicate that the unmodified bentonite has little reinforcement action on NBR, while OMB has obvious reinforcing effects on NBR. At different contents of fillers, the tensile strength at 300% and hardness of OMB filled NBR vulcanizates are higher than those of original bentonite or carbon black filled NBR vulcanizates.

Table 1. Mechanical properties of original bentonite filled NBR vulcanizates

Mechanical properties	Original bentonite content (phr)					
	0	5	10	20	30	40
Tensile strength at 300% elongation (MPa)	1.12	1.45	1.40	1.60	1.72	2.10
Tensile strength (MPa)	5.87	6.30	6.80	7.10	7.90	7.80
Elongation at break (%)	800	820	805	791	784	759
Tear strength (kN • m ⁻¹)	11.2	–	12.8	–	–	–
Permanent set	4	4	4	8	8	12
Shore A hardness	45	45	47	51	51	57

Table 2. Mechanical properties of OMB filled NBR vulcanizates

Mechanical properties	OMB content (phr)					
	0	5	10	20	30	40
Tensile strength at 300% elongation (MPa)	1.12	3.90	8.50	13.1	16.1	–
Tensile strength (MPa)	5.87	14.2	16.10	17.80	17.17	20.50
Elongation at break (%)	800	585	500	451	354	291
Tear strength (kN • m ⁻¹)	11.2	19.81	21.7	26.77	35.52	40.10
Permanent set	4	8	8	12	16	28
Shore A hardness	45	48	55	62	70	73

The effects of fillers on the tensile strength and elongation at break of NBR vulcanizate are shown in Fig. 1. With the same amount of fillers, the tensile strength of NBR vulcanizate filled with OMB is equal to or higher than that of NBR vulcanizates reinforced by carbon black (N330). From Table 3, we can see that when 10 phr of OMB was added to NBR vulcanizates, its reinforcing effects were close to the level of 30 phr carbon black

(N330). These results show that OMB is a light-colored and efficient reinforcing filler for rubbers.

Table 3. Mechanical properties of carbon black (N330) filled NBR vulcanizates

Mechanical properties	Carbon black content (phr)				
	0	10	20	30	40
Tensile strength at 300% elongation (MPa)	1.12	1.54	2.10	3.00	4.90
Tensile strength (MPa)	5.87	8.30	12.70	16.10	20.20
Elongation at break (%)	800	772	723	690	675
Tear strength (kN • m ⁻¹)	11.2	15.37	18.00	24.30	33.26
Permanent set	4	4	8	8	12
Shore A hardness	45	48	54	58	63

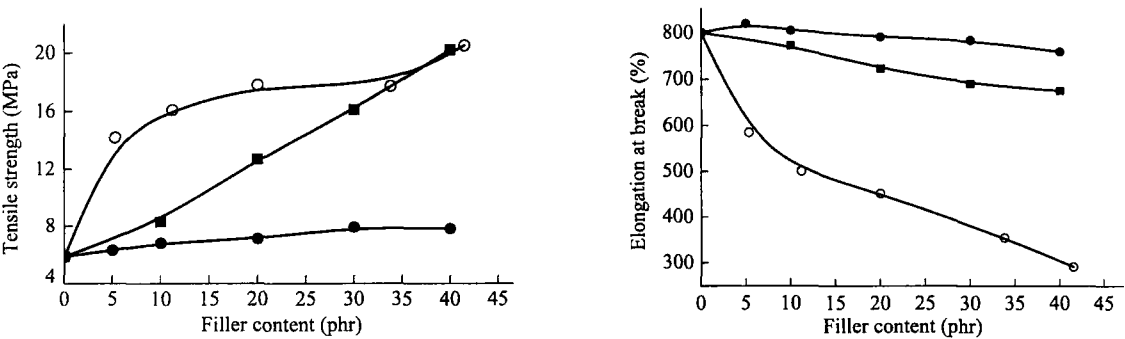


Fig. 1 The effects of fillers on the mechanical properties of NBR vulcanizate
● Bentonite; ○ OMB; ■ Carbon black N330

Structural Analysis of NBR/OMB Hybrids

Figure 2 shows the XRD patterns of original bentonite, OMB and NBR/OMB hybrids. Before mixing with NBR, the interlayer spaces of original bentonite and OMB were 1.26 nm (curve A) and 2.06 nm (curve B), respectively. XRDs of the vulcanizates filled with 10 phr and 40 phr of OMB hybrids, respectively showed some new diffraction peaks ($3^{\circ} < 2\theta < 11^{\circ}$) which correspond to interlayer spaces about 3.95 nm, 2.06 nm, 1.45 nm, 1.36 nm and 1.26 nm. It is suggested that NBR molecules could be intercalated into the galleries of OMB (3.95 nm); but some of the organomodified agents still remained inside the galleries (2.06 nm) and a small amount of original bentonite was left in the vulcanizates. The latter may belong to free bentonite layers which were originally distributed in water and combined together again during NBR coagulation and drying.

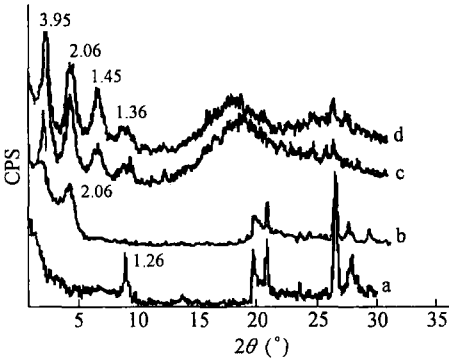


Fig. 2 X-ray diffraction patterns of NBR/OMB hybrids
a) Original bentonite; b) OMB; c) NBR/OMB (10 phr); d) NBR/OMB (40 phr)

More direct evidence for demonstrating the formation of the hybrids is provided by TEM ultramicrotomed sections. Figure 3(a) shows a TEM micrograph of vulcanizate prepared by mixing OMB and block NBR, which reveals that OMB dispersed unevenly in NBR with micro size (about 10 μm). Mechanical tests did not show much improvement in the mechanical properties of the vulcanizate (Table 4). It is suggested that the mechanical force used to mix the NBR block was not large enough to disperse bentonite adequately and at the same time it was difficult for macromolecules of the NBR block to enter the bentonite galleries.

Figure 3(b) shows the TEM micrograph of vulcanizate prepared by the coprecipitation of OMB and NBR latex. Particles of different sizes were distributed in the vulcanizate. Most of them were small stripes with certain orientation. They were about 300 nm in length and 40 nm in width. A few bigger ones measuring several hundred nm in width were surrounded by the small ones. Comparing Fig. 3(b) with Fig. 3(a), the particles in NBR/OMB vulcanizates obtained by latex coprecipitation were dispersed more homogeneously in NBR matrix. The thickness of most dispersed phase was about 30–60 nm, which was equal to the thickness of 25–50 layers of bentonite.

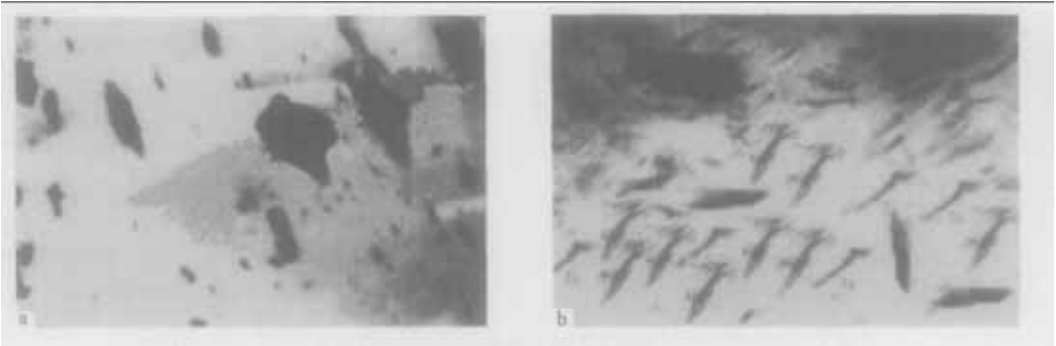


Fig. 3 TEM photographs of NBR/OMB vulcanizates
a) Vulcanizate prepared by mixing OMB and block NBR (Magnification = $\times 2000$);
b) Vulcanizate prepared by the coprecipitation of OMB and NBR latex (Magnification = $\times 32000$)

Table 4. Mechanical properties of OMB filled block NBR vulcanizates

Mechanical properties	OMB content (phr)				
	0	5	10	20	30
Tensile strength at 300% elongation (MPa)	0.89	1.54	1.62	2.0	2.48
Tensile strength (MPa)	1.34	3.00	3.63	5.22	6.37
Elongation at break (%)	534	546	567	670	676
Tear strength ($\text{kN}\cdot\text{m}^{-1}$)	7.14	10.20	11.78	17.06	20.50
Permanent set	7	8	12	16	44
Shore A hardness	46	48	50	58	64

PVC Reinforced by NBR/OMB Hybrids

Table 5 shows the effects of NBR on the mechanical properties of PVC/NBR blends. The tensile strength and flexural strength of the blends are decreased when the amount of NBR is increased. For example, at 10.5 phr of NBR, the tensile strength and flexural strength of the blends were decreased by 29.6% and 26.3%, respectively, while elongation at break was increased from 2.6% (pure PVC) to 53.1% (14 phr of NBR). The notched impact strength of PVC/NBR blends increased from 4.0 kJ/m^2 to 59.8 kJ/m^2 . Because the tensile strength and flexural strength are decreased when the amount of NBR is increased, a higher content of NBR in the blends can enhance their impact strength but will sacrifice other properties of the materials.

Table 5. Mechanical properties of PVC/NBR composites

NBR (phr)	0	2.1	3.5	7	10.5	14
Tensile strength (MPa)	59.6	55.9	52.2	40.8	42.0	36.3
Flexural strength (MPa)	104.2	103.3	93.6	75.9	76.8	66.9
Elongation at Break (%)	2.6	3.9	10.1	14.0	24.6	53.1
Notched impact strength ($\text{kJ} \cdot \text{m}^{-2}$)	4.0	5.3	8.7	36.4	59.8	53.9

Some mechanical properties of PVC/(NBR/OMB) composites are given in Table 6. The tensile strength and flexural strength of the composites were decreased very slowly with an increase in the amount of NBR/OMB (70/30) hybrids. For example, at 15 phr of NBR/OMB, tensile strength and flexural strength were decreased by 18.2 and 23.0, respectively. However the impact strength was significantly enhanced up to 70.2 kJ/m^2 . Comparing Table 6 to Table 5, it is easy to find that at the same amount of NBR, the reinforcing effects of NBR/OMB hybrids on PVC are much better than those of NBR. On the one hand, NBR/OMB hybrids improve the toughness of PVC. On the other hand, the tensile strength and flexural strength can be maintained fairly well.

Table 6. Mechanical properties of PVC/(NBR/OMB) composites

Mechanical properties	NBR/OMB (70/30) hybrids wt%					
	0	3.0	5.0	10	15	20
Tensile strength (MPa)	59.6	58.6	55.7	53.4	48.8	42.8
Elongation at break (%)	2.65	2.90	4.22	4.43	4.63	5.28
Flexural strength (MPa)	104.2	105.9	106.6	97.7	80.2	77.7
Notched impact strength ($\text{kJ} \cdot \text{m}^{-2}$)	4.0	13.6	29.7	47.9	70.2	90.6

SEM micrographs of impact-fractured surfaces are presented in Fig. 4. In the case of PVC/NBR (100/10.5) composite (Fig. 4a), the average NBR particle size was smaller than 1 μm and the particles were spherical in shape; the interphases between PVC and NBR were blurred. Figure 4(b) shows a SEM micrograph of PVC/(NBR/OMB) (100/15) composite. The interphases between matrix and dispersed phase became more blurred. These results suggest that the adhesion between PVC and NBR/OMB hybrids is strong.

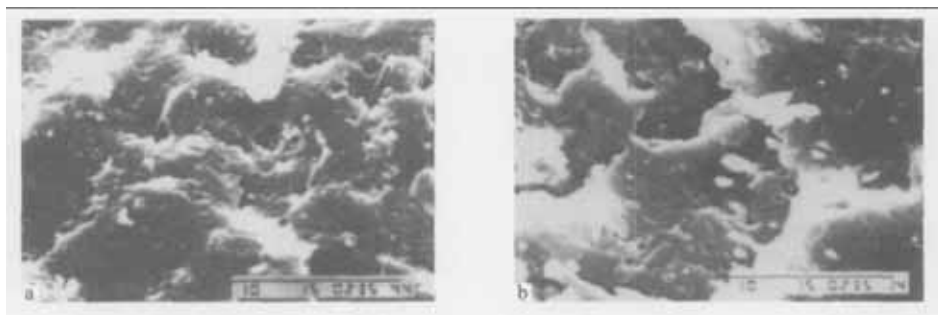


Fig. 4 SEM microphotographs of impact-fractured surface of the composites
a) PVC/NBR (100/10.5) composite; b) PVC/(NBR/OMB) (100/15)

There are two reasons why NBR/OMB hybrids have a reinforcing effect. Firstly, NBR molecules are intercalated into the galleries of organomodified bentonite which act as crosslinking points, the reinforcing effects of NBR are obviously enhanced by bentonite, and the strength and modulus of elastomer particles are increased, the toughening effects of NBR elastomer are significantly improved. Secondly, some of the OMB will remain in the NBR/OMB hybrids, which may allow PVC molecules to have a chance to be melt intercalated into bentonite galleries or to play the role of reinforcing rigid inorganic particles, and cause changes in the ability to absorb the impact energy in the composite. Therefore, the reinforcing effect of NBR/OMB hybrids on PVC is better than that of NBR and the tensile strength and flexural strength of the composites can be maintained fairly well.

CONCLUSIONS

Latex intercalation is one of the most effective ways to prepare NBR/bentonite hybrids. NBR macromolecules can enter the galleries of OMB. The mechanical properties of the vulcanizates are better than those of NBR/unmodified bentonite composite.

OMB is a new highly effective, light-colored reinforcing agent. The reinforcing effects of vulcanizates filled with 10 phr of OMB are closed to the level of 30 phr carbon black (N330).

The reinforcing effects of NBR/OMB hybrids on PVC are better than those of NBR, and the tensile strength and flexural strength of the composites can be maintained fairly well.

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