

# Preparation and Structure and Mechanical Properties of Poly(styrene-*b*-butadiene)/Clay Nanocomposites

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**ABSTRACT:** Star-shaped and linear block thermoplastic poly(styrene-*b*-butadiene) copolymer (SBS)/organophilic montmorillonite clays (OMMT) were prepared by a solution approach. The intercalation spacing in the nanocomposites and the degree of dispersion of nanocomposites were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. The mechanical properties, dynamic mechanical properties, and thermal stability of these nanocomposites were determined. Results showed that SBS chains were well intercalated into the clay galleries and an intercalated nanocomposite was obtained. The me-

chanical strength of nanocomposites with the star-shaped SBS/OMMT were significantly increased. The addition of OMMT also gave an increase of the elongation, the dynamic storage modulus, the dynamic loss modulus, and the thermal stability of nanocomposites. The increase of the elongation of nanocomposites indicates that SBS has retained good elasticity. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3430–3434, 2004

**Key words:** SBS; montmorillonite; nanocomposites; structure; properties

## INTRODUCTION

Polymer/clay nanocomposites have attracted considerable attention from both a fundamental research and an applications point of view in recent decades because they frequently exhibit unexpected properties synergistically derived from the two components.<sup>1–6</sup> Depending on the degree of intercalation of the polymer chain into the gallery of clay, nanocomposites are obtained with structures ranging from intercalated to exfoliated, which is influenced by various factors such as the method of preparation, the structure and polarity of virgin polymer, the source of clay, and the length and number of alkyl groups of the cationic modifier molecule, etc. However, usually it is difficult to prepare nanocomposites with exfoliated structure because of very strong electrostatic interactions between silicate layers.

Until the present time, numerous studies have focused on plastics/clay nanocomposites: in contrast, few articles related to elastomer/clay were reported. Burnside and Giannelis<sup>7</sup> described the two-step preparation of silicon rubber based nanocomposites. Wang et al.<sup>8</sup> prepared a series of intercalated nanocompos-

ites based on the same type of silicon rubber. Okada and coworkers<sup>9,10</sup> obtained a nitrile rubber (NBR)-based nanocomposite in a two-step synthesis.

In this research, we have prepared thermoplastic elastomer [poly(styrene-*b*-butadiene) copolymer (SBS)]/clay nanocomposites by solution blending; the nanocomposites consist of a commercial product of block poly(styrene-*b*-butadiene) copolymer and a commercial organophilic clay containing ammonium salt. The microstructure, mechanical properties, and thermal stability of nanocomposites are described.

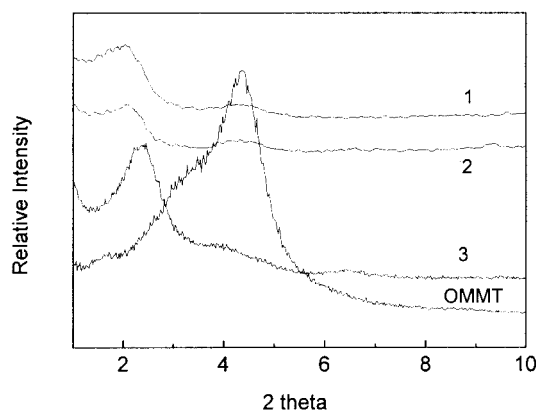
## EXPERIMENTAL

### Materials

Organophilic montmorillonite clays (OMMT; trade name NANNOLIN DK1) was supplied by Fenghong Clay Chemical Corp. (China). This clay is an organophilic MMT, which is exchanged by a quaternary, long (estimated 16–18 carbons), organic ammonium salt with cation exchange capacity of 110 meq/100 g, and an average particle size of 25 × 1000 nm in the dry state. The SBS, supplied by Beijing Yanshan Petrochemical Corp. SBS4303, is a star-shaped block copolymer which contains 30 wt % polystyrene with number-average molecular weight of about 300,000. SBS1401 is a linear block copolymer, in which the polystyrene block percentage is about 40 wt % and the number-average molecular weight is about 100,000. Toluene was commercially available.

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**Figure 1** XRD patterns of organophilic MMT and SBS4303-based nanocomposite.

### Preparation of poly(styrene-*b*-butadiene)/clay nanocomposites

Different amounts of OMMT were dispersed in toluene at 50°C for 3 h with stirring in a 2-L resin kettle; 100 phr poly(styrene-*b*-butadiene) was added into the slurry. After stirring vigorously for at least 8 h, the resulting composites were poured into ethanol to yield white precipitates, and the precipitates were filtered and dried under vacuum at 50°C.

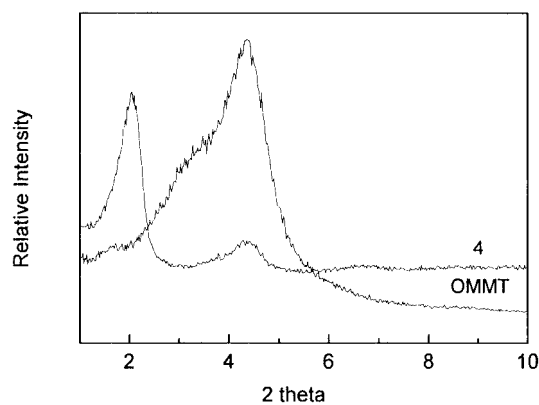
### Characterization of poly(styrene-*b*-butadiene)/clay nanocomposites

The change in basal spacing of the nanocomposites was measured by using an X-ray diffractometer (D/max RB). CuK $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) was used as an X-ray source at a generator voltage of 40 kV and a current of 100 mA. Diffraction angle was scanned from 1 to 10° at a rate of 0.2°/min. The basal spacing of MMT was estimated from the position of the (001) plane peak in the XRD pattern by using the Bragg's equation,  $d = \lambda/2 \sin \theta$ .

TEM investigations were performed by using a FEI Co. TECNAI G220 TEM with a Cu filament operating at 200 kV. Extra precautions were taken to minimize sample motion and beam damage of the samples. The TEM grids were mounted in a liquid nitrogen cooled sample holder and the brightness of the electron beam was minimized (low-dose mode).

All specimens were kept in a sealed desiccator under vacuum for 24 h before mechanical property measurements were performed. The values reported reflect an average from five measurements. Tensile tests were conducted according to ASTM D638 by using an Instron model 5567 testing machine.

Dynamic mechanical properties were measured by using a TA 2980 DMA dynamic mechanical analyzer with multi-frequency-film-tension module. The specimens (size 1.5 × 4.5 × 20 mm) were cut from the center of the samples. A temperature sweep at 5°C/



**Figure 2** XRD patterns of organophilic MMT and SBS1401-based nanocomposite.

min from -150 to 150°C at a frequency of 1 Hz was used to determine the  $\tan \delta$  for all samples in addition to the dynamic modulus.

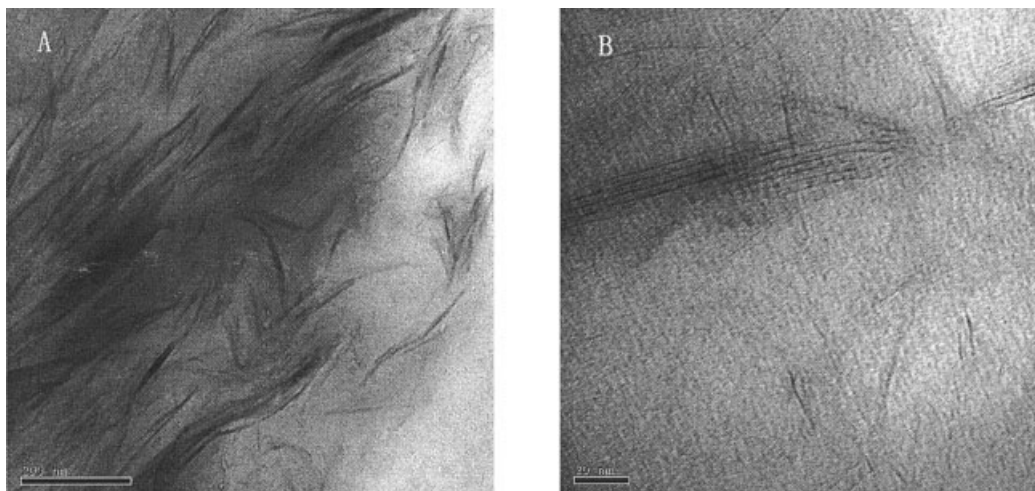
## RESULTS AND DISCUSSION

### XRD patterns of nanocomposites and TEM observation

Figures 1 and 2 show the XRD patterns of organoclay and nanocomposites based on different SBS, respectively. The characteristic peaks and basal spacing estimated by the Bragg's equation for nanocomposites with different OMMT content are shown in Table I. The OMMT has a large characteristic peak at low  $2\theta$  equal to 4.38°, and the peak corresponds to a basal spacing of 20.2 Å. After OMMT is added to the SBS, the shift of the XRD reflection peak to lower angles is observed, which implies an increase of the basal spacing. As shown in Figure 1, nanocomposites containing 2.5 phr OMMT have a 41.8 Å basal spacing, and the basal spacing is obviously increased compared with OMMT. However, with further increase in OMMT content, the basal spacing decreases. When the nanocomposite contains 7.5 phr OMMT (sample 3), the characteristic peak has shifted from 4.38 to 2.38°, whose corresponding basal spacing is 37.1 Å. Those results indicate that SBS chains intercalate into the

**TABLE I**  
Component of Every System and Basal Spacing of OMMT and Nanocomposites

Sample No.	OMMT(SBS) (phr)	Diffraction angle	Basal spacing (Å)
OMMT		4.38°	20.2
1	2.5 (SBS4303)	2.08°	41.8
2	5 (SBS4303)	2.22°	39.8
3	7.5 (SBS4303)	2.38°	37.1
4	2.5 (SBS1401)	2.06°	42.9



**Figure 3** TEM pattern of SBS4303-based nanocomposite (No. 3).

gallery of OMMT, which is swollen; thus, an intercalated nanocomposite was obtained. Similarly, Figure 2 shows a shift of the characteristic peak for nanocomposites based on SBS1401 containing 2.5 phr OMMT as for nanocomposite based on SBS4303. Sample 4 has 42.9 Å basal spacings, a little larger than that of sample 1 containing the same OMMT. However, the characteristic peaks exist in all cases, indicating that intercalated nanocomposites could be achieved by this solution approach, which may be attributed to that the Van der Waals forces between clay galleries dominating polymer clay interactions, resulting in a finite expansion of clay galleries and retention of clay structure. It seems that an increase of OMMT content does not affect the larger expansion of clay galleries.

The intercalated morphology of the SBS/OMMT nanocomposites was also supported by TEM (Fig. 3), in which the dark lines represent the intersections of OMMT. It was observed that the MMT layers were dispersed randomly in SBS matrix and the stacked silicate layers still exist, but part of it seems to be flocculation, as shown in Figure 3(A). In Figure 3(B), the stacking of only three or four layers with a distance of less than 3.8 nm composed of dark band and bright field is observed in the SBS matrix (light region). This is consistent with the change of basal spac-

ing estimated by XRD. The SBS chains are intercalated in the narrow space of the oriented collections of parallel silicate layers as revealed by the XRD pattern. Some single layers were also found in the SBS matrix as shown in Figure 3(B). It indicates that there exists some exfoliation of OMMT. This may be attributed to the intensive stirring during preparation and the stronger interaction between some SBS chains and OMMT layers.

### Mechanical properties of nanocomposites

The mechanical properties of nanocomposites were measured and summarized in Table II. The pure SBS4303 has a tensile strength of 16.5 MPa and modulus at 300% of 3.11 MPa. The tensile strength of nanocomposites increases rapidly with increasing OMMT content. When only 2.5 phr OMMT is added, the tensile strength of nanocomposites is 29.3 MPa: an approximately 77% increase in tensile strength is obtained. The increasing trend is less when the OMMT content increases beyond 2.5 phr. Sample 3, containing 7.5 phr OMMT, has a tensile strength of 30.6 MPa, which is increased approximately 80% compared with pure SBS4303. A similar phenomenon is observed in Table II for elongation at break. The addition of

**TABLE II**  
Mechanical Properties of SBS and the Nanocomposites

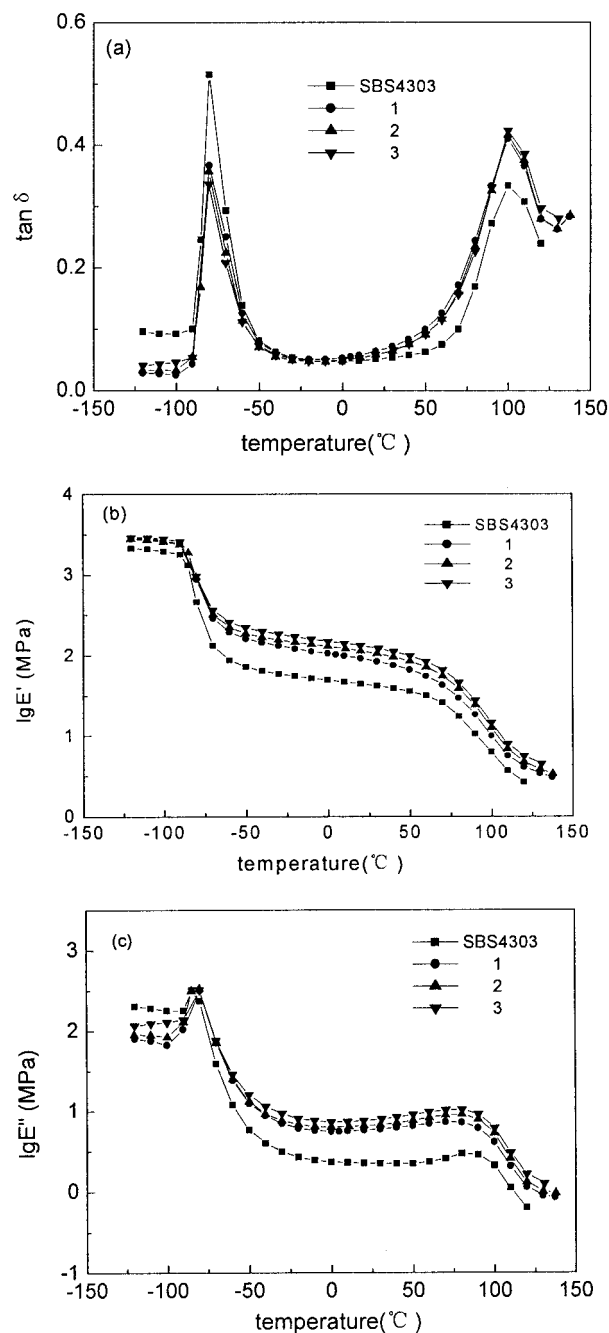
Sample No.	Tensile strength (MPa)	Modulus at 300% (MPa)	Elongation at break (%)
SBS4303	16.5	3.11	500
1	29.3	4.61	742
2	28.1	6.12	782
3	30.6	6.33	789
SBS1401	31.5	4.89	700
4	31.8	6.22	620

OMMT gives the obvious effect on the elongation, which increases with increasing OMMT content. These results are in good agreement with the basal spacing. The modulus at 300% increases along with increasing OMMT content and its modulus increases more than 100% when 7.5 phr OMMT is added. This indicates that the addition of OMMT produces a significant reinforcement effect and does not damage the elasticity of SBS. The reason may be that the OMMT preferentially disperses in the PS phase of SBS, leading to reduced interaction between PS macromolecules chains and chains of PB, which move more easily under tensile force. For the SBS1401/OMMT nanocomposites, the tensile strength was almost unchanged, whereas elongation at break and the modulus at 300% increased with the addition of OMMT. The different effects of addition of OMMT into SBS4303 and SBS1401 on mechanical properties of nanocomposites may be because of the difference of the chemical structure. The mechanism of how the addition of OMMT affects mechanical properties of nanocomposites needs to be studied further.

#### Dynamic mechanical properties of nanocomposites

The loss factor ( $\tan \delta$ ), dynamic storage modulus ( $E'$ ), and dynamic loss modulus ( $E''$ ) versus temperature for SBS4303 and nanocomposites are plotted in Figure 4. As shown in Fig. 4(a), in all cases, two transitions are observed. The lower temperature transition at  $-80^\circ\text{C}$  is characteristic of the polybutadiene domains, whereas the higher temperature transition, at about  $100^\circ\text{C}$ , is characteristic of the polystyrene domains. As the OMMT content increases, the value of  $\tan \delta$  relevant to the polybutadiene domains decreases, while the value of  $\tan \delta$  relevant to the polystyrene domains increases and the mechanical relaxation is widened, which also slightly shifts toward higher temperature. This may be attributed to the OMMT platelets dispersing at a greater degree in the polystyrene domains block.

In the  $E'$  and  $E''$  curves [Fig. 4(b, c)], the trend of dynamic storage modulus and dynamic loss modulus as a function of temperature for the unfilled SBS and for the nanocomposites containing different OMMT amounts are apparent. The dynamic moduli of the nanocomposites are much higher than pure SBS, and a considerable increase is observed in the range of temperature from  $-50$  to  $100^\circ\text{C}$ . It is probable that the addition of OMMT could induce the reinforcement effect on polystyrene. The increasing trend becomes more significant when 2.5 phr OMMT is added, but it is less so with increasing OMMT content further. This is consistent with an increase of the basal spacing and mechanical properties of nanocomposites. The same results were also obtained when Laus et al.<sup>11</sup> melt

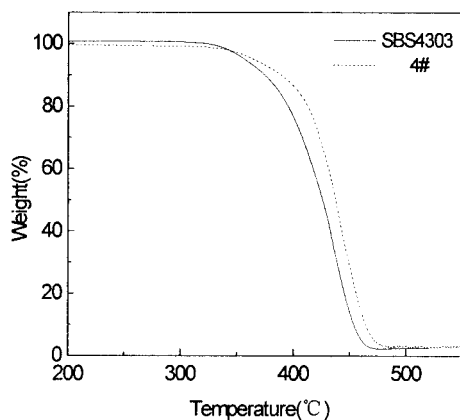


**Figure 4** Dynamic mechanical spectra of the SBS4303 and nanocomposites (a) temperature dependence of  $\tan \delta$ ; (b) temperature dependence of  $E'$ ; (c) temperature dependence of  $E''$ .

blended a commercial SBS with a kind of OMMT and prepared an intercalated nanocomposite.

#### Thermal characterization of nanocomposites

Figure 5 shows the TGA results for pure SBS4303 and for the nanocomposites containing 2.5 phr OMMT. Approximate decomposition temperatures of these materials were  $434.8$  and  $440.6^\circ\text{C}$ . These were signifi-



**Figure 5** Thermogravimetric results (relative weight loss of temperature) for SBS4303 and nanocomposites (No. 1).

cant increases in thermal stability resulting from the intercalated clay platelets. This may be partly due to kinetic effects, with the platelets retarding diffusion of oxygen into the polymer matrix.

### CONCLUSION

A series of poly(styrene-*b*-butadiene)/OMMT nanocomposites were prepared by a solution approach. XRD patterns and TEM observation indicated that

intercalated nanocomposites were achieved. The mechanical properties for SBS4303/OMMT nanocomposites were significantly improved by the clay added. Dynamic storage modulus and dynamic loss modulus increased with increasing clay content and the decomposition temperature also increased with the clay added.

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