

# Studies on the Poly(*Styrene-*b*-Butadiene-*b*-Styrene*)/Clay Nanocomposites Prepared by Melt Intercalation

Hongde Xu,<sup>1,2</sup> Yang Li,<sup>2</sup> Dingsheng Yu<sup>1</sup>

<sup>1</sup>The Key Laboratory of Preparation and Processing of Novel Polymers of Beijing City, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

<sup>2</sup>Research Institute of Beijing Yanshan Petrochemical Co. Ltd., Beijing 102500, People's Republic of China

Received 10 September 2004; accepted 12 January 2005

DOI 10.1002/app.22029

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Two types of SBS/OMMT composites are prepared by melt blending using a twin-screw extruder. An X-ray diffractometer indicates that polymer chains have intercalated into the gallery of the clay. It is shown in TEM photos that the thickness of the layer aggregate in the SBS1301 matrix is approximately 200 Å, but in the SBS4402 matrix the size of the filler particle is in micrometers. When SBS1301 is intermingled into SBS4402/OMMT, the particle size is reduced obviously. The tensile strength and elongation at break of the nanocomposite, SBS1301/OMMT, in-

crease with the addition of OMMT; and when addition is 5phr, they achieve maximum. A small content of OMMT (less than 5phr) can prevent the deterioration of the mechanical properties of the SBS1301/MMT. In addition, a small content of SBS4402 (less than 20 wt %) can improve the mechanical properties of the SBS1301/OMMT composites. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 146–152, 2005

**Key words:** nanocomposites; melt intercalation; SBS; clay; properties

## INTRODUCTION

Nanocomposites are a fascinating class of composites—particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. In recent years nanocomposites have attracted considerable attention because they frequently exhibit unexpected properties synergistically derived from the nano-scale inorganic filler and the polymer matrix.<sup>1–6</sup> Among all the nanocomposite precursors, those based on clay have been more widely investigated,<sup>7–12</sup> probably because the starting clay materials are easily available and because their intercalation chemistry has been studied for a long time.<sup>13</sup> Layers of clay can easily slide past each other under shear during compounding; then large aggregates are broken into smaller entities or are even exfoliated into individual platelets of very high aspect ratio having about 1nm thickness and a diameter of several hundred nanometers. There are two main types of nanocomposites when a layered clay is associated with a polymer: intercalated nanocomposites and exfoliated nanocomposites.

One of the most commercial thermoplastic elastomers (TPE) is the poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (SBS), which exhibits the characteristics of plastic and rubber, and include good

resistance to low temperature, good processability, and outstanding elasticity. There are few studies based on SBS/clay nanocomposites. Laus<sup>14</sup> prepared SBS/clay nanocomposites by a Brabender. He found that the storage modulus value, in the plateau region between the glass transition processes of the PB and PS, and the glass transition temperature of the PS increased as both the organophilic clay content and the annealing time increase. Chen and Gong<sup>15</sup> first synthesized a polyacrylate/clay by multistep exchange reactions and a diffusion polymerization method, then SBS/clay nanocomposites were prepared on a two-roll mill. They just studied the dynamic mechanical property of the composites and found that partial polystyrene segments of the SBS intercalated into the modified clay interlayer and exhibited a new glass transition at about 157°C (glass transition of the polystyrene segments out of the clay interlayer was 94°C). Liao and his coworkers<sup>16</sup> prepared SBS/clay nanocomposites by solution blending. In their work, the microstructure, mechanical properties, and thermal stability of the nanocomposites were described. Results showed that intercalated nanocomposites were obtained; mechanical properties and thermal stability were improved, too.

In this research, we prepared an SBS/OMMT nanocomposite by melt blending using a twin-screw extruder; this preparation technique is more favored in practical manufacture compared to solution blending. Organophilic montmorillonite clay is a commercial product. Here, for the first time, we provide the mor-

Correspondence to: D. Yu (yuds@mail.buct.edu.cn).

phology of the phase separated structure of the nanocomposite, discuss the relationship between the structure and the properties of the nanocomposites, and get some interesting results.

## EXPERIMENTAL

### Materials

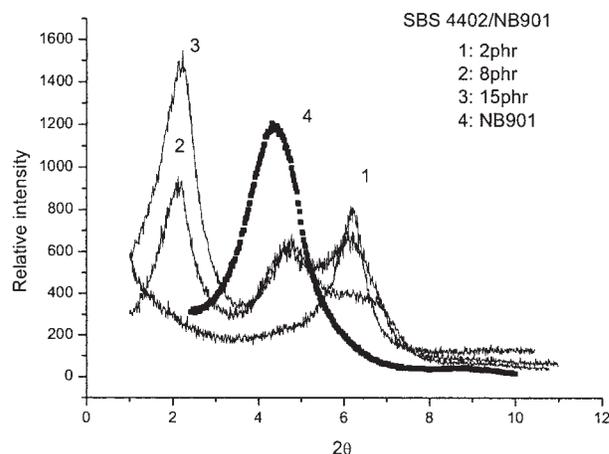
Organophilic montmorillonite clay (OMMT; HuaTe Group, China) is an organophilic MMT, which is exchanged by an octadecyl trimethyl ammonium with cation exchange capacity of 110 meq/100 g, and an average particle size of  $25 \times 1000$  nm in the dry state. Montmorillonite clay (MMT; HuaTe Group, China) also has an average particle size of  $25 \times 1000$  nm in the dry state. SBS is supplied by Beijing Yanshan Petrochemical Corp. The ODT temperature of the SBS lies between  $126^\circ\text{C}$  and  $131^\circ\text{C}$ <sup>17</sup> (when the polymer is heated above the ODT temperature, the microstructure will be destroyed and then form a homogeneous phase). SBS4402 is a star-shaped block copolymer that contains 40 wt % polystyrene with number average molecular weight of about 200,000. SBS1301 is a linear block copolymer, in which the polystyrene block percentage is about 30 wt % and the number average molecular weight is about 100,000.

### Preparation of SBS/clay nanocomposites

SBS/clay nanocomposites are prepared by melt blending using a twin-screw extruder (Coperion, ZSK25). The preparation condition is as follows: melt segment temperature is  $180^\circ\text{C}$ , screw rotating speed is 200rpm. Composites with different formulation, SBS1301/OMMT, SBS4402/OMMT, SBS1301/OMMT/MMT, and SBS4402/SBS1301/OMMT, are prepared in one-step melt compounding.

### Characterization of SBS/clay nanocomposites

The change in basal spacing of the nanocomposites is measured by using an X-ray diffractometer (D/ma  $\times$  RB). CuK ( $\lambda = 1.54\text{\AA}$ ) is used as an X-ray source at a generator voltage of 40 kV and a current of 100 mA. Diffraction angle is scanned from  $1$  to  $10^\circ$  at a step of  $0.02^\circ$ . The basal spacing of MMT is estimated from the position of the (001) plane peak in the XRD pattern by using Bragg's equation,  $d = \lambda/2 \sin\theta$ . TEM investigations are performed by a FEI Co. TECNAI G<sup>2</sup>20 TEM with a Cu filament operating at 200 kV. Extra precautions are taken to minimize sample motion and beam damage of the samples. The TEM grids are mounted in a liquid nitrogen cooled sample holder, and the brightness of the electron beam is minimized (low-dose mode). Tensile tests are conducted according to ASTM D638 by using an Instron model 5567 testing

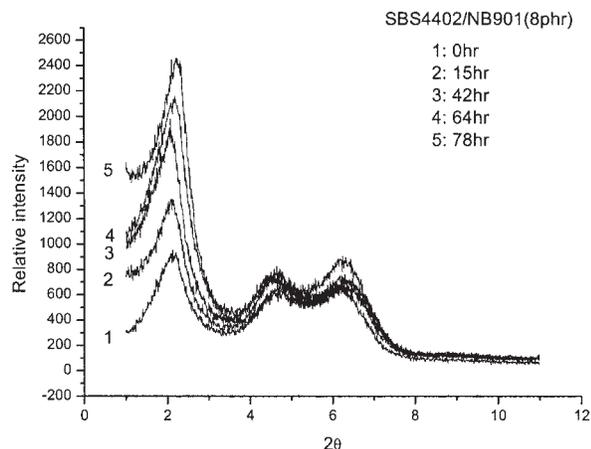


**Figure 1** XRD patterns of OMMT and SBS4402/OMMT with different OMMT content.

machine. Dynamic mechanical properties are measured by using a TA 2980 DMA dynamic mechanical analyzer with multi-frequency-film-tension module. The specimens (size  $1.5 \times 4.5 \times 20$  mm) are cut from the center of the samples. A temperature sweep at  $5^\circ\text{C}/\text{min}$  from  $-120$  to  $150^\circ\text{C}$  at a frequency of 2 Hz is used to determine the  $\tan \delta$  for all samples in addition to the dynamic modulus.

## RESULTS AND DISCUSSION

An X-ray diffractometer and TEM are usually used to characterize polymer/clay nanocomposites. When the polymer chain intercalates into the interlayer of the clay, the basal spacing of the clay should increase, and the position of the (001) plane peak in the XRD pattern should shift towards lower angle. Figure 1 shows the XRD patterns of the SBS/clay. The raw organophilic montmorillonite (OMMT) has a large peak at  $2\theta$  equal to  $4.46^\circ$ , which corresponds to a basal spacing of  $19.8\text{\AA}$ . After 8phr OMMT is added into the SBS matrix, and the position of the (001) plane peak shifts from  $4.46^\circ$  to a lower angle,  $2.20^\circ$ , which corresponds to a basal spacing of  $40.1\text{\AA}$ , nearly two-fold of the OMMT's. Peaks at  $6.22^\circ$  and  $4.66^\circ$  are attributed to the diffraction of the 003 and 002 plane (001 plane diffraction peak of the nanocomposite and OMMT is at  $2.20$  and  $4.46$ , respectively). The peaks of the 003 and 002 planes indicate that the nanocomposites exhibit expansion of the interlayer gallery spacing with the preservation of long-range order. From Figure 1, when the addition of the OMMT is 2phr, there is no reflection peak in the lower angle area, but as the addition of OMMT increases, reflection peaks at lower angles appear and the position of the peaks at lower angles seems to be steady and does not shift with the OMMT loadings. This result indicates that SBS chains have intercalated into the gallery of the clay, and the



**Figure 2** XRD patterns of SBS4402/OMMT with different anneal times.

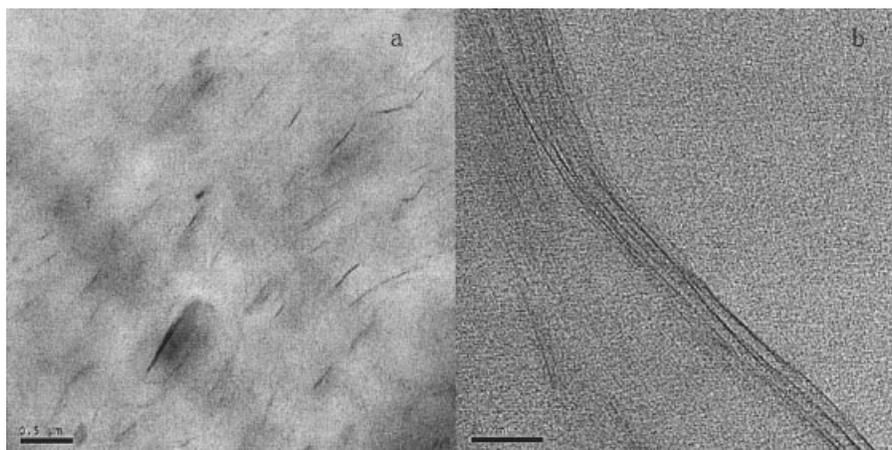
amount of the SBS chains that have intercalated into the gallery of the clay increases with the increasing of the OMMT loading. At lower loading of the OMMT, the relative intensity is too low and there is no reflection peak at the lower angles. In general, nanocomposites need to anneal at lower temperature after they have been prepared so as to get a satisfying intercalation. Figure 2 is the XRD patterns of the SBS/clay after annealing (at 120°C under nitrogen) at different times. With the increase of the anneal time, the relative intensity increases on the whole, and the position of the plane peaks (001) shifts towards higher angles in some degree. These results imply that the layers of the clay have a trend of adjacency under the annealing condition, which may be attributed to the strong polarity of the clay surface.

Comparable to the X-ray diffractometer, TEM can get more direct structure characterization of the nanocomposites. Figure 3(a) is a TEM photo of the SBS1301/OMMT composite in which the dark lines

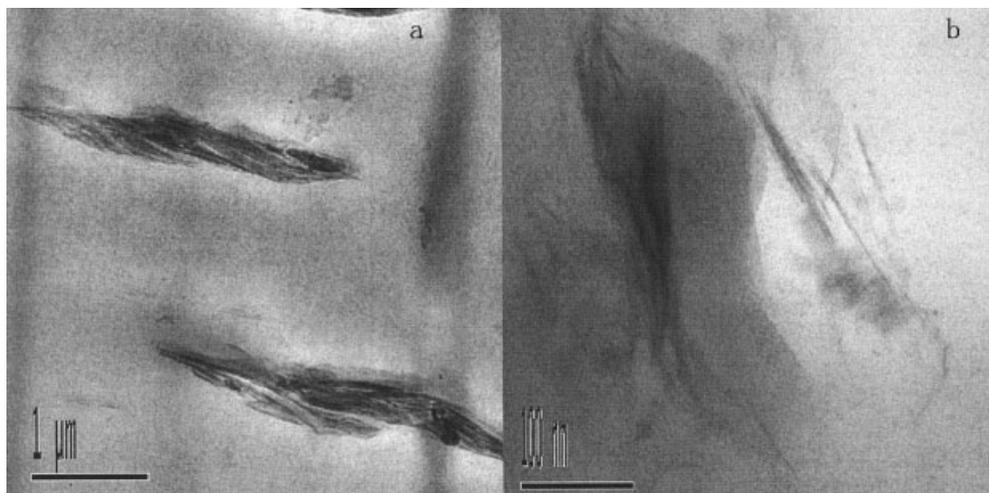
represent the clay layer aggregates. From Figure 3(b), it can be observed that the thin filigree-like layer aggregates are just three or four layers, the distance between layers is about 40 Å, and the thickness of the layer aggregate is approximately 200 Å. It is obvious that clay is dispersed in the SBS matrix in nano scale and the macromolecular chain has intercalated between the clay sheets. Figure 3(a) also shows the perfect orientation of layer aggregates along shear direction and the layer aggregates that uniformly disperse in the SBS matrix.

Figure 4(a) is a TEM photo of the SBS4402/OMMT. Unexpectedly, the layer aggregates are so large that the order of magnitude of the layer aggregate is micrometer, which is far out of the nano range and is similar to the general inorganic filler. In fact, whatever changes we make in the melt temperature and the screw rotating speed, the clay exists in granules. From the results of the XRD, the basal spacing of the OMMT has increased clearly and the polymer chain must have intercalated between the clay layers. These seem to be contradictory. The explanation may arise from the viscosity of the matrix in the molten state. Under the same processing condition, the viscosity of the star-shaped SBS4402 is much less than that of the molten linear SBS1301 and the shear is not strong enough to smash the bigger particle to smaller particles, but the polymer chain has intercalated. This is why the results of the XRD demonstrate that the basal height increases, but the photo of the TEM finds that the size of clay aggregate is so large. To verify this conclusion, an amount of SBS1301 is intermingled into SBS4402/OMMT. Figure 4(b) is the TEM photo of this composite. Obviously, the filler particle size is much smaller than that in the pure SBS4402 matrix.

It is known that the triblock SBS has a well separated phase structure. According to the relative contributions of the different blocks, SBS can exhibit a

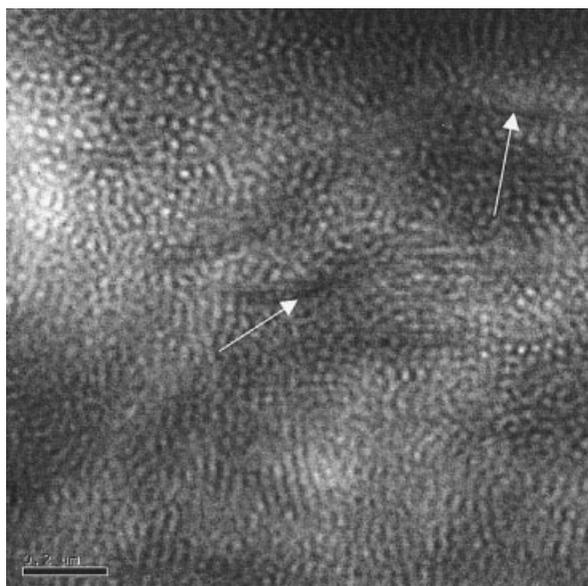


**Figure 3** TEM micrographs of SBS1301/OMMT (OMMT content is 2phr).



**Figure 4** TEM micrographs of SBS/OMMT (OMMT content is 3phr): (a) SBS4402/OMMT, (b) SBS4402/SBS1301/OMMT (mass ratio of SBS1301 to SBS4402 is 4 : 6).

variety of morphologies, such as alternating lamellar, cylindrical, and spherical microdomains.<sup>18,19</sup> Until now, there has been no article to discuss whether the clay dispersed in the SBS matrix in nano-scale has any effect on the morphology of the SBS matrix. Figure 5 is the TEM micrograph of SBS1301/OMMT. The specimen film is stained by  $\text{OsO}_4$  and cut under liquid nitrogen. In the Figure, the deep dark lines are clay layers. Obviously, the matrix retains its typical cylindrical morphology and the nano-scale clay layers (as shown with arrows) do not destroy the matrix structure. This indicates that the SBS matrix can retain its excellent mechanical properties, and nano-scale clay particles can improve the properties of the composite.



**Figure 5** TEM micrographs of SBS1301/OMMT (OMMT content is 1phr, stained by  $\text{OsO}_4$ ).

The dynamic mechanical behavior of the SBS1301/OMMT nanocomposites is studied in the linear viscoelasticity region between  $-120^\circ\text{C}$  and the temperature at which samples lose their dimensional stability. The relationship between storage modulus and loss modulus and OMMT content is shown in Figures 6(a,b). By and large, with the increase of the OMMT, both moduli increase in the measured temperature range. It is probable that the addition of OMMT could induce the reinforcement effect on the matrix. The loss factor ( $\tan \delta$ ) curves are plotted in Figure 6(c). Peaks at the lower temperature and the higher temperature correspond to the glass transition of the PB and PS block domain, respectively. To all samples with different addition of OMMT, glass transition temperature ( $T_g$ ) of the PB keeps constant and the amount of the OMMT has no effect on that. In contrast, the  $T_g$  of the PS increases gradually with the increase of the OMMT; detailed data is listed in Table I.

According to the block structure of SBS, both ends of the block copolymer are PS blocks. Now that polymer chains have intercalated into the clay galleries, many PS segments must have intercalated into the galleries. Whether the PB block intercalates into the galleries, we are not sure, but the length of the clay slice is far longer than that of the PS block (the polymerization degree of the PS block is about 150), so we cannot exclude the possibility of the intercalation of the PB. But the butadiene molecular is apolar and the styrene molecular is weak polar, so the polar clay layers will have stronger interaction with the PS chains and have nearly no interaction with the PB chains. Then the confined PS chain is thus expected to resist flow even at temperatures higher than the corresponding  $T_g$  of the bulk PS. In some scope of OMMT loadings, the intercalation of the PS chains increases

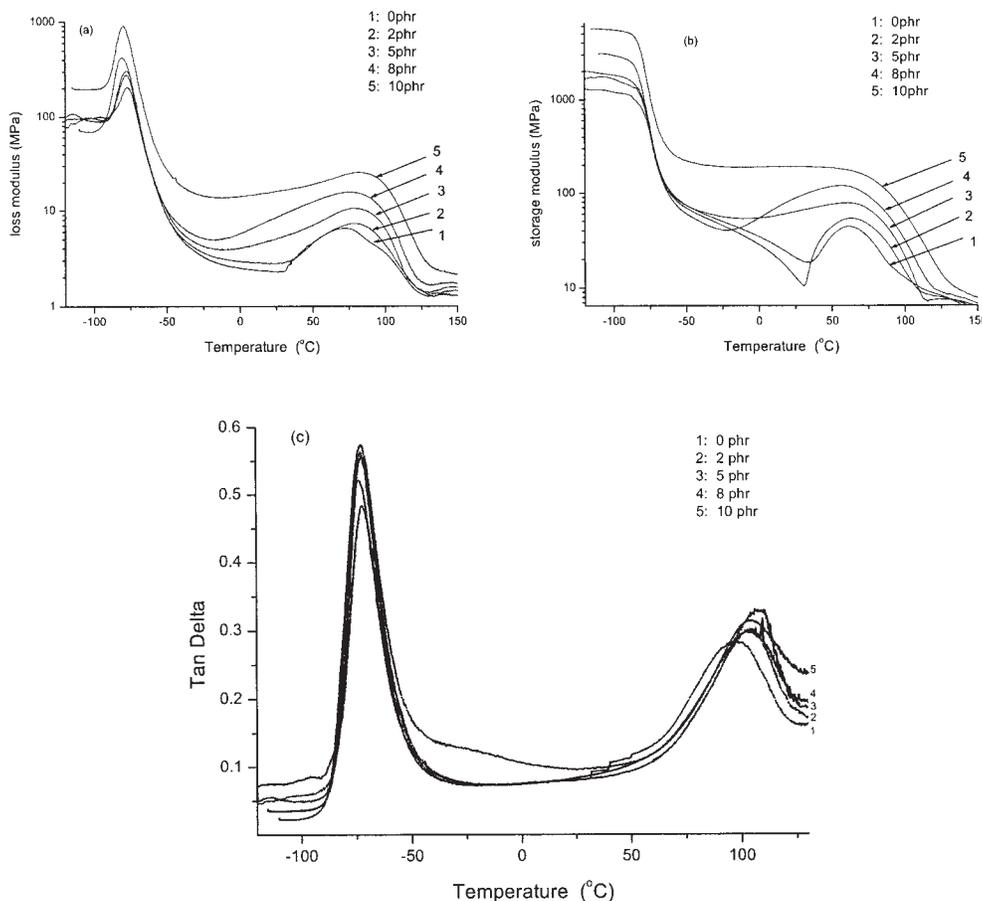


Figure 6 Dynamic mechanical spectra of SBS1301/OMMT nanocomposites with different OMMT contents.

with the increase of the OMMT content. So, in a macroscopic view, the  $T_g$  of the PS increases gradually with the increase of the OMMT.

Some mechanical properties of the SBS/clay are measured. Figure 7 shows the tensile strength and elongation at break of the SBS1301/OMMT and SBS4402/OMMT. With SBS1301/OMMT, the tensile strength first increases rapidly with increasing OMMT content; then when the OMMT content is 5 phr, the strength achieves the maximum value. Elongation at break of the SBS1301/OMMT has a similar trend. The maximum tensile strength of the SBS1301/OMMT is 25.9 MPa, which has an approximately 70% increase over that of the neat SBS1301 (15.5 MPa). The maximum elongation at break is 770%, an increase of about 20% more than that of the neat SBS1301 (660%). This

indicates that the addition of OMMT produces a significant reinforcement effect and does not damage the elasticity of the matrix. For SBS4402/OMMT, the result is widely divergent from that of the SBS1301/OMMT. The mechanical properties of SBS4402/OMMT deteriorate with the addition of the OMMT. The effect of the OMMT is similar to the ordinary

TABLE I  
Relationship Between  $T_g$  of the PS Block and the Amount of OMMT in SBS1301/OMMT Nanocomposites

OMMT content/phr	0	2	5	8	10
$T_g/^\circ\text{C}$	97.4	104.5	106.2	107.2	104.2

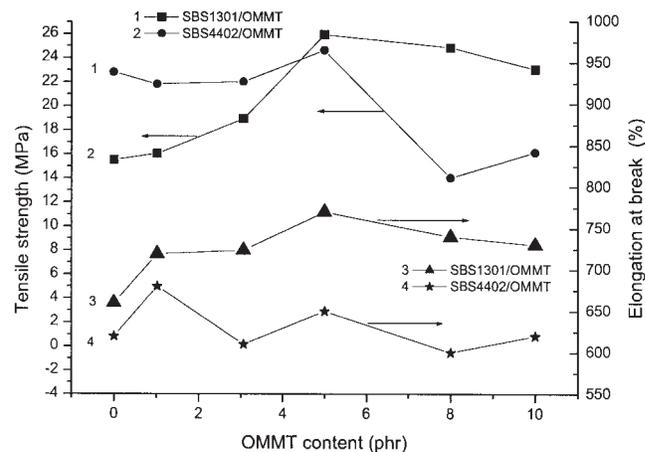


Figure 7 Mechanical properties of SBS/OMMT.

inorganic filler. This is not surprising; in Figure 4(a), the particle size is so large that it will have no reinforcement, notwithstanding the existence of some intercalations.

The mechanical properties of the blend of SBS1301 and SBS4402 are measured and shown in Figure 8. For all samples, OMMT content is 3phr. For tensile strength and elongation at break, there are two maximum values when addition of SBS1301 or SBS4402 is 20 wt %, respectively. The result indicates that a small content of another type of SBS can improve the mechanical properties of both the SBS/OMMT composites.

In many cases, inorganic fillers, such as clay,  $\text{CaCO}_3$ ,  $\text{TiO}_2$ , and so forth, have been used in polymer composites for saving polymer consumption and reducing composite cost. But cost reduction is at the expense of sacrifice of the composite properties. Usually, the addition of the inorganic filler results in the loss of strength and elasticity. In Figure 9, the tensile strength and elongation at break of the SBS1301/MMT are less than those of the pure SBS1301. With the increase of the MMT, the strength and the elongation tend to decrease, which indicates that the MMT filler not only does not reinforce the matrix but also damages the elasticity of the matrix. But when OMMT is employed at the same time, the deterioration of the properties will be avoided; this result is also shown in Figure 9. This may be attributed to the dispersion in nano-scale of the OMMT particles, the reinforcement of which can compensate the negative effect of the MMT fillers in some degree. For all SBS1301/OMMT/MMT samples, the amount of OMMT is 3phr, but the amount of MMT changes from 2phr to 15phr. Although the trend of the strength and the elongation tends to descend, too, the descent is based on a higher foundation. Even if the level of the MMT is 15phr, the strength and the elongation are not less than those of the pure SBS. So,

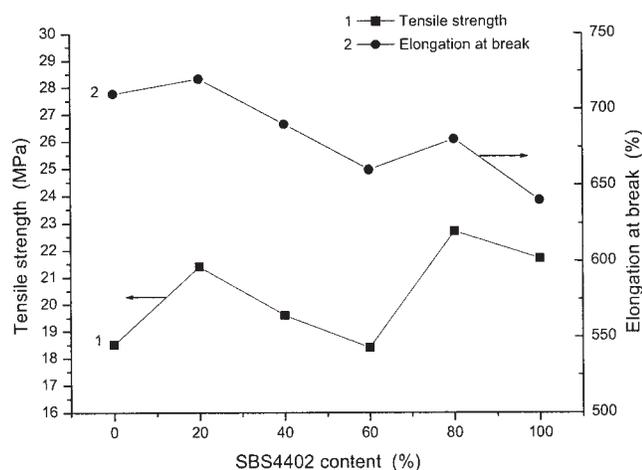


Figure 8 Mechanical properties of SBS4402/SBS1301/OMMT.

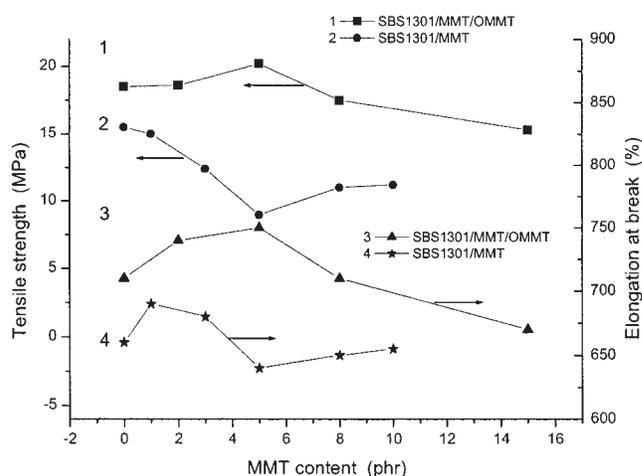


Figure 9 Mechanical properties of SBS1301/OMMT/MMT.

in case of a requirement of a large amount of inorganic fillers, the extra addition of a small amount of OMMT can prevent the drastic property deterioration of the composite. In the case of no requirement of inorganic fillers, the addition of a small amount of OMMT can improve the property of the composite remarkably.

## CONCLUSIONS

SBS/clay composites are prepared by melt blending using a twin-screw extruder. An X-ray diffractometer indicates that the polymer chains have intercalated into the gallery of the clay. It is shown in TEM photos that the thickness of the layer aggregate in SBS1301 is approximately 200 Å, but in SBS4402 the layer aggregate is so large that the size of is far out of the order of nano scale. So SBS1301/OMMT is a nanocomposite, but SBS4402/OMMT is not a nanocomposite proper. When SBS1301 is intermingled into SBS4402/OMMT, the filler particle size diminishes obviously. The tensile strength and elongation at break of the SBS1301/OMMT nanocomposite increase with the addition of OMMT; and when addition is 5phr, they achieve maximum. A small content of OMMT (less than 5phr) can prevent the deterioration of the mechanical properties of the SBS1301/MMT. In addition, a small content of SBS4402 (less than 20 wt %) can improve the mechanical properties of the SBS1301/OMMT composites.

Financial support of this work by the SINO Petrochemical Co. Ltd. through a contract (No. 402051) is gratefully acknowledged.

## References

1. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
2. Morgan, A. B.; Harris, Jr., R. H.; Kashiwagi, T.; Chyall L. J.; Gilman, J. W. *Fire Mater* 2002, 26, 247.

3. Nah, C.; Ryu, H. J.; Kim, W. D.; Choi, S. S. *Polym Adv Technol* 2002, 13, 649.
4. Koo, C. M.; Kim, M. J.; Choi, M. H.; Kim, S. O.; Chung, I. J. *J Appl Polym Sci* 2003, 88, 1526.
5. Tjong, S. C.; Meng, Y. Z. *J Polym Sci Part B: Polym Phys* 2003, 41, 2332.
6. Zhang, J. Z.; Wang, X.; Lu, L.; Li, D.; Yang, X. J. *J Appl Polym Sci* 2003, 87, 381.
7. Kalgaonkar, R. A.; Jog, J. P. *J Polym Sci Part B: Polym Phys* 2003, 41, 3102.
8. Zengjun, L.; Peilin, Z.; Deyue, Y. *J Appl Polym Sci* 2004, 91, 1834.
9. You-Ping, W.; Qing-Xiu, J.; Ding-Sheng, Y. *J Appl Polym Sci* 2003, 89, 3855.
10. Liangming, W.; Tao, T.; Baotong, H. *J Polym Sci Part A: Polym Chem* 2004, 42, 941.
11. Zhen, W.; Pinnavaia, T. J. *Chem Mater* 1998, 10, 1820.
12. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Macromolecules* 1995, 28, 8080.
13. Ogawa, M.; Kuroda, K. *Bull Chem Soc Jpn* 1997, 70, 2593.
14. Laus, M. *J Mater Res* 1997, 12, 3134.
15. Chen, Z.; Gong, K. *J Appl Polym Sci* 2002, 84, 1499.
16. Liao, M. Y.; Zhu, J. D.; Xu, H. D.; Li, Y.; Shan, W. *J Appl Polym Sci* 2004, 92, 3430.
17. Mohammady, S. Z.; Mansour, A. A.; Stoll, B. *J Appl Polym Sci: Part B* 2001, 39, 2198.
18. Kimishima, K.; Jinnai, H.; Hashimoto, T. *Macromolecules* 1999, 32, 2585.
19. Hashimoto, T.; Shibayama, M.; Fujimura, M.; Kawai, H. In: *Block Copolymers, Science and Technology*; Meser, D. J., Ed.; Harwood Academic: London, 1983.