

Amphiphilic Poly(styrene-*b*-ethylene oxide)-Block-Copolymer-Intercalated Layered Silicate and Its Nanocomposites with Acrylonitrile-Butadiene-Styrene Resin

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ABSTRACT: Amphiphilic poly(styrene-*b*-ethylene oxide) block copolymers were synthesized by sequential anionic copolymerization. Layered silicates intercalated by the block copolymers were prepared via melt intercalation. The effects of the intercalated clay on an acrylonitrile-butadiene-styrene resin were characterized with X-ray diffraction, transmission electron microscopy, stress-strain measurements in elongation, and thermogravimetric analysis. X-ray and microscopy results demonstrated that the main structure of the

dispersed block-copolymer-intercalated clay in the acrylonitrile-butadiene-styrene resin matrix was mono- and bundle-layered. Further studies demonstrated that the resin showed considerable improvement in its tensile strength, modulus, and thermal stability. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 238–242, 2004

Key words: block copolymers; nanocomposites

INTRODUCTION

Blending polymers with layered silicates for the preparation of nanocomposites has attracted much attention in recent years because it produces unexpected properties, including improvements in the composite strength, stiffness, and thermal and barrier properties, when small amounts of silicates are added to the polymer matrix.^{1–16} Montmorillonite in nature consists mainly of layered silicates carrying negative charges that form ionic bonds with metal cations in the intergallery of the layered silicates and also dangling hydroxyl end groups on their surfaces.^{17,18} The existence of ionic bonds and the ability to form hydrogen bonds with water make montmorillonite highly hydrophilic and, therefore, incompatible with organic polymers. To improve the affinity of montmorillonite toward low-polar organic materials, we must modify montmorillonite by replacing the metal cations in the intergallery of the silicates with various organic cation molecules. There are two reasons for this modification: (1) the addition of an intercalating agent to increase the space between the layered silicates and make it more uniform and (2) the addition of small organic

molecules bonded to silicates to make montmorillonite more miscible with the polymer matrix. Therefore, polymer molecules are allowed to enter the enlarged intergallery of silicates for further intercalation or exfoliation. In general, the intercalated agents are small molecules of cationic surfactants, such as dodecyl ammonium chloride and 1-hexadecyl ammonium bromide.^{19,20} Although the surface activity of the clay can be modified with these surfactants, no strong interaction between the clay and bulk polymer can take place because short molecular chains are difficult to form, entangling with polymeric macromolecules. However, macromolecular intercalating agents can enhance interfacial activity and interfacial adhesion between the clay and bulk polymer simultaneously.²¹

In this investigation, we synthesized a series of amphiphilic block copolymers {poly(styrene-*b*-ethylene oxide) [P(S-*b*-EO)]} as macromolecular intercalating agents. Poly(ethylene oxide) (PEO) block chains replaced the weakly adsorbed water, which filled in the space between hydrated exchangeable cations. The amount of the intercalating agent adsorbed onto the clay was mainly controlled by the layer charge density (i.e., the surface area covered by the hydrated cations vs the surface area covered by weakly adsorbed water).^{22,23}

Acrylonitrile-butadiene-styrene resin (ABS) is a widely used engineering plastic because it is inexpensive and has comprehensive properties. However, improving its mechanical and thermal properties is a permanent theme for researchers. In this work, a poly-

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TABLE I
Characterization of the P(S-*b*-EO) Copolymers

Sample	Composition (wt %)		$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
	Styrene	EO			
SbEO1	30	70	5.54	6.68	1.2
SbEO2	40	60	10.28	12.56	1.22
SbEO3	30	70	7.13	8.5	1.19

M_n = number-average molecular weight; M_w = weight-average molecular weight.

(styrene-*b*-ethylene oxide)/sodium montmorillonite (SbEO–MMT) hybrid was investigated as a reinforcement filler for ABS.

EXPERIMENTAL

Materials

ABS (PA-747) was obtained from Chi Mei Corp. (Taiwan, China). Sodium montmorillonite (MMT) was supplied by Liu Fang Zi Clay Co. (Jilin, China). The cation-exchange capacity of MMT was 90 mequiv/100 g.

Preparation of the amphiphilic block copolymers

P(S-*b*-EO) was synthesized via sequential anionic copolymerization. All reagents were strictly purified before use. Dry tetrahydrofuran (THF) and styrene were added to a 500-mL capped bottle. The bottle was purged with high-purity nitrogen (99.999%) and degassed for 0.5 h. The solution was cooled to -78°C with an ethanol/liquid-nitrogen bath. Diphenyl methyl potassium in THF was then added. The fresh red solution was agitated and maintained at -78°C . After the reaction had proceeded for 0.5 h, purified ethylene oxide, twice distilled in the presence of CaH_2 , was added. The temperature of the reactor was then slowly increased from -78 to 35°C (ca. 1 h). The color changed from deep red to light yellow-green. The solution was agitated to maintain the temperature at 35°C for 24 h. The reaction was quenched with acidified methanol, and the solution was poured into a large excess of petroleum ether at a low temperature (ca. -10°C). The precipitate was filtered, washed and then dried *in vacuo*. The product was extracted successively with cyclohexane and water. The final copolymer was characterized with gel permeation chromatography and $^1\text{H-NMR}$. The results are shown in Table I.

Preparation of P(S-*b*-EO)-intercalated MMT

MMT with P(S-*b*-EO) was mixed with a mortar and pressed in a mold on a hot press at 120°C for 1 h and 15 MPa; it was then cooled to the ambient temperature in air. The intercalated SbEO–MMT hybrid was

treated for 24 h at 80°C in a vacuum oven. Finally, it was porphyzied into powder with a crusher.

Preparation of the ABS/P(S-*b*-EO)-intercalated MMT nanocomposites

ABS and P(S-*b*-EO)-intercalated MMT were dried at 40°C for 4 h *in vacuo* before use. ABS and various amounts of P(S-*b*-EO)-intercalated MMT were dry-mixed and melt-blended at 200°C for 5 min with an internal mixer system. Then, the samples of the ABS/layered-silicate nanocomposite were compression-molded at 180°C and 15 MPa for measurements of the mechanical and thermal properties.

Instrumentation

X-ray diffraction (XRD) measurements were collected on a Rigaku Dmax-3A (Japan) diffractometer with $\text{Cu K}\alpha$ radiation (40 kV and 100 mA). The scanning speed was $1^\circ/\text{min}$. Powdered char samples were ground to a particle size of less than $37 \mu\text{m}$.

The samples for transmission electron microscopy (TEM) were also prepared in a compression mold. The resulting samples were ultrathin-sectioned with a microtome equipped with a diamond knife. The sections were about 60 nm thick, and TEM micrographs were obtained with a Philips EM-400-ST (Holland) apparatus running at an acceleration voltage of 100 kV.

The tensile properties of the ABS/layered-silicate nanocomposite were measured according to the specifications of ASTM D 1708 at a crosshead speed of 20 mm/min with a Testometric (United Kingdom) M500-10AX tester.

Thermogravimetric analysis (TGA) was performed with a Netzsch TG209 (Germany) instrument under a nitrogen atmosphere. A heating rate of $10^\circ\text{C}/\text{min}$ was used.

RESULTS AND DISCUSSION

To obtain high-performance organic–inorganic hybrid materials, we must achieve significant improvements in the interfacial adhesion between the polymer matrix and the reinforcing material because the organic polymer matrix is relatively incompatible with the inorganic phase. Generally, better interfacial bonding will impart better properties, such as high modulus and high tensile strength, to a polymer composite.

For the good dispersion of hydrophilic MMT in ABS, sodium ions on its surface should be exchanged with organic cations through an ion-exchange process to render the surface hydrophobic. Thus, the hydrophobic environment in the clay galleries can accommodate the hydrophobic ABS matrix. In this study, amphiphilic P(S-*b*-EO) (Table I) has been studied for the surface modification of MMT for the preparation

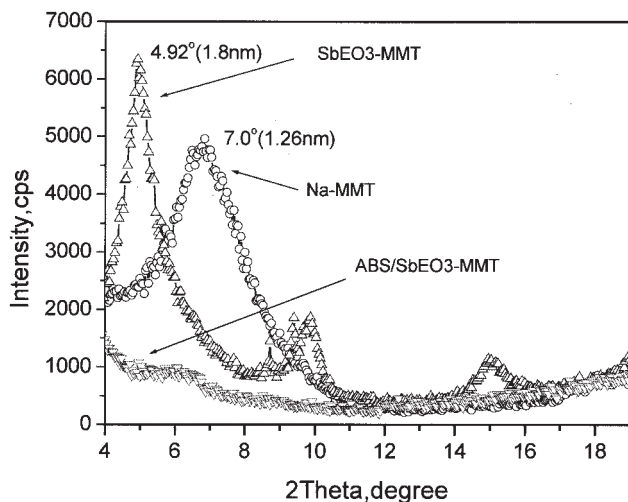


Figure 1 XRD patterns of montmorillonite clay, its P(S-*b*-EO)-intercalated form, and their nanocomposite with a 5 wt % loading of the modified clay.

of organic MMT. The diffraction patterns and data for MMT and organic MMT intercalated with different P(S-*b*-EO) samples are presented in Figure 1 and Table II.

The 001 basal reflections for the original MMT are at $2\theta = 7.0^\circ$, and the corresponding d_{001} value is 1.26 nm; for the P(S-*b*-EO)-intercalated samples, the reflections are at $2\theta = 4.92^\circ$, and the corresponding d_{001} value is about 1.8 nm, which represents an increase of approximately 0.6 nm. There are no obvious reflections for the modified ABS composites below $2\theta = 18^\circ$, and this implies that there is some exfoliation of the intercalated clay in the composites. That is, to some extent, some disorder and loss of structural regularity of the clay layers exist, and this makes the clay layers disperse well in the ABS matrix.

The influence of the molecular weight of the block copolymers on the intercalating effect has also been examined. Figure 2 shows that there are no obvious differences in the 001 basal reflections of SbEO2 and SbEO3, and for SbEO1, the d_{001} value only slightly increases. This indicates that the molecular size in this range of molecular weights has no distinct effect on the intercalation process.

TABLE II
XRD Data of Pristine MMT and MMT Intercalated with different P(S-*b*-EO) Copolymers

Sample	2θ ($^\circ$)	d_{001} (nm)
Pristine MMT	7.0	1.26
SbEO1-MMT (1/2 w/w)	4.84	1.82
SbEO2-MMT (1/2 w/w)	4.92	1.79
SbEO3-MMT (1/2 w/w)	4.92	1.79
SbEO3-MMT (1/1 w/w)	4.86	1.81

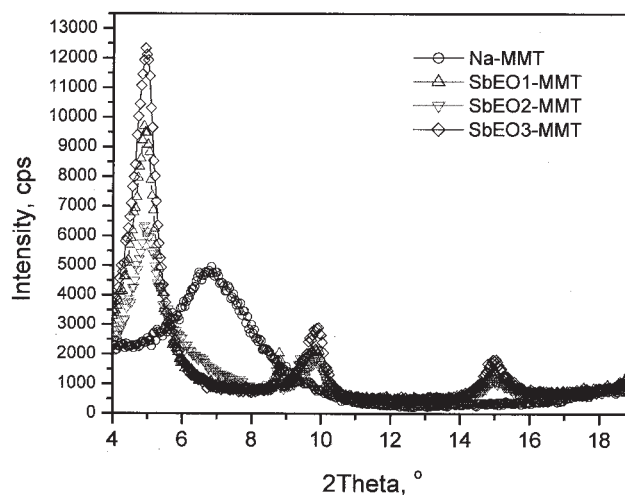


Figure 2 XRD patterns of montmorillonite clay and its forms intercalated with different P(S-*b*-EO) block copolymers.

Morphology

The modification of montmorillonite is mainly used to create a desired morphology for nanocomposites and consequently results in enhanced properties for polymer nanocomposites. Intercalated structures are self-assembled, well-ordered, multilayered structures in which the extended polymer chains are inserted into the gallery space between individual, parallel silicate layers. In the exfoliated cases, the interlayer spacing can be on the order of the radius of gyration of the polymers; therefore, the silicate layers may be considered to be well dispersed in the organic polymer. Both of these hybrid structures can also coexist in the polymer matrix; this mixed nanomorphology is very common for composites based on smectite silicates and clay minerals.

A TEM image of the cross section from the ABS/SbEO3-MMT composite (5 wt %) is shown in Figure 3. The composite has individual silicate layers with a mixture of nanomorphologies, along with multilayer stacks. SbEO3-MMT is dispersed well in the polymer matrix.

This strong interaction possibly comes from the strong hydrogen bonds between the layered silicate and PEO block chain segments, which make P(S-*b*-EO) adhere to the interlayer and act as an intercalating agent.

Mechanical properties

The tensile strength and tensile modulus of pristine ABS are 38.4 MPa and 1.37 GPa, respectively. There are no obvious reductions in the tensile strength of ABS/P(S-*b*-EO) when the concentration of P(S-*b*-EO) is less than 3 wt %. The tensile mechanical properties of

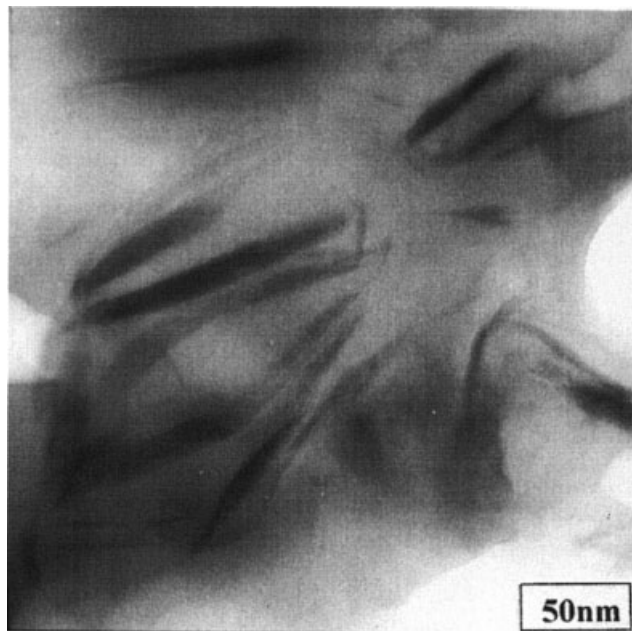


Figure 3 TEM micrograph of nanocomposites containing a 5 wt % loading of the modified montmorillonite (SbEO3-MMT, 1/2 w/w).

these nanocomposites and the corresponding results for pristine ABS are given in Figures 4 and 5. The tensile strength increases by approximately 16% in the modified ABS when the concentration of SbEO3-MMT is 2 wt %. Young's modulus of ABS/SbEO3-MMT (5 wt %) is higher than that of pristine ABS. Thus, the tensile strength measurements reveal that the effect of the clay is more pronounced on the tensile strength and Young's modulus. The obvious increase in the tensile modulus reflects the reinforcement effect attained by the dispersion of the clay nanolayer into

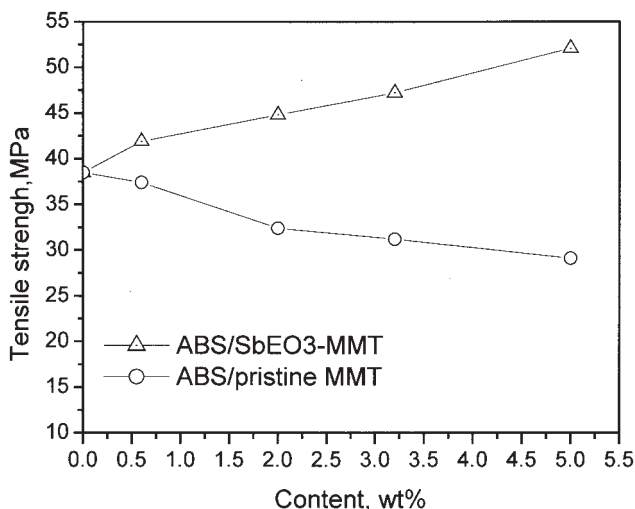


Figure 4 Tensile strength of ABS/SbEO3-MMT (1/2 w/w) and ABS/pristine MMT composites.

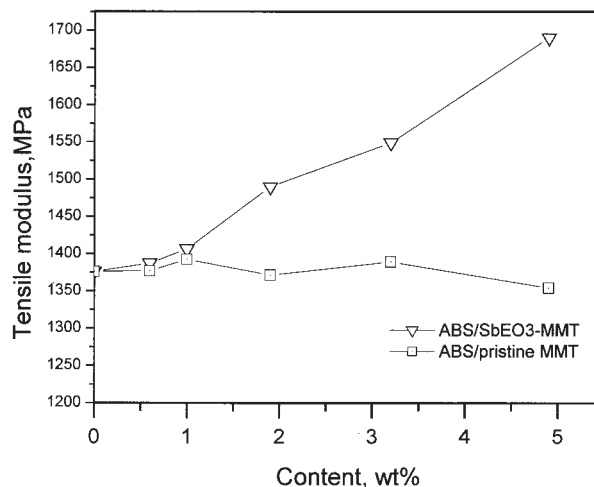


Figure 5 Tensile modulus of ABS/SbEO3-MMT (1/2 w/w) and ABS/pristine MMT composites.

the ABS matrix. The increase in Young's modulus of the ABS/SbEO3-MMT composites can mainly be attributed to the stiffness of the silicate, but the extent of the increase depends on the bonding between the layered silicates and ABS matrix. In addition, the results indicate that both the tensile strength and tensile modulus of the ABS/SbEO3-MMT nanocomposites are higher than those of ABS/pristine MMT blends (Figs. 4 and 5).

Thermal properties

The thermal properties of the ABS/SbEO3-MMT nanocomposites (Fig. 6) have been examined with TGA. Figure 6 shows that the thermal stability increases with the SbEO3-MMT loading. The temperatures at a 5% weight loss are shown in Figure 7, which indicates that the thermal stability of ABS/SbEO3-

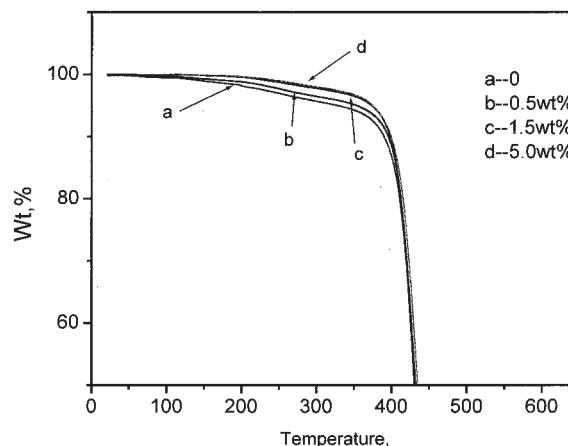


Figure 6 TGA of ABS/SbEO3-MMT (1/2 w/w) nanocomposites and pristine ABS.

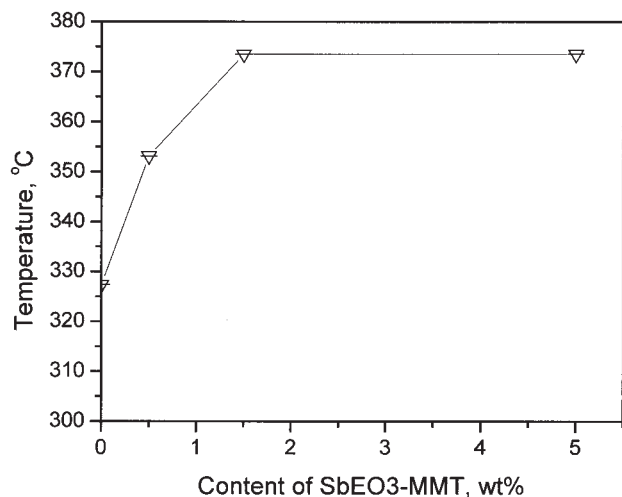


Figure 7 Temperatures at 5% weight loss for ABS/SbEO3-MMT (1/2 w/w) nanocomposites.

MMT is enhanced by the incorporation of 5 wt % SbEO3-MMT into ABS. The 5 wt % decomposition temperature is about 10°C higher than that of the corresponding pristine ABS. The reason may be the homogeneous distribution of the silicate sheets, which increases the total path of the volatile gases out of the composite in comparison with pristine ABS.

CONCLUSIONS

Amphiphilic P(S-*b*-EO) block copolymers have been synthesized as macromolecular intercalated agents for layered silicates. XRD results indicate that amphiphilic P(S-*b*-EO) has an obvious intercalating effect on layered silicates.

The measurements of the mechanical properties indicate that intercalated silicate can effectively improve

the properties of ABS, such as the tensile strength, Young's modulus, and thermal stability.

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