

Preparation and Dynamic Mechanical Properties of Poly(styrene-*b*-butadiene)-Modified Clay Nanocomposites

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ABSTRACT: Polybutyl acrylate (PBA) was intercalated into clay by the method of multistep exchange reactions and diffusion polymerization. The clay interlayer surface is modified, and obtaining the modified clay. The structures of the clay-PBA, clay-GA (glutamic acid), and the clay-DMSO (dimethyl sulfoxide) were characterized using X-ray diffraction (XRD). The new hybrid nanocomposite thermoplastic elastomers were prepared by the clay-PBA with poly(styrene-*b*-butadiene) block copolymer (SBS) through direct melt intercalation. The dynamic mechanical analysis (DMA) curves of the SBS/modified clay nanocomposites show that partial polystyrene segments of the SBS have intercalated into the modified clay interlayer and exhibited a new glass transition at about 157°C (T_{g3}). The glass transition temperature of polybutadiene segments (T_{g1}) and polystyrene segments out of the modified clay interlayer (T_{g2}) are about -76 and 94°C, respectively, compared with about -79 and 100°C of the neat SBS, and they are basically unchanged. The T_{g2} intensity of the SBS-modified clay decreases with increasing the amounts of the modified clay, and the T_{g3} intensity of the SBS-modified clay decreases with increasing the amounts of the modified clay up to about 8.0 wt %. When the contents of the modified clay are less than about 8.0 wt %, the SBS-modified clay nanocomposites are homogeneous and transparent. The T_{gb} and T_{gs} of the SBS-clay (mass ratio = 98.0/2.0) are -78.39 and 98.29°C, respectively. This result shows that the unmodified clay does not essentially affect the T_{gb} and T_{gs} of the SBS, and no interactions occur between the SBS and the unmodified clay. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1499–1503, 2002; DOI 10.1002/app.10353

Key words: SBS; clay; intercalate; nanocomposites

INTRODUCTION

The poly(styrene-butadiene-styrene) copolymer (SBS) is a type synthetic polymeric material that

was developed at the beginning of the 1960s. SBS thermoplastic elastomers (TPE) exhibit the characteristic of plastic and rubber, and include a good resistant to low temperature, good permeability, elongation percentage, and outstanding elasticity. There are four major TPE materials of commercial importance, each consisting of hard blocks (crystalline or glassy) coupled to rubbery soft blocks: polyamide/elastomer, polyurethane/elastomer, polyester/elastomer, and polyamide/

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elastomer. The former is a simple triblock, while the latter three are made up of segmented multiblocks of the indicated constituents.¹ A key attribute of most TPEs is the ability to tailor toughness and large strain elasticity by varying the ratio of hard/soft fractions, so the TPEs have been used in many fields.

Hybrid organic–inorganic composites typically exhibit mechanical properties superior to those of their separate components, because they combine the structure and physical properties of both inorganic host material and the organic guest at a nanometer scale, so many polymer–silicate nanocomposites can be synthesized by direct melt intercalation even with high molecular weight polymers.^{2–10} Because nonpolar polystyrene can be intercalated into modified layered silicate, and the thermal properties of the polystyrene may be increased greatly,^{11–14} we consider that the PS chain segments of the poly(styrene–butadiene–styrene) copolymers (SBS) can be intercalated into modified layered silicate by a melt-blended method, and SBS will acquire unprecedented properties, but little work on SBS–silicate nanocomposites has been reported.^{5,15,16}

In this article, we successfully synthesized a polyacrylate/nature clay (mixture of kaolinite and muscoite) by multistep exchange reactions and a diffusion polymerization method.⁴ The SBS-modified clay nanocomposites have been prepared using melt blending. Here, we mainly study the dynamic mechanical property.

EXPERIMENTAL

Materials

The clay used in this study was from Yinhua, Guangdong. Purification was carried out by a sedimentation method, and possible phases of the clay were examined by the XRD technique; diffraction peaks of the phases were determined by the fingerprint method. The chemical composition of the clay is 32.75% Si, 5.3% Al, 0.46% Fe, 0.35% Ca, and 0.24% Mg, which was determined by atomic absorption spectrometry. The SBS copolymer was supplied by Yueyang Petrochemical Corporation, China and is characterized by a number-average molar mass $M_n = 70,000 \text{ g mol}^{-1}$; the polystyrene block percentage is about 30% by weight. DMSO, GA, and BA were commercially available.

Nanocomposites Preparation

The preparation of clay–PBA hybrids was carried out via a three-step process. First, 30 g clay and 100 mL DMSO were placed in a 250-mL vessel and stirred with a magnetic stirrer at 80°C for 24 h. The product was filtered and dried in vacuum at 50°C and crushed in a mortar. Then a clay–DMSO composite was obtained. Then GA 6 g, 6 mL of concentrated hydrochloric acid and 100 mL water were added in a 250-mL vessel, heated, and made the GA dissolve completely. Then 30 g clay–DMSO and 100 mL water were added to the mixture, stirred with a magnetic stirrer at 80°C for 12 h. The product was filtered, washed three times with 100 mL hot water, freeze dried, and dried in vacuum at 50°C, and crushed in a mortar. A clay–DMSO composite was obtained. Finally, a 500-mL three-necked separable flask coupled with a mechanical stirrer was used as the reaction vessel. In this vessel, 30 g of clay–GA, 13.5 mL of BA, 0.1 g of benzoyl peroxide (BPO), and 150 mL of toluene were mixed and stirred at 30°C for 48 h, then the condensation condenser and nitrogen pipe were connected, the mixture was heated in an oil bath at 60°C for 1 h, 70°C for 1 h, 80°C for 3 h, and 100°C for 3 h. At the end of reaction, the product was filtered, washed three times with toluene, dried in vacuum at 80°C, and crushed in a mortar. A clay–PBA hybrid materials were obtained.

SBS/modified clay nanocomposites were prepared by melt blending on a two-roll mill at 160°C, the total amount of SBS and clay–PBA was 100 g for all the preparations, but the amount of clay–PBA was 0, 0.5, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0, and 10.0 g, respectively. The preparation condition was followed, and mixing was continued for 10 min on a two-roll mill at 160°C; the compression molded was preheat for 4 min in an electric-heat curing press at 4 MPa and 170–175°C, heat pressed for 4 min at 15 MPa, and cold pressed for 10 min at 15 MPa. The preparation condition of the SBS/clay was the same for contrast.

Characterization

An X-ray diffraction measurement on the power samples were performed using the D/MAX-III power diffractometer equipped with Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$). Dynamic mechanical analysis (DMA) was carried out on a TA Instruments DMA-2980 with a double cantilever geometry at the frequency of 10 Hz and at the heating rate of 3°C/min from –130–180°C.

RESULTS AND DISCUSSION

Figure 1(a), (b), (c), and (d) are the X-ray diffraction patterns of the clay, clay-DMSO, clay-GA, and clay-PBA, respectively. The results show that the peaks of 7.162, 4.350, and 3.579 Å of kaolinite disappear completely after reaction of the clay with DMSO, and diffraction intensity of the muscovite decreases, the new peaks of 11.232 and 3.994 Å are observed, and diffraction intensity of 11.232 Å is very strong. This result indicates that DMSO is intercalated into the interlayer space of clay, and the clay-DMSO composite is formed. In addition, DMSO is mainly intercalated into the kaolinite phase of the clay.

Figure 1(c) shows that the as group peaks appear (25.545, 23.198, and 20.790 Å) and the peak of 11.232 Å of the clay-DMSO disappear, DMSO in the interlayer of the clay is displaced by GA, and the gallery height increases, forming the clay-GA composite.

With BA diffused and polymerized in the clay-GA composite, forming the clay-PBA composite, the peaks of 25.546, 23.198, and 20.790 Å are replaced by 15.494 and 14.029 Å; on the contrary, the gallery heights of the clay decrease.

Why the gallery height of the clay-PBA decreases and the clay-GA and clay-PBA have multipeaks is unknown. We consider that the structure of GA contains two carboxyl groups (—COOH) and an amino group (amino acid). The hydrogen bond may form intermolecularly, and a crosslinking acrylamide may happen during heating, and because the degrees of polymerization of

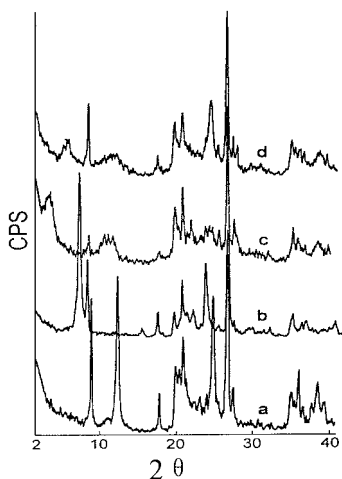


Figure 1 X-ray diffraction patterns of (a) the clay, (b) the clay-DMSO; (c) the clay-GA; and (d) the clay-PBA.

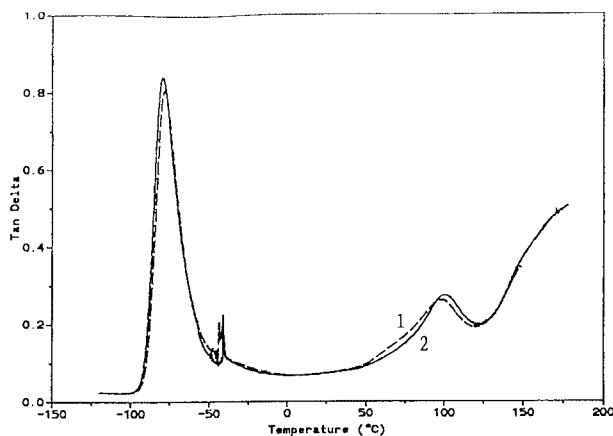


Figure 2 DMA curves of (1) for #1 and (2) for #10.

the PBA are different, the clay-GA and clay-PBA composites have multipeaks. Depending on the packing density, temperature, and chain length, the chains are thought to lie either parallel to the host layers forming lateral mono- or bilayers, or radiate away from the surface form extended (paraffin-type) mono- or bimolecular arrangement.¹⁷ In some cases, individual chains are thought to adopt a hybrid arrangement with both lateral and paraffin-type segments, leading to a pseudotrilinear. We consider that the chains of GA are thought to lie in a bimolecular arrangement (paraffin-type) in the clay interlayer, but the chains of PBA are thought to lie in a monomolecular arrangement (paraffin-type), so the gallery height of the clay-GA is higher than of the clay-PBA.

Because SBS has a character of a two microdomain structure, so polystyrene (PS) and polybutadiene (PB) chain segments retain the respective part of the physical properties. For example, for the glass transition temperature, SBS has two the glass transition temperatures. Figures 2 and 3 are DMA curves of the #1, #2, #4, #5, and #10 sample.

Figure 2 indicates that the glass transition temperature of the polybutadiene segment (T_{gb}) and the polystyrene segment (T_{gs}) of neat SBS are -79.73 and 100.62°C , respectively, and the T_{gb} and T_{gs} of the SBS/clay (mass ratio = 98.0/2.0) are -78.39 and 98.29°C , respectively. This result shows that the unmodified clay does not essentially affect the T_{gb} and T_{gs} of the SBS, and no interactions occur between the SBS and the unmodified clay.

In contrast, Figure 3 shows that there are three the glass transition temperatures in the

SBS/PBA–clay (modified clay) systems; the position of the T_{g_b} does not essentially change, but the intensity of the T_{g_2} decreases with increasing the amounts of the modified clay, and there is a new glass transition temperature (T_{g_3}) at about 157°C. The intensity of the T_{g_3} increases with increasing the amounts of the modified clay. This result indicates that the polystyrene segment of the SBS have reacted with the modified clay only and intercalated into the interlayer of the modified clay; the thermal property of the SBS/modified clay nanocomposites has been improved.

The SBS thermoplastic elastimers is a triblock copolymer, so if the middle block of polybutadiene segments react with the modified clay and intercalate into the interlayer of the modified clay, the polybutadiene segments must be loop conformations, but the polystyrene segments may be line conformations. In accordance with the interlayer space size of the modified clay, the polystyrene segments are more easily intercalated into the modified clay interlayer than the polybutadiene segments. We consider that the modified clay (or the organophilic clay) has a selective localization with the polystyrene segments. It is not only that the PBA (or other long alkyl chain in the ammonium salt), which modifies the surface characteristics of the clay, increases the compatibility between the polystyrene segments and the modified clay. But it is decision for the polystyrene segments conformations in the SBS.

The SBS-modified clay has two glass transitions, which are T_{g_2} (about 98°C) and T_{g_3} (about 157°C), respectively. This result indicates that a part of the polystyrene segments have intercalated into the modified clay interlayer only, as the

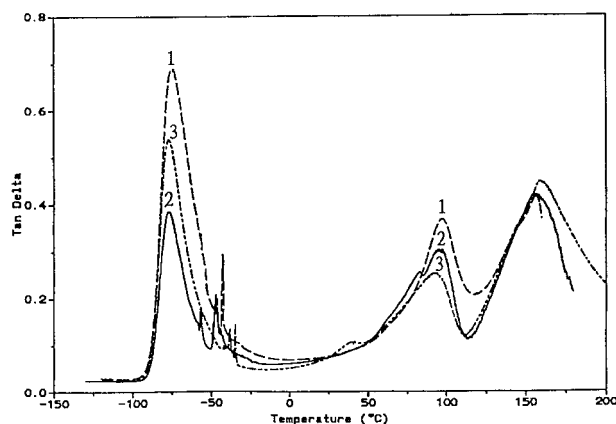


Figure 3 DMA curves for SBS/clay–PBA nanocomposites: (1) for #2, (2) for #4, and (3) for #5.

Table I Component of Every System

No	SBS/Clay-PBA (Mass Ratio)	SBS/Clay (Mass Ratio)
1 [#]	100 : 0	
2 [#]	99.5 : 0.5	
3 [#]	99.0 : 1.0	
4 [#]	98.5 : 1.5	
5 [#]	98.0 : 2.0	
6 [#]	96.0 : 4.0	
7 [#]	94.0 : 6.0	
8 [#]	92.0 : 8.0	
9 [#]	90.0 : 10.0	
10 [#]		98.0:2.0

intercalated polystyrene segments must establish numerous segment–host contacts to offset the large decrease in conformational energy that opposes intercalation. These interactions severely impede the rotational and translational motions of the polymer. The physical picture is analogous to chemical crosslinks in bulk polymers, which have the effect of increasing the glass transition. As the density of crosslinks, or polymer–host interactions in this case, increases, the transition is broadened, and it may not occur at all in highly crosslinks materials. The confined polymer is thus expected to exhibit dimensional stability and resist flow even at temperatures above the corresponding glass transition of the bulk polymer (or microdomain structure polymers, such as SBS). So the glass transition of the polystyrene segments increases to about 157°C in the clay interlayer, but the glass transition of the polystyrene segments is basically retained in the clay interlayer.

When the modified clay contents are less than 8.0wt %, the SBS/modified clay nanocomposites are homogeneous and transparent. But when the modified clay contents are in excess of 10.0 wt %, the modified clay evidently gathers in the SBS-modified clay nanocomposites. These results show that the contents of intercalated into the modified clay do not increase with the modified clay increase. The mechanical properties of the SBS-modified clay nanocomposites also show that the breaking strength, breaking elongation, 300% elongation modulus, and 500% elongation modulus increase as the contents of the modified clay increase up to about 6.0 wt %, ⁶ corresponding to the above results.

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