

Arranged Microdomain Structures Induced by Clay Silicate Layers in Block Copolymer-Clay Nanocomposites

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Summary

We propose a novel scheme for controlling the nanostructures of organic polymer materials by using nanoparticles as templates and we also demonstrate a spontaneous formation of arranged microdomain structures in block copolymers controlled by clay silicate layers dispersed at the nanometer level. Block copolymer-layered silicate nanocomposites were prepared by melt compounding of hydrogenated styrene-butadiene-styrene triblock copolymer with organophilic layered silicates intercalated with stearylammonium. Their morphologies were observed by transmission electron microscopy. The triblock copolymer microdomain structures were found to be arranged along the dispersed silicate layers. Such structures did not exist in the original block copolymer. TEM images suggest that the formation of the arranged microdomain structures are induced and controlled by the interaction of the silicate layers, which act as templates. It is thought that these controlled nanostructures were formed through the selective absorption of the polystyrene segments on dispersed silicate surfaces followed by segregation of each segment.

Introduction

Nanostructure control in organic polymers is of great importance for many technological applications, such as optical, electrical, biochemical fields. Various types of nanocomposite systems based on organic polymers and inorganic nanoparticles, i.e. metals, ceramics, have been reported [1-10]. These nanocomposites, with only a few percent nanoparticle loading, have a large amount of interfaces between the organic polymer and the nanoparticle. It is known that organic polymers at the interfaces or surfaces often have specific structures, which are different from those of polymer bulk [11]. In this paper we propose a novel scheme for controlling nanostructures in organic polymers through the interactions induced by the nanoparticle interfaces.

Some of the most promising nanocomposite systems are based on organic polymers and inorganic clay minerals consisting of silicate layers [5-10]. It is well known that the silicate layers modified with alkylammonium salt are uniformly dispersed in

organic polymers at the nanometer level. Montmorillonite is one of the most widely used clay minerals for preparing polymer-clay nanocomposites. The individual montmorillonite silicate layer $[\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{O})_2]$ consists of two silicate tetrahedral sheets sandwiching an aluminum hydroxide octahedral sheet. It is approximately 1nm thick and 200nm in length.

Block copolymers are composed of two or more chemically distinct segments and known to form various kinds of the microdomain structures owing to segregation of their different segments [11]. The microdomain structures of block copolymers are usually determined by the molecular structure species, contents and block types, i.e., A-B, A-B-A. In this paper, we demonstrate the spontaneous formation of ordered microdomain structures in block copolymers induced by silicate layers.

Experiment

Materials

The materials used for the preparation of the samples are purified sodium montmorillonite (Kunipia-F) from Kunimine Ind. Co., stearylamine from Wako Pure Chemical Co., hydrogenated styrene-butadiene-styrene copolymer (SEBS, TaftecTM H1030) from Asahi Chemical Co. SEBS is A-B-A type triblock copolymer consisting of 30Wt% polystyrene (PS) segments and 70Wt% hydrogenated polybutadiene (PEB) segment. These materials were used without further purifications.

Organophilic clay

Organophilic montmorillonite was prepared as follows. Sodium montmorillonite (80 g, cation exchange capacity: 119 meq / 100 g) was dispersed into 5000 mL of hot water (about 80°C) using a homogenizer. Stearylamine (31.1 g, 115 mmol) and conc.HCl (11.5 mL) were dissolved into hot water, which was poured into the montmorillonite-water solution under vigorous stirring using a homogenizer for 5 minutes, producing a white precipitate. The precipitate was collected and washed with hot water three times, and freeze-dried to yield an organophilic montmorillonite intercalated with stearylammunium. It is termed C18-Mt. The inorganic content was 69.2Wt% by measuring the weights before and after burning its organic component. The interlayer spacing of C18-Mt was 2.20 nm measured by X-ray diffraction (XRD) methods.

Preparation of nanocomposites

SEBS-clay nanocomposite (SEBS-CN) samples were prepared by melt-compounding SEBS pellets with C18-Mt powder using a twin-screw extruder at 210-240°C. The twin-screw extruder was a TEX30 α -45.5BW from Japan Steel Works LTD. Its screw length was 1365 mm and its L/D was 45.5. The obtained strands were pelletized and dried under vacuum at 60°C. The inorganic content of the sample was 5.0Wt% by measuring the weights before and after burning its organic component. The films used for evaluation were prepared by compression molding using a hot press. The samples were preheated to 250°C for 3 minutes, pressed at 250°C for 1 minute and cooled to ambient temperature. The films were 0.4-0.6 mm thick.

Characterization

XRD measurements were performed on the compression molded films using a Rigaku RAD-B diffractometer with Cu-K α radiation generated at 30 kV and 30 mA. Small angle X-ray scattering (SAXS) measurements were performed on the films using a Rigaku Ultrax-18 with Cu-K α radiation generated at 40 kV and 250 mA. Transmission electron microscopy (TEM) observations were performed using ultra thin sections of films stained with RuO $_4$. TEM observations were taken by Jeol-2000EX TEM using an acceleration voltage of 200 kV.

Results and Discussions

Figure 1 shows the TEM images of SEBS and SEBS-CN. There are apparently no ordered microdomain structures observed in SEBS shown in Figure 1a. Figure 1b-d are TEM images of the SEBS-CN in which arranged microdomain structures around the dispersed silicate layers are clearly observed. The microdomain structures consisting of PS layers and PEB layers were found to be alternatively arranged along the silicate layers. The shapes of the ordered structures were dependent on the shapes of the silicate layers. The straight-layered structures of the microdomain were formed on the straight silicate layers, while the curved layered structures were formed on the curved silicate layers (Figure 1d). These facts suggest that the formation of the arranged microdomain structures were induced and controlled by the interaction of the silicate layers acting as templates. Around the isolated silicate layers, it was observed that there were 10 layers of alternatively stacked segments (Figure 1c). The interactions of these silicate layers were extended to 150 nm in the block copolymer. Observing the arranged structures in detail, the PS layers consisted of dots and/or lines in the PS domains. These layered structures are formed two-dimensionally on the silicate layers. Figure 2 is a TEM image of a larger area on the SEBS-CN. The layered structures were observed around most of the dispersed silicate layers. There are 3-10 layers of PS domains stacked on the silicate layers. Silva et. al., reported silicate layer template effects in nanocomposites which consisted of SEBS, SEB and organophilic montmorillonite [10]. In their work, they mentioned that cylindrical and spherical microdomains are arranging on the silicate layers as observed by TEM, but there were apparently no multi-layered microdomain structures along the silicate layers.

Figure 3 shows the SAXS patterns of SEBS and SEBS-CN, where $q=4\pi\sin\theta/\lambda$ ($\lambda=0.1541\text{nm}$). The SAXS pattern of SEBS has an apparent peak at $q=0.36\text{ nm}^{-1}$, while that of SEBS-CN showed an apparent peak at $q=0.32\text{ nm}^{-1}$. This indicates that SEBS-CN consists mainly of different microdomain structures from those of SEBS.

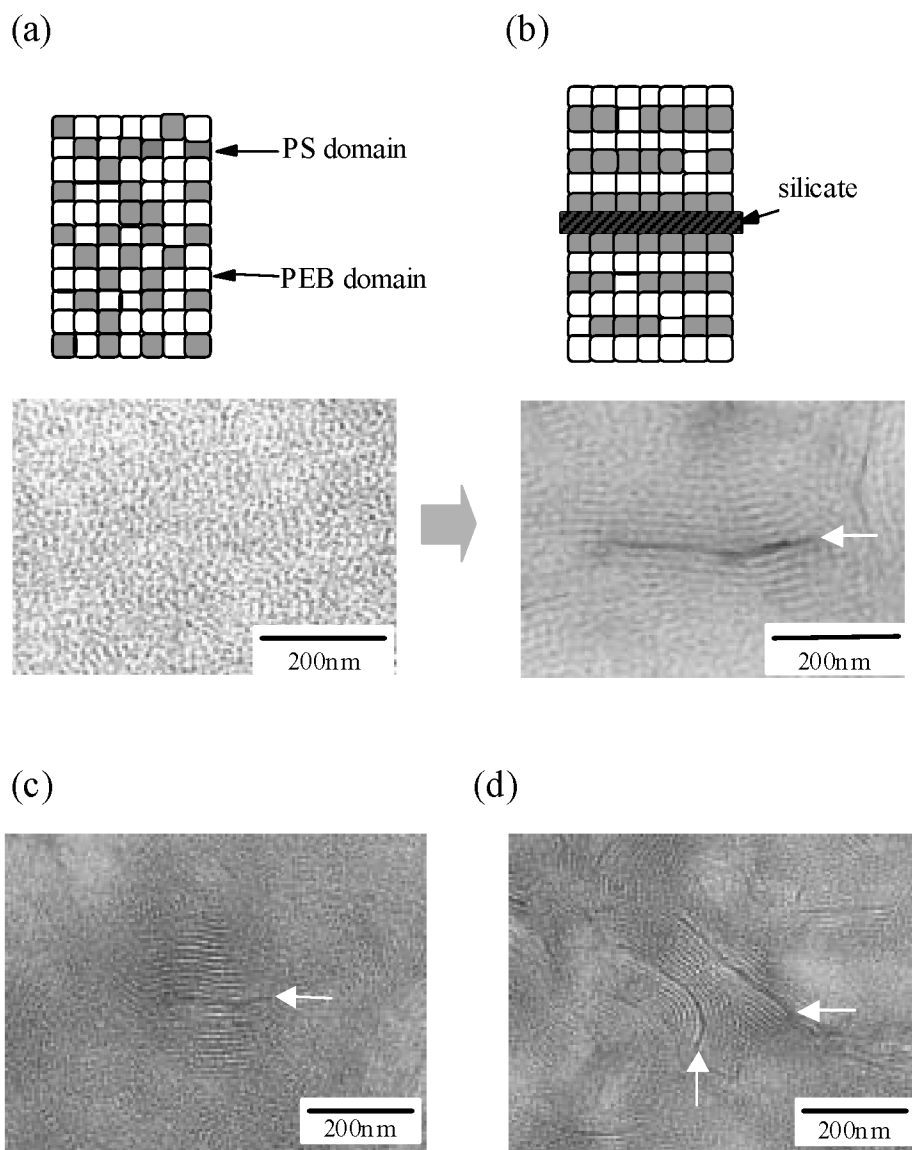


Figure 1. TEM images of SEBS-CN and SEBS stained with RuO_4 . White arrows in the figures indicate silicate layers. (a) SEBS contains the gray regions which correspond to segregated microdomains of polystyrene segments stained with RuO_4 and the lighter regions which correspond to hydrogenated polybutadiene segments. (b) SEBS-CN has ordered microdomain structures arranged along the silicate layers. The black lines are the cross sections of the silicate layers. (c) Ordered structures around an isolated silicate sheet. (d) Ordered structures along the straight and curved silicate layers.

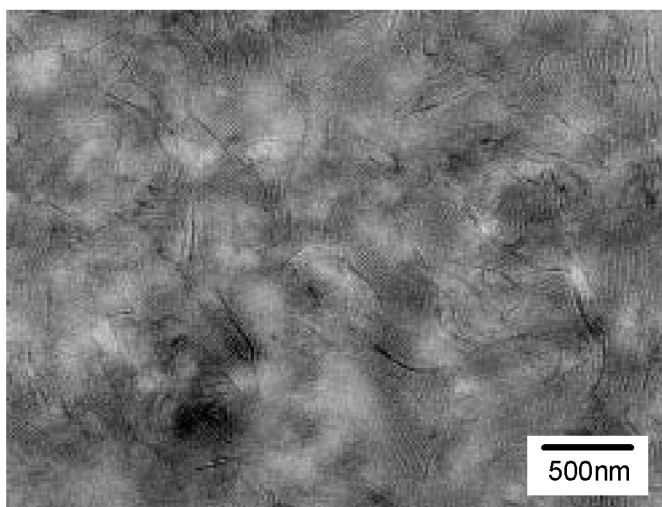


Figure 2. TEM image of a larger area of SEBS-CN.

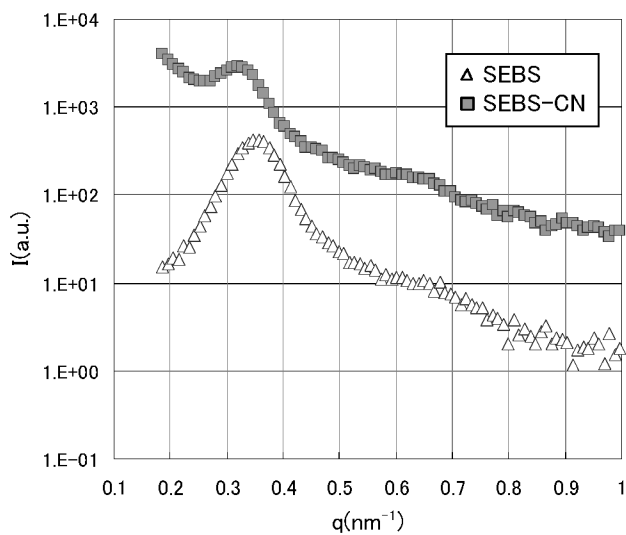


Figure 3. SAXS patterns of SEBS and SEBS-CN.

Silicate layers are homogeneously dispersed in SEBS-CN. The silicate layers are typically 2-5 layers stacked together but there are also some individual silicate layers present. The interlayer spacing between the silicate layers was determined by XRD measurements which show that the 2θ value has shifted from 4.02° to 2.70° in C18-Mt to SEBS-CN as shown in Figure 4. This corresponds from a 2.20 nm to a 3.3 nm expansion between the silicate layers. Thus it indicated that the SEBS polymer chains intercalated into the galleries of stacked silicate layers.

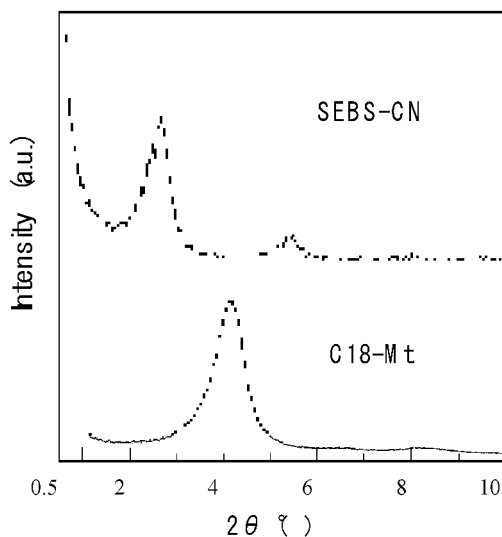


Figure 4. X-ray spectrum of SEBS-CN and C18-Mt.

The structure evolution of this system is schematically depicted in Figure 5. The PS segments first, selectively absorb on the silicate surfaces and then form PS domains on the silicate surfaces [12]. This is supported by the gray PS regions stained with RuO_4 existing around the silicate layers as shown in the TEM images. Following the PS domain absorption, the regions of PEB segments connected with PS segments arranges on the initial PS regions. Then, another PS segment forms the dots or plates of PS regions arranged along the silicate layers. Such segregations continuously occur and the controlled stacking-microdomain structures are formed along the silicate layers. It is thought that this phenomenon occurs by both selective absorption on the silicate layers and spontaneous segregation by the block copolymer.

Conclusions

We demonstrated the control of the block copolymer microdomain structures induced by the silicate layers. In SEBS-CN, the microdomain structures of the SEBS were found to be arranged along the silicate layers acting templates. It is thought that the controlled microdomain structures were formed through the selective absorption of the

PS segments on the dispersed silicate surfaces followed by the segregation of each segment. Further studies to analyze these high-ordered microdomain structures of this nanocomposite is in progress.

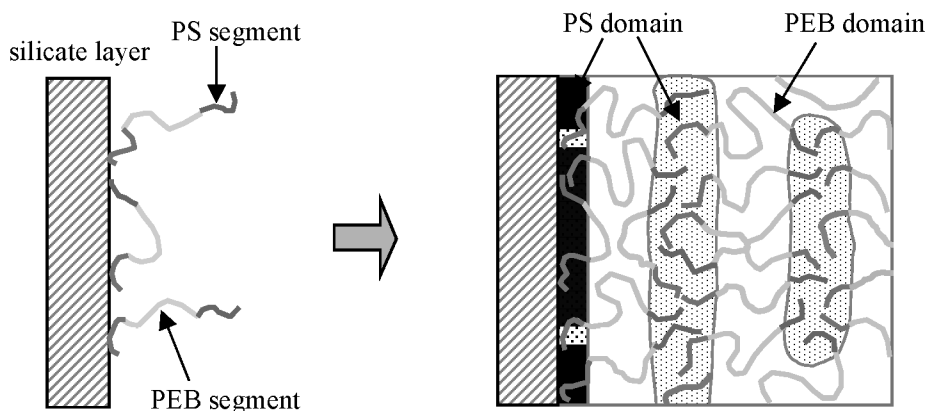


Figure 5. Schematic representations showing structural evolution on the silicate layer. (a) Initial selective absorption of the PS segment on the silicate surface. (b) Segregation of the SEBS controlled by the silicate layer.

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- It suggested that PS segments have better affinity for the silicate layer surfaces compared to PEB segments, because polystyrene intercalates into the galleries of the C18-Mt [13] and polyolefins such as polyethylene, polypropylene do not intercalate[9].
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