Korean J. Chem. Eng., **18**(1), 21-25 (2001)

Microstructure and Rheological Behavior of Block Copolymer/Clay Nanocomposites

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(*Received 21 March 2000 • accepted 13 December 2000*)

Abstract−Organic/Inorganic hybrid nanocomposites based on poly(styrene-butadiene-styrene) copolymer (SBS) and clay are fabricated by melt intercalation. The degree of intercalation is dependent on the surface properties of clay and SBS. The epoxized block in epoxized SBS acts as a strong attractive site with the clay surface, which yields the increased interlayer space in the layered silicates. It is also shown that the thermal stability of clay as well as the surface properties is very important in fabricating the polymer/clay nanocomposites. The rheological behavior of the SBS/clay nanocomposites is quite different from that of SBS itself. Both storage moduli and complex viscosity of the SBS/layered silicate nanocomposites increase and show non-terminal flow behavior.

Key words: Block Copolymer, SBS, Epoxidized SBS, Clay, Nanocomposites, Rheology, Non-terminal Behavior

INTRODUCTION

Nanostructured organic-inorganic hybrid composites have attracted considerable attention from both fundamental research and application points of view [Krishnamoorti and Giannelis, 1997; Vaia et al., 1995; Kim et al., 1995; Lyu et al., 1999; Tucker et al., 2000]. The intercalation of polymer melts in mica-type layered silicates has recently been reported as a means to synthesize composite materials consisting of alternating nanometer-thick layers of polymer and ceramic [Krishnamoorti and Giannelis, 1997; Vaia et al., 1993]. The process involves annealing a mixture of polymer and layered silicate powders above the glass transition temperature or melting point of the polymer. By judiciously engineering the polymer-silicate interactions, composites have been produced from a broad range of polymers with varying degrees of polarity and crystallinity such as polystyrene, poly(vinylpyridine), poly(ethylene oxide), polysiloxanes, polyphosphazenes, polyamide, and liquid crystalline copolyesters. As a synthetic approach, polymer melt intercalation is appealing because of its versatility and compatibility with current polymer processing techniques, and its environmentally benign character due to the absence of solvent. Applications of the resulting polymer-layered silicate nanocomposite hybrids range from studying polymer chains in a confined environment to industrial exploitation of novel mechanical and electrical properties resulting from the nanometer periodicity of the constituents.

However, few studies have been reported for block copolymer/layered silicate nanocomposites. Block copolymers made with incompatible blocks form equilibrium domain structures of various types. These structures and their distinctive properties have steadily attracted increasing interest. These copolymers have proven great practical use in improving properties of homopolymer blends and of adhesives [Baek and Han, 1992; Moon et al., 1999]. The use of block copolymers in such applications is affected by their flow properties. Thus, it is very important to understand the relationship of the microstructure and the rheological behavior of block copolymer in various application areas. The flow behaviors with their different microstructure have been investigated by a number of researchers [Wang et al., 1999; Pinherio and Winey, 1998]. Block copolymer/layered silicate nanocomposites can be used to facilitate blending with appropriate homopolymers. It was shown that block or graft copolymers combining one part of the polymer that is identically and/or completely miscible with the organic polymer and another part that is compatible with layered silicate are applied to act as compatibilizer. The examples of such are poly(ethyleneoxide-block-styrene), poly(ethyleneoxide-block-methyl methacrylate) and poly(styrene-block-vinylpyridine) [Fischer et al., 1999].

In this study, a few important results of the block copolymer/layered silicate nanocomposites which can find a useful industrial application will be reported. Commercialized clays with different surface properties are mixed with two different types of SBS to fabricate the nanolayer reinforced block copolymer nanocomposite. The microstructure of each nanocomposite is characterized and then the rheological behavior of the nanocomposites is discussed. The block copolymer/layered silicate nanocomposite has shown anomalous rheological behavior, which is very similar to that other polymer/layered silicate nanocomposites [Lim and Park, 2000].

EXPERIMENTAL

1. Materials

Two types of poly(styrene-block-butadiene-block-styrene) copolymer (hereafter SBS) were used. One is a commercialized poly (styrene-block-butadiene-block-styrene) copolymer (hereafter SBS46, average molecular weight is 180,000) and the other is its epoxidized poly(styrene-block-butadiene-block-styrene) copolymer (hereafter ESBS), which are produced by Daiseru Chemical Corporation. The polystyrene block percentage is about 40% by weight in both SBS and ESBS polymers. ESBS is divided into three samples (ESBS1, ESBS2 and ESBS3) depending on the content of ep-

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oxy group. The content of epoxy based on polybutadiene block is 5 wt%, 10 wt% and 20 wt% in ESBS1, ESBS2 and ESBS3 samples, respectively.

The commercialized organophilic clays (Cloisite 20A and Cloisite 30B) produced by Southern Clay Products were used. The pristine Na^+-Montmorillonite was modified to organophilic by cation exchange reaction with dimethyl dihydrogenated-tallow ammonium ion (hereafter M20A) and methyl tallow bis-2 hydroxyl ethyl ammonium ion (hereafter M30B). The cationic exchange capacity (CEC) of M20A and M30B was found to be 95 meq/100 g and 90 meq/100 g, respectively.

2. Preparation of SBS/Clay Nanocomposites

Each series of SBS nanocomposites were prepared by mixing two types of SBS block copolymers with the organoclay in a Brabender batch mixer. The weight percents of the clay were fixed at 3 and 5 wt% in each composite series. The physically premixed mixture was introduced into the heated mixer at 180 °C. Mixing was maintained for 10 min at a 45 rpm mixing speed. The obtained lumps of the composites were compression molded into test species (20 mm diameter disk with roughly thickness 2 mm) at 180 °C, to be used for X-ray diffraction and rheological measurements.

3. Microstructure

The degree of swelling and the interlayer distance of clay in the nanocomposites were studied by means of wide angle X-ray diffraction. The X-ray diffraction spectra were collected on a Rigaku Inc. θ-θ diffractometer equipped with an intrinsic germanium detector system using Cu-Kα (λ=1.54 Å) radiation at a generator voltage 45 kV and current of 40 mA. The scanning rate is 2^o/min from 1.2^o to 10^o.

4. Rheometry

The rheological properties of each nanocomposite series were measured by ARES (Advanced Rheometric Expansion System) in oscillatory mode with a parallel plate geometry using 25 mm diameter plates. All measurements were performed with 2 K FRTN1 transducer with a lower resolution limit of 0.02 g-cm over a wide frequency range. Typical sample thickness ranged from 1.5 to 1.8 mm. Some measurements were also performed with thinner samples (thickness: from 0.7 to 1.0 mm), to ensure the negligible surface effects that may be due to the possible surface-induced ordering of the layered structure. The data for thinner samples were in good agreement with those from the thicker samples, indicating little or no influence of the contacting surface on the microstructure.

RESULTS AND DISCUSSION

1. Microstructure of SBS/Clay Nanocomposite

Figs. 1 and 2 illustrate the XRD patterns for nanocomposites of each SBS and clay (M20A, M30B) series. Quite different microstructures are formed according to the combination of SBS and clay species. For the M20A-based nanocomposite series, intercalated structures are observed in all the composite series, although the degree of intercalation varies with each SBS. We found that the degree of swelling in ESBS/M20A is larger than that in SBS46/M20A.

The basal reflections from the unintercalated M20A, p-(001) and p-(002) are observed at 2θ=3.74 and 2θ=7.40, respectively, and correspond to a repeat distance perpendicular to the layers of d_{001}= 2.36 nm. After the fabrication of SBS46/M20A composites, the intensity of the reflections corresponding to the initial M20A disappears while a set of new peaks appear corresponding to the SBS46/M20A intercalated hybrid. In the SBS46/M20A nanocomposites, the basal reflections from the intercalated M20A, i-(001), i-(002) and i-(003), are observed at 2θ=2.53, 2θ=5.17 and 2θ=7.56, respectively. And the repeat distance perpendicular to the layer is d_{001}= 3.49 nm.

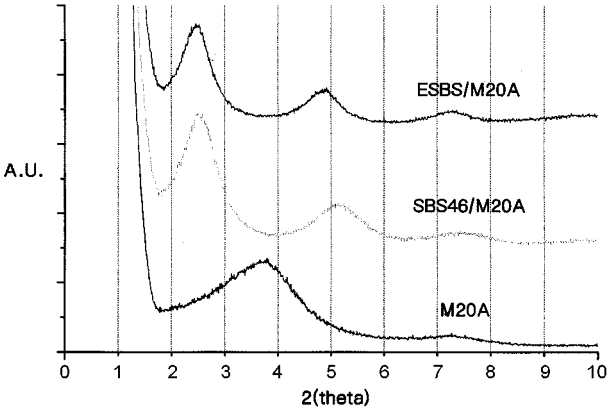

Fig. 1. X-ray diffraction spectra of SBS/M20A series. Note that the repeat distance (d_{001}=2.36 nm) of unintercalated M20A is increased to d_{001}=3.49 nm (SBS46/M20A) and d_{001}=3.67 nm (ESBS/M20A).

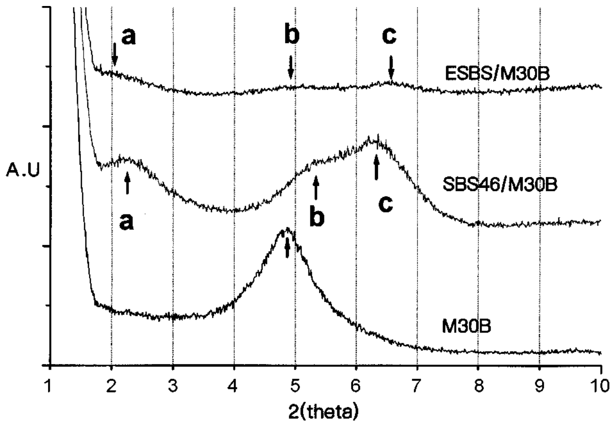

Fig. 2. X-ray diffraction spectra of SBS/M30B series.

The X-ray diffraction peak (001) of the ESBS/M20A nanocomposites is observed even at a lower angle. In the ESBS/M20A nanocomposites, the basal reflections from the intercalated M20A, i-(001), i-(002) and i-(003), are observed at 2θ=2.40, 2θ=4.88 and 2θ=7.31, respectively. The repeat distance perpendicular to the layer is, d_{001}=3.67 nm. The epoxidized blocks in ESBS, which carries a block with polar character, act as a more attractive moieties to polar group such as hydroxyl or oxygen groups which reside on the surface of M20A. A schematic explanation for the different degree of intercalation between SBS/M20A and ESBS/M20A is shown in Fig. 3. When SBS copolymers are mixed with clay particles, styrene blocks intercalate into the interlayer via Lewis acid-base interaction [Lim and Park, 2000]. But, the butadiene blocks possess no interaction with clay and are immiscible with clay particles. In case of ESBS, the epoxidized part in butadiene block has also interaction with the polar group of clay and some of the butadiene

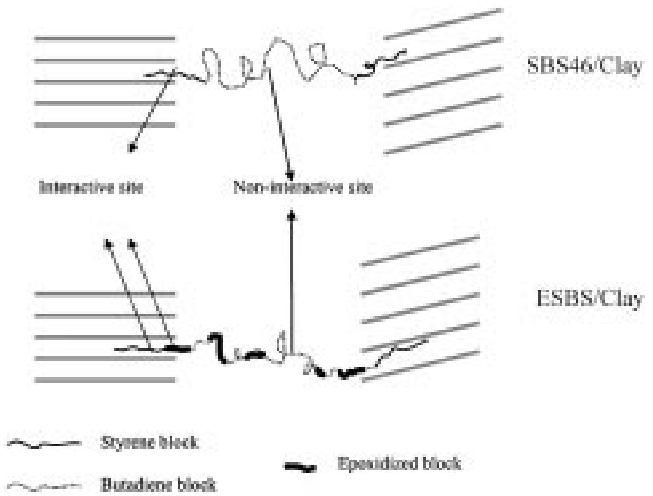

Fig. 3. Schematic explanation for the different degree of intercalation in SBS46/M20A and ESBS/M20A nanocomposites.

block which contains epoxidized block would also intercalate into the interlayer of silicate. Consequently, the degree of interlayer swelling is larger in case of ESBS/M20A than SBS/M20A. This result shows that the surface character of the polymer affects the degree of intercalation.

Quite different results for the microstructure of SBS/M30B series nanocomposites are shown in Fig. 3. The main peak (001) of M30B ($2\theta=4.86$) is shifted to a lower angle ($2\theta=2.22$) in SBS/M30B nanocomposite series compared with that in SBS/M20A nanocomposite series although the interlayer space ($d_{001}=1.82$ nm) of the initial M30B is smaller than that of M20A ($d_{001}=2.36$ nm). This is due to the attractive interaction of SBS polymer with polar hydroxyl group of M30B which resides in the interlayer of clay. In particular, a partially exfoliated structure is observed in ESBS/M30B, while partially intercalated structure is observed in the case of SBS46/M30B composite series. The interaction between epoxidized block in ESBS and polar group of M30B is responsible for the different microstructure.

Another interesting aspect in the X-ray diffraction spectrum is the second and third peak (designated with **b** and **c**). The X-ray data measured after heat-treatment clearly shows the evidence of thermal collapse of the silicate layer. The pristine M30B is thermally treated at the same condition with the processing of nanocomposite fabrication. It is annealed in an oven at 180 °C for 10 min. As shown in Fig. 4, the sharp main peak shifts to a larger angle at 180 °C. During the process, the oxidative decomposition of the oligomer which is residing in the gallery of the silicate surface occurred and the silicate layer eventually collapsed as reported in previous works [Lee et al., 2000; Ogawa, 1994]. In our previous work, the collapsed microstructure was also observed by transmission electron microscopy [Lee et al., 2000]. In fact, the oligomers with hydroxyl groups possess poor thermal stability compared with other alkane groups. As a result, we believe that the peak of (b) in the SBS/M30B nanocomposite series represents the (002) peak of alternating lamellar layers. The peak of (c) is assigned to the collapsed silicate peak. The broadened peak between (b) and (c) results from the overlap of both (b) and (c) peaks.

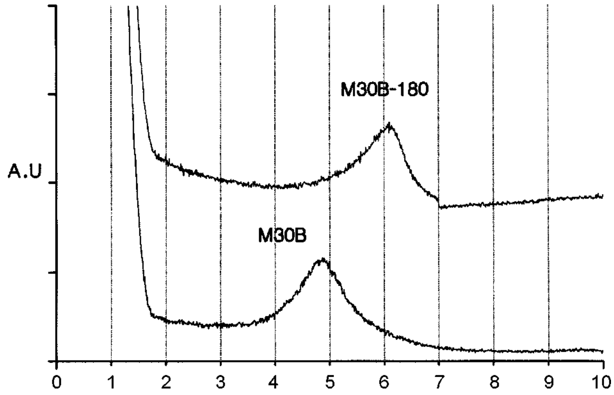

Fig. 4. Effect of heat treatment on the microstructure of M30B. Heat treatment was performed in a heating oven at 180 °C for 10 min.

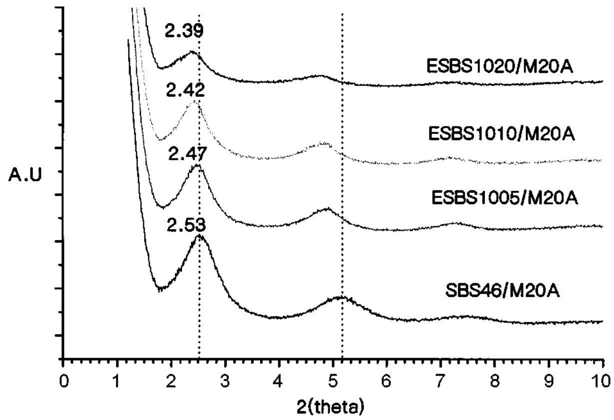

Fig. 5. X-ray diffraction spectra of ESBS/M20A nanocomposites with different contents of epoxidized block.

The above results suggest that the thermal stability of clay as well as the polar characteristics of the modified surface should be carefully considered in fabricating useful polymer/layered silicate.

2. Effect of Epoxidized Block on the Degree of Intercalation

To study the effect of epoxidized block on the degree of intercalation, three different ESBS are fabricated with M20A. The swelling of the interlayer distance in the ESBS/M20A nanocomposite series is shown in Fig. 5. The main peaks shift to lower angles as the content of epoxidized block is increased. And, the intensity of the peaks decreases and width of each peak is broadened with the increase of epoxized block, implying more disordered structure formed. The epoxidized block in ESBS carries polar moieties, which acts as interacting sites with the modified silicate surface. Consequently, more chains can intercalate into the interlayer of the silicate and more disordered structures are formed due to the strong interaction and corresponding efficient shear force during the compounding process in the mixer.

3. Rheological Behavior of SBS/Clay Nanocomposites

Fig. 6 shows the rheological behavior of SBS46/M20A and SBS46/M30B nanocomposites with different silicate loadings. The storage moduli increase and the frequency dependence of the storage moduli decrease with clay loading in the SBS46/M20A nanocomposites. The zero shear viscosity, which is one of the parameters characterizing the terminal zone, is not observed in SBS46/M20A

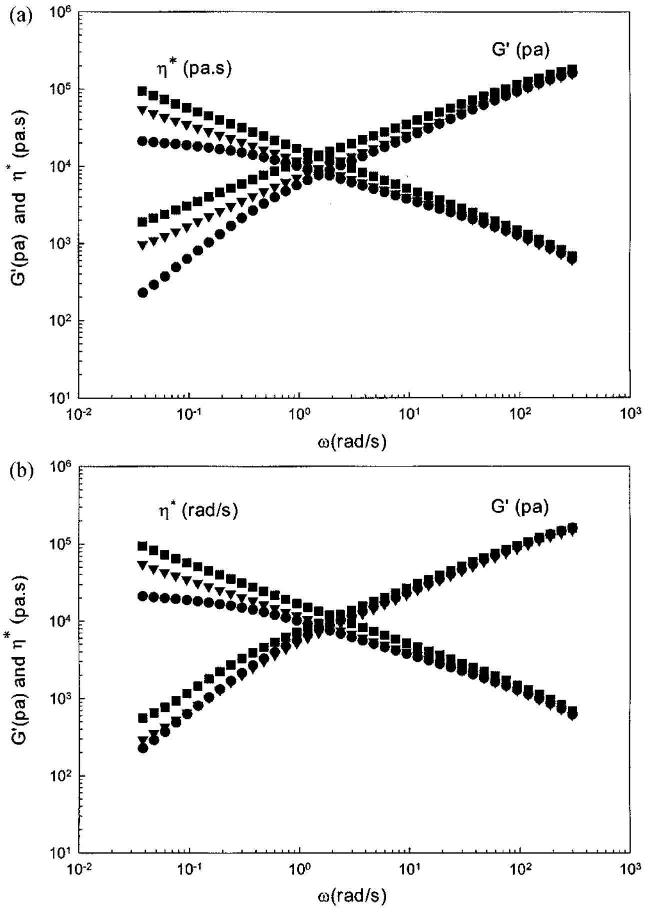

Fig. 6. (a) Storage modulus and complex viscosity of SBS46 and SBS46/M20A nanocomposite series (Each symbol denotes: ●: SBS46, ▼: SBS46/M20A-03 (3 wt%), ■: SBS46/M20A-05 (5 wt%)). (b) Storage modulus and complex viscosity of SBS46 and SBS46/M30B nanocomposite series (Each symbol denotes: ●: SBS46, ▼: SBS46/M30B-03 (3 wt%), ■: SBS46/M30B-05 (5 wt%)).

nanocomposites. However, very different rheological behavior is observed for the SBS46/M30B. The storage moduli increase slightly and the tendency of non-terminal behavior is very weak even with a high clay loading. In fact, the non-terminal flow behavior has been observed in filled-polymer systems exhibiting yield phenomena [Gandhi and Salovey, 1998; Aoki, 1987], but only in the cases where the filler and polymer are actively interacting and in a dynamic regime controlled by much larger length scales (i.e., lower frequencies) than those observed in this study. Thus, we can infer that the different microstructure observed in X-ray diffraction data in Fig. 2 is responsible for the different rheological behavior between SBS46/M20A and SBS46/M30B nanocomposites. Recently, rheological evidence for the intercalated polymer/clay nanocomposites was proved with simple quantitative analysis [Lim and Park, 2000].

In the SBS46/M20A nanocomposites, most of the layered silicates are swollen due to the intercalation of polymer chains, and the polymer chains are in close contact with the host surface in the gallery of the layered silicates. The non-terminal rheological behavior shown in SBS46/M20A may be due to the interaction of polymer chains with the filler. Additionally, the interaction is more remarkable because the nanofiller, which has very large interfacial area compared to the conventional micro or macro-sized filler, touches the polymer chains. On the other hand, SBS46/M30B nanocomposites are not only partially intercalated but also have some collapsed silicate layers in the polymer matrix. Since the collapsed

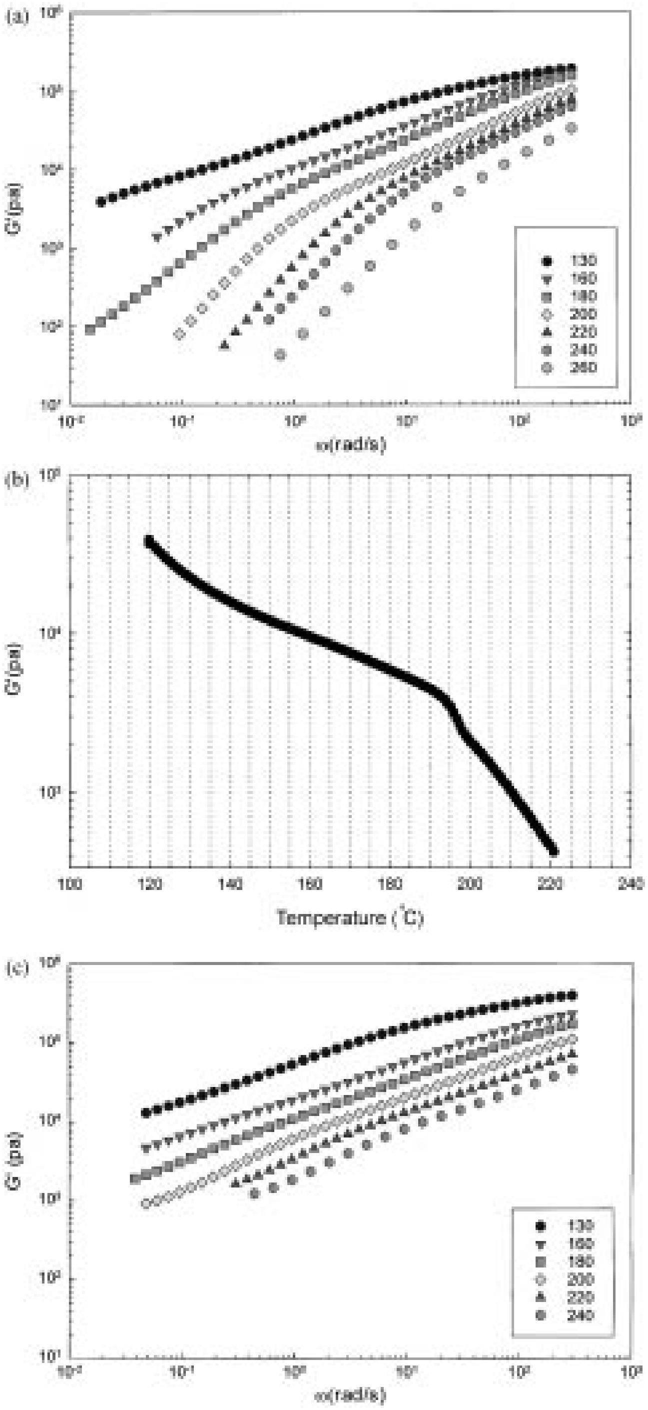

Fig. 7. (a) Changes in storage modulus of SBS46 at various temperatures. (b) Temperature dependence in storage modulus of SBS46 at 1 rad/s, 4% strain, and heating rate 3 °C/min for SBS and SBS/M20A-05. (c) Changes in storage modulus of SBS46/M20A-05 at various temperatures.

silicate is immiscible with the polymer matrix and does not seem to contribute to the non-terminal rheological behavior, the partially intercalated portion of the nanocomposites is only responsible for the slight enhancement of the storage moduli of the SBS46/M30B nanocomposites.

The rheological behavior of SBS46/M20A nanocomposites which have intercalated nanostructure is studied at several temperatures to investigate the relationship between microstructure and rheological behavior in a wide frequency range. Fig. 7 shows the storage moduli of SBS46 and SBS46/M20A nanocomposites as a function of oscillation frequency, ω, at different temperatures. The G' of SBS46 is a typical behavior for a phase-mixed block copolymer [Kais et al., 1995] where, at high temperatures, G' follows a limiting low-frequency power law behavior close to ω^2 behavior. As shown in Fig. 7(a), the slope of the storage modulus at T=180 °C shows non-terminal behavior at low frequency, which is a typical property of a micro-phase separated structure. The slope of the storage modulus at T=200 °C, however, changes abruptly reflecting the order-disorder transition temperature (T_{ODT}) located between the two temperatures. The order-disorder transition temperature ($T\approx195$ °C) was also identified by G' vs T method as shown in Fig. 7(b), which is consistent with the rheological behavior shown in Fig. 7(a). On the other hand, there is no appreciable change for the frequency dependence of the storage modulus for SBS46/M20A nanocomposites in the entire experimental temperature range as shown in Fig. 7(c). The non-terminal low-frequency rheological behaviors shown in SBS46/M20A nanocomposites, even above T_{ODT} of SBS46 itself, are similar to those behaviors in ordered block copolymers ($T<T_{ODT}$) and smectic liquid-crystalline small molecules [Larson et al., 1993; Rosedale and Bates, 1990].

In fact, more detailed characterization is needed for the microstructure of block copolymer/clay nanocomposites in order to elucidate the relation between the microstructure and rheological behavior more clearly.

CONCLUSIONS

SBS/clay nanocomposites are prepared by conventional melt processing and the rheological behaviors of the nanocomposites are discussed in terms of their microstructures. The degree of intercalation is dependent on the surface properties of both clay and SBS. In addition, it is learned that the thermal stability of clay particles should be also considered in order to produce SBS/clay nanocomposites properly. Both the storage moduli and complex viscosities of SBS/clay nanocomposites increase and show non-terminal behavior as the clay content is increased.

ACKNOWLEDGEMENT

Authors are thankful for the financial support of the Center for Advanced Functional Polymers (CAFPoly) appointed by the Korea Science and Engineering Foundation. This work is also partially supported by the Brain Korea 21 Project of the Ministry of Education of Korea.

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