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Polymer 45 (2004) 1267–1273

polymer

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Effect of heat treatment on the microstructural change of syndiotactic polystyrene/poly(styrene-*co*-vinyloxazolin)/clay nanocomposite

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Received 31 July 2003; received in revised form 30 November 2003; accepted 4 December 2003

Abstract

The fabrication of a syndiotactic polystyrene (sPS)/organoclay nanocomposite was conducted via a stepwise mixing process using poly(styrene-*co*-vinyloxazolin) (OPS), i.e. melt intercalation of OPS into organoclay followed by blending with sPS. The effects of several parameters, including type of organoclay and mixing temperature on the microstructure of the nanocomposite were investigated through X-ray diffraction patterns and rheological properties. The microstructure of the nanocomposite mainly depended on the arrangement type of the organic modifiers in the clay gallery. Using organoclays having lateral a bilayer arrangement exfoliated structure was obtained, whereas intercalated structure were obtained when organoclay with a paraffinic monolayer arrangement was employed in our sPS/OPS/organoclay system. In this work, a simple heat treatment on a previously prepared OPS/organoclay nanocomposite induced microstructural evolution with a favorable direction from intercalation to exfoliation. This phenomenon is attributed to a strong interaction between OPS and the clay surfaces, which is revealed by plateau behavior of the storage modulus in rheological properties. When heat is applied to the OPS/organoclay, the OPS chains and clay layers move together by promoted thermal motion of OPS chains, which results in disordering of stacked clay layers and exfoliation.

Keywords: Syndiotactic polystyrene; Clay; Nanocomposite

1. Introduction

There have been numerous studies on polymer/clay nanocomposites due to interest in their superior properties over conventional microcomposites, including strength, stiffness, flame retardancy and barrier properties. In the case of atactic polystyrene (PS), various preparation methods for nanocomposites have been attempted such as in situ solution polymerization [1–4], in situ emulsion polymerization [5,6], and melt intercalation [7–12]. Doh and Cho showed that free radical polymerization of a styrene monomer in the presence of organophilic clay treated with an apolar alkylammonium chain yielded a nanocomposite with intercalated structure [2]. When a reactive organic modifier such as a vinyl alkylammonium chain was used instead of a non-reactive modifier, exfoliated nanocomposites were obtained [4]. However, intercalated nanocomposites were obtained when a reactive organic modifier of a vinyl monomer not having a long alkyl chain was used [1]. Recently, exfoliated PS nanocomposites were synthesized by using a silicate anchored initiator via living free radical polymerization [3].

PS/clay nanocomposites with different microstructures are also obtained by the melt intercalation method according to the type of organic modifier in the clay gallery and the polarity of the matrix polymer. Melt mixing or annealing of only two components of PS and organoclay yields nanocomposites with intercalated structure [7,8]. However, exfoliated PS nanocomposites could be obtained by increasing the polarity of the matrix polymer [9] or introducing another polar polymer miscible with PS [10].

In this work, the fabrication of a syndiotactic polystyrene (sPS)/clay nanocomposite was attempted via melt intercalation. sPS is a semi-crystalline polymer with high melting point (about 270 °C) due to its stereo-regularity, whereas atactic polystyrene (PS) is an amorphous polymer.

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doi:10.1016/j.polymer.2003.12.011

Thus, direct melt intercalation of sPS into organoclay is problematic due to thermal instability of the organic modifiers treated on the inner layer surface of the clay at high temperature [12–14]. In general, the clay should be swelled by an alkyl ammonium material via a cation exchange reaction between the metal ions in the clay gallery and alkyl ammonium ions in order to increase the wettability between the polymer and clay surface. However, the interaction between alkyl ammonium and the silicate layer of clay is not thermally stable enough to resist the high melt processing temperature of sPS, which makes intercalation of sPS into the clay gallery difficult. To solve this problem, we utilized the indirect approach of melt intercalation of amorphous polystyrene into organophilic clay followed by blending with sPS. We used poly(styrene-*co*-vinyloxazoline) (OPS) as an amorphous polystyrene. OPS can be melt-intercalated above the glass transition temperature which is within the thermally stable range of the organic modifier.

On the basis of the above stepwise fabrication method, we investigated the effect of organoclay type on the microstructure of nanocomposites by using three organoclays with different chemical structures and conformations. The microstructures of the obtained nanocomposites were examined by XRD spectra and transmission electron microscopy (TEM) images. The rheological properties were measured and discussed in relation to their microstructures. Since the fabrication of sPS nanocomposites includes high temperature processing, the heat has a significant effect on the microstructures. Therefore, heat treatment on the OPS/organoclay nanocomposites was performed in order to observe the structural change of these nanocomposites at the high melt processing temperature of sPS.

2. Experimental part

2.1. Materials

sPS was supplied by Samsung General Chemical Co. and used as received. OPS was a commercial product of Nippon Schokubai Co. with the grade name of Epocros RPS1005 in which 5 wt% oxazolin unit was included. Three montmorillonite type organophilic clays were used. These organoclays were prepared by ion exchanging sodium-montmorillonite with alkyl ammonium cations. The inner layer surfaces of the organoclays were treated with dimethyl dihydrogenated tallow ammonium (MHT), dimethyl benzyl hydrogenated tallow ammonium (BHT), and trimethyl octadecyl ammonium (TMO), respectively. Hydrogenated tallow alkyl chain consisted of 65 wt% of C_{18}, 30 wt% of C_{16} and 5 wt% of C_{14}. From here on, organoclays are termed according to their organic modifier. Two organoclays, MHT and BHT, were donated by Southern Clay Co. and TMO was prepared in our laboratory by adopting the common procedure as outlined elsewhere [10]. All organoclays were used after drying in a vacuum oven at 80 °C for two days. The properties of materials used in this work are summarized in Table 1.

2.2. Preparation of nanocomposite

First, OPS and organophilic clay were mixed in a Brabender roller mixer at a temperature of 200 °C for 10 min with 50 rpm rotor speed. OPS was inserted and melted completely in the mixing chamber. The organophilic clay was then loaded into the molten polymer. After completion of mixing, the mixed composite was ejected from the mixing chamber, then cooled and crushed at room temperature. sPS nanocomposites were fabricated by blending sPS with the above products in a Brabender roller mixer at 280 °C for 5 min with 50 rpm rotor speed.

Heat treatment of the OPS/organoclay nanocomposites was performed through annealing in a small vial of a mini-molder (CSI co.) for 5 min with varying temperature.

2.3. Characterization

The dispersed state of the clay layers in the matrix polymer was evaluated using XRD and TEM. XRD spectra were obtained using a Rigaku X-ray generator (Cu Kα radiation with $\lambda = 1.5406$ Å) with 2θ scan range of 0–10° at room temperature. The specimens of nanocomposites for XRD measurement were obtained in sheet form using a hydraulic press. TEM images were obtained using a Jeol JEM-2000EX TEM. The specimens were cut into ultra thin slices using a Reichert-Jung Ultracut Microtome at room temperature without any staining process. The dynamic moduli as rheological properties were measured using ARES (Rheometrics Co.) with parallel plate geometry. Frequency sweep was carried out at 280 °C with the 10% strain, which was within the linear viscoelastic regime. All measurements were conducted under an inert nitrogen environment to avoid degradation of the polymers at high temperature.

3. Results and discussion

In fabricating OPS/organoclay nanocomposites, the

Table 1
Properties of materials used in this work

Materials	M_w	T_g (°C)	T_m (°C)	CEC (mequiv./100 g)	d-spacing (nm)
SPS	617,900	100	265	–	–
OPS	156,000	108	–	–	–
MHT	–	–	–	125	2.97
BHT	–	–	–	125	1.93
TMO	–	–	–	119	1.81

organoclay content was maintained at 10 wt%. The blend ratio of sPS and the OPS/organoclay nanocomposite was 7:3 in all cases. Thus the organoclay content in the sPS nanocomposite was 3 wt%. First, we investigated the effect of organic modifier type on the microstructure of the nanocomposites by using two organoclays having the same cation exchange capacity (CEC), MHT and BHT. The compositions of the fabricated nanocomposites are summarized in Table 2.

The XRD patterns of organoclay and polymer/organoclay nanocomposites are shown in Fig. 1. When only two components of sPS and organoclay were mixed at 280 °C of sPS melting temperature, the (001) peak of clay layers remained at its initial position or shifted to a higher 2θ value. This indicates that the clay interlayer spacing did not change or even decreased, which resulted in phase separated microcomposites not intercalated nanocomposite. This result is attributed to a thermal rupture of bonds or thermal desorption of the organic modifier followed by a decrease of wettability between the polymer and clay, which corresponds with other reports [12–14].

However, two organoclays showed different XRD patterns in sPS/organoclay composite. Although considerable weight loss of organic modifier occurred in both organoclays at sPS melt temperature by TGA experiment (Fig. 2), only BHT showed a decrease of d-spacing, from 1.93 nm ($2\theta = 4.58°$) to 1.43 nm ($2\theta = 6.18°$). The peak around $2\theta = 6.7°$ is the diffraction peak of the hexagonal crystallographic structure of sPS. Considering previous theoretical and experimental results [15,16], the tilted paraffinic monolayer is most likely for the arrangement of organic modifier in MHT in view of its d-spacing (2.97 nm) and the lateral bilayer for BHT with d-spacing (1.93 nm). Recently, it was reported that organoclay with a paraffinic monolayer structure maintained its d-spacing after thermal treatment, whereas the d-spacing of organoclay with a lateral bilayer structure reduced to a lateral monolayer [14], which is consistent with our results. Most relevantly, intercalated or exfoliated nanocomposite could not be obtained by simply melt mixing sPS and organoclay.

Table 2
Compositions of nanocomposites and their d-spacings

Sample	sPS (wt%)	OPS (wt%)	Organoclay (wt%)			d-spacing (nm)
			MHT	BHT	TMO	
SPOPS	70	30	0	0	0	–
SPSM	97	0	3	0	0	3.01
OPSM	0	90	10	0	0	3.22
SPOPSM	70	27	3	0	0	3.53
SPSB	97	0	0	3	0	1.43
OPSB	0	90	0	10	0	3.31
SPOPSB	70	27	0	3	0	Exfoliation
OPST	0	90	0	0	10	3.16
SPOPST	70	27	0	0	3	Exfoliation

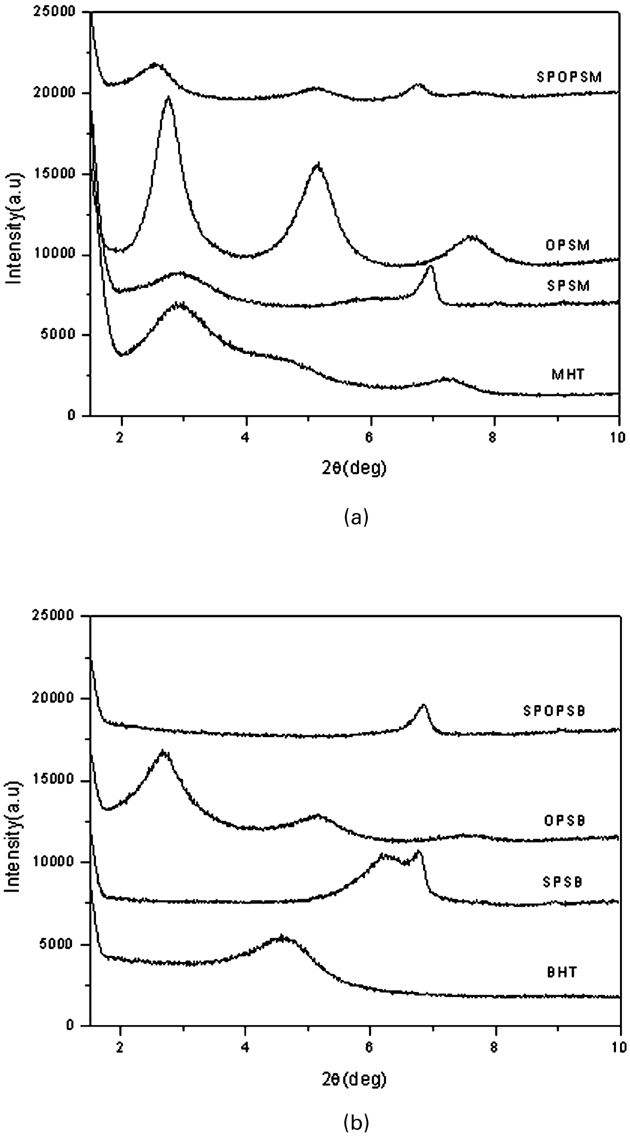


Fig. 1. XRD patterns of composites with different organoclays, (a) MHT series, (b) BHT series.

When OPS and organoclay are melt-mixed at 200 °C as a first step of the fabrication method, intercalated nanocomposites were obtained irrespective of the type of organoclay. The d-spacing increased from 2.97 to 3.22 nm for MHT and from 1.93 to 3.31 nm for BHT. This is similar to the previous result of Yoon et al. [12], who obtained an intercalated nanocomposite by annealing or melt mixing OPS and organoclay. Hasegawa et al. [10], however, reported that a nearly exfoliated (or disordered intercalated) nanocomposite could be obtained by mixing OPS and organoclay in a twin-screw extruder. This high degree of dispersion is thought to result from the relative intensities of the mixing equipment in comparison to Yoon's and our results, which were obtained using roller blade mixer.

When sPS and above the OPS/organoclay nanocomposite were mixed at 280 °C of sPS melting temperature, we could obtain intercalated or exfoliated nanocomposites

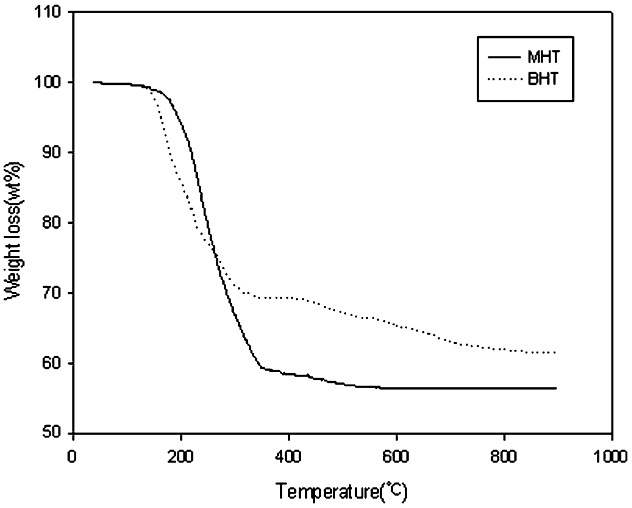


Fig. 2. TGA curves of two organoclays under air environment.

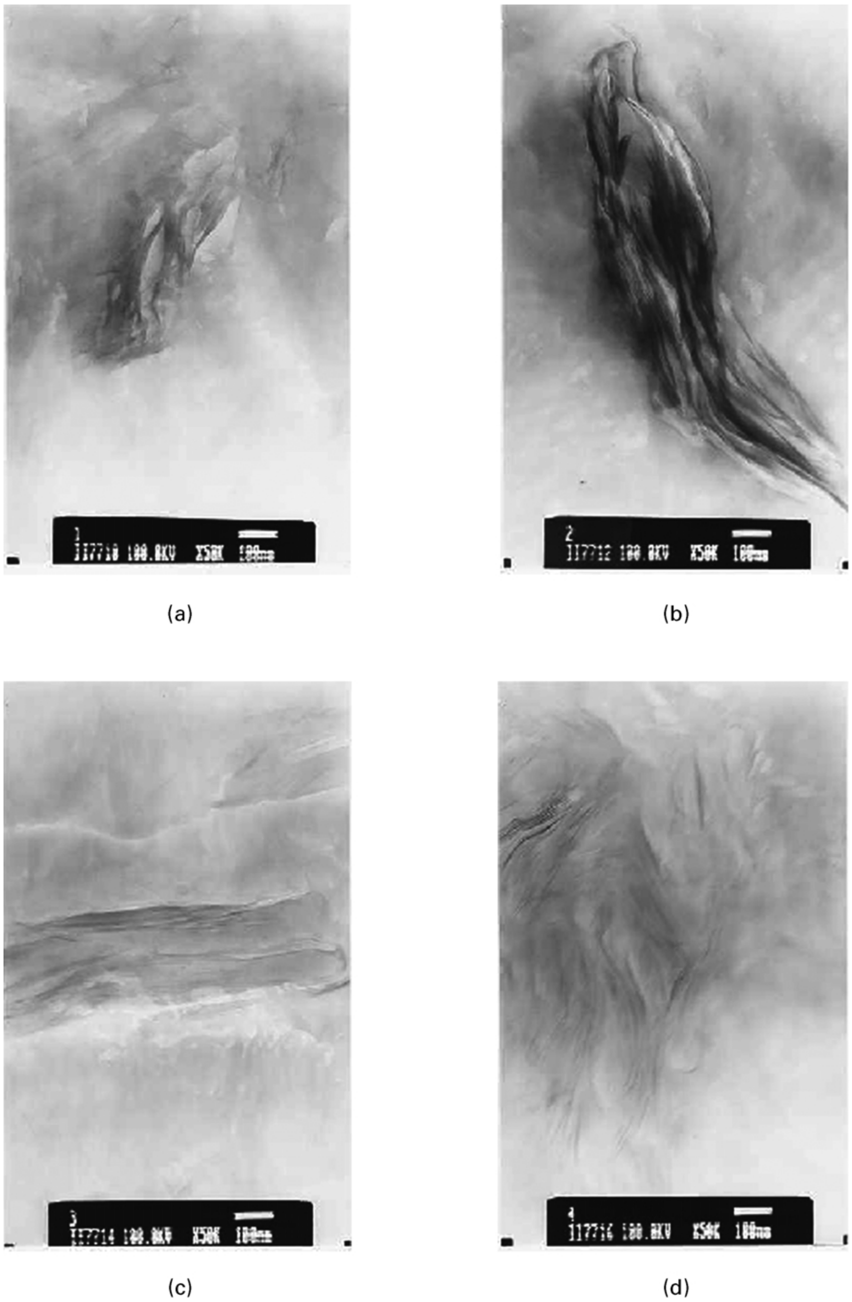
according to the type of organoclay without any collapsed clay layers. In the case of using MHT, the intercalation peak appeared at $2\theta = 2.5°$, corresponding to 3.53 nm of d-spacing. This value is 0.3 nm higher than that of OPS/MHT, and thus it is believed that some sPS intercalated into the clay gallery. However, a completely exfoliated nanocomposite without any intercalation peak in the XRD pattern was obtained in the case of using BHT. Differences in the microstructure between the two organoclays can be clearly observed by the TEM images in Fig. 3. The composites obtained by melt-mixing of only two components of sPS and organoclay showed agglomerated clay particles as expected in the XRD patterns. Individual layers of clay are visible as regions of alternating, narrow dark and light bands within the particle. The clay layers in BHT were more severely agglomerated than that of MHT, as dark bands of clay layers were presented more closely together, which is consistent with the result of the decrease of d-spacing in the XRD pattern. However, sPS nanocomposites obtained by stepwise mixing showed typical intercalated and exfoliated structure in MHT and BHT, respectively. We observed that the face-to-face stacking of clay layers was maintained in the MHT case while the individual clay layers were delaminated in the BHT case. On the basis of the results of the XRD and TEM analyses, stepwise mixing using OPS is determined to be a useful method in obtaining a nanocomposite for a sPS/organoclay system.

At this time, it is worthwhile to note microstructural change of the nanocomposite induced by simply melt-mixing OPS/organoclay with sPS at high temperature. To our knowledge, there has been no report on the microstructural change of a nanocomposite by processing at high temperature, which is a favorable direction from intercalation to exfoliation, without any collapsed clay layers. Thus, in order to investigate the effect of heat on the microstructural change, heat treatment on an OPS/organoclay nanocomposite was performed for 5 min with varying temperature from 200 to 280 °C. The XRD patterns according to the heat treatment temperature are shown in Fig. 4. In the case of OPS/MHT, a higher temperature results in a lower (001) peak with, maintenance of the peak position at $2\theta = 2.5°$, which indicates microstructural change from ordered intercalation to disordered. However, the (001) peak of the OPS/BHT nanocomposite disappeared above 230 °C, which corresponds to an exfoliated structure.

The microstructural change of the OPS/organoclay nanocomposite caused by heat can be explained as follows. When heat is applied, the OPS chains previously intercalated in the clay gallery become more energetic and have promoted thermal motion. This increased thermal motion makes it easier for OPS chains to move out from the clay gallery due to the thermodynamic tendency of the gain of conformational entropy. The oxazolin group in OPS has a strong interaction with hydroxyls in clay surface. Thus the layered structure of clay becomes disordered or exfoliated as OPS and clay layer move together by heat treatment.

Comparing two organoclays, MHT and BHT, we observed that the microstructural change to an exfoliated state occurred more rapidly for BHT. In previous reports [15], it was revealed that organoclay with a lateral bilayer arrangement of organic modifier had a twice larger surface area per alkylammonium molecule than that of organoclay with a paraffinic monolayer. This means that the former organoclay has lower packing density than the latter. Thus BHT with a lateral bilayer structure has relatively large empty spaces in the clay gallery and as a result a high amount of OPS can intercalate and interact with the clay surface, leading to an exfoliated structure at the relatively low temperature of 230 °C. This could be confirmed by the XRD data in Table 2, which shows that the net increase of d-spacing in OPS/BHT was 1.38 nm while there was only a 0.25 nm increase in the case of OPS/MHT.

The chemical affinity between OPS and the benzene group in BHT may be another reason for the exfoliated structure of the OPS/BHT nanocomposite. In order to investigate the effect of a pendant group in the organic modifier, TMO having a lateral bilayer arrangement of organic modifier consisting of only a C_{18} aliphatic chain was compared to the BHT. As revealed in the XRD patterns shown in Fig. 5, the OPS/TMO nanocomposite showed an intercalated structure as the (001) peak shifted from $2\theta = 4.89°$ to $2\theta = 2.79°$. This corresponds to an increase of d-spacing from 1.81 to 3.16 nm. When this OPS/TMO nanocomposite was thermally treated or mixed with sPS at 280 °C, a nearly exfoliated structure was obtained while a small intercalation peak remained. This result is nearly identical as that obtained when using BHT. As such, the arrangement of organic modifier in the clay gallery strongly appears to be the main factor in affecting the microstructure of the sPS/OPS/organoclay nanocomposite. However, the chemical affinity between organic modifier and polymer may be another factor in considering that a small intercalation peak remained in OPS/TMO, whereas a completely exfoliated structure without any intercalation



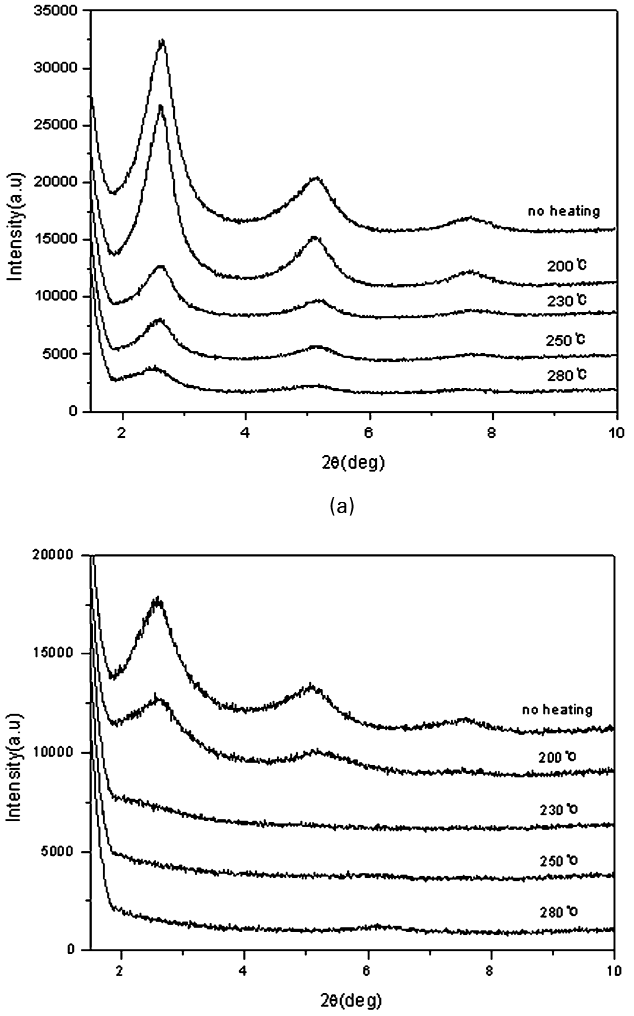
(a) (b)

(c) (d)

Fig. 3. TEM images of nanocomposites, (a) SPSM, (b) SPSB, (c) SPOPSM, (d) SPOPSB.

peak was obtained in OPS/BHT. The chemical affinity between polymer and organic modifier promotes intermixing of the two chains and consequently the clay layers are delaminated more completely by the thermal motion of OPS during heat treatment. This result is consistent with the theoretical study that an interaction between organic modifier and matrix polymer is advantageous in terms of obtaining an exfoliated structure [17].

Finally, dynamic moduli as rheological properties were measured and studied in relation to the microstructure of the nanocomposites revealed previously by XRD and TEM. The storage moduli and loss moduli vs. frequencies are shown in Fig. 6. When we focused on the nanocomposite obtained by stepwise mixing, we found that the storage moduli increased greatly at the low frequency region in comparison to the matrix polymer sPS/OPS blend. An enhanced modulus at the low frequency region in an intercalated nanocomposite has been reported in some previous studies. This phenomenon could be explained by the retarded relaxation dynamics of polymer chains in a confined geometry [18,19] or the mesoscopic structure of clay tactoids [20]. However, the exfoliated nanocomposite created using BHT showed more enhanced storage moduli and even plateau behavior at low frequency region as compared to the intercalated nanocomposite made using MHT. Krishnamoorti et al. reported that the rheological



(a)

(b)

Fig. 4. XRD patterns of heat treated OPS/organoclay nanocomposite at different temperature for 5 min, (a) MHT series, (b) BHT series.

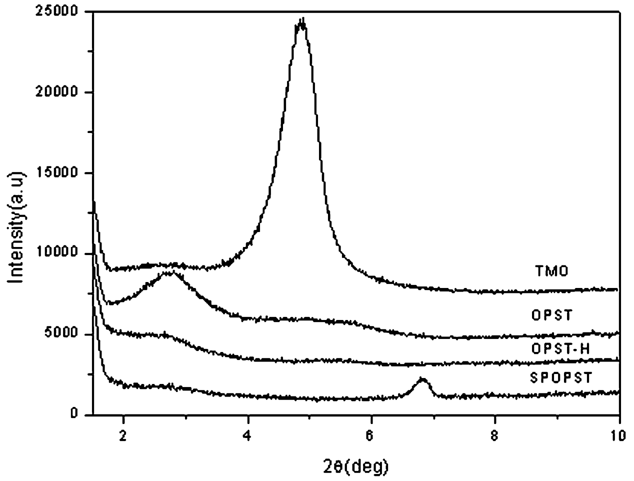
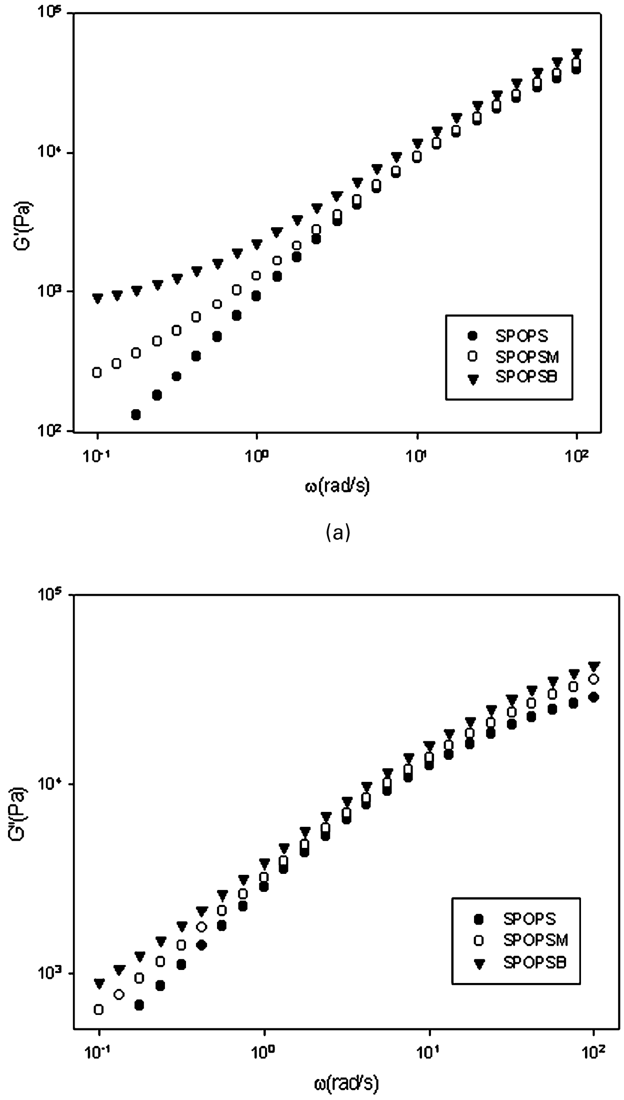


Fig. 5. XRD patterns of nanocomposites using TMO (OPST-H represents the heat treated OPST nanocomposite at 280 °C for 5 min).



(a)

(b)

Fig. 6. Dynamic rheological properties of nanocomposites at 280 °C, (a) storage moduli, (b) loss moduli.

properties of exfoliated nanocomposites showed different behavior according to the interactions between the polymer and the clay surface. Simply delaminated clay layers without any interaction between polymer and clay surface showed no difference in rheological properties from the matrix polymer whereas end-tethered nanocomposites such as an in situ polymerized nylon-6/organoclay hybrid showed decreased frequency dependence of storage modulus in the low frequency region [18]. This plateau behavior of the storage modulus could be found in other end-tethered polymer/organoclay system, poly(ε-caprolactone)/organoclay [21] and polystyrene/organoclay [11], and has been attributed to the network formation between polymers and clay layers. Based on previous reports, sPS/OPS/BHT nanocomposite is believed to be a pseudo end-tethered nanocomposite, due to the strong interaction between OPS and the clay surface in view of the rheological properties. The loss modulus showed a similar trend to the storage modulus but with a reduced difference due to the viscous character of the loss modulus.

4. Conclusions

The fabrication of nanocomposites based on sPS and organoclay as polymer and filler, respectively, was performed by melt intercalation. Intercalated or exfoliated nanocomposites without any collapsed clay could be obtained by using OPS via a stepwise mixing method. Previously intercalated OPS played an important role in preventing the clay layers from collapsing during melt-mixing with sPS at high temperature. The microstructure of the nanocomposites mainly depended on the arrangement type of organic modifier in the clay gallery. Organoclays having a lateral bilayer arrangement were advantageous in terms of obtaining an exfoliated nanocomposite in our sPS/OPS/organoclay system. We could obtain more complete exfoliated nanocomposites by using an organoclay having chemical affinity between polymer and organic modifier, as revealed in a comparative study of BHT and TMO. One notable result was that the microstructural evolution occurred in a favorable direction from intercalation to exfoliation by high temperature. This phenomenon could be explained as follows. OPS/organoclay is believed to exist in a pseudo end-tethered state due to the strong interaction between OPS and the clay surfaces. When heat is applied to the OPS/organoclay, OPS chains and clay layers move together by promoted thermal motion of the OPS chains, which results in disordering of the stacked clay layers and exfoliation.

Acknowledgements

The authors are very grateful for the financial support provided by Samsung General Chemical Ltd. and the Center for Advanced Functional Polymers through KOSEF. In addition, this work is also partially supported by the Brain Korea 21 project of the Ministry of Education (MOE) of Korea.

References

[1] Akelah A, Moet A. J Mater Sci 1996;31:3589.
[2] Doh JG, Cho I. Polym Bull 1998;41:511.
[3] Weimer MW, Chen H, Giannelis EP, Sogah DY. J Am Chem Soc 1999;121:1615.
[4] Fu X, Qutubuddin S. Polymer 2001;42:807.
[5] Noh MW, Lee DC. Polym Bull 1999;42:619.
[6] Laus M, Camerani M, Lelli M, Sparnacci K, Sandrolini F, Francescangeli O. J Mater Sci 1998;33:2883.
[7] Vaia RA, Ishii H, Giannelis EP. Chem Mater 1993;5:1694.
[8] Sikka M, Cerini LN, Ghosh SS, Winey KI. J Polym Sci Part B: Polym Phys 1996;34:1443.
[9] Vaia RA, Giannelis EP. Macromolecules 1997;30:8000.
[10] Hasegawa N, Okamoto H, Kawasumi M, Usuki A. J Appl Polym Sci 1999;74:3359.
[11] Hoffmann B, Dietrich C, Thomann R, Friedrich C, Mulhaupt R. Macomol Rapid Commun 2000;21:57.
[12] Yoon JT, Jo WH, Lee MS, Ko MB. Polymer 2001;42:329.
[13] McAtee Jr JL, Concilio CB. Am Mineral 1959;44:1219.
[14] Lee JW, Lim YT, Park OO. Polym Bull 2000;45:191.
[15] Vaia RA, Teukolsky RK, Giannelis EP. Chem Mater 1994;6:1017.
[16] Hackett E, Manias E, Giannelis EP. J Chem Phys 1998;108:7410.
[17] Balazs AC, Singh C, Zhulina E. Macromolecules 1998;31:8370.
[18] Krishnamoorti R, Vaia RA, Giannelis EP. Chem Mater 1996;8:1728.
[19] Lim YT, Park OO. Macromol Rapid Commun 2000;21:231.
[20] Ren J, Silva AS, Krishnamoorti R. Macromolecules 2000;33:3739.
[21] Krishnamoorti R, Giannelis EP. Macromolecules 1997;30:4097.