ELSEVIER

Polymer 42 (2001) 329–336

polymer

www.elsevier.nl/locate/polymer

Effects of comonomers and shear on the melt intercalation of styrenics/clay nanocomposites

J.T. Yoon[a], W.H. Jo[a,*], M.S. Lee[b], M.B. Ko[c]

[a]*Hyperstructured Organic Materials Research Center and Department of Fiber and Polymer Science, Seoul National University, Kwanak-ku, Sun 56-1, Shinlim-Dong, Seoul 151-742, South Korea*
[b]*Department of Textile Engineering and Advanced Materials Research Institute, Chonnam National University, Kwangju 500-757, South Korea*
[c]*Polymer Hybrid Research Center, Korea Institute of Science and Technology, Seoul 130-650, South Korea*

Received 28 December 1999; received in revised form 6 March 2000; accepted 12 April 2000

Abstract

The effect of polar comonomers introduced into polystyrene (PS) chains on the melt intercalation into organosilicate is investigated in terms of shear and annealing time. In the case, where the interaction between polymers and silicate layers is relatively weak, e.g. PS/organosilicate hybrids, it is difficult for the polymer chains to diffuse into interlayers of organosilicate and the hybrids are unstable under shear. For hybrids in which the interaction is enhanced by incorporating polar comonomers, e.g. acrylonitrile (AN) and methylvinyl oxzoline (OZ), their structures are stable even after a long mixing time. However, they do not show an exfoliated structure under the mixing conditions used in this study. The interaction between the comonomer and the silicate surface is investigated indirectly via both X-ray diffractional and FTIR spectral analyses. It is concluded that the structural stability of polymer/organosilicate hybrids is very dependent on the relative magnitude of the interactions between polymers, organic modifiers, and silicate layers.

Keywords: Clay; Intercalation; Exfoliation

1. Introduction

Polymer/inorganic hybrids based on the intercalation of polymer chains into layered silicates, form a class of nanocomposites that has recently received considerable attention from both academia and industry as an effective way to overcome the shortcomings of conventional mineral-filled composites [1]. They can be classified into three categories according to the degree of dispersion and/or exfoliation of silicates: conventional, intercalated, and exfoliated composites. In an intercalated structure, silicate sheets maintain their layered stacking, but the gallery height has increased to accommodate the intercalated polymer chains. In an exfoliated structure, individual silicate sheets lose their layered geometry and are dispersed in the polymers, resulting in excellent physical properties only with a small amount of loading.

The polymer/layered-silicate hybrids have been synthesized in three different ways, i.e. solution intercalation [2], in situ polymerization [3] or direct melt intercalation [4]. For commercial production, the first two approaches are limited because neither a suitable monomer nor a compatible polymer–silicate solvent system is always available. Moreover, they are not always compatible with current polymer processing techniques. These disadvantages drive the researchers to the direct melt-intercalation method [4–6]. To exfoliate the silicate layers into layer by layer on a nanometer scale using a melt process, the factors such as the interaction between polymers and organosilicate and mixing condition should be considered.

Various aspects of polymer/organosilicate hybrids obtained by melt intercalation have been investigated in recent years: interlayer structure of modified silicates [7], structural evolution during polymer melt intercalation [8], mobility of intercalated polymer chains described by both the glass transition behavior [9,10] and initial positron annihilation life time [11] and kinetics of polymer intercalation [12]. The effects of factors such as the length and number of alkyl groups of the cationic modifier molecule and the change in the polarity of matrix polymer on the intercalation behavior were also investigated [13]. Some attempts to predict the phase diagram and structural characteristics of nanocomposites in terms of the above-mentioned parameters were performed using thermodynamics based on the lattice model [14], the Onsager based approach [15],

---

* Corresponding author. Tel.: +82-2-8807192; fax: +82-2-8851748.
E-mail address: whjpoly@plaza.snu.ac.kr (W.H. Jo).

0032-3861/01/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00333-5

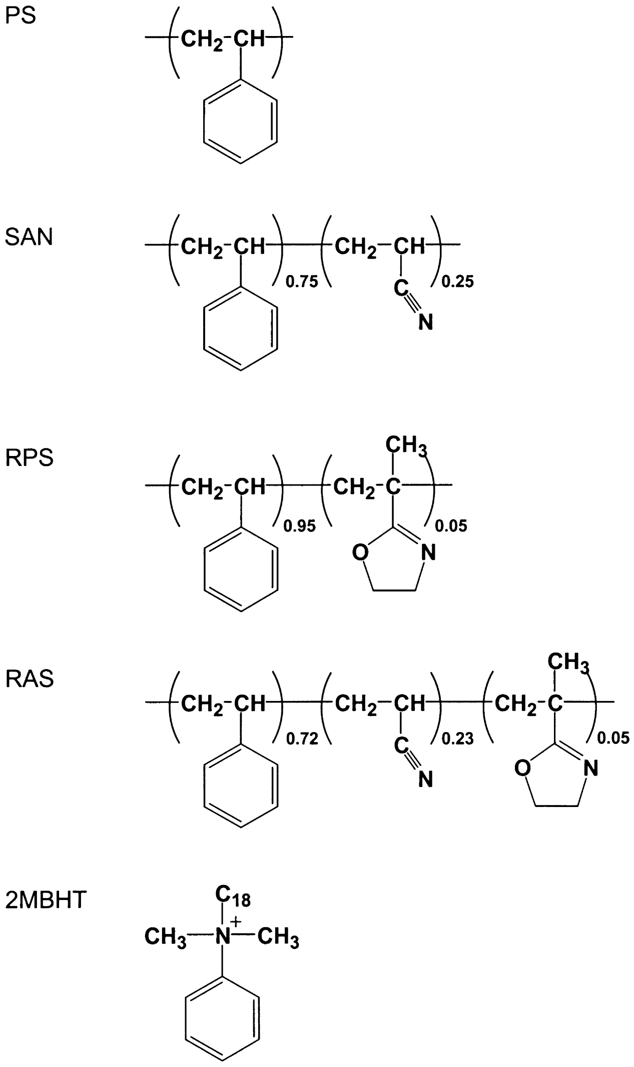

Fig. 1. Chemical structures of the polymers and organic modifier used in this study.

the self-consistent field (SCF) theory [16,17] and the molecular simulation method [18–20]. It has been reported [10,12] that the intercalation of organosilicate by PS takes place in a very short time and the equilibrium gallery height is independent of the molecular weight of PS, even though the intercalation rate is slower when the molecular weight is higher. Moreover, the gallery height is significantly lower than the radius of gyration of the polymers used, indicating that the polymer chains have flattened conformations in the gallery [9–11].

In this study, we investigate the effect of comonomers on the intercalation behavior of styrenic polymers/organosilicate hybrids because the introduced comonomers may change the degree of intermolecular interactions and the stress-transfer during mixing. Polystyrene homopolymer and three styrenic copolymers composed of styrene (ST), acrylonitrile (AN) and methylvinyloxazoline (OZ) were used. To investigate the effect of mixing condition, hybrids were prepared using two different methods: simple annealing without shear; and shear mixing using an internal mixer. The degree of intercalation is estimated using a wide-angle X-ray diffraction (XRD) technique and the interaction between polymer and organosilicate is investigated using a Fourier transform infrared (FTIR) spectroscopy.

2. Experimental

2.1. Materials

The organosilicate (C10) used in this study was a sodium montmorillonite (MMT) modified with dimethyl benzyl hydrogenated tallow ammonium (2MBHT), supplied by Southern Clay Products Inc. Inorganic content and cation exchange capacity of C10 were 61 and 125 meq./100 g, respectively, and its basal lattice spacing (d_{001}) by XRD was 1.91 nm. PS and three different styrenic copolymers, which are used as guest polymers, are commercially available and used without further purification. The chemical structures of the polymers are shown in Fig. 1 and their properties are listed in Table 1. All polymers in pellet or bead form were milled into fine powder with a narrow particle-size distribution, collected using a Cu mesh sieve (180 mesh), and then dried in a vacuum oven at 85°C for at least 24 h before mixing with organosilicate.

2.2. Hybrid preparation

Styrenic copolymer/organosilicate hybrids were prepared by two different methods. One is to prepare hybrids by simple annealing of the mixture without shear. Mixtures

Table 1
Characteristics of the polymers used in this study

Code	Source	Composition (wt%)			T_g[a] (°C)	M_w[b] (g/mol)
		ST	AN	OZ		
PS	Cheil Industries	100	–	–	108	220k
SAN	Cheil Industries	75	25	–	111	107k
RPS	Nippon Shokubai	95	–	5	105	188k
RAS	Nippon Shokubai	72	23	5	106	49k

[a] Measured by differential scanning calorimetry at the heating rate of 10°C/min.
[b] Measured by gel permeation chromatography using THF at 23°C; PS standard.

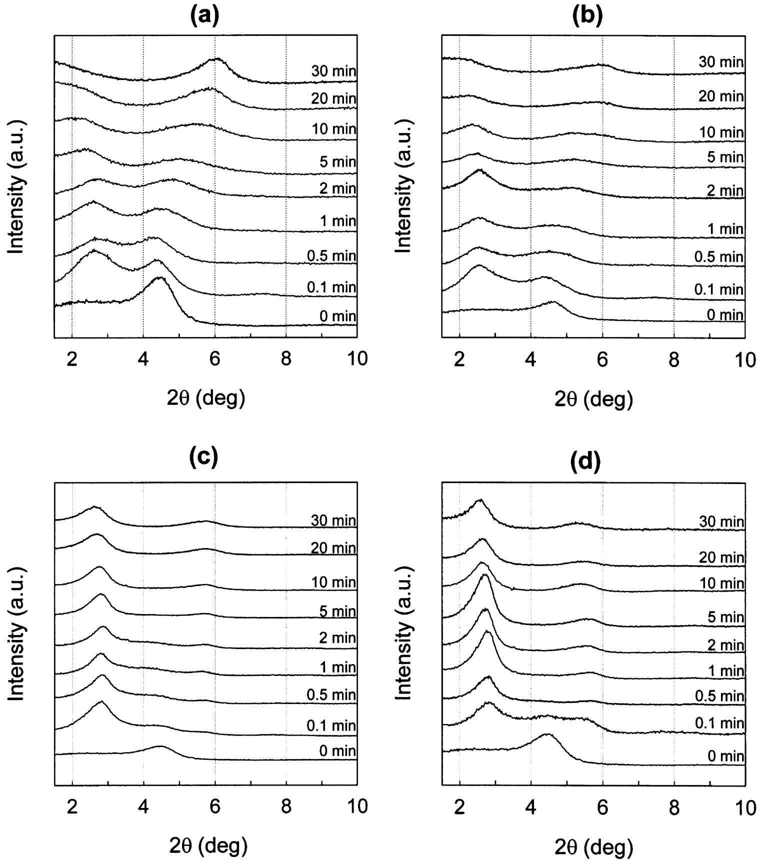

Fig. 2. Variation of the XRD intensity profiles with the annealing time for polymer/C10 hybrids prepared without shear at 210°C: (a) PS/C10; (b) RPS/C10; (c) SAN/C10; and (d) RAS/C10; Annealing times in minutes are indicated in each figure.

of polymers and C10 were dry-blended and then pressed into solid pellets using a hydraulic press at room temperature. Intercalated structure was developed by annealing the pellet at 210°C for a specified period of time under pressure. The resultant samples were quickly quenched to room temperature. The other is to prepare hybrids by using a Haake internal mixer with roller blades operating at 210°C for a specified mixing time. The rotor speed was 50 rpm, which corresponds to a shear rate of 65 s^{-1}. After mixing, the samples were quenched in liquid nitrogen. The fraction of C10 in hybrids was fixed at 5 wt% for melt-mixed hybrids and 20 wt% for annealed hybrids.

2.3. Characterization

The change in the basal spacing of the hybrids prepared with mixing time or annealing time was measured using an X-ray diffractometer (XRD, MAC Science MXP 18A-HF). CuK_α radiation ($\lambda = 0.154$ nm), generated at a voltage of 40 kV and a current of 100 mA, was used as an X-ray source. The diffraction angle was scanned from 1.5° at a rate of 2°/min. The basal lattice spacing of silicates was estimated from the position of the (001) plane peak in the XRD intensity profile using the Bragg's law, $d = \lambda/2 \sin \theta_{max}$. Specimens of shear-mixed hybrids for XRD were made by pressing the mixed sample at 200°C for 1 min, followed by quenching to room temperature. The interlayer structure of organosilicate was examined by an FTIR spectrometer (Perkin–Elmer FT-IR 1725X). Thirty-two scans at a resolution of 4 cm^{-1} are signal-averaged. To examine the interlayer structure of organosilicate, un-intercalated polymers were extracted from the hybrids by the Soxhlet method using methylethylketone (MEK) as an extraction solvent at 100°C for 12 days. The resultant silicates were filtered and then dried at 65°C for 3 days under vacuum.

3. Results and discussion

3.1. Hybrids prepared by simple annealing without shear

The finite expansion in interlayer height of organosilicate associated with intercalation results in the development of a new basal reflection in XRD intensity profiles. When powder mixtures of C10 and polymers are annealed without shear for 0.1 min, new peaks located around $2\theta = 2.5$–3° are observed regardless of the polymer type used, as shown in Fig. 2. Since the shift of the peaks to the lower diffraction-angle side indicates the increase in gallery height

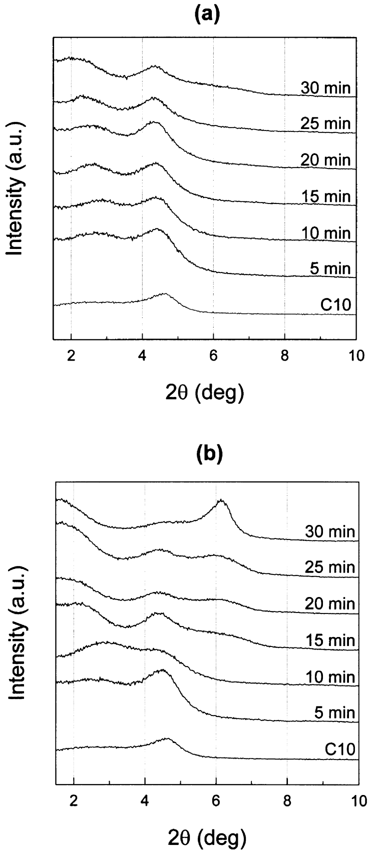

Fig. 3. Variation of the XRD intensity profiles from the neat organosilicate, C10, with the annealing time at: (a) 210°C; and (b) 220°C.

of the organosilicate, it is clear that all polymers used in this study are intercalated into the silicate interlayers in a short time. Quick disappearance of the peak at 4.7°, a characteristic peak of neat C10, also supports that the initial intercalation is a fast process.

When annealing time is increased, however, the structural change of hybrids becomes different depending upon the type of polymers used. For SAN and RAS, the positions of peaks corresponding to the intercalated structure ($2\theta =$ 2.6–2.9°) show only slight changes with annealing, indicating that the hybrid structures prepared from them are stable at the annealing temperature, 210°C. The peak at about 5.7° corresponds to the 002 reflection of the intercalated hybrids. On the other hand, for the PS and RPS copolymers, as the annealing time increases, the peaks at a high angle shift gradually to the higher angle side, and the low-angle peaks corresponding to the intercalated structure which are relatively strong and sharp shift slightly to the lower angle side. The high-angle peaks for PS/C10 and RPS/C10, as can be seen in Fig. 2a and b, are not considered as the 002 reflection of the intercalated organosilicate, because the peaks do not correspond to the scattering angle two times that for the first peak.

The shift of the high-angle peak to the higher angle side may be explained by the structural instability of C10. The interlayer structure of C10 may collapse from the bilayer arrangement of alkyl chains to monolayer one during annealing, which results in the reduction in the gallery height. It will be discussed in detail in the following section. Since the polymer chains experience a significant loss of conformational entropy when the chains are intercalated into a narrow interlayer of organosilicate, a large negative change of enthalpy is needed to overcome the entropy loss in order for the chains to be intercalated into the interlayer. Fig. 2c and d shows that the monomers AN and/or OZ used in this study may favorably interact with organosilicates and thus can stabilize the structure of hybrid during annealing. However, in the case that the interaction is not strong enough or the content of functional group in polymers is small, e.g. PS/C10 and RPS/C10, the interlayer structure of organosilicate may collapse during annealing, as can be seen in Fig. 2a and b. Therefore, it is summarized that when the intermolecular interactions between polymers, organic modifiers and the surface of silicate layers are not controlled in an optimum manner, two different processes take place competitively during melt annealing: the intercalation of polymer chain into the silicate interlayer; and the collapse of interlayer structure from the bilayer arrangement of alkyl chains to monolayer one. From these results, it is conjectured that there are two types of organosilicates: the one which is not intercalated with PS chains and whose interlayer alkyl chains are collapsed during annealing; and the other, intercalated with PS chains. It is not clear at present whether this observation is specific or general for polymer-intercalated hybrids. Although the collapse of interlayer structure of organosilicate itself under heat, of course, has been reported by McAtee et al. [21], there has been no report, to the best of our knowledge, to show the instability of interlayer structures in polymer/organosilicate hybrids during annealing. In the following sections, we will show the effect of thermal treatment on the interlayer structure of C10 and the effect of shear applied during mixing on the structural change.

When the positions of the first peaks of copolymer hybrids are compared with each other, it is revealed that the diffraction angle corresponding to the first scattering peaks becomes smaller in the order of RAS $\sim$ SAN $>$ RPS, which coincides with the order of the molecular weight of polymers. However, this difference in peak position seems to be relatively small, because the change in gallery height is much smaller than the radius of gyration of polymer chains at the annealing temperature.

3.2. Effect of thermal treatment of organosilicate

To examine the thermal stability of C10 itself, a neat C10 was annealed for a specified period of time in an oven under atmospheric environment at two different temperatures, 210 and 220°C. For C10 annealed at 210°C, as shown in Fig. 3a, the peak at $2\theta = 4.7°$ corresponding to the basal spacing for the bilayer arrangement of alkyl chains remains almost

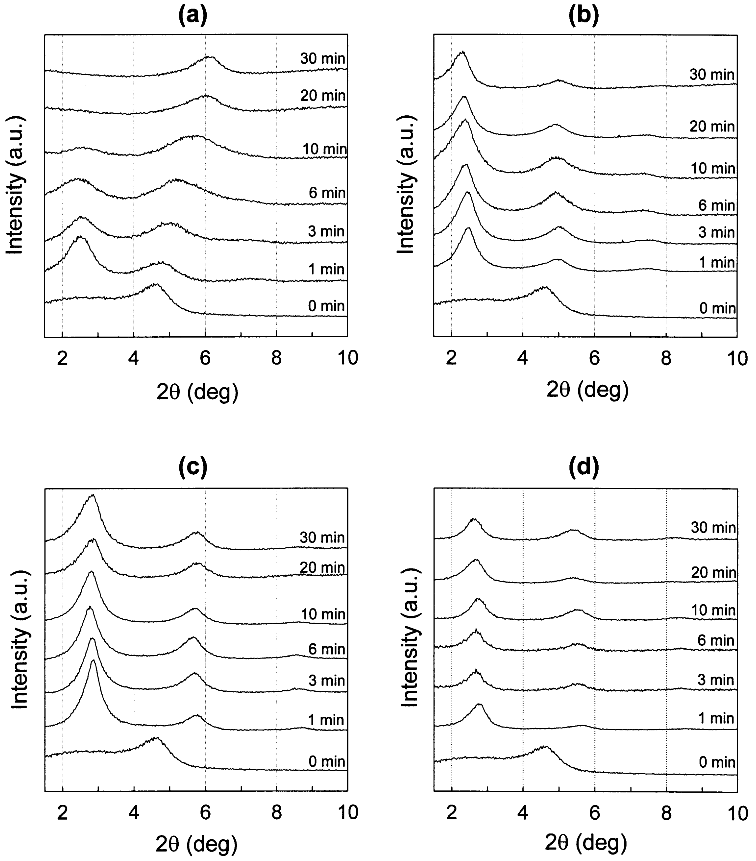

Fig. 4. Variation of the XRD intensity profiles with the mixing time for polymer/C10 hybrids prepared with an internal mixer at 210°C under a shear rate of 65 s^{-1}: (a) PS/C10; (b) RPS/C10; (c) SAN/C10; (d) RAS/C10. Mixing times in minutes are indicated in each figure.

constant even after 30 min of mixing, and a weak and broad peak at a lower angle around $2 \sim 3^\circ$ evolves, the origin of which is not clear at present. Annealing at 220°C, by the way, casts different XRD intensity profiles, as shown in Fig. 3b. The intensity of the peak at 4.7° becomes weaker as the annealing time increases. A weak and broad peak at a lower angle is also observed. Another new peak begins to develop at 6.2° after 15 min of annealing. It becomes abruptly sharp and strong after 30 min of mixing, which is expected to correspond to the monolayer arrangement of alkyl chains in the interlayer probably due to the breakup of coulombic interaction between modifier ammonium and negative charge of silicate surface. These results indicate that the interlayer structure of bilayer arrangement is relatively stable at 210°C and an increase of only 10°C is critical enough to break the ionic bond resulting in the collapse to the monolayer arrangement. Simple calculation on the gallery heights of C10 with monolayer or bilayer arrangements of alkyl chains in organic modifier may support the above-mentioned explanation: $d_{\text{monolayer}} = 0.96 + 0.46 = 1.42$ nm (corresponding to $2\theta \sim 4.7^\circ$) for monolayer, and $d_{\text{bilayer}} = 0.96 + 2 \times 0.46 = 1.88$ nm (corresponding to $2\theta \sim 6.2^\circ$) for bilayer. In these calculations, 0.96 and 0.46 nm were used as the thickness of silicate layer and that of alkyl chain, respectively [22,23]. Vaia et al. [7], however, reported that the gallery height of organosilicate moderately increases as the temperature increases from 80 to 130°C. They explained that the increase arises from the transition from solid-like to liquid-like environment of alkyl chains. Their result is not in much contradiction with our results, considering that their experimental temperature was lower than that of ours and the annealing time was not specified in their report.

In order to check whether or not the collapse of the interlayer structure of organosilicate arises from the thermal degradation of organic moiety during annealing, the weight loss of organosilicate was measured after the neat C10 was annealed at 210 or 220°C for 30 min. Since the weight loss was less than 0.5 wt% of organic components at both temperatures, it is believed that the collapse does not come from the thermal degradation of organic moiety in C10. Therefore, it is believed that the organic molecules (2MBHT) are exuded from the gallery during annealing. Thermodynamically, organic modifiers can be exuded from the interlayer of organosilicate when the entropy gain owing to the exudation is greater than the coulombic interaction energy between the modifiers and silicate layer at the annealing temperature.

When Fig. 2a and b is compared with Fig. 3a, it is revealed that the time evolutions of monolayer silicates in all polymer/C10 hybrids are much faster than in the neat C10. This implies that the interaction between organic modifiers and polymer chains accelerates the exudation of organic modifiers from the interlayer and that the collapse of interlayer structure is controlled by both the entropic gain of exuded 2MBHT molecules and enthalpic interaction between polymer and modifier. The stability of intercalated structure might affect the preparation of clay-dispersed nanocomposite through melt intercalation. If the ionic bond between modifier and silicate layer is broken, and therefore, the collapse into the monolayer-arrangement is predominant upon mixing, it becomes more difficult for polymer chains to penetrate into the collapsed interlayer due to the entropy barrier. Therefore, to minimize the collapse of interlayer, care should be given to the determination of the process temperature, at which the massive breakage of coulombic interactions is not initiated, and the selection of a polymer for the intercalated hybrid, which may interact weakly with the modifier and strongly with the silicate surface.

3.3. Hybrids prepared by melt mixing

For the copolymer hybrids, most silicates are intercalated within 1 min of mixing and the peak positions remain almost unchanged during longer mixing, as shown in Fig. 4. Comparison of Figs. 2 and 4 shows that the shear does not give a significant change in the intercalation behavior of polymer chains under our experimental condition except for RPS/C10. Under shear, RPS/C10 hybrids show only diffraction peaks associated with intercalation without any symptom of chain collapse in interlayer. The stabilization of intercalated structures in the SAN, RPS, and RAS hybrids is believed to arise from the interaction between silicate layers and incorporated comonomers. The OZ units may interact with hydroxyl groups on the surface of silicate layer through hydrogen-bonding [15,16,24,25] and AN units interact with N^+ of ammonium through polar interaction [26]. For the PS hybrid, the XRD intensity profiles show a different behavior from the others. As the mixing time increases, the peak located around $2\theta = 4.7°$ moves to the higher angle side and finally settles at the angle of 6.2°, which corresponds to the monolayer arrangement of alkyl chains in the intergallery as said above. A noteworthy point for the PS/C10 hybrid (weak interaction between polymer and silicate surface) is that the peak intensity at 2.5° decreases and becomes broader with increasing mixing time and disappears after 20 min of mixing. Since the intercalated structure of PS hybrids from simple annealing is maintained to some extent for a longer annealing time, as shown in Fig. 2a, it is clear that the shear applied during mixing rather accelerates the collapse of interlayer structure of organosilicate and also pulls the intercalated PS chains out of the gallery.

Very recently, Hasegawa et al. [27] reported that an exfoliated hybrid of RPS and organosilicate was prepared by melt mixing. They suggest that the strong hydrogen bonding between OZ and oxygen groups of silicate surface plays a critical role in delaminating and dispersing the silicate layers of clay on a nanometer scale. However, the RPS hybrids prepared in our study seem to be very stable under the mixing conditions applied in this study, and therefore, only intercalated hybrids with an enlarged gallery height are obtained. Comparing our results with their results, one of the reasons for this discrepancy is the different mixing devices and hence the different shear rate and field during mixing. Lower processing temperature in their experiment (180°C) compared to ours (210°C) might be another effective factor both to retard the interlayer collapse and to effectively transfer shear force owing to higher melt viscosity. From these results, it is summarized that the shear applied during the mixing does not give any significant effect on the intercalation behavior when the interaction between the polymer and the silicate surface is absent or very weak as in PS hybrids.

The effect of shear on the formation of nanocomposite of polymer/clay via melt intercalation has been studied experimentally in a qualitative sense [12]. They reported that the presence of an externally applied shear would promote the exfoliation of silicate layers. Huh and Balazs [28] also investigated the effect of shear on the intercalated polymer/clay nanocomposites via a Monte Carlo simulation method. They found that the bridging chains between two confining layers in silicate are converted to loops or free chains under shear. As a consequence, the bridging force is removed and the mixture can readily form an exfoliated composite. This suggests that an optimum combination of external shear and the interaction between polymer and silicate layer is the prerequisite for exfoliated nanocomposite. Further works are required to quantitatively investigate the effect of the shear field on exfoliation of silicate layers.

From the thermodynamic point of view, it is expected that the strong interaction between polymer and silicate layers may lead to stable intercalated hybrids rather than exfoliated ones. Recently, Balazs and co-workers [15–17] have investigated the intercalation- and exfoliation-phenomena of polymer/organosilicate hybrids by examining the phase behavior in polymer–clay mixtures based on the Onsager approach [15] and the SCF theory [16,17] using a computer simulation technique. From a free energy expression for a mixture of polymer and thin disks, they concluded that an intercalated and stable structure is expected from kinetic consideration when the Flory–Huggins interaction parameter, χ, between polymer and disk is negative. As a polymer chain diffuses into the energetically favorable interlayer, it maximizes the contact with the two confining layers. In effect, the polymer chain ‘glues’ the two surfaces together as it moves into the interlayer. This ‘fused’ condition could represent a kinetically trapped structure, and as a result, an increase in the attraction between the polymer and the silicate layer would lead only to an intercalated structure, rather than an exfoliated one.

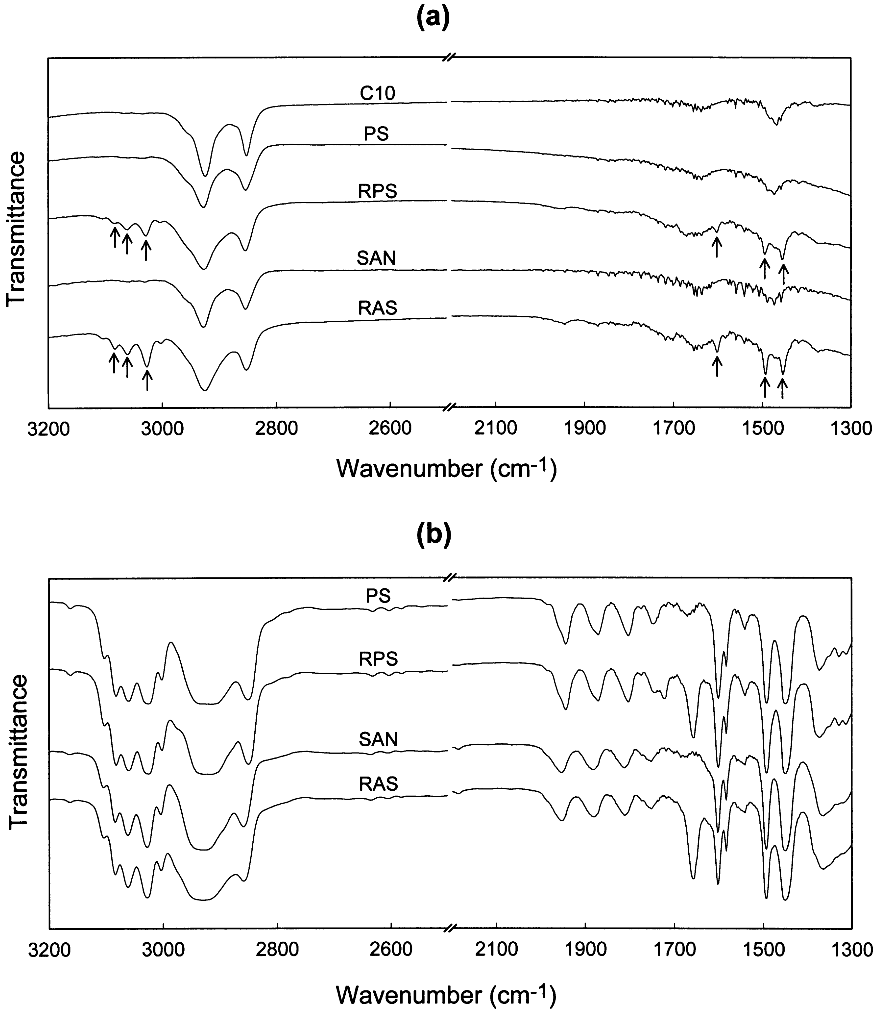

Fig. 5. FTIR spectra of extracted silicates and polymers: (a) extracted silicates; and (b) virgin polymers.

3.4. Analysis of extracted silicates

Whether or not polymer chains are strongly attached to the silicate surface, may be identified using FTIR and XRD analyses for the solvent-extracted silicates. Fig. 5 shows the FTIR spectra of the residual silicates after extraction of polymer from hybrids using MEK. Spectra of the silicates from the PS/C10 and SAN/C10 are nearly identical to the neat C10 (Fig. 5a and b). The bands at ~2920 and 2850 cm^{-1} are assigned to the CH_2 asymmetric and symmetric stretching mode of alkyl group in cationic modifier molecules, respectively. The band around 1470 cm^{-1} is due to the CH_2 bending (scissoring) vibration. However, the silicates extracted from RPS/C10 and RAS/C10 show characteristic bands of the polymers: 1600, 1490 and 1450 cm^{-1} due to the stretching vibration of –C=C– in benzene ring. The characteristic bands around 3000–3100 cm^{-1} associated with the stretching vibration of CH in the aromatic ring are also observed, although, the stretching vibration of –C=N– in the OZ ring at 1660 cm^{-1} was not clearly identified in extracted silicates. These results indicate that the PS and SAN chains intercalated during mixing are solved out of gallery while the RPS and RAS chains still reside within interlayer. The polymers attached to the silicates may affect

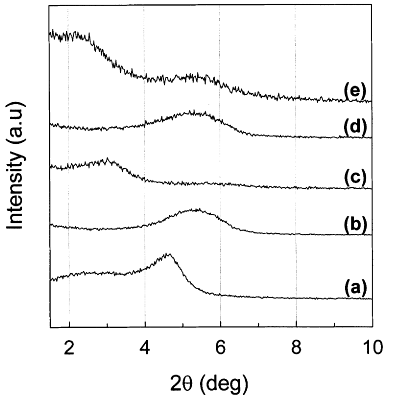

Fig. 6. The XRD intensity profiles of silicates extracted from polymer/C10 hybrids by the Soxhlet method at 100°C for 12 days. Silicates were extracted from: (a) C10; (b) PS/C10; (c) RPS/C10; (d) SAN/C10; and (e) RAS/C10.

the gallery height of the silicates extracted. Fig. 6 shows the XRD intensity profiles of the same extracted silicates as those used for the FTIR analysis. As expected from FTIR results, the extracted silicates from the PS and SAN hybrids have reduced values of *d* spacings compared to that of the neat C10 itself, whereas the *d* spacings from the RPS and RAS hybrids are comparable to the *d*-values before extraction. These results provide another evidence confirming that polymer chains of RPS and RAS be strongly entrapped within the interlayer during melt intercalation of polymers even under shear. Although simple polar interaction between the nitrile group in AN units and the oxygen group of the silicate surfaces contributes to form stable hybrids of SAN/C10, it does not seem to impart the permanent stability which can survive under the extraction condition. On the origin and role of the interactions between OZ units in RAS and RPS and the organosilicate, further studies are under progress.

4. Conclusions

Using X-ray diffraction and FTIR spectroscopy, we investigated how the type and content of comonomers and/or preparation method of hybrids affect the melt intercalation of styrenics/organosilicate hybrids. PS and three different styrenic copolymers with OZ and/or AN units were used as matrix polymers. The organic modifier used in this study, 2MBHT, does not seem to impart thermal stability to the organosilicate during melt annealing at 210°C. When the hybrids were prepared by two different methods, i.e. the simple annealing without shear and the shear mixing in an internal mixer at the same temperature, all polymers used in this study were successfully intercalated into the gallery of organosilicate in a very short time, irrespective of the preparation method. However, the hybrids show different structural stability during simple annealing or shear mixing. For the PS hybrids, simple annealing causes the change in interlayer structure of organosilicate, which is not intercalated with PS, whereas the intercalated structures are still stable during annealing. The shear applied during mixing was detrimental to the structural stability of the PS hybrids. The gallery height of the PS hybrids after 20 min of mixing was reduced to that of the organosilicate with monolayer arrangements. From these results, we may conclude that when the interaction between the polymer chain and the silicate surface (not organic modifiers) is not strong enough, the interlayer structure of resulting hybrids is unstable under shear, and thus, polymer chains are exuded out from the interlayer of organosilicate during mixing, which is unfavorable for exfoliation.

The structures of copolymer hybrids are very stable under both simple annealing and shear mixing. It is clear that polar comonomers introduced into PS contribute to enhance the interaction between the polymers and the silicate surfaces, and thus to stabilize the resultant hybrids. However, the stability of the intercalated structure may be rather unfavorable for the exfoliation of silicate layers under the experimental conditions used in this study.

References

[1] LeBaron PC, Wang Z, Pinnavaia TJ. Appl Clay Sci 1999;15:11–29.

[2] Ogata N, Jimenez G, Kawai H, Ogihara T. J Polym Sci Part B: Polym Phys 1997;35:389–96.

[3] Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, Kamigaito O. J Mater Res 1993;8:1179–84.

[4] Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A. Macromolecules 1997;30:6333–8.

[5] Giannelis EP. Appl Organomet Chem 1998;12:675–80.

[6] Fischer HR, Gielgens LH, Koster TPM. Acta Polym 1999;50:122–6.

[7] Vaia RA, Teukolsky RK, Giannelis EP. Chem Mater 1994;6:1017–22.

[8] Vaia RA, Giannelis EP. Chem Mater 1996;8:2628–35.

[9] Vaia RA, Giannelis EP. Chem Mater 1993;5:1694–6.

[10] Sikka M, Cerini LN, Ghosh SS, Winey KI. J Appl Polym Sci 1996;34:1443–9.

[11] Olson BG, Peng ZL, Srithwatpong R, McGervy JD, Ishida H, Jamieson AM, Manias E, Giannelis EP. Mater Sci Forum 1997;255–257:336–8.

[12] Vaia RA, Jandt KD, Kramer EJ, Giannelis EP. Macromolecules 1997;28:8080–5.

[13] Vaia RA, Giannelis EP. Macromolecules 1997;30:8000–9.

[14] Vaia RA, Giannelis EP. Macromolecules 1997;30:7990–9.

[15] Lyatskaya Y, Balazs AC. Macromolecules 1998;31:6676–80.

[16] Balazs AC, Singh C, Zhulina E. Macromolecules 1998;31:8370–81.

[17] Zhulina E, Singh C, Balazs AC. Langmuir 1999;15:3935–43.

[18] Lee JY, Baljon ARC, Loring RF. J Chem Phys 1998;109:10 321–30.

[19] Baljon ARC, Lee JY, Loring RF. J Chem Phys 1999;111:9068–72.

[20] Lee JY, Baljon ARC, Loring RF. J Chem Phys 1999;111:9754–60.

[21] McAtee Jr JL, Concilio CB. Am Mineral 1959;44:1219–29.

[22] Lagaly G. Clay Miner 1981;16:1–21.

[23] Török B, Bartók M, Dékány I. Colloid Polym Sci 1999;227:340–6.

[24] Hasegawa N, Kawasumi M, Kato M, Usuki A, Okada A. J Appl Polym Sci 1998;67:87–92.

[25] Karaboni S, Smith B, Heidug W, Urai J, van Oort E. Science 1996;271:1102–4.

[26] Noh MH, Jang LW, Lee DC. J Appl Polym Sci 1999;74:179–88.

[27] Hasegawa N, Okamoto H, Kawasumi M, Usuki A. J Appl Polym Sci 1999;74:3359–64.

[28] Huh J, Balazs AC. ACS Polym Mater Sci Engng 1999;81:449–50.