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Preparation of clay-dispersed poly(styrene-*co*-acrylonitrile) nanocomposites using poly(ϵ-caprolactone) as a compatibilizer

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Abstract

Poly(styrene-*co*-acrylonitrile) (SAN)/organoclay nanocomposites were prepared using poly(ϵ-caprolactone) (PCL) as a compatibilizer. Two-step mixing sequence was used to prepare the SAN nanocomposites: PCL/organoclay master batches with different degree of intercalation were prepared by melt mixing first, and then they were melt-mixed with SAN, where PCL is miscible with SAN. The intercalation behavior of PCL in the master batches was investigated in terms of the type of organic modifier and mixing conditions such as shear rate, mixing temperature and mixing time. Longer mixing time and lower mixing temperature were required to prepare exfoliated PCL master batches. As the degree of exfoliation of clays becomes better, the stiffness reinforcement effect of the organoclays increases in both PCL/organoclay master batches and their blends with SAN. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocomposites; Organoclay; Poly(styrene-*co*-acrylonitrile)

1. Introduction

In recent years, the polymer/silicate hybrid nanocomposites have been of considerable interest as an effective method to develop new composite materials [1–4]. When the silicate layers, which are the basic building unit of natural or synthetic clays, are exfoliated in nano-scale and randomly distributed into polymer matrix, physical properties of the resultant composites are significantly enhanced. For example, polyamide nanocomposites with nano-scale silicate plates have been known to have extraordinarily good mechanical properties and heat stability compared to neat polyamides or conventional clay composites [5].

Among various methods, the following two are considered as commercially attractive approaches for preparing polymer/clay nanocomposites: in-situ polymerization and melt exfoliation. The latter is especially important in practical interests, because normal processing condition can be applied without requirement of additional equipment. However, it is not always possible to directly introduce polymer chains into gallery of silicate layers and then to exfoliate them during melt mixing, because the electrostatic interactions between silicate layers are very strong. Thus, before compounding with polymers, pristine clays should be modified in order to facilitate the introduction of polymer chains into the intergallery of silicate layers. Introducing low molecular weight organic modifier into the intergallery can make the silicate layers organophilic. To prepare the nanocomposites with exfoliated silicate layers, the organic modifier introduced should interact favorably with matrix polymer. For example, polyamide nanocomposites with exfoliated silicate layers can be prepared by simple mixing only when the organic modifiers with polar functional moiety such as hydroxyl group, which is able to interact with amide group in polyamide via hydrogen bonding, are introduced into intergallery. However, it is not always possible to prepare exfoliated nanocomposites, even though the interaction between matrix polymer and organic modifier is favorable. In other words, optimized mixing conditions should be applied for obtaining exfoliated nanocomposites, and relative magnitude of the interactions between polymer, organic modifier, and silicate layer should also be considered [6]. If such factors could not be carefully controlled, only intercalated nanocomposites would be obtained.

More recently, it has been reported by Hasegawa and his coworkers [7,8] that polypropylenes with exfoliated silicate layers were successfully prepared when the polymer

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compatibilization technique for immiscible polymer blends was used. They used the functional polymers with small amount of functional moiety as a compatibilizer to enhance the affinity of polymer to organosilicate. For example, maleic anhydride (Mah) modified polypropylene (Mah-PP) was used for preparing exfoliated PP nanocomposites [8] and poly(styrene-*co*-oxazoline) copolymers was also used for polystyrene nanocomposites [9]. The amount of functional groups in compatibilizers should be controlled to give the optimized interaction of compatibilizer with matrix polymer or organic silicate.

In this study, we investigate another compatibilizing approach to prepare polymer hybrid nanocomposite by melt-exfoliation. Instead of using functionalized polymers, a polymer miscible with the matrix polymer, is used as a compatibilizing component. As a prerequisite condition for this purpose, the polymer, selected as a compatibilizer, is required to exfoliate the silicate layers during melt mixing. As a model system, we select poly(styrene-*co*-acrylonitrile) (SAN)/clay hybrid in which the silicate layers are not exfoliated during melt mixing [6]. Poly(ϵ-caprolactone) (PCL) is chosen as a compatibilizer, because it is well known that PCL is miscible with SAN, if the AN content in SAN copolymer is in the range of 8–28 wt% [10], and because it was reported that PCL can exfoliate silicate layers of clay during melt mixing [11].

2. Experimental

2.1. Materials

PCL ($M_w = 80,000$ g/mol, $T_g = -60$°C, and $T_m = 62$°C) was obtained from Sigma-Aldrich Chem. Co. Ltd. The SAN copolymer containing 25 wt% of acrylonitrile was obtained from Cheil Industries Inc. The molecular weight of SAN is 69,000 g/mol and its glass transition temperature is 106°C. Three different organoclays were used in this study: Cloisite® 30A, C16, and C18. Cloisite® 30A, organics-treated montmorillonite (MMT), was obtained from Southern Clay Products Inc. It contains methyl tallow bis-2-hydroxyethyl ammonium ion as an organic modifier. The C16 and C18 were synthesized by ion-exchange reaction. The interlayer cations of natural Na-MMT, supplied by southern Clay Product Inc, were exchanged with cetyltrimethyl ammonium ion (C16) or octadecyltrimethyl ammonium ion (C18). The details of the alkylammonium ion exchange reactions are described elsewhere [12]. The chemical structures of organic modifiers used in this study are shown in Fig. 1.

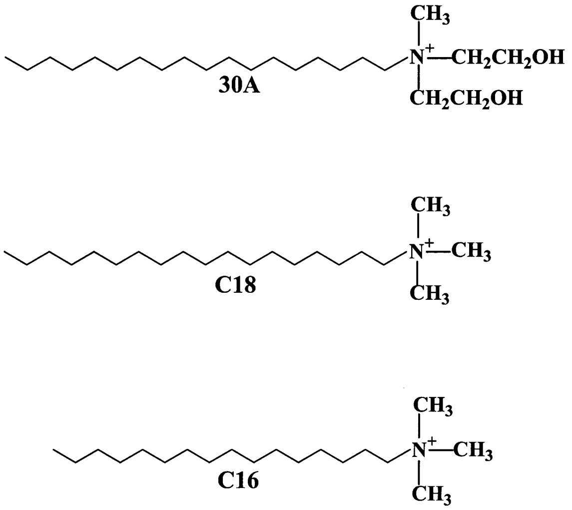

Fig. 1. Schematic representation of structure of organic modifiers used in this study.

2.2. Preparation of hybrid nanocomposites

To use PCL/organoclay hybrids as a master batch for preparing SAN/organoclay nanocomposites, PCL and organosilicates were melt-mixed first. The master batch of PCL/organoclay was then melt-mixed with SAN. In order to investigate the effect of processing conditions on the intercalation/exfoliation of the silicate layers in the master batch, some experiments were performed as follows. First, to investigate the effect of organic modifier on the melt intercalation and/or exfoliation of PCL, PCL was melt-mixed with three different organoclays, i.e. 30A, C16, and C18, at 100°C for 10 min using a Mini-Max molder. Second, to investigate the effect of shear rate, PCL was melt-mixed with 30A under different rotor speeds at 100°C for 10 min. For comparison, intercalation and/or exfoliation without shear was also examined by annealing the mixture of fine polymer powder and 30A on a hot plate. Third, the effect of mixing temperature was investigated by varying the mixing temperature (100 and 190°C) for the specified mixing time and under constant rotor speed (120 rpm). For all the experiments, the organoclay content was fixed at 5 wt%. The PCL/30A hybrid as a master batch was mixed with SAN at 180°C for 8 min using a Mini-Max molder. The sample code of (PCL/30A)/SAN denotes this procedure. The SAN content in SAN hybrid nanocomposites was fixed at 60 wt%.

2.3. Calculation of the maximum shear rate at wall

A mixture (1.5 g) of PCL and organosilicate was dry-blended and then was melt-mixed using a Mini-Max molder (rotor diameter of 1.5 cm) for a specific period of time. In order to quantitatively examine the effect of shear stress on the degree of exfoliation of silicate layers, different rotor speed was applied during mixing process in the Mini-Max molder. Assuming that the geometry of the molder is of two parallel disks with radius *r*, the maximum shear rate at wall can be expressed as $\gamma_{max} = 2\pi\Omega/(h \times 60)$ (rad/s), where *h* is the height of polymer melt confined between the parallel disks, and Ω is the mixing rotor speed in rpm. The melt density of PCL ($\rho_{melt} = 1.1$ g/cm^3) is used for the calculation of *h*. The melt viscosity of PCL was measured using a Rheometrics mechanical spectrometer (Model 800) in the oscillatory mode with parallel plate fixture of 25 mm in diameter. Dynamic frequency sweep experiments were performed with the frequency sweep ranging from 0.1 to 100 rad/s in linear viscoelastic region at two different temperatures of 100 and 190°C.

2.4. Characterization

The change in basal spacing of the nanocomposites was measured using an X-ray diffractometer (MAC Science, MXP 18A-HF). Ni-filtered CuK_α ($\lambda = 1.54$ Å) radiation, generated at a voltage of 40 kV and current of 30 mA, was used as an X-ray source. Diffraction angle was scanned from 1.5° at a rate of 2°/min. The basal spacing of silicate layers was estimated from the position of (001) plane peak in XRD pattern using the Bragg's law, $d = \lambda/2\sin\theta_{\max}$. Dynamic mechanical properties of hybrids were measured by a Rheometric scientific dynamic mechanical thermal analyzer (DMTA) with a bending mode at the frequency of 1 Hz. The temperature range was between −100 and 130°C.

3. Results and discussion

Fig. 2(A) shows the XRD patterns of organoclays used in this study, indicating that the (001) reflection position is dependent on the type of organic surface modifiers. The XRD patterns for PCL/organoclay hybrids, which were prepared by melt mixing at 100°C for 10 min using a Mini-Max molder, are shown in Fig. 2(B). Although *d*-spacing calculated from the peak position of XRD pattern of 30A is smaller than that of C18, *d*-spacing of 30A in the PCL/30A hybrid is larger than that of C18 in the PCL/C18 hybrid after melt mixing with PCL. This is probably because the organic modifier 30A with hydroxyl groups interacts more favorably with carbonyl groups in PCL than non-polar C18 or C16 does. For this reason, 30A was selected as the organoclay for this study.

The shear rate during mixing may affect the intercalation and/or exfoliation of polymer/clay nanocomposites. Fig. 3 shows how the shear rate during mixing affects the intercalation of the PCL/30A master batch, when the master batch was prepared at 100°C for 10 min. Here we assume that the shear rate applied to the master batch is proportional to the rotor speed of Mini-Max molder. Moreover, since the shear stress is proportional to the shear rate, it is expected that exfoliation would take place more readily as the shear rate during mixing increases. However, only intercalated structures are obtained under the conditions employed in this experiment, as shown in Fig. 3. Therefore, it seems that the melt intercalation of PCL into the silicate layers does not depend upon the magnitude of shear rate within the shear range used in this study. Thus, the rotor speed was fixed at 120 rpm in this study.

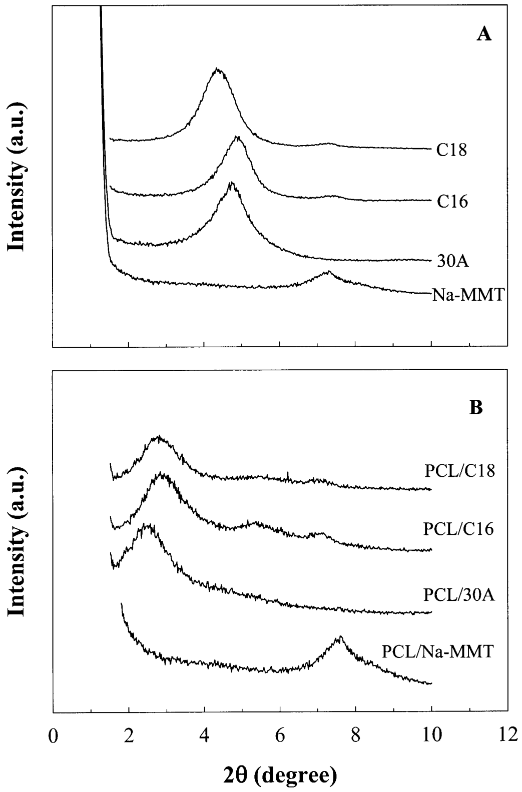

Fig. 2. Effects of the organic modifiers on the melt intercalation of PCL: (A) XRD patterns of pristine clay and organoclay used in this study and (B) XRD patterns of PCL/organoclay hybrids after melt intercalation of PCL. Melt mixing was performed at 100°C for 10 min under constant rotor speed of 120 rpm. The calculated maximum shear rate and the shear viscosity are 12.2 rad/s and 8300 Pa s, respectively.

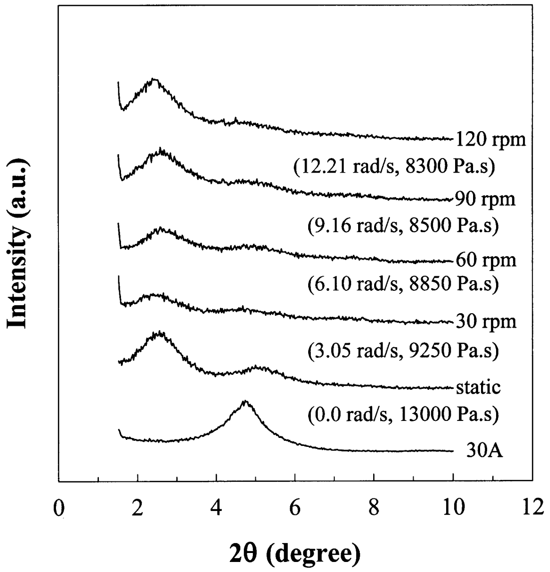

Fig. 3. Effects of shear rate (static, 30, 60, 90 and 120 rpm) during mixing on the melt intercalation of PCL/30A hybrids. Melt mixing was performed at 100°C for 10 min. For comparison, XRD pattern of 30A is presented. The calculated maximum shear rate at wall and the shear viscosity are indicated in parenthesis for each rotor speed.

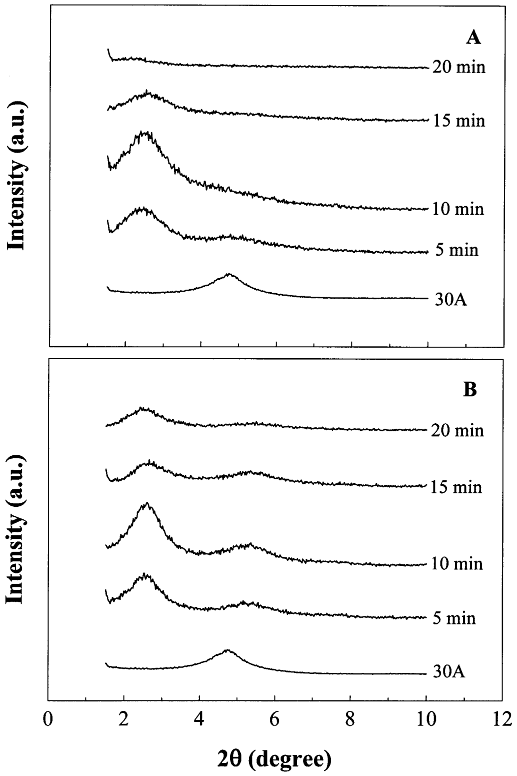

Fig. 4. Effect of mixing temperature and mixing time on the melt intercalation of PCL/30A. Melt mixing was performed at (A) 100°C and (B) 190°C under constant rotor speed of 120 rpm. Mixing time in minutes is indicated. The calculated maximum shear rate at wall and the shear viscosity at 190°C are 12.2 rad/s and 1150 Pa s, respectively.

Fig. 4 shows the effect of mixing time and mixing temperature on the intercalation and/or exfoliation of PCL in the PCL/30A hybrid. Mixing was performed at two different temperatures, 100 (Fig. 4(A)) and 190°C (Fig. 4(B)), for the specified mixing time. From the peak positions of the XRD patterns, it is found that *d*-spacing of the PCL/30A hybrid does not significantly change with the mixing temperature or mixing time. However, the peak area corresponding to (001) plane of silicate layers gradually decreases with the mixing time for the samples prepared at 100°C, and finally the diffracted peak becomes indiscernible after 20 min of mixing. This means that more disordered structure of layered silicates is developed within 20 min. Similar trend is observed at 190°C, but the peak still remained after 20 min of mixing. The shear stress applied to silicate layers is expressed as the product of the melt viscosity of system and the shear rate, if the hybrid melt is a Newtonian fluid. When an equal shear rate (or rotor speed) is applied, the shear stress transmitted to silicate layers is proportional to the melt viscosity of system. Since the melt viscosity increases with decreasing the processing temperature, the shear stress transmitted to the silicate layers increases with decreasing the mixing temperature. Therefore, more disordered structure could be developed at the lower temperature, i.e. 100°C. This suggests the possibility that PCL/30A nanocomposites with different degree of exfoliation can be prepared by varying processing conditions.

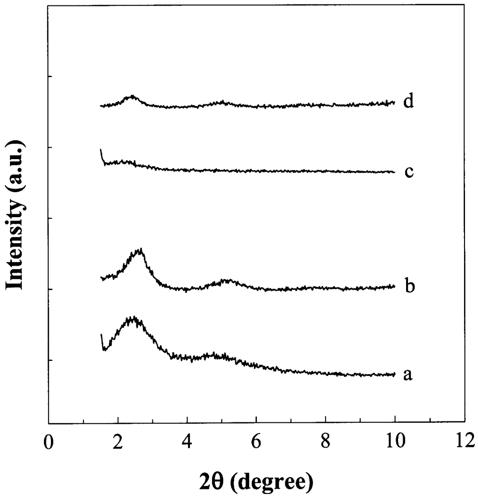

Fig. 5. XRD patterns for (a) intercalated PCL/30A master batch, mixed at 100°C for 5 min under constant rotor speed of 120 rpm; (b) (intercalated PCL/30A master batch)/SAN nanocomposite; (c) partially exfoliated PCL/30A master batch, mixed at 100°C for 20 min under constant rotor speed of 120 rpm; (d) (partially exfoliated PCL/30A master batch)/SAN nanocomposite. Mixing SAN with the master batch was performed at 180°C for 8 min under constant rotor speed of 120 rpm.

SAN/organoclay nanocomposites with PCL as a compatibilizer were prepared by melt mixing SAN with the PCL/organoclay nanocomposite prepared above. The degree of exfoliation of silicate layers in the (PCL/organoclay)/SAN nanocomposites may be dependent upon the degree of exfoliation of PCL/30A used as the master batch: exfoliated (PCL/organoclay)/SAN nanocomposites are expected when the exfoliated PCL/organoclay hybrid is mixed with SAN. Fig. 5 shows the XRD patterns for the SAN nanocomposites prepared by mixing SAN with PCL/organoclay nanocomposite at 180°C for 8 min. When the intercalated PCL/clay is mixed with SAN, any change in the position and shape of the diffracted peak is not observed, as shown in Fig. 5(a) and (b), indicating that mixing of SAN with PCL/clay does not affect the intercalation into the organosilicate. On the other hand, when partially exfoliated PCL/30A was mixed with SAN, weak and broad peaks appeared again, as can be seen in Fig. 5(d). It may be attributed to the aggregation and/or reordering of silicate layers during further mixing of PCL/organoclay with SAN. Since the lower critical solution temperature (LCST) of the PCL/SAN blend is located near 90°C, as shown in Fig. 6, the mixing temperature of this study, 180°C, is higher than the LCST. Here, the phase diagram of PCL/SAN blend was determined by the cloud point measurement. Therefore, the two polymers are not mixed at the molecular level during mixing. The immiscibility between SAN and PCL may decrease the affinity of organoclay to matrix SAN copolymers and thus cause the aggregation of the nanoscale building blocks in the

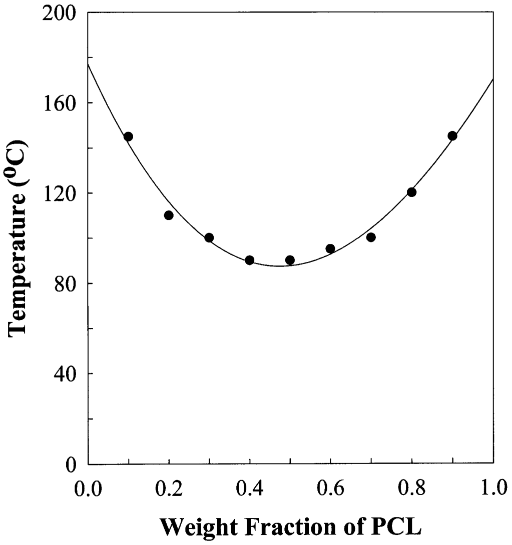

Fig. 6. Phase diagram of PCL/SAN blend, showing the LCST.

SAN-rich domains. It is clear from Fig. 5 that the phase separation between matrix and compatibilizer during melt mixing is critical for preparing exfoliated nanocomposite using a polymer miscible with the matrix polymer as a compatibilizer. More detailed work to examine the effect of phase separation during melt mixing on the reaggregation of organosilicate will be needed. The scanning electron micrograph shows that the blend of SAN and PCL prepared at 180°C is homogeneous when the sample is cooled to room temperature, as can be seen in Fig. 7. This indicates that the blend is homogeneous below the LCST, even though the mixing temperature is higher than the LCST. This is because the phase separation of PCL/SAN blend is a thermoreversible process across the LCST. Indeed, the blend at 180°C is opaque, but the blend film becomes clear when the blend is cooled to lower temperature than the LCST.

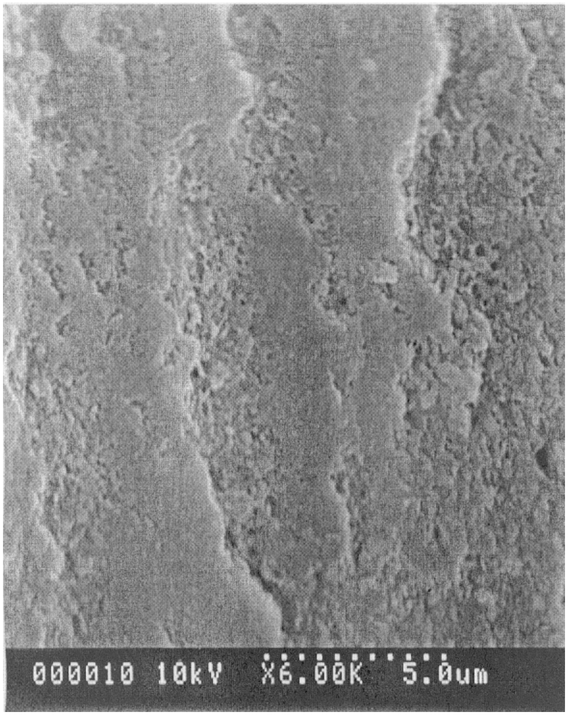

Fig. 7. Scanning electron micrograph of PCL/SAN blend prepared at 180°C.

Dynamic storage moduli of the PCL/30A master batches and their blends with SAN are plotted against temperature in Fig. 8. Intercalated PCL/30A master batch shows higher modulus than the neat PCL over entire temperature range examined, as shown in Fig. 8(A). It is also noteworthy that partially exfoliated PCL/30A master batch shows higher modulus than intercalated PCL/30A one at the same 5 wt% organoclay content. This greater reinforcing effect is attributed to better dispersion of silicate layers in partially exfoliated PCL/30A master batch. Dynamic storage moduli of the (PCL/30A)/SAN blends are shown in Fig. 8(B). For comparison, dynamic storage modulus of (PCL/Na-MMT)/SAN hybrid is measured and presented in Fig. 8(B). It is assumed that among the three hybrids, the (PCL/Na-MMT)/SAN hybrid has the lowest degree of intercalation or exfoliation. The inorganic content in (PCL/30A)/SAN blend was about 1.5 wt% whereas the inorganic content in (PCL/Na-MMT)/SAN blend was about 1.9 wt%. Even though (PCL/Na-MMT)/SAN blend contains higher inorganic content, the dynamic storage modulus is lower than those of the

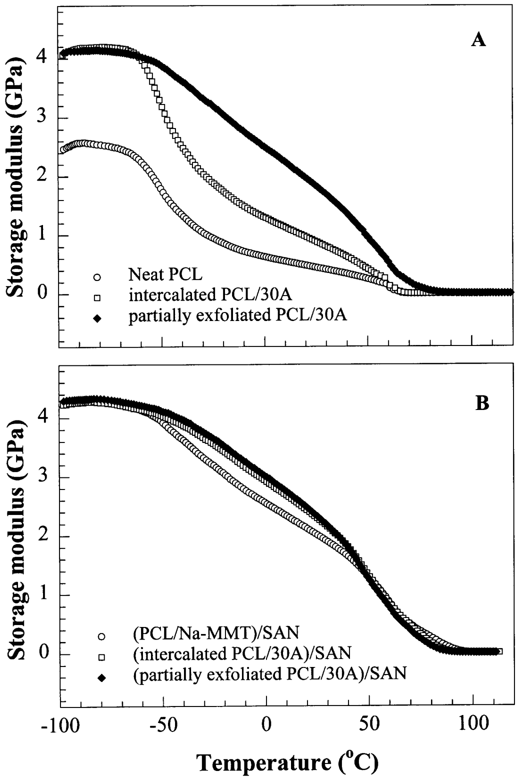

Fig. 8. DMTA measurements of (A) PCL/30A master batches and (B) (PCL/30A)/SAN nanocomposites. For comparison, DMTA measurements of neat PCL and (PCL/Na-MMT)/SAN are presented in (A) and (B), respectively.

others. This is attributed to the lowest dispersion of clay in (PCL/Na-MMT)/SAN blend. Closer examination of Fig. 8(B) shows that (partially exfoliated PCL/30A)/SAN hybrid has slightly higher modulus than (intercalated PCL/30A)/SAN hybrid.

4. Conclusions

A new approach to prepare exfoliated polymer/silicate nanocomposite was attempted using a polymer miscible with matrix polymer as a compatibilizer. As a prerequisite, the compatibilizer should be able to effectively exfoliate the organosilicate into the nano-scale building block before mixing with matrix polymer. In this study, PCL was selected as a compatibilizer for preparing SAN/organoclay nanocomposites. By carefully controlling the mixing conditions such as mixing time and temperature, it was possible to prepare PCL/30A master batches with different degree of intercalation. Lower mixing temperature and longer mixing time are desirable to prepare exfoliated PCL nanocomposite. The elastic modulus of the exfoliated PCL nanocomposite is higher than that of the intercalated one. Weak XRD peaks corresponding to the intercalated structure of organosilicate appear again when the exfoliated PCL master batch was mixed with SAN. This was attributed to the phase separation of SAN and PCL during melt mixing. To obtain completely exfoliated nanocomposite, the phase separation during melt mixing should be considered.

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