

Evaluation of Polymethacrylic Ionomer as Compatibilizers for MCPA6/Clay Composites

Tongfei Wu,^{1,2} Andong Liu,³ Tingxiu Xie,³ Guisheng Yang^{1,3}

¹CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Technology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

²Graduate University of the Chinese Academy of Sciences, Beijing, 100039, People's Republic of China

³Shanghai Genius Advanced Materials Co., Ltd, Shanghai 201109, People's Republic of China

Received 11 March 2008; accepted 15 May 2008

DOI 10.1002/app.28709

Published online 26 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The compatibilization effects provided by polymethacrylic ionomer (PMMA ionomer) on monomer-casting polyamide6 (MCPA6)/clay (pristine sodium montmorillonite) composites were studied in this work. The PMMA ionomer used in this study was sodium polymethacrylate ionomer (PMMA Na⁺-ionomer), which is a copolymer of methyl methacrylate and sodium methacrylate, prepared using emulsion polymerization. MCPA6/clay/PMMA Na⁺-ionomer composites were prepared by *in situ* anionic ring-opening polymerization (AROP) of ϵ -caprolactam (CLA). X-ray diffraction (XRD) and transmission electron microscopy (TEM) plus rheological measurement were used to characterize those composites. The results

indicated that PMMA Na⁺-ionomer is a good compatibilizer for this system. With increasing PMMA Na⁺-ionomer content, a better dispersion of clay layers was successfully achieved in the MCPA6 matrix. Furthermore, differential scanning calorimetry (DSC) and XRD results indicated that well dispersed silicate layers limit the mobility of the MCPA6 molecule chains to crystallize, reduce the degree crystalline, and favor the formation of the γ -crystalline form of the MCPA6 matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2727–2732, 2008

Key words: compatibilizer; ionomer; PA6/clay nanocomposites

INTRODUCTION

Clay nanocomposites represent a potentially attractive approach for improving some performance characteristics (mechanical, thermal, barrier, etc) of polymers without a significant increase in material mass because the high aspect ratio of the clay platelets permits significant reinforcement when just a few weight percent of clay mineral was randomly and homogeneously dispersed on a molecular level in the polymer matrix. However, the key challenge to realizing this potential is to achieve a higher degree of exfoliation of the silicate layers within the polymer matrix using a convenient and economical process.¹

PA6/montmorillonite nanocomposites were the first successful examples, as pioneered by the Toyota research group.^{2,3} In last 20 years, great success has been achieved in the preparation of exfoliated polymer/clay nanocomposites using organically modified montmorillonite (OMMT), including polyamide-based,^{2–5} epoxy-based,^{6,7} polyimide-based,⁸ and poly-aniline-based⁹ nanocomposites. To obtain exfoliated

polymer/pristine Na⁺-MMT nanocomposites; some attempts have been made via melt blending.^{10–12}

A method for preparing exfoliated PA6/Na⁺-MMT nanocomposites using anionic ring opening polymerization was developed in our lab.¹³ The study revealed that water and ϵ -caprolactam was a couple of good dispersants for exfoliated Na⁺-MMT. However, when the MMT content is increased up to 2 wt %, the silicate layers began to flocculate with increasing MMT content. Clearly, more extensive utilization of PA6-based nanocomposites would be possible if a more effective or less expensive compatibilizer was available. The purpose of this study is to explore the possibility of PMMA ionomer serving as a better compatibilizer. The presence of the pendant ionic groups in the ionomer creates favorable interactions between the ionomers and the silicate layers. It has been reported that ionomers, e.g., Surlyn,^{14–16} PBT ionomer,¹⁷ PET ionomer,¹⁸ polyethylene-based ionomer,¹⁹ and isobutylene-based ionomer²⁰ formed fully exfoliated nanocomposites when combined with clay using a static melt intercalation technique. It demonstrated that the remarkably improved exfoliation was successfully achieved compared with the corresponding nonionic polymers. In this work, we prepared PMMA Na⁺-ionomer using emulsion polymerization and test their effectiveness as compatibilizers for PA6 nanocomposites prepared by *in situ* anionic ring-opening polymerization of ϵ -caprolactam.

Correspondence to: G. Yang (ygs@geniuscn.com).

MATERIALS AND METHODS

Materials

ϵ -Caprolactam (CLA) was obtained from Joint Stock Company, Republic of Belarus. Methyl methacrylate (MMA), methacrylic acid (MA), NaOH, ϵ -caprolactam sodium salt (CLNa) and toluene-2,4-diisocyanate (TDI) used as activator in this work were purchased from Shanghai Chemical Reagents Company and used without further treatment. Ammonium persulfate was used as initiator for acrylic polymerization. Na⁺-MMT (BP-180) with a cation exchange capacity (CEC) of 85 mequiv. 100 g⁻¹ was supplied by Zhejiang Fenghong Clay Chemicals.

Preparation of PMMA Na⁺-ionomer

PMMA Na⁺-ionomer was prepared using a typical emulsion polymerization. MMA and MA were mixed in molar proportion of 3 : 1. The prescribed amounts of water and part of the mixture of MMA and MA were placed in a 500-mL flask equipped with a stirrer and heated to and kept at 80°C under a nitrogen atmosphere. After the addition of ammonium persulfate (0.2 wt % relative to amounts of MMA and MA) and the completion of emulsification, the rest part of the mixture was dropped into water and the value of pH was kept between 9 and 11 through adding NaOH. The polymerization was continued till it was substantially completed. The solid content of emulsion is 10 wt %.

Preparation of MCPA6/clay/PMMA Na⁺-ionomer nanocomposites

A desired amount of pristine montmorillonite was added to 50 times the amount of boiling deionized water at 70°C and stirred for 3 h. Then prescribed amounts of CLA and PMMA Na⁺-ionomer lattices were added, and the mixture was stirred for 0.5 h till CLA was dissolved completely. Afterwards, a rotary evaporator was used under a vacuum at 80°C to remove most of the water of the mixture. And then the mixture was kept under another vacuum at 140°C for 20 min to remove traces of water remaining. About 1 wt % of CLNa as a catalyst for AROP and TDI as an activator was then added. The final mixture was then immediately poured into a mold preheated to 180°C, and polymerized in the oven at 180°C for 10 min. After polymerization, the products were cooled to room temperature slowly and extracted with boiling water to eliminate the residual monomer (the equilibrium conversion was about 92–95%). Finally, MCPA6/clay/PMMA Na⁺-ionomer nanocomposites with various amounts of PMMA Na⁺-ionomer (weight ratio: 97/3/0, 97/3/1.5, 97/3/3, 97/3/4.5) were obtained.

Characterization

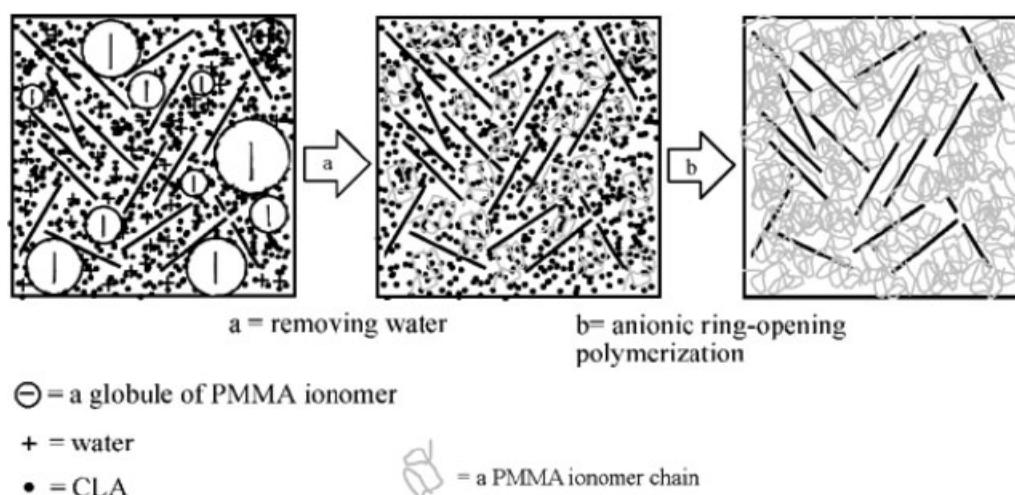
XRD was performed on a Rigaku D/Max-III X-ray diffraction analyzer equipped with a rotating Cu anode generator system using Cu/K- α_1 ($\lambda = 1.540 \text{ \AA}$) radiation. XRD data were measured at room temperature. Differential scanning calorimetry measurements were performed on a Perkin-Elmer diamond DSC in a nitrogen atmosphere with heating and cooling rates of 10 K min⁻¹. Calibration was achieved using indium standard samples. All the measurements were performed from room temperature to 523 K with a standstill for 5 min to erase any previous thermal history and then subsequent cooling and second heating cycles were recorded, respectively. The melt enthalpy (ΔH_f) in the second heating scan was used to measure the degree of crystallization (X_c), according to the following equation:

$$X_c = \Delta H_f / F\Delta H_f^* \times 100\%$$

where ΔH_f is the melting enthalpy of MCPA6 (or PA6) in the sample, F is the homopolymer weight fraction in the blend, and ΔH_f^* is the melting enthalpy of the matrix polymer of 100% crystallization ($\Delta H_f^* = 230 \text{ Jg}^{-1}$).²¹ Transmission electronic microscopy was carried out on a Hitachi H-800 microscope. The samples were ultramicrotomed with a diamond knife on a Leica Ultracut UCT microtome at -20°C to give about 80-nm-thick sections. Then the sections were transferred to carbon-coated Cu grids of 200 meshes. An ARES strain-controlled dynamic mechanical spectrometer was used to measure the linear and nonlinear viscoelastic response of the MCPA6/clay/PMMA Na⁺-ionomer nanocomposites. The oscillatory shear measurements were carried out at frequencies from 0.1 to 100 rad s⁻¹, with a strain of 0.5% and a parallel plate flow cell of 25 mm in diameter.

RESULTS AND DISCUSSION

For all hybrids, the weight ratio of MCPA6/clay was fixed to 97/3 and the content of PMMA Na⁺-ionomer was changed to test its effectiveness as compatibilizer for PA6 nanocomposites. Scheme 1 shows the clay dispersing process. PMMA Na⁺-ionomer improved the dispersion of clay in CLA after removing water. X-ray diffraction spectra for nanocomposites with various amounts of PMMA Na⁺-ionomer (MCPA6/clay/PMMA Na⁺-ionomer: 97/3/0; 97/3/1.5; 97/3/3; 97/3/4.5) and pristine clay are presented in Figure 1. Pristine clay used in this work has a basal spacing of the intercalated clay with 1.5 nm, calculated from the Bragg formulation $\lambda = 2d\sin\theta$, $2\theta = 5.7$. It is clear that at low PMMA Na⁺-



Scheme 1 Preparation of MCPA6/clay/PMMA ionomer nanocomposites contains three steps: First, mix prescribed amounts of Na⁺-MMT water suspension, CLA and PMMA ionomer latex together; second, remove water; and finally, anionic ring-opening polymerize CLA.

ionomer contents (below 97/3/3), there are weak and broad diffraction peaks at about $2\theta = 4.7$ ($d_{001} = 1.9$ nm, calculated as the difference of the d_{001} distance obtained by XRD and the individual layer thickness (0.95 nm)²²), which is characteristic of the d -spacing of the intercalated silicate layers and suggests that the silicate layers aggregated. Further, the interlayer gallery spacing with a typical value of 1.9 nm for various representative hybrids is independent of the PMMA Na⁺-ionomer content, as evidenced from Figure 1. And the intensity of d_{001} diffraction peak becomes weaker with PMMA Na⁺-ionomer content increasing. When the PMMA Na⁺-ionomer content is increased up to 97/3/4.5 (1.5 times to clay), there are hardly any visible diffraction peaks, which demonstrates that the silicate layers

are exfoliated, or the clay layers has been pushed apart to be larger than 4.52 nm.²³ PMMA Na⁺-ionomer intercalates the interlayer galleries due to the presence of the pendant ionic groups in the ionomer, leading to favorable interactions with the silicate layers, which indicated PMMA Na⁺-ionomer steadied the exfoliated silicate layers and avoid aggregating in CLA. The exfoliated clay structures in MCPA6/clay/PMMA Na⁺-ionomer nanocomposites (97/3/4.5) are also verified with transmission electron microscopy (TEM) as shown in Figure 2.

TEM is often used to differentiate two classes of relative separation of clay layers in the exfoliated state: disorderly exfoliated structure and intercalated

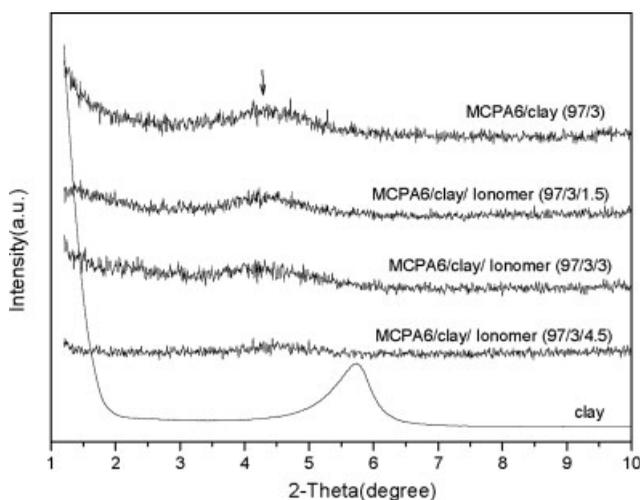


Figure 1 X-ray diffraction spectra for MCPA6/clay/PMMA Na⁺-ionomer composites with various amounts of PMMA Na⁺-ionomer and pristine clay.

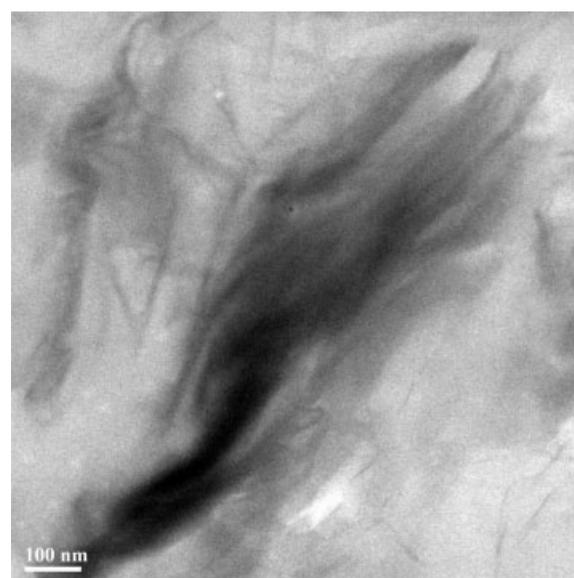


Figure 2 TEM micrographs of MCPA6/clay/PMMA Na⁺-ionomer composite (97/3/4.5).

structure. In Figure 2, the silicate layers were found in both these two states and they are all dispersed at the monolayer level. Intercalated structure might be caused by an absence or insufficiency of the intercalation of PMMA Na⁺-ionomer into the interlayer galleries. The platelet thickness in Figure 2 appears to be ~ 2 nm or over while the average length is about 100–200 nm. The thickness deduced from these photomicrographs is somewhat higher than that of a silicate layer.

The rheological properties of our various representative hybrids were measured to prove the ability of PMMA Na⁺-ionomer to exfoliate silicate layers, as evidenced from Figure 3(A,B). Comparison of the viscoelastic response of various representative hybrids shows a significant effect of compatibilizer. In the whole frequency region, when the PMMA Na⁺-ionomer content increase up to 97/3/3, the storage modulus G' and complex viscosity η rose observably. The reason for the increasing of G' and η might arise from the increased surface areas because of an enhanced dispersion of layered silicate aggregates. Furthermore, for MCPA6/clay/PMMA Na⁺-ionomer nanocomposites 97/3/3 and 97/3/4.5, the complex viscosity of composites does not reach a plateau value and it tends to show leveling-off in G' at low frequencies. This gel-like characteristic of the nanocomposites is due to the network structuring from the well dispersed silicate layers.²³ It is worth to note that the value of G' and η for 97/3/3 is much higher than that for 97/3/4.5. This may be due to the fact that, although the exfoliation of clay for MCPA6/clay/PMMA Na⁺-ionomer composite (97/3/4.5) is better than that for 97/3/3 from XRD result, the superfluous PMMA Na⁺-ionomer would make the network structure more incompact and reduce G' and η .

To detect the stability of the three-dimensional superstructure of exfoliated MCPA6/clay/PMMA Na⁺-ionomer composites (97/3/4.5), the rheological measurement was used, which is described to be very sensitive to elastic properties of network-like superstructures.^{22,24–30} Therefore, the validity of the time–temperature superposition principal (TTS) was checked applying the van Gurp's plot³¹ ($\delta = \text{atan } G''/G'$ versus $|G^*| = (G'^2 + G''^2)^{1/2}$) to the isothermal frequency sweeps of pure MCPA6 and MCPA6/clay/PMMA Na⁺-ionomer composites (97/3/4.5). The corresponding data are shown in Figure 3(C). For MCPA6 (solid symbols), all isotherms merged in one curve and, therefore, TTS holds. For MCPA6/clay/PMMA Na⁺-ionomer composites (97/3/4.5) (open symbols), it reveals that TTS does not hold in this case because the isotherms do not merge into a common curve. Such a behavior is typical for samples with properties changing during the experiment. With proceeding experiment time from the

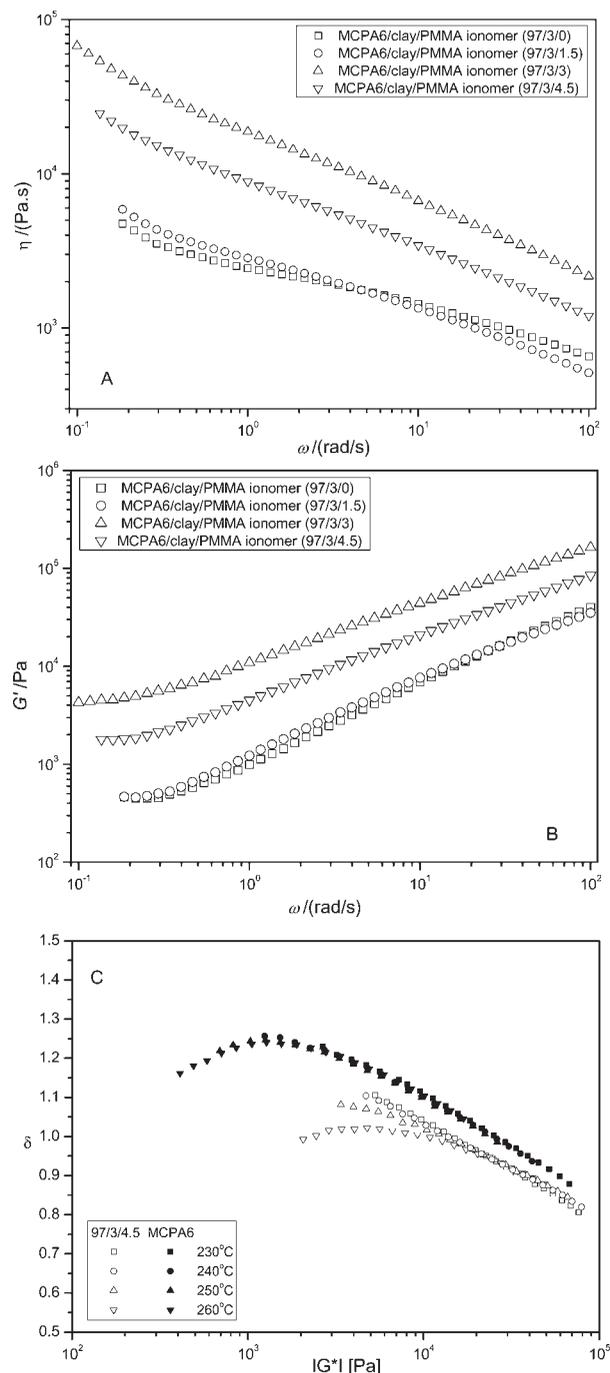


Figure 3 The viscoelastic properties of MCPA6/clay/PMMA Na⁺-ionomer composites with various amounts of PMMA Na⁺-ionomer at 240°C: (A) plots of log η versus log ω ; (B) plots of log G' versus log ω . (C) Van Gurp's plots of MCPA6 and MCPA6/clay/PMMA Na⁺-ionomer composites (97/3/4.5).

first isotherm at 230°C to the last at 260°C, the material becomes more and more elastic. The thus obtained level of elasticity refers to some flocculation of clay layers with increasing temperature.³⁰

The effect of degree of exfoliation and dispersion of composites on the crystallization behavior was investigated using DSC and XRD, respectively. The

heating and cooling thermograms of neat MCPA6 and MCPA6/clay/PMMA Na⁺-ionomer composites with various PMMA Na⁺-ionomer contents are compared in Figure 4(A,B). The data are summarized in Table I in detail.

As far as composite systems are concerned, the degree of exfoliation and dispersion of silicate layers play a major role in the crystallization behavior of the MCPA6 matrix. DSC cooling scans of MCPA6 and MCPA6/clay/PMMA Na⁺-ionomer composites are shown in Figure 4(A). The crystallization temperatures (T_c) of various representative hybrids tend to show a monotonic drop with the PMMA Na⁺-ionomer content increasing. Furthermore, at low PMMA Na⁺-ionomer contents (below 97/3/1.5), the hybrids show just one crystallization peak at $\sim 181^\circ\text{C}$ (see Table I). When the PMMA Na⁺-ionomer content is increased up to 97/3/3, there is one more crystallization peak at lower temperature, about 178.3°C . With the PMMA Na⁺-ionomer content increasing up to 97/3/4.5, the crystallization peak at higher temperature disappears. This may be due to the fact that with PMMA Na⁺-ionomer content increase, more silicate layers were exfoliated and well dispersed in the MCPA6 matrix. Then the well dispersed silicate layers limit the mobility of the MCPA6 molecule chains to crystallize. PMMA Na⁺-ionomer content of 97/3/3 may be a critical value for the formation of network-like superstructure form silicate layers, which is in good agreement with rheological results.

The second heating DSC traces are presented in Figure 4(B), in which peaks at around 211 and 218°C may be attributed to the melting peaks of the γ -crystalline form and the α -crystalline form, respectively.³² With PMMA Na⁺-ionomer content increase, the melting peak (T_m) of the γ -crystalline form swells (see Table I), which is a more evidence that the well dispersed silicate layers limit the mobility of the MCPA6 molecule chains to form the more stable α -crystalline form. This suggests that the well dispersed silicate layers favor the formation of the γ -crystalline form and prohibit the formation of the α -crystalline form. The effect of composites on crystalline form is also verified with XRD as shown in Figure 4(C). MCPA6/clay/PMMA Na⁺-ionomer composites with various amounts of PMMA Na⁺-ionomer were cooled to room temperature with the same cooling rate after the second heating of DSC and were used to perform XRD. Peaks at about 20.1° and 23.8° can be assigned to (200 + 002) and (002) planes of the α -crystalline form, respectively, and the peak at around 21.3° is characteristic of (200) and (101) planes of the γ -crystalline form.^{32,33} With PMMA Na⁺-ionomer content increasing, the γ -crystalline form appeared and became stronger. The crystalline degree (X_c) of MCPA6 matrix for 97/3/

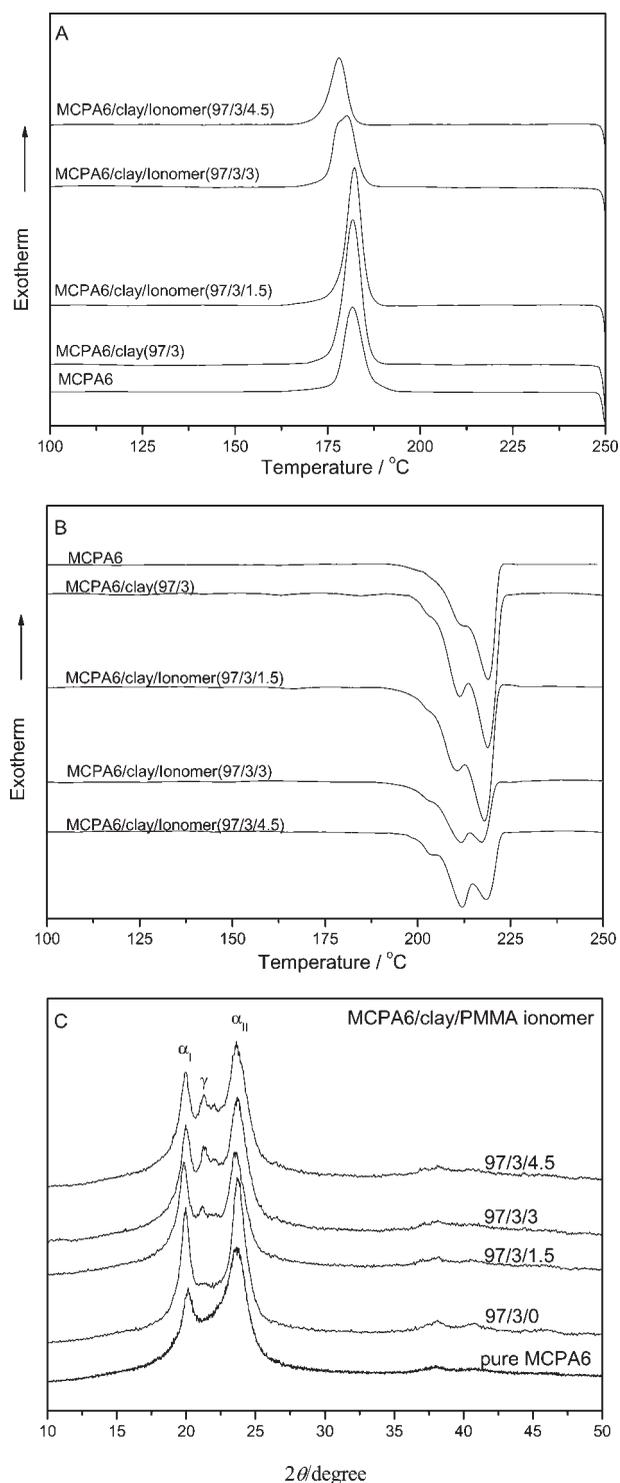


Figure 4 Thermograms of MCPA6/clay/PMMA Na⁺-ionomer composites with various amounts of PMMA Na⁺-ionomer: (A) Cooling; (B) The second heating. (C) The XRD patterns of MCPA6/clay/PMMA Na⁺-ionomer nanocomposites cooled to room temperature with the same cooling rate after the second heating of DSC.

4.5 is higher than that for 97/3/3. This suggests that nanocomposite 97/3/4.5 has a more incompact network-like superstructure which could not limit the

TABLE I
Characteristic Values of Crystallization and Melting Behavior of
MCPA6/Clay/PMMA Na⁺-Ionomer Nanocomposites

	Na ⁺ -ionomer Content x	T _{m1} /°C	T _{m2} /°C	T _c /°C	ΔH _m /(J/g)	X _c /%
Pure MCPA6	–	211.5	218.9	181.7	44.7	19.4
MCPA6/clay/PMMA	0	211.3	218.7	181.8	37.8	16.4
Na ⁺ -ionomer	1.5	210.7	218.0	182.2	42.7	18.6
(97/3/x)	3	211.4	217.3	180.2, 178.3	27.0	11.7
nanocomposites	4.5	212.0	218.5	178.2	37.6	16.3

mobility of the MCPA6 molecule chains to crystallize effectively. This is in good agreement with rheological results.

CONCLUSIONS

We prepared PMMA Na⁺-ionomer using emulsion polymerization and tested their effectiveness as compatibilizers for MCPA6 composites prepared by *in situ* anionic ring-opening polymerization to see if this provides a viable approach to form well-exfoliated composites. X-ray and TEM plus rheological measurement results show that PMMA Na⁺-ionomer is a good compatibilizer for this system. With PMMA Na⁺-ionomer content increase, a better dispersion of nanoscale clay was successfully achieved in the MCPA6 matrix. When PMMA Na⁺-ionomer content was increased up to equivalence with clay, a tough network-like superstructure of silicate layers formed. However, for this composite, TTS does not hold. The superstructure is not stable and changes at melting state during the experiment. Furthermore, analysis using DSC and XRD indicated that well dispersed clay layers limit the mobility of the MCPA6 molecule chains to crystallize, reduce the crystalline degree, and favor the formation of the γ-crystalline form of the MCPA6 matrix.

References

- Cui, L.; Paul, D. R. *Polymer* 2007, 48, 1632.
- Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
- Okada, A.; Usuki, A. *Mater Sci Eng* 1995, C3, 109.
- Fornes, T. D.; Yoon, P. J.; Hunter, D. L.; Keskkula, H.; Paul, D. R. *Polymer* 2002, 43, 5915.
- Wang, K.; Wang, L.; Wu, J. S.; Chen, L.; He, C. B. *Langmuir* 2005, 21, 3613.
- Ma, J.; Yu, Z. Z.; Zhang, Q. X.; Xie, X. L.; Mai, Y. W.; Luck, I. *Chem Mater* 2004, 16, 757.
- Yano, K.; Usuki, A.; Okada, A. *J Polym Sci Part A: Polym Chem* 1997, 35, 2289.
- Yeh, J. M.; Liou, S. J.; Lai, C. Y.; Wu, P. C.; Tsai, T. Y. *Chem Mater* 2001, 13, 1131.
- Yu, Z. Z.; Yang, M. S.; Zhang, Q. X.; Zhao, C. G.; Mai, Y. W. *J Polym Sci Part B: Polym Phys* 2003, 41, 1234.
- Yu, Z. Z.; Hu, G. H.; Varlet, J.; Dasari, A.; Mai, Y. W. *J Polym Sci Part B: Polym Phys* 2005, 43, 1100.
- Hasegawa, N.; Okamoto, H.; Kato, M.; Usuki, A.; Sato, N. *Polymer* 2003, 44, 2933.
- Liu, A.; Xie, T.; Yang, G. *Macromol Chem Phys* 2006, 207, 701.
- Liu, H.; Lim, H. T.; Ahn, K. H.; Lee, S. J. *J Appl Polym Sci* 2007, 104, 4024.
- Shah, R. H.; Hunter, D. L.; Paul, D. R. *Polymer* 2005, 46, 2646.
- Shah, R. H.; Paul, D. R. *Macromolecules* 2006, 39, 3327.
- Chisholm, B. J.; Moore, R. B.; Barber, G.; Khouri, F.; Hempstead, A.; Larson, M.; Olson, E.; Kelley, J.; Balch, G.; Caraher, J. *Macromolecules* 2002, 35, 5508.
- Barber, G. D.; Calhoun, B. H.; Moore, R. B. *Polymer* 2005, 46, 6706.
- Lee, J. A.; Kontopoulou, M.; Parrent, J. S. *Polymer* 2005, 46, 5040.
- Parent, J. S.; Liskova, A.; Resendes, R. *Polymer* 2004, 45, 8091.
- Evstatiev, M.; Schultz, J. M.; Petrovich, S.; Georgiev, G.; Fakiov, S.; Friedrich, K. *J Appl Polym Sci* 1998, 67, 723.
- Ren, J.; Silva, A. S.; Krishnamoorti, R. *Macromolecules* 2000, 33, 3739.
- Zhong, Y.; Zhu, Z.; Wang, S. Q. *Polymer* 2005, 46, 3006.
- Krishnamoorti, R.; Giannelis, E. P. *Macromolecules* 1997, 30, 4097.
- Giannelis, E. P.; Krishnamoorti, R.; Manias, E. *Adv Polym Sci* 1999, 138, 107.
- Hoffmann, B.; Kressler, J.; Stoepplmann, G.; Friedrich, C.; Kim, G. M. *Colloid Polym Sci* 2000, 278, 629.
- Hoffmann, B.; Dietrich, C.; Thomann, R.; Friedrich, C.; Muelhaupt, R. *Macromol Rapid Commun* 2000, 21, 57.
- Lim, Y. T.; Park, O. *Macromol Rapid Commun* 2000, 21, 231.
- Solomon, M. J.; Almusallam, A. S.; Seefeldt, K. F.; Varadan, P. *Polym Mater Sci Eng* 2000, 82, 263.
- Reichert, P.; Hoffmann, B.; Bock, T.; Thomann, R.; Muelhaupt, R.; Friedrich, C. *Macromol Rapid Commun* 2001, 22, 519.
- Honerkamp, J.; Weese, J. *Rheol Acta* 1993, 32, 57.
- Kyotani, M.; Mitsuhashi, S. *J Polym Sci Part A-2: Polym Phys* 1972, 10, 1497.
- Coppola, G.; Pallesi, B. *Polymer* 1974, 15, 130.