

Morphology and Properties of Polyacrylonitrile/Na-MMT Nanocomposites Prepared via *in-situ* Polymerization with Macroazoinitiator

Han Mo Jeong*, Mi Yeon Choi, and Young Tae Ahn

Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea

Received January 3, 2006; Revised February 15, 2006

Abstract: In the preparation of a polyacrylonitrile (PAN)/sodium montmorillonite (Na-MMT) nanocomposite via an *in-situ* polymerization method, macroazoinitiator (MAI) was intercalated in the gallery of Na-MMT to enhance the delamination of silicate layers by intergallery polymerization. The exfoliated fine dispersion observed by X-ray diffraction pattern and transmission electron microscopy, the enhanced tensile storage modulus and the thermal decomposition temperature showed that the intercalated MAI was effective in inducing intergallery polymerization and that a poly(ethylene glycol) block linked to a PAN block improved the dispersion of hydrophilic Na-MMT in the polymer matrix.

Keywords: polyacrylonitrile, sodium montmorillonite, nanocomposite, macroazoinitiator, intergallery polymerization.

Introduction

A great deal of research on organic polymer-layered silicate nanocomposites has been carried out over the past decade due to their substantially enhanced physical properties over pristine polymers, even when prepared with a very small amount of layered silicate.¹⁻¹⁰ These nanocomposites demonstrate improved thermal, mechanical, barrier, and flame-retardant properties. These unique properties of nanocomposites arise from the maximized interfacial contact between the organic and inorganic phase, so fillers with high surface-to-volume ratio are commonly used. Layered silicates such as montmorillonite, which are composed of stacks of parallel lamellae with a 1 nm thickness and a high aspect ratio, are typically used.

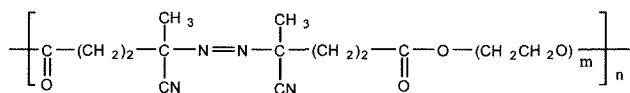
In general, two idealized polymer-layered silicate nanocomposites structures are possible: intercalated and exfoliated.¹¹⁻¹³ Intercalated structures are self-assembled, well-ordered, and multilayered structures in which the extended polymer chains are inserted into the gallery space between parallel individual silicate layers. Because these structures usually retain multilayered features with alternating polymer-silicate layers, an increased *d*-spacing between the silicate layers can be detected by X-ray diffraction (XRD). In the exfoliated structure, the individual silicate layers are delaminated and randomly dispersed in the polymer matrix separately. The exfoliated structures no longer give a coherent wide-angle ($2\theta > 1^\circ$) XRD signal, because the

distances between the silicate layers are expanded far apart and the layers are sufficiently disordered. Many nanocomposites have both the morphologies of intercalated and exfoliated structures, together with partially exfoliated structures, where small stacks of 2~4 silicate layers are dispersed in the polymer matrix.

Because the exfoliated nanocomposites usually provide the best property enhancements due to a large interfacial area and homogeneous dispersion, many efforts were devoted to design methods that improved the delamination of silicate layers in the polymer matrix. Polymerization at the galleries between the silicate layers can promote exfoliation because the growing polymer chain can push apart and eventually delaminate the silicate layers. Therefore, the initiator, or comonomer, anchored at the gallery induces intergallery polymerization and can be utilized for exfoliation.¹⁴⁻¹⁷ The surface of a natural silicate such as sodium montmorillonite (Na-MMT) is polar and hydrophilic in nature, so the dispersion of Na-MMT in the hydrophobic polymer matrix requires a large favorable enthalpic contribution to overcome this discrepancy in polarity as well as the entropy loss in order for the chain to diffuse into the gallery. Block or graft copolymers containing a block which is miscible with the matrix polymer and another block which is compatible with Na-MMT can be utilized for the favorable enthalpic contribution.^{18,19} The macroazoinitiator (MAI) containing a poly(ethylene glycol) (PEG) segment as shown in the following chemical structure can be easily intercalated at the gallery of Na-MMT, because the high stability of the intercalated PEG/Na-MMT compound prevents PEG from being washed out after inter-

*Corresponding Author. E-mail: hmjeong@mail.ulsan.ac.kr

calation, even with solvents which have high affinity toward Na-MMT.^{20,21} It is therefore anticipated that intercalated MAI can be utilized to prepare exfoliated nanocomposites by inducing inter-gallery radical polymerization of vinyl monomers and the polymerized PEG-vinyl monomer multi-block copolymer will have an affinity to Na-MMT due to the presence of PEG block.²²



To the authors' best knowledge, the following three papers report on nanocomposites of polyacrylonitrile (PAN)/hydrophilic silicate. A paper about intercalated PAN/kaolinite nanocomposite was reported by Y. Sugahara *et al.*,²³ and the other papers by Y. S. Choi *et al.* and T. Yu *et al.* described the preparation of exfoliated PAN/Na-MMT nanocomposites via emulsion polymerization.^{24,25} In this paper, we report on the morphology and physical properties of PAN/Na-MMT nanocomposites prepared by our new method utilizing MAI.

Experimental

Na-MMT (Southern Clay) was used after drying at 60 °C in a vacuum for 2 days. MAI (Wako Pure Chemical, VPE-0201), the condensation polymer of 4,4'-azobis(4-cyanopentanoic acid) and PEG diol (molecular weight 2,000),²⁶ had a molecular weight of about 22,000 and an azo group content of 0.45 mmol/g. MAI, acrylonitrile (AN, Aldrich), 2,2'-azobisisobutyronitrile (AIBN, Aldrich), acetonitrile (Aldrich), methanol (Aldrich), and dimethylsulfoxide (DMSO, Aldrich) were used as received.

Na-MMT intercalated with MAI (MAI/Na-MMT) was

prepared using an acetonitrile/methanol mixture (1/1 by volume) as a solvent.^{20,21} Three grams of MAI were dissolved in 100 mL of solvent and stirred with 7 g of Na-MMT for 1 day at room temperature. The intercalated compound was separated with a centrifuge, and repeatedly washed with acetonitrile and methanol to remove nonintercalated physisorbed MAI.¹⁸ It was dried at 25 °C for 48 hrs in a vacuum before use.

The recipes for the preparation of PAN/Na-MMT nanocomposites are shown in Table I. In Series I, AIBN was dissolved in AN, and the bulk radical copolymerization of AN in the presence of Na-MMT was carried out by stirring with a magnetic bar at 60 °C under N₂ atmosphere for 48 hrs. In Series III, Na-MMT intercalated with MAI was swelled in a reactor with water, and then AN was added drop-wise into the reactor while stirring with a magnetic stir bar at room temperature. The volume of swelling water was adjusted to equal the volume of AN. After the feeding of AN, this heterogeneous system was heated to 60 °C and polymerization was carried out at 60 °C under N₂ atmosphere for 48 hrs. Series II was prepared by the same method as Series III, with the exception that MAI was not intercalated in Na-MMT when fed into the reactor. The prepared PAN/Na-MMT nanocomposites were crushed into powder and dried at 100 °C for 12 hrs in a vacuum to remove low molecular weight components.

The reduced viscosity of the 0.50 g/dL polymer solution in DMSO was measured with an Ostwald viscometer at 50 °C. Na-MMT was removed before the measurement by a previously reported method.²⁴

XRD patterns were obtained with an X-ray diffractometer (X'PERT, Philips) using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) as the X-ray source. The diffraction angle was scanned from 1.2 ° at a rate of 1.2 °/min.

The morphology of the nanocomposites was examined

Table I. Recipe for the Preparation of PAN/Na-MMT Nanocomposite

Designation Code	Feed					Concentration of Azo group (mmol/100 g-AN)
	AN (wt %)	AIBN (wt %)	MAI (wt %)	Na-MMT (wt %)	MAI/Na-MMT (wt %)	
<i>Series I</i>						
C0E0	99.69	0.31	-	-	-	1.86
C5E0	95.19	0.08	-	4.73	-	0.48
<i>Series II</i>						
C5E10	94.23	-	1.04	4.73	-	0.50
<i>Series III</i>						
C3E06N	96.35	-	-	-	0.66/2.99	0.31
C5E10N	94.23	-	-	-	1.04/4.73	0.50
C7E14N	92.09	-	-	-	1.43/6.48	0.70

with a transmission electron microscope (TEM, Hitachi H-8100) with an accelerating voltage of 200 kV. The TEM samples were prepared by putting a polymerized nanocomposite powder into an epoxy capsule and curing the epoxy at 25 °C for 24 hrs in a vacuum oven. Then the cured epoxy containing a nanocomposite was microtomed by a diamond knife into 80 nm-thick slices.

Dynamic mechanical properties were determined using a dynamic mechanical thermal analyzer (Rheometry Scientific DMTA MK), with a bending mode at a heating rate of 4 °C/min and 10 Hz. Samples were compression molded at 160 °C.

Thermogravimetric analysis (TGA) was carried out with a thermogravimetric analyzer (TA Instruments, TGA 2950) at a heating rate of 10 °C/min under O₂ atmosphere with a 30 mg sample in a platinum crucible.

Results and Discussion

XRD. Figure 1(a) and (b) show the XRD patterns of Na-MMT and Na-MMT intercalated with MAI (MAI/Na-MMT), where it is evident that Na-MMT and MAI/Na-MMT have peaks at $2\theta=7.9^\circ$ and $2\theta=5.0^\circ$, respectively, as we previously reported.²² This shows that the gallery height calculated by Bragg's law, $d=\lambda/2 \sin\theta$, increased from 11.2 to 17.7 Å by the intercalation of MAI into the gallery of Na-

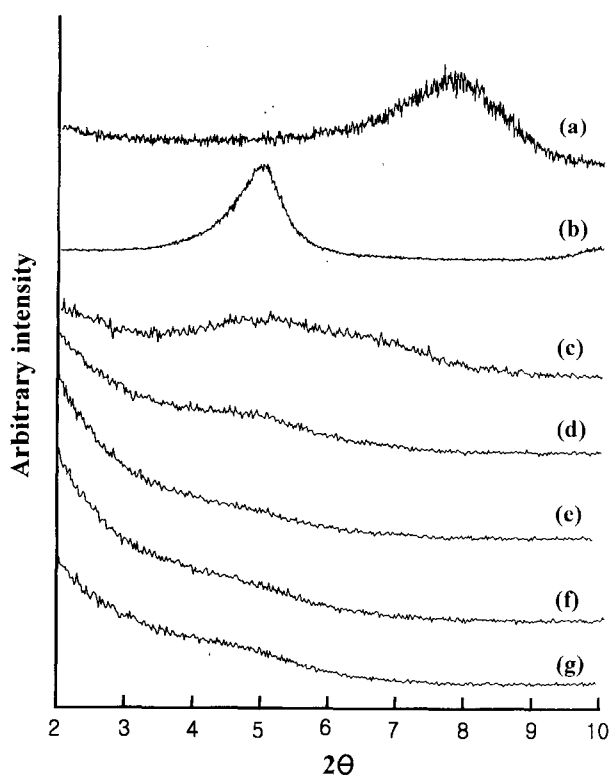


Figure 1. XRD patterns of (a) Na-MMT, (b) MAI/Na-MMT, (c) C5E0, (d) C5E10, (e) C3E06N, (f) C5E10N, and (g) C7E14N.

MMT. The weight loss by pyrolysis in a furnace at 600 °C showed that the amount of MAI intercalated in the gallery was 0.22 g/g-Na-MMT, as we reported before.²² In Figure 1(c), C5E0 has a broad peak at $2\theta=5.1^\circ$, demonstrating that the ordered parallel face-face morphology of Na-MMT is retained. However, the gallery height is increased to 17.2 Å by the intercalation of polymerized molecules. In the XRD pattern of C5E10 in Figure 1(d), only a shoulder around $2\theta=4.5^\circ$ is present instead of a peak, and the intensity at the lower angle below $2\theta=4.5^\circ$ is increased compared to Figure 1(c). This suggests that much of the ordered morphology of Na-MMT is scattered and the gallery height is expanded by the insertion of matrix polymers. We observed that viscosity increase due to the polymerization of AN was trivial up to 48 hrs at 60 °C, when MAI/Na-MMT was used without swelling water. This suggested that the polymerization of AN could occur mostly at the initiating sites of MAI when AN could approach to this active site after swelling the gallery of Na-MMT with water. If we consider the fact that MAI yields the multiblock copolymer of PAN and PEG,^{26,27} the result of Figure 1(d) supports the assertion that the PEG block linked to PAN improves the interaction between the matrix polymer and Na-MMT, and enhances the insertion of PAN molecules into the gallery. In the XRD patterns of Series III (Figures 1(e)~(g)), the intensity increase at the low angle is more evident and the shoulder becomes obscure. This suggests that MAI intercalated at the gallery of Na-MMT induces inter-gallery polymerization, causing the expansion of gallery height and the disordering of silicate layers. Figure 1(e) does not show any distinguishable peak or shoulder, which suggests that this disordering is more evident at a lower content of Na-MMT.^{3,28}

TEM. Figure 2 shows the transmission electron micrographs of PAN/Na-MMT nanocomposites. The dark lines are intersections of silicate layers, and the other region is the polymer matrix. Figure 2(a), the TEM morphology of C5E0, shows very large, unevenly dispersed Na-MMT particles, with a thickness around 300 nm. This suggests that Na-MMT is immiscible with the PAN matrix polymer.¹² Figure 2(b), the TEM morphology of C5E10, also shows heterogeneously dispersed particles of Na-MMT. However, the size is reduced compared to that in Figure 2(a), and the thickness is less than 100 nm. In addition, the expanded gallery gap can also be easily observed in Figure 2(b). This morphology of C5E10 suggests that the PEG segment linked to PAN improves the compatibility of PAN with Na-MMT. The TEM morphology of C5E10N in Figure 2(c) shows almost homogeneously dispersed silicate layers of Na-MMT. However, the TEM morphology of C5E10N observed at high magnification in Figure 2(d) suggests that this is a partially exfoliated structure, where small stacks of less than 5 silicate layers are observable. The TEM morphology of C5E10N is consistent with the results of XRD, which suggest that the delamination of silicate layers was enhanced by the

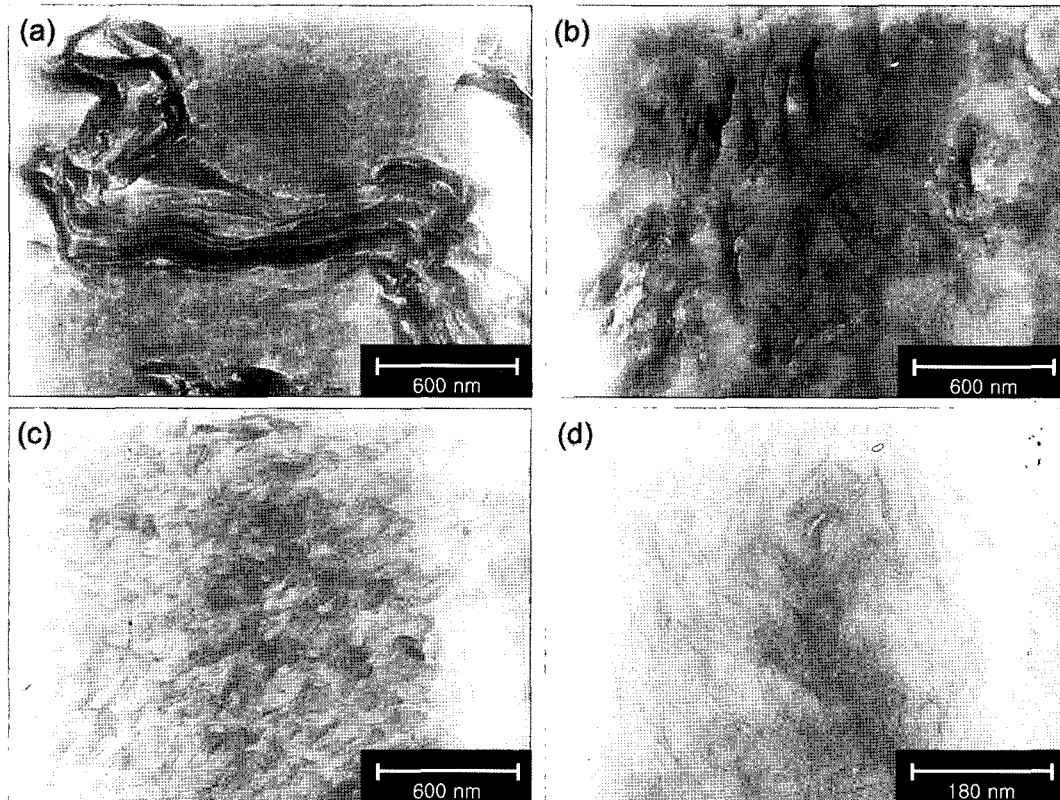


Figure 2. TEM micrographs of PAN/Na-MMT nanocomposites: (a) C5E0, (b) C5E10, (c) and (d) C5E10N.

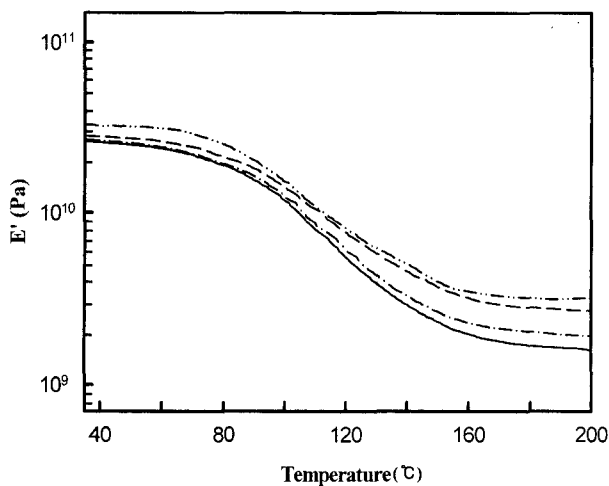


Figure 3. Tensile storage modulus of PAN/Na-MMT nanocomposites: (—) C0E0; (---) C5E0; (-·-·) C5E10, (····) C5E10N.

inter-gallery polymerization induced by the MAI that was intercalated before polymerization at the gallery of Na-MMT.

Dynamic Mechanical Property. The tensile storage modulus measured by DMTA in Figure 3 shows that E' increases according to the order, C0E0 < C5E0 < C5E10 <

C5E10N. This indicates that the reinforcing effect of Na-MMT is enhanced as the dispersion of Na-MMT in polymer matrix improves. Figure 3 also shows that the enhancement of E' by added Na-MMT is more evident above the glass-rubber transition temperature, T_g compared to that below T_g ; similar results were observed for polyurethane/clay nanocomposites⁴ and epoxy/clay nanocomposites.²⁹ The shear deformation and stress transfer to the silicate are enhanced by the increased elasticity of the matrix at the temperature region above T_g . Additionally, even though silicate layers are ceramic in nature, because of their very large aspect ratio and nanometer thickness, they may behave mechanically more like flexible sheets of paper than rigid plates, most likely when the matrix polymer is in the glassy state.³⁰ This may explain the above results. The E' values at 40 and 180 °C are given in Table II, where we can see that the E' value increases as the content of Na-MMT is increased in Series III.

TGA. The thermal decomposition patterns of PAN/Na-MMT nanocomposites analyzed by thermogravimetry are shown in Figure 4, where it can be seen that the initial 5 wt% weight loss temperature increases according to the order C0E0(264.2 °C) < C5E0(267.5 °C) < C5E10(270.5 °C) < C5E10N (278.2 °C). The increase in decomposition temperature is more evident as the dispersion of Na-MMT in the

Table II. Characteristics of PAN/Na-MMT Nanocomposite

Sample	Polymerization Yield (%)	Reduced Viscosity of Matrix Polymer (dL/g)	Content of Na-MMT ^a (wt%)	E' (Pa)	
				40 °C	180 °C
<i>Series I</i>					
C0E0	62.6	1.17	-	2.58×10^{10}	1.69×10^9
C5E0	64.5	0.70	7.0	2.64×10^{10}	2.04×10^9
<i>Series II</i>					
C5E10	58.6	1.00	7.6	2.78×10^{10}	2.81×10^9
<i>Series III</i>					
C3E06N	57.5	1.05	4.5	3.02×10^{10}	3.05×10^9
C5E10N	63.3	0.75	7.2	3.20×10^{10}	3.21×10^9
C7E14N	64.7	0.85	9.5	3.25×10^{10}	3.65×10^9

^aDetermined by the weight of residue after pyrolysis in a furnace at 600 °C.

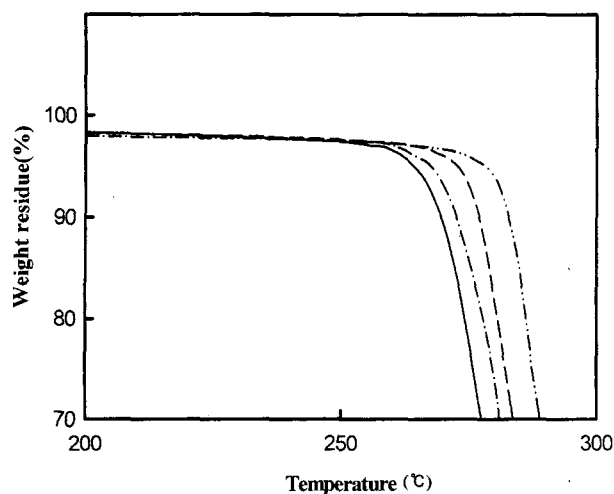


Figure 4. TGA thermograms of PAN/Na-MMT nanocomposites: (—) C0E0; (---) C5E0; (····) C5E10, (-·-·-·) C5E10N.

polymer matrix is enhanced. Similar results have been reported for other nanocomposites, and this enhanced thermal stability was attributed to the thermal insulation effect or hindered diffusion of volatile decomposition products by the presence of silicate layers.³¹⁻³³

Conclusions

In the preparation of a PAN/Na-MMT nanocomposite, Na-MMT intercalated with MAI was effective to bring about the delamination of silicate layers, which was confirmed by XRD, the morphology observed by TEM, and the mechanical and thermal properties. The results showed that the intergallery polymerization was induced by the intercalated radical initiator, MAI, and that the PEG block linked

PAN block enhanced the interaction between the matrix polymer and the hydrophilic Na-MMT.

Acknowledgements. This work was supported by the University of Ulsan Research Fund of 2004.

References

- (1) H. Ishida, S. Campbell, and J. Blackwell, *Chem. Mater.*, **12**, 1260 (2000).
- (2) P. C. Le Baron, Z. Wang, and T. J. Pinnavaia, *Appl. Clay Sci.*, **15**, 11 (1999).
- (3) H. M. Jeong, K. H. Jang, and K. Cho, *J. Macromol. Sci.-Phys.*, **B42**, 1249 (2003).
- (4) B. K. Kim, J. W. Seo, and H. M. Jeong, *Eur. Polym. J.*, **39**, 85 (2003).
- (5) H. M. Jeong, B. C. Kim, and E. H. Kim, *J. Mater. Sci.*, **40**, 3783 (2005).
- (6) J. H. Park, W. N. Kim, H.-S. Kye, S.-S. Lee, M. Park, and J. Kim, *Macromol. Res.*, **13**, 367 (2005).
- (7) S. Subramani, J. M. Lee, J. H. Kim, and I. W. Cheong, *Macromol. Res.*, **13**, 418 (2005).
- (8) Y. S. Choi, Y. K. Kim, and I. J. Chung, *Macromol. Res.*, **11**, 418 (2003).
- (9) G. Khang, S. J. Lee, Y. M. Lee, J. H. Lee, and H. B. Lee, *Korea Polym. J.*, **8**, 179 (2000).
- (10) M. B. Ko, J. Kim, and C. R. Choe, *Korea Polym. J.*, **8**, 120 (2000).
- (11) C. Zeng and L. J. Lee, *Macromolecules*, **34**, 4098 (2001).
- (12) A. B. Morgan and J. W. Gilman, *J. Appl. Polym. Sci.*, **87**, 1329 (2003).
- (13) J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris, Jr., E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, and S. H. Phillips, *Chem. Mater.*, **12**, 1866 (2000).
- (14) H. Böttcher, M. L. Hallensleben, S. Nuß, H. Wurm, J. Bauer, and P. Behrens, *J. Mater. Chem.*, **12**, 1351 (2002).
- (15) M. W. Weimer, H. Chen, E. P. Giannelis, and D. Y. Sogah, *J.*

- Am. Chem. Soc.*, **121**, 1615 (1999).
- (16) Q. Zhou, X. Fan, C. Xia, J. Mays, and R. Advincula, *Chem. Mater.*, **13**, 2465 (2001).
- (17) M. Laus, M. Camerani, M. Lelli, K. Sparnacci, F. Sandrolini, and O. Francescangeli, *J. Mater. Sci.*, **33**, 2883 (1998).
- (18) B. Liao, M. Song, H. Liang, and Y. Pang, *Polymer*, **42**, 10007 (2001).
- (19) H. R. Fisher, L. H. Gielgens, and T. P. M. Koster, *Acta Polym.*, **50**, 122 (1999).
- (20) P. Aranda and E. Ruiz-Hitzky, *Chem. Mater.*, **4**, 1395 (1992).
- (21) J. Wu and M. M. Lerner, *Chem. Mater.*, **5**, 835 (1993).
- (22) H. M. Jeong and Y. T. Ahn, *Macromol. Res.*, **13**, 102 (2005).
- (23) Y. Sugahara, S. Satokawa, K. Kuroda, and C. Kato, *Clays and Clay Minerals*, **36**, 343 (1988).
- (24) Y. S. Choi, K. H. Wang, M. Xu, and I. J. Chung, *Chem. Mater.*, **14**, 2936 (2002).
- (25) T. Yu, J. Lin, J. Xu, T. Chen, and S. Lin, *Polymer*, **46**, 5695 (2005).
- (26) A. Ueda and S. Nagai, *J. Polym. Sci., Polym. Chem.*, **24**, 405 (1986).
- (27) T. O. Ahn, J. H. Kim, J. C. Lee, H. M. Jeong, and J. -Y. Park, *J. Polym. Sci., Polym. Chem.*, **31**, 435 (1993).
- (28) T.-K. Chen, Y.-I. Tien, and K.-H. Wei, *Polymer*, **41**, 1345 (2000).
- (29) T. Lan and T. J. Pinnavaia, *Chem. Mater.*, **6**, 2216 (1994).
- (30) R. Krishnamoorti, R. A. Vaia, and E. P. Giannelis, *Chem. Mater.*, **8**, 1728 (1996).
- (31) X. Huang and W. J. Brittain, *Macromolecules*, **34**, 3255 (2001).
- (32) J. G. Doh and I. Cho, *Polym. Bull.*, **41**, 511 (1998).
- (33) P. Uthirakumar, K. S. Nahm, Y. B. Hahn, and Y. -S. Lee, *Eur. Polym. J.*, **40**, 2437 (2004).