Effect of Matrix Viscosity on Clay Dispersion in Preparation of Polymer/Organoclay Nanocomposites

Moon Bae Ko[1], Jae Young Jho[1], Won Ho Jo*, and Moo Sung Lee[2]

Hyperstructured Organic Materials Research Center and School of Material Science and Engineering,
Seoul National University, Seoul 151-742, Korea
[1]*Hyperstructured Organic Materials Research Center and School of Chemical Engineering,*
Seoul National University, Seoul 151-742, Korea
[2]*Department of Textile Engineering and Advanced Materials Research Institute, Chonnam National University,*
Kwangju 500-757, Korea

Abstract: The viscosity effect of matrix polymer on melt exfoliation behavior of an organoclay in poly(ε-caprolactone) (PCL) was investigated. The viscosity of matrix polymer was controlled by changing the molecular weight of poly(ε-caprolactone), the processing temperature, and the rotor speed of a mini-molder. Applied shear stress facilitates the diffusion of polymer chains into the gallery of silicate layers by breaking silicate agglomerates down into smaller primary particles. When the viscosity of PCL is lower, silicate agglomerates are not perfectly broken into smaller primary particles. At higher viscosity, all of silicate agglomerates are broken down into primary particles, and finally into smaller nano-scale building blocks. It was also found that the degree of exfoliation of silicate layers is dependent upon not only the viscosity of matrix but thermodynamic variables.

Introduction

Polymer/layered silicate nanocomposites have recently received considerable attention from both academia and industry as an effective way to overcome the shortcomings of conventional mineral-filled nanocomposites[1,2]. When the silicate layers are exfoliated and randomly distributed in polymer matrix, the nanocomposites exhibit improved mechanical, thermal, and barrier properties even at a loading level of 5 wt%. Among several approaches which are currently proposed to make exfoliated nanocomposites, the melt-compounding method is especially attractive because current polymer processing techniques can be used with a minimal modification. The method would allow us to prepare directly nanocomposites using conventional compounding devices used for commercial polymers.

There are many factors to be considered for preparing nanocomposites with exfoliated silicate layers using the melt-compounding method. First of all, the interaction between polymer and silicate layer should be controlled for polymer chains to diffuse into silicate layers by reducing strong attractive force between silicate layers. This may be achieved by modifying hydrophilic silicate with an organic modifier, which can favorably interact with hydrophobic polymers[3-7]. Beside the favorable interaction between polymer and silicate layers, the shear stress applied during melt mixing may also affect the exfoliation of silicate layers. It has been expected that exfoliated nanocomposites can be

prepared only when the shear stress large enough to overcome the van der Waals force between silicate layers is applied. However, as revealed in our previous study[8], the exfoliation of organoclay becomes faster as the molecular weight decreases and the mixing temperature increases. This indicates that exfoliation of silicate layers is strongly dependent upon the diffusion of matrix polymers through the inter-crystalline region of silicate layers, because the diffusion becomes faster as the molecular weight of polymers decreases and the mixing temperature increases. To our knowledge, it has not been completely understood how the melt viscosity applied during mixing affects the exfoliation degree of silicate layers. Therefore, it is very interesting to find a critical viscosity for exfoliating silicate layers. In this study, we choose poly(ε-caprolactone)/organosilicate nanocomposites as a model system, because it has been known that PCL has good ability to intercalate into organosilicate layers compared with other polymers and that exfoliated nanocomposites could be easily obtained under a proper condition of melt processing[9,10]. The viscosity effect of matrix polymer on the melt exfoliation behavior of an organoclay in PCL is investigated systematically by changing the molecular weight of PCL, processing temperature, and shear rate.

Experimental

Materials

Three PCLs with different molecular weight, $M_n = 10000$ (PCL10K), 42500 (PCL43K) and 80000 (PCL80K) g/mol, were supplied from Sigma-Aldrich Chem. Co. Polymers

---

provided in pellet form were milled in the form of powder of 250 μm size using a Thomas-Wiley Intermediate mill and then vacuum-dried. Cloisite® 30A (C30A) was obtained from Southern Clay Products Inc. and used as received. The interlayer sodium cations of montmorillonite were exchanged with methyl tallow bis-2-hydroxyethyl ammonium for an organic modifier, whose chemical structure is available in reference 11. The powder sizes of organosilicates are distributed as: 10 vol.% less than 2 μm, 50 vol.% less than 6 μm and 90 vol.% less than 13 μm.

Preparation of PCL/Organosilicate Hybrids

PCL/organosilicate nanocomposites were prepared under shear using a mini-molder with the cup diameter of 1.5 cm. The mixing ratio of PCL/organosilicate was 93/7 by weight and the total amount of sample was fixed at 0.5 g. Mixing time was varied from 6 min to 60 min, and the mixing temperature was varied from 80 °C to 180 °C. The maximum shear rate during melt mixing can be calculated from the rotor speed of the mini-molder, the amount of sample, and the diameter of mixing cup as follows:

$$\dot{\gamma}_{max} = 2\pi\Omega r/(h \times 60)[s^{-1}] \qquad (1)$$

where h is the height of polymer melt confined in the cup, r is the radius of the cup and Ω is the rotor speed in rpm. The density of PCL melt ($\rho_{melt} = 1.1$ g/cm^3) is used for the calculation of h.

Characterizations

A polarized light microscope (Leitz, ORTHOLUX II) equipped with a hot stage (Mettler, FP82HT) was utilized to observe the primary particles of organosilicate distributed in PCL. At 80 °C, only the primary particles of organoclay in μm-size can be observed by polarized light microscope, because the crystals of PCL are melted at that temperature.

The change in the degree of exfoliation of silicate layers with mixing conditions was observed using an X-ray diffractometer (MAC Science, MXP 18A-HF). CuK$_\alpha$ (λ = 1.5405 Å), generated at a voltage of 40 kV and current of 30 mA, was used as a source. Diffraction angle was scanned from 1.5 ° to 10 ° at a rate of 2 °/min. After subtracting the background intensity from raw diffraction profiles, the crystallinity is calculated assuming that the crystallinity is proportional to the peak area of (001) plane.

Melt viscosity of PCL was measured using a Rheometrics rheometer (RMS 800) under the oscillatory mode with a parallel-plate fixture. Dynamic frequency sweep experiments were performed in linear viscoelastic region at the temperatures of 80, 100, 120, 140, 160, and 180 °C under nitrogen atmosphere to minimize thermal degradation of polymer. The frequency sweep employed was in the range of 0.1-100 rad/s.
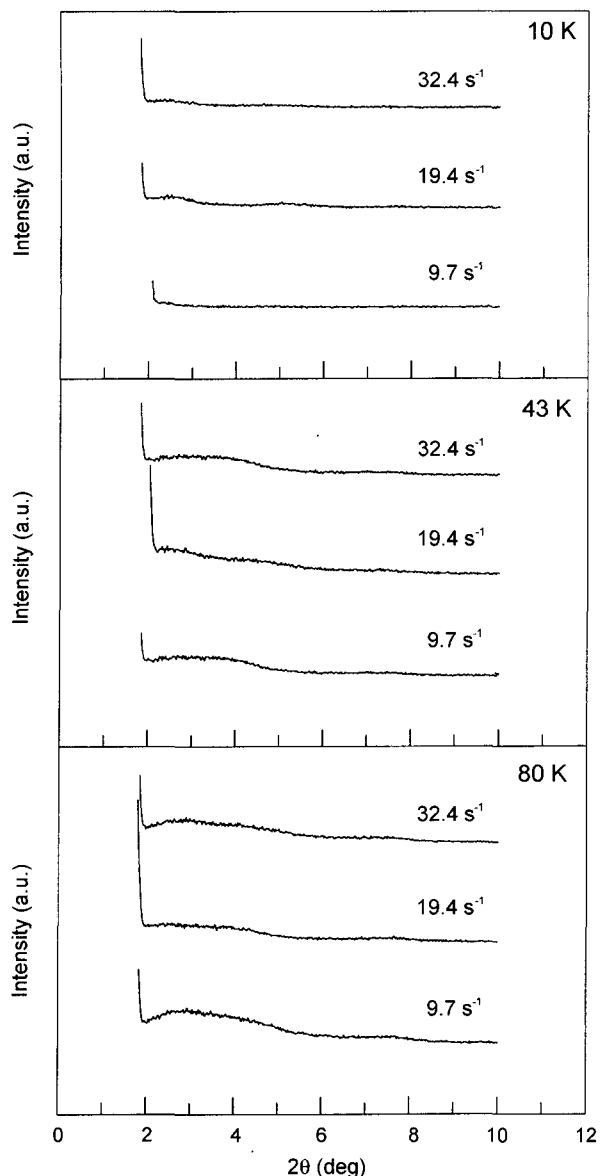
Results and Discussion

For non-Newtonian fluids, the viscosity is a function of shear rate. The maximum shear rates applied during preparation of nanocomposites using a mini-molder are in the range of 9.7 s^{-1} to 32.8 s^{-1}. The range is indicated by two vertically dashed lines in Figure 1. As a natural consequence, the PCL of higher molecular weight has higher melt viscosity at the same shear rate and temperature, and the melt viscosity decreases with increasing temperature, as shown in Figure 1. The PCL of lower molecular weight (PCL10K) shows nearly the Newtonian behavior, while the others show shear-thinning behavior in the range of shear rate examined in this study. For quantitative analysis of shear stress effect, the maximum shear stress (τ_{max}) applied during melt-mixing was calculated using the relation $\tau_{max} = \eta \cdot \dot{\gamma}_{max}$. First, the maximum shear rate ($\dot{\gamma}_{max}$) was calculated from the rotor speed applied using equation (1), and then it was multiplied by the melt viscosity (η) at the maximum shear rate to give the maximum shear stress.

When the PCL is mixed with C30A for short period of time, e.g., 6 min, any distinct XRD diffraction peak of C30A in the hybrid is not observed irrespective of the molecular weight of PCL and shear rate as shown in Figure 2. This leads us to speculate two possibilities. The first possibility is that silicate layers are well dispersed in nanoscale due to exfoliation of silicate layers. The second possibility is that polymer chains are not intercalated at all into gallery of
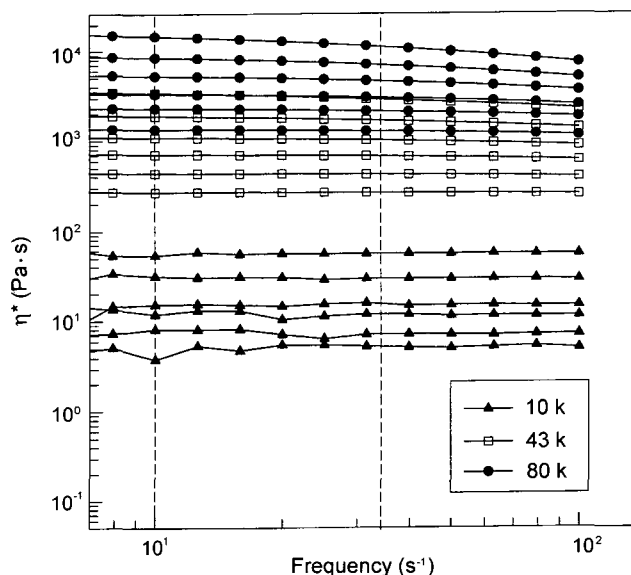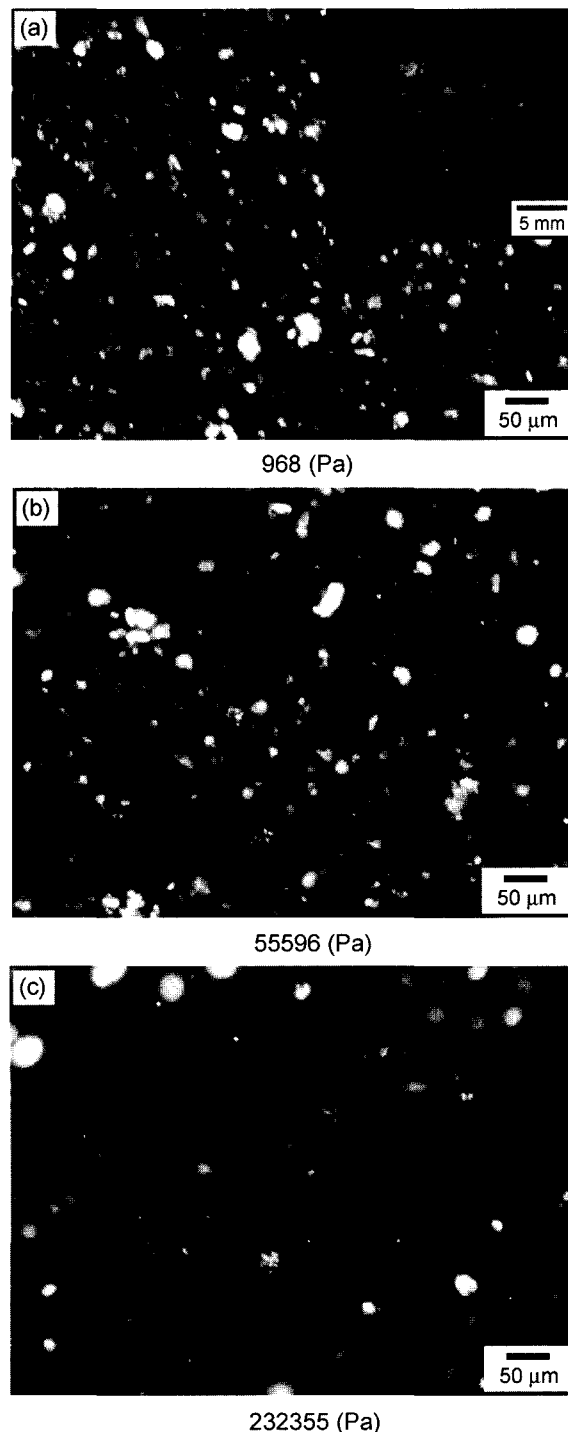

Figure 1. Melt viscosities of neat PCLs with different molecular weight at different temperatures. Measuring temperatures are 80, 100, 120, 140, 160, and 180 °C from the top for each PCL. Two vertically dashed lines represent the shear rate range used for the preparation of clay-hybrid in this study.

**Figure 2.** XRD patterns for the samples mixed for 6 minute under various shear rates for three PCLs.

Figure 3. Polarized optical microscopy of Cloisite® 30A in the hybrids prepared at 100 °C and 32.8 rad/sec with the mini-molder: (a) 10K, (b) 43K, (c) 80K. The number below each photograph indicates the applied maximum shear stress. OM observations were done at 80 °C.

silicate layers. This is because diffraction peaks by silicate alone are not often observed when the amount of silicate in hybrid is small[11]. Nevertheless, when polymer chains are intercalated into gallery of silicate layers, the diffraction peak is observed at lower angle. Therefore, it is unclear whether the absence of diffraction peak arises from either exfoliation or no intercalation.

The conversion of organosilicate layers to an intercalated hybrid requires polymer chains to be transported from the molten bulk into the silicate interlayer. According to Vaia *et al.*[6], the silicate particles are composed of an agglomeration of smaller particles. The larger silicate particle is referred to

as an agglomerate and the smaller one as a primary particle. The primary particle is generally formed by a compact face-

to-face stacking or low-angle intergrowth of individual silicate crystallites. Thus, it is expected that a silicate agglomerate is broken down into many primary particles, and subsequently the resulting primary particles are broken down into small silicate crystallites and/or individual silicate layer, when polymer chains diffuse into inter-crystalline region and/or the gallery between two adjacent silicate layers.

Morphologies of three hybrids prepared from PCLs with different molecular weight and the same amount of organoclay (7 wt%), were observed with a polarized optical microscope. The outgoing light is elliptically polarized after passage through the stacks of silicate layers with crystalline ordering. The analyzer reduces the intensity of outgoing light but an appreciable fraction of the incoming light is transmitted, so that the primary particles of organoclay of μm-size can be observed with the polarized optical microscope, as shown in Figure 3. However, some association of agglomerates in mm-order is also found in a part of the hybrid prepared with PCL10K (see the inset of Figure 3(a)). The breakdown of agglomerates under shear flow is described quantitatively by Tadmor and Gogos[12]. It has been shown that the maximum force to separate a dumbbell-shaped agglomerate into primary particles in a fluid occurs when the dumbbell axis is at an angle of 45 ° to the direction of shear, and is proportional to the shear stress. As a result, mixing is enhanced as the shear stress increases. Thus, poor breakdown of clay agglomerate in PCL10K hybrid into primary particles may be due to the lower viscosity of PCL10K. It should be noted that the shear stress is proportional to the viscosity at a given shear rate. It is also observed from Figures 3(b) and (c) that the fraction of primary particles is smaller in PCL80K rather than in PCL43K. This indicates that the breakdown of primary particles into building block of submicron size is more effective in PCL80K rather than in PCL43K. Therefore, it is tentatively concluded that the shear stress applied during mixing plays an important role in clay-dispersion by breaking silicate agglomerates down into primary particles, which could then facilitate polymer chains to diffuse easily into the gallery of layered silicates.

As the mixing time becomes longer than 6 min, the XRD peak of (001) plane is observed at around 2.5 °, as seen in Figure 4. This indicates that intercalation takes place when the mixing time is longer than 6 min. It is expected that a large entropy loss is accompanied when a polymer chain with a radius of gyration about a few tens of nanometer is intercalated into a narrow gallery with a height of about 1 nm. Therefore, the diffusion of PCL into the gallery of silicate layers becomes more difficult as the molecular weight of PCL increases. As a result, the silicate layers may not be exfoliated and thus the intensity of (001) reflection for the hybrid of PCL80K does not disappear even for longer mixing time, i.e., 60 min, as shown in Figure 4. Unlike PCL80K hybrid, however, the XRD peak for PCL43K disappears completely when the mixing time is longer than
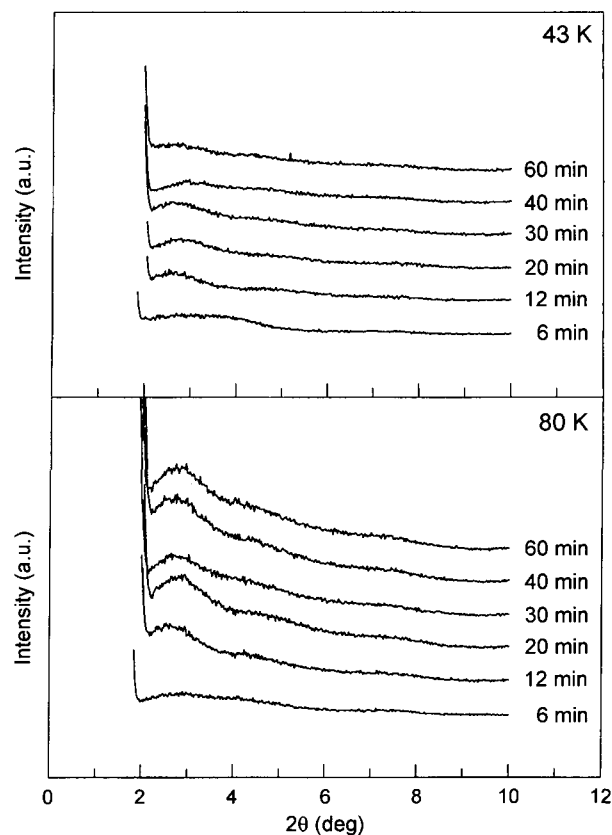
Figure 4. XRD patterns for the hybrids prepared under the shear rate of 32.8 rad/sec for various mixing times.

40 min. This indicates that the stacking of silicate layers is loosened by the diffusion of polymer chains into the gallery of organoclay during melt mixing, and finally the silicate layers are exfoliated.

It can be seen from the Figures 3 and 5 that primary particles of μm-size disappear gradually as the mixing time increases. Most of primary particles observed in the hybrid mixed for 6 min (Figure 3) are broken down into building blocks of submicron size in both PCL43K and PCL80K after mixing for 20 min. Here the area of XRD peak of (001) reflection may be used for examining the dispersion behavior of organoclay in the hybrids melt-mixed for longer than 20 min. It is assumed that the integrated intensity of XRD peak is proportional to the crystallinity as follows:

$$\text{crystallinity} \propto \int s^2 I(s)\,ds \qquad (2)$$

where s $(=2\sin\theta/\lambda)$ is a scattering vector. Thus the peak area, $\beta H/2$, where β and H are the half-width in radian and the peak intensity in count per second, respectively, may be used as a measure for the crystallinity of intercalated silicate layers[13].

When the peak area in two PCL-hybrids (PCL43K- and
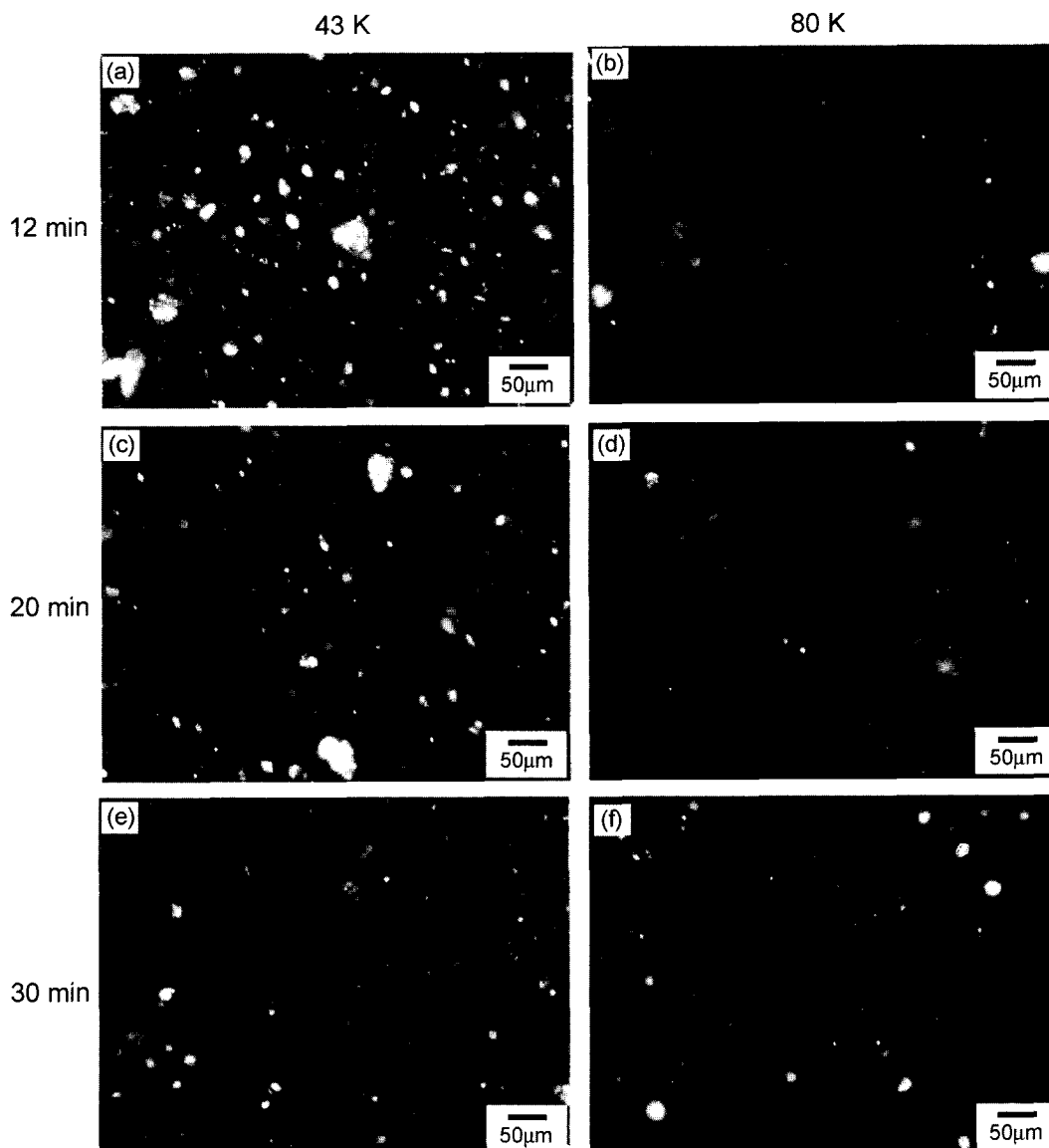
Figure 5. Polarized optical microscopy of Cloisite® 30A in the hybrids prepared at 100 °C and 32.8 rad/sec with the mini-molder for various mixing time: (a) 43K, 12 min, (b) 80K, 12 min, (c) 43K, 20 min, (d) 80K, 20 min, (e) 43K, 30 min, (f) 80K, 30 min. OM observations were done at 80 °C.

PCL80K-hybrid) is plotted against $1/\eta^*$, the crystallinity fluctuates at a given value of $1/\eta^*$ as the maximum shear rate varies in the range from 9.7 rad/s to 32.8 rad/s, as shown in Figure 6. Fluctuation of crystallinity seems to arise from the inhomogeneity of sample and/or experimental error. Here the value of $1/\eta^*$ is assumed to be proportional to the diffusion rate of polymer chain into silicate layers. It is also found from Figure 6 that the average value of crystallinity does not change with $1/\eta^*$ of matrix polymer. This indicates that the exfoliation of silicate layers is not related to the diffusion rate of matrix polymers through the inter-crystalline region of silicate layers. It is obvious from Figure 6 that the

crystallinity of PCL80K-hybrid is larger than that of PCL43K-hybrid at the same viscosity of matrix polymer, indicating that silicate layers in PCL43K-hybrid are more easily exfoliated than in PCL80K. It is expected that larger PCL chain, i.e., PCL80K, is more difficult to penetrate into the gallery of silicate layers rather than smaller one (PCL43K), because larger entropy loss must be accompanied for PCL80K than for PCL43K. Therefore, it is concluded that clay-exfoliation is controlled mainly by a thermodynamic variable, i.e., the entropy, while the shear stress applied during mixing seems to enhance clay-dispersion by breaking silicate agglomerates down into primary particles.
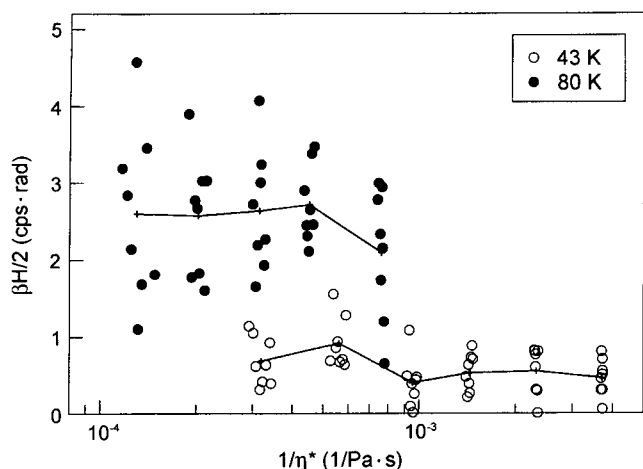
Figure 6. Plots of crystalinity versus $1/\eta^*$. Data points are clustered at each mixing temperature, showing that the crystallinities are fluctuating. Mixing temperatures are 80, 100, 120, 140, 160, and 180 °C from left for PCL43K, and 100, 120, 140, 160, and 180 °C from left for PCL80K. The average values of $1/\eta^*$ and crystallinity for each cluster of data are connected with solid lines only for visualization.

Conclusions

We investigated the viscosity effect of matrix polymer on the exfoliation of organosilicate layers in PCL matrix. The viscosity of matrix polymer was controlled by changing the molecular weight of PCL, the mixing temperature, and the rotor speed of a mini-molder. The XRD peak area pertaining to (001) reflection was used as a measure of the degree of intercalation and/or exfoliation. Applied shear stress could facilitate polymer chains to diffuse into the gallery of silicate layers by breaking silicate agglomerates down into smaller primary particles. When the matrix viscosity is lower, however, silicate agglomerates are not perfectly broken into smaller primary particles, but some agglomerates in mm-order can be found in the hybrid prepared from the PCL of low molecular weight. When the matrix viscosity is higher, all of silicate agglomerates are broken down into primary particles, and finally into smaller crystallites. The higher shear stress or higher viscosity seems to play an important role in clay-dispersion by breaking silicate agglomerates into primary particles. However, the degree of exfoliation of silicate layers is dependent upon not only the viscosity of matrix, but also thermodynamic variables.

References

1. T. J. Pinnavaia and G. W. Beall, "Polymer-Clay Nanocomposites", John Wiley and Sons, New York, 2000.
2. J. M. Garces, D. J. Moll, J. Bicerano, R. Fibiger, and D. G. McLeod, *Adv. Mater.*, **12**, 1835 (2000).
3. R. A. Vaia, R. K. Teukolsky, and E. P. Giannelis, *Chem. Mater.*, **6**, 1017 (1994).
4. R. A. Vaia and E. P. Giannelis, *Chem. Mater.*, **8**, 2628 (1996).
5. M. Sikka, L. N. Cerini, S. S. Ghosh, and K. I. Winey, *J. Polym. Sci., Part B, Polym. Phys.*, **34**, 1443 (1996).
6. R. A. Vaia, K. D. Jandt, E. J. Kramer, and E. P. Giannelis, *Macromolecules*, **28**, 8080 (1995).
7. R. A. Vaia and E. P. Giannelis, *Macromolecules*, **30**, 8000 (1997).
8. S. W. Kim, W. H. Jo, M. S. Lee, M. B. Ko, and J. Y. Jho, *Polymer J.*, **34**, 103 (2002).
9. M. B. Ko, *Korea Polymer J.*, **8**, 186 (2000).
10. S. W. Kim, W. H. Jo, M. S. Lee, M. B. Ko, and J. Y. Jho, *Polymer*, **42**, 9837 (2001).
11. M. B. Ko, *Polymer Bulletin*, **45**, 183 (2000).
12. Z. Tadmor and C. G. Gogos, "Principles of Polymer Processing", John Wiley and Sons, New York, 1979.
13. M. B. Ko, M. Park, J. Kim, and C. R. Choe, *Korea Polymer J.*, **8**, 95 (2000).