Effects of Shear on Melt Exfoliation of Clay in Preparation of Nylon 6/Organoclay Nanocomposites

Seong Woo KIM, Won Ho JO,[†] Moo Sung LEE,* Moon Bae KO,** and Jae Young JHO**

Hyperstructured Organic Materials Research Center and School of Material Science and Engineering, Seoul National University, Seoul 151–742, Korea

**Department of Textile Engineering and Advanced Materials Research Institute, Chonnam National University, Kwangju 500–757, Korea*

***Hyperstructured Organic Materials Research Center and School of Chemical Engineering, Seoul National University, Seoul 151–742, Korea*

(Received May 21, 2001; Accepted October 10, 2001)

ABSTRACT: The effect of shear stress on the exfoliation of organosilicate layers in the polyamide 6 (PA6) matrix was investigated using an X-Ray diffractometer (XRD). Shear stress was controlled by changing the molecular weight of PA6, mixing temperature, and rotor speed of a mini-molder. When Cloisite[®] 30 B (30 B), which favorably interacts with PA6, was used as organosilicate, silicate layers were exfoliated even at zero shear stress when annealing time was long enough. When shear stress was applied, the exfoliation of clay took place in a much shorter time compared to the statically annealed sample, and was dependent on molecular weight of matrix and mixing temperature. For poorly interacting PA6/ Cloisite[®] 25 A nanocomposites, only well ordered intercalated ones were obtained under high shear conditions. Shear stress applied during mixing thus plays a secondary role. Breaking silicate agglomerates into primary particles facilitates polymer chains to diffuse easily into the gallery of layered silicates, and thus enhances the degree of exfoliation at a given mixing condition. Thermodynamics, especially the diffusion of polymer chain into the silicate layers, plays primary roles in preparing the nanocomposites with exfoliated structure.

KEY WORDS Silicate / Polyamide 6 / Nanocomposite / Shear / Intercalation / Exfoliation /

Polymer/layered silicate nanocomposites have recently received considerable attention as an effective way to overcome the shortcomings of conventional mineral-filled nanocomposites.^{1,2} When 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%.

To make exfoliated nanocomposites, the melt-compounding method is especially attractive because current polymer processing techniques can be applied with minimal modification. The method allows us to prepare directly nanocomposites using conventional compounding devices such as extruders used for commercial polymers. There are many factors to be considered for preparing nanocomposites with exfoliated silicate layers using the method. First, interactions between polymer and silicate should be controlled for polymer chains to diffuse into silicate layers by reducing strong electrostatic force between silicate layers. This may be achieved by modifying hydrophilic silicate with an organic modifier, which favorably interacts with hydrophobic polymer. Some aspects on polymer/organosilicate nanocomposites, prepared by melt processing, have been investigated in recent years: interlayer structure of modified silicates,³ structural evolution

during polymer melt intercalation,⁴ mobility of intercalated polymer chains described by glass transition behavior,⁵ and kinetics of polymer intercalation.⁶ The effect of the chemical structure of organic modifier such as the length and number of alkyl groups and the polarity of polymers on the intercalation behavior has been investigated.⁷ More recently, we reported that polymers could be modified by copolymerization to tune the degree of interaction between organosilicate and polymer and to control the diffusion of polymer chains into gallery of silicate layers.⁸

Shear stress applied during melt mixing may affect the exfoliation of silicate layers. It is expected that exfoliated nanocomposites can be prepared only when the shear stress is applied enough to overcome the electrostatic force between silicate layers. Mixing conditions such as high shear rate, low temperature to keep the viscosity of polymer melt high, and long mixing time are recommended. The type of mixer also affects exfoliation and dispersion of silicate layers and thus the mechanical properties of nanocomposites.^{9,10} Therefore, the preparation of nanocomposites with exfoliated structure is governed by several coupled factors. Hence it is not always possible to prepare nanocomposite with the same degree of exfoliation even when the same polymers and organosilicate are used. The results

[†]To whom correspondence should be addressed (Tel: +82-2-880-7192, Fax: +82-2-885-1748, E-mail: whjpoly@plaza.snu.ac.kr).

Table I. Characteristics of organoclays

Code	Organic modifier	CEC ^a	% Moisture	% Weight on ignition
NaMMT	—	98	4	7
30 B	MT2EtOH ^b	95	2	32
25 A	2MHTL8 ^c	95	2	32

^aCation exchange capacity (meq/100 g). ^bMethyl tallow bis-2-hydroxyethyl ammonium.^cDimethyl hydrogenated tallow 2-ethyl-hexyl ammonium.

of ref 8 differ from those in ref 11. To our knowledge, it is not completely understood how the shear stress applied during mixing affects the degree of exfoliation of silicate layers.

This study investigates the effects of shear stress on the exfoliation of silicate layers. From the viewpoint of force balance, the dispersion of organosilicate agglomerates can be achieved when the cohesive force of agglomerates is exceeded by the hydrodynamic separating force or shear stress applied by the matrix polymer during melt processing. Therefore, it is very significant to find a critical shear stress, *i.e.*, a minimum stress for exfoliating silicate layers. In this study polyamide 6 (PA6)/organosilicate nanocomposites were used as a model system, because PA6 has better ability to intercalate into organosilicate layers compared to other polymers and that exfoliated nanocomposites could be obtained under a proper condition of melt processing.^{10, 12}

EXPERIMENTAL

Materials

Three PA6s with different molecular weights, $M_n = 14000$ (14 K), 22500 (22 K) and 48000 (48 K) g mol⁻¹, were obtained from Sumitomo Co. The polymers in pellet form were milled in the form of powder of 250 μ m size using a Thomas–Wiley Intermediate mill and then were vacuum-dried. Two organic-modified montmorillonites were obtained from Southern Clay Products Inc. and used as received. Sodium cations in the interlayer of montmorillonite were exchanged with methyl tallow bis-2-hydroxyethyl ammonium (30 B) or dimethyl-hydrogenated tallow (2-ethylhexyl)ammonium (25 A) for organic modifiers. Powder size of the organosilicate was *ca.* 8 μ m. Characteristics of organosilicates are shown in Table I and their chemical structures in Figure 1.

Preparation of Nylon 6/Organosilicate Hybrids

PA6/orgnosilicate nanocomposites without shear were prepared by simple annealing at melt state. A mixture of polymer and organosilicate (93/7 by weight) was dry blended, and placed on a hot plate for a specified annealing time under pressure. Annealing temperature was varied from 230°C to 250°C. After annealing,

Figure 1. Chemical structures of organic modifiers.

the samples were quenched to room temperature.

PA6/organosilicate nanocomposites were prepared under shear using a mini-molder composed of a cup with the inner-diameter of 1.5 cm and the depth of 2.0 cm and a rotor with nearly the same diameter. The mixing ratio of PA6/organosilicate was 93/7 by weight and total amount of samples per batch was fixed at 0.5 g. Mixing time was varied from 4 min to 20 min, and the rotor was moved up and down every 10 s during the mixing in order to increase mixing efficiency. Mixing temperature was varied from 230°C to 250°C. In all cases, a heat stabilizer (IRGANOX 1010) of 1 wt% was added in order to prevent thermal degradation of PA6. The maximum shear rate during melt mixing can be calculated from rotor speed, amount of sample, and diameter of mixing cup as follows:

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

where h is height of polymer melt confined in the cup, and Ω , rotor speed in rpm. The densities of PA6 melt ($\rho_{\text{melt}} = 0.96 \text{ g cm}^{-3}$) and organosilicate ($\rho_{\text{silicate}} = 2.2 \text{ g cm}^{-3}$) were used for calculation of h .

Characterizations

Change in the degree of exfoliation of silicate layers with mixing conditions was observed using an X-Ray diffractometer (MAC Science, MXP 18A-HF). Films for X-Ray diffraction were prepared by pressing the mixed powder of PA6 and organosilicate at 230°C for 1 min, followed by quenching to room temperature.

Figure 2. Melt viscosities of neat PA6s with different molecular weights at: (a) 230°C, (b) 240°C, and (c) 250°C. Two vertical dashed lines represent shear rate range.

Cu- K_{α} ($\lambda = 1.5405 \text{ \AA}$), 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 $2^{\circ} \text{ min}^{-1}$. After subtracting the background intensity from raw diffraction profiles, the profiles were curve-fitted using a Gaussian peak fitting method. d -spacing of silicate layers was estimated from the peak position of (001) plane in XRD profiles using the Bragg's law:

$$d_{(001)} = \lambda / 2 \sin \theta_{\max} \quad (2)$$

where λ is wavelength of X-Ray source and $\theta_{\max}$ is maximum peak position, *i.e.*, Bragg's angle. Apparent crystallite size of layered silicates (D_c) as

$$D_c = K \lambda / \beta \cos \theta_{\max} \quad (3)$$

was estimated, where K is a Scherrer shape factor close to unity, and β is full width at half maximum in radian.

Melt viscosity of PA6 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 230, 240, and 250°C under nitrogen atmosphere to minimize thermal degradation of polymers. The frequency sweep was 0.1 to 100 rad s^{-1} .

Thermal properties of PA6/organosilicate nanocomposites were measured using a differential scanning calorimeter (DSC, Perkin–Elmer DSC 7) under nitrogen atmosphere. 5 mg samples were heated to 250°C at a heating rate of $20^{\circ} \text{C min}^{-1}$ and maintained at this temperature for 3 min to eliminate thermal history. After cooling to -20°C at a cooling rate of $-20^{\circ} \text{C min}^{-1}$, they were heated again to 250°C at $20^{\circ} \text{C min}^{-1}$ to monitor crystallization and melting behavior. The endothermic peak on the second heating run and exothermic peak on cooling were identified as melting and crystallization temperature, respectively.

RESULTS AND DISCUSSION

Shear stress (τ) applied to polymer is expressed as product of shear rate ($\dot{\gamma}$) and melt viscosity (η): $\tau = \eta \times \dot{\gamma}$. For non-Newtonian fluids, viscosity is a function of shear rate. Figure 2 shows melt viscosity data for three different PA6 at three temperatures of melt mixing. Shear rates applied during preparation of samples are in the range of two vertically dashed lines in each figure. As a natural consequence, PA6 with higher molecular weight has higher melt viscosity at the same shear rate, and melt viscosity decreases with increasing temperature. PA6 of 14 K shows nearly the Newtonian behavior, while the others, shear thinning in the range of shear rate of this study.

Two distinct diffraction peaks, corresponding to (001) and (002) plane of 30 B, were observed irrespective of molecular weight of PA6 and annealing temperature, when the sample was annealed for a short period, as shown in Figure 3. As annealing time increased, the peak of (001) plane observed at around 2.4° became broad accompanying by decrease in intensity. The peaks disappear completely when the molecular weight of PA6 is low and the annealing time is long. These results indicate the loosening in stacking order of silicate layers, caused by the diffusion of polymer chains into the gallery of organosilicate during melt annealing.

It is expected that a large entropy loss takes place when a polymer chain with a radius of gyration about a few tens of nanometer is intercalated into a narrow gallery with height of about 1 nm. Therefore, the diffusion of PA6 into the gallery of silicate layers becomes more difficult as molecular weight of PA6 increases and intensity of (001) reflection decreases more slowly as

Figure 3. Changes in XRD profiles with annealing time for PA6/30B series prepared by simple annealing without shear: (a) 14 K/30 B, 250°C; (b) 14 K/30 B, 240°C; (c) 14 K/30 B, 230°C; (d) 22 K/30 B, 250°C; (e) 22 K/30 B, 240°C; (f) 22 K/30 B, 230°C; (g) 48 K/30 B, 250°C; (h) 48 K/30 B, 240°C; (i) 48 K/30 B, 230°C. Annealing times in minutes are indicated in each figure.

observed for 48 K/30 B series in Figure 3. For a long polymer chain to diffuse into a narrow gallery of silicate layers and form a thermodynamically stable intercalation, strong interaction between polymer chain and organic modifiers is required. As expected from the chemical structure of 30 B, hydrogen bonds between amide group in PA6 and hydroxyl group in 30 B may be formed and contribute to the stability of resultant intercalation.

Unlike PA6/30 B, when PA6 is melt mixed with 25 A under no shear at 240°C, peaks corresponding to the (001) plane of silicate layers remain nearly unchanged even after 60 min annealing, as shown in Figure 4. This is because 25 A does not contain a functional moiety, which favorably interacts with PA6. Better interaction between polymer and organic modifiers facilitates the diffusion of polymer chains into the gallery of silicates. As annealing temperature increases and/or molecular weight of polymer decreases, the rate of polymer diffu-

sion into the gallery of organosilicate increases.

Shear stress affects the intercalation and/or exfoliation of polymer clay nanocomposites. Even at a rotor speed of 25 rpm, corresponding to the maximum shear rate of about 7 s^{-1} , peak intensity of (001) plane decreased significantly compared to that of the nanocomposites prepared without shear. Shear stress thus effectively contributes to the diffusion of polymers into the gallery of silicate layers and finally exfoliation of the layers. When critical rotor speeds, at which diffraction peaks of (001) plane disappear, estimated from Figure 5, were about 35, 55, and 110 rpm for 14 K, 22 K, and 48 K, respectively. At the same shear rate, shear stress increases with molecular weight of polymer due to its higher melt viscosity. Exfoliation of organoclay in the matrix of high molecular weight polymer would thus appear to take place more easily than in the matrix of low molecular weight polymer. However, Figure 5 shows the opposite result. Therefore, similarly to the

Figure 4. Changes in XRD profiles with annealing time for PA6/25 A series prepared by simple annealing without shear at 240°C: (a) 14 K/25 A; (b) 22 K/25 A; (c) 48 K/25 A. Annealing times in minutes are indicated in each figure.

Figure 5. Changes in XRD profiles for PA6/30 B series, prepared by melt-mixing, with various rotor speeds: (a) 14 K/30 B; (b) 22 K/30 B; (c) 48 K/30 B. Mixing was performed at 240°C for 6 min. For comparison, XRD profiles for samples prepared without shear at the same temperature and time are inserted.

case of static annealing, exfoliation of organosilicate under shear seems controlled mainly by diffusion of polymer chains into the gallery of silicates rather than amount of shear stress applied.

Figure 6 shows the effects of shear stress on exfoliation of silicate layers when interaction between polymer (PA6) and organic modifier (25 A) is not favorable. Although the peak corresponding to (001) plane becomes broad slightly on increasing mixing rotor speed, ordered intercalated structures are still observed. 48 K/25 A showed the (001) plane peak at very high rotor speed of 300 rpm. This indicates that it is difficult to prepare exfoliated nanocomposite only by shear stress for poorly interacting polymer/organosilicate systems. From Figure 6c, 48 K/25 A nanocomposites prepared at above 120 rpm produce much better ordered intercalated structures than at 90 rpm, *i.e.*, the (002) reflection becomes sharper. According to eq 1, shear rate corre-

sponding to 200 rpm is about 110 rad s^{-1} , located in the shear thinning region. Since the viscosity is inversely proportional to shear rate in shear thinning region, increase of shear stress at 200 or 300 rpm may not be as large as increase in shear rate due to lowering of viscosity. This relatively low viscosity may be a reason why (002) reflection becomes sharper at high shear rate, although decrease in viscosity is not enough to decrease shear stress.

For quantitative analysis of shear stress effect, maximum shear stress applied during melt-mixing was calculated using the relation $\tau_{\max} = \eta \times \dot{\gamma}_{\max}$. Maximum shear rate ($\dot{\gamma}_{\max}$) was calculated with the rotor speed applied, and then multiplied by the melt viscosity at the shear rate to give the maximum shear stress. The degree of exfoliation is estimated by two parameters: Bragg's $d_{(001)}$ and apparent crystallite size of silicate (D_c). The diffraction angle (2θ) of (001) reflection represents the

Figure 6. Changes in XRD profiles for PA6/25 A series, prepared by melt-mixing, at various rotor speeds: (a) 14 K/25 A; (b) 22 K/25 A; (c) 48 K/25 A. Mixing was performed at 240°C for 6 min. For comparison, XRD profiles for samples prepared without shear at the same temperature and time are inserted.

Figure 7. Effects of maximum shear stress on: (a) d -spacing ($d_{(001)}$) and (b) apparent crystallite size (D_c) of silicate layers in PA6/30 B series. Mixing was performed at 240°C for 6 min.

interlayer spacing, and full width at half maximum of the (001) reflection represents the thickness of silicate layers. The broader the width of diffraction peak, the smaller the thickness of silicate layers, indicating silicate layers are chopped more finely. Here, we assume that the thickness of silicate layers is related to the degree of exfoliation in a qualitative sense. The results for PA6/30 B and PA6/25 A prepared at 240°C for 6 min are shown in Figure 7 and Figure 8, respectively, where the statically annealed sample corresponds to the nanocomposite prepared under zero shear stress. As expected from Figure 5, Bragg's spacing $d_{(001)}$ increases and D_c decreases as maximum shear stress increases. The rates of change in $d_{(001)}$ and D_c are dependent on the molecular weight of PA6. Formation of exfoliated nanocomposites may be determined by whether polymer chains effectively diffuse into the gallery of silicate layers and then reduce van der Waals force between silicate layers during a given mixing time. As the molec-

ular weight of the polymer decreases, conformational entropy loss for confinement of a polymer chain in the gallery of silicate layers becomes smaller, so that small shear stress is enough to disperse the silicate layers in the polymer matrix. Increase in mixing temperature might induce faster diffusion of polymer chains into the gallery of silicate layers due to chain mobility, resulting in larger d -spacing and smaller crystallite size, as shown in Figure 9. Diffusion of polymer chain into the silicate host is thus a major factor for exfoliating silicate layers. Here, as a prerequisite the interaction between polymer and organic modifier should be favorable.

PA6 has two crystal forms: thermodynamically stable α -form (melting temperature, $\sim 217^\circ\text{C}$) consisting of fully extended planar zigzag chains, in which adjacent antiparallel chains are jointed to each other by hydrogen bond¹³ and the γ -form (melting temperature, $\sim 210^\circ\text{C}$) composed of pleated sheets of parallel chains jointed by hydrogen bonds.^{13,14} The silicate surface in

Figure 8. Effects of maximum shear stress on: (a) d -spacing (d_{001}) and (b) apparent crystallites size (D_c) of silicate layers in PA6/25 A series. Mixing was performed at 240°C for 6 min.

Figure 9. Effects of maximum shear stress on: (a) d -spacing (d_{001}) and (b) apparent crystallite size (D_c) of silicate layers in 48K/30B series, prepared at different mixing temperatures. Mixing was performed for 6 min.

PA6/organosilicate nanocomposite induces conformational changes of the polymer chains due to restriction of chain mobility near the surface. This limits the formation of hydrogen-bonded sheets leading to the γ -form.^{15, 16} Figure 10a shows that the ratio of γ -form to α -form increases for the sample of PA6/organosilicate, compared with that for neat PA6 (48 K). The melt crystallization temperature upon cooling also shifts to higher one, as shown in Figure 10b. It is clear that the silicate surface acts as a heterogeneous nucleation site and increases the crystallization rate of PA6.

To investigate shear effects on the thermal properties of PA6/organosilicate nanocomposites, DSC measurements were performed for melt-mixed 48 K/25 A nanocomposites. As shown in Figure 11, the ratio of γ -form to α -form crystal is maximum at a rotor speed of 90 rpm. Shear stress breaks up silicate agglomerates and helps the polymer chain diffuse easily into the gallery of silicate layers. Therefore, as rotor speed increases, polymer chains can be more easily introduced in the gallery of 25 A. The fraction of polymer chains

confined in the gallery thus becomes larger, leading increase in γ -crystalline phase. However, as the rotor speed increases further over 200 rpm, 48 K shows shear thinning behavior and thus the melt viscosity of 48 K begins to decrease significantly and shear stress may decrease. This limits polymer diffusion into the silicate layers, resulting in dominance of more stable α -form. This explanation is also supported by change in melt crystallization temperature with rotor speed. As shown in Figure 11b, the melt crystallization temperature of nanocomposites increases to a rotor speed of 90 rpm, and then decreases above 200 rpm.

CONCLUSIONS

We investigated the effects of shear stress on the exfoliation of organosilicate layers in the PA6 matrix. Shear stress was controlled by changing the molecular weight of PA6, mixing temperature, and rotor speed of a mini-molder. As a measure of intercalation and/or exfoliation, d -spacing of silicate layers (d_{001}) and ap-

Figure 10. DSC thermograms for 48 K/organosilicate nanocomposites, prepared by melt mixing at 240°C for 6 min under a constant rotor speed of 90 rpm: (a) heating scans; (b) cooling scans. Heating and cooling scan rates were 20°C min⁻¹ and -20°C min⁻¹, respectively.

Figure 11. DSC thermograms for 48 K/25 A, prepared by melt mixing at 240°C for 6 min at different rotor speeds: (a) heating scans; (b) cooling scans. Heating and cooling scan rates were 20°C min⁻¹ and -20°C min⁻¹, respectively.

parent crystallite size (D_c) of layered silicates were used. By carefully controlling mixing conditions, it was possible to prepare PA6/organosilicate nanocomposites with different degrees of exfoliation. When 30 B, which favorably interacts with PA6 through hydrogen bonding, was used as organosilicate, silicate layers were exfoliated even at zero shear stress when annealing time was long enough. Clay exfoliation is dependent on the molecular weight of PA6 and mixing temperature. Exfoliation of 30 B becomes faster, as molecular weight decreases and mixing temperature increases. This indicates exfoliation of silicate layers is closely related to diffusion of matrix polymers into the gallery of silicate layers because diffusion becomes faster as molecular weight of matrix decreases and mixing temperature increases. The shear stress applied seems to contribute to breaking up of silicate agglomerates and improve sample uniformity. The shear stress applied during mixing seems to play a secondary role. Breaking silicate agglomerates into primary particles facilitates polymer chains to diffuse easily into the gallery of lay-

ered silicates and enhances the degree of exfoliation under given mixing conditions.

Acknowledgments. The authors thank the Korea Science and Engineering Foundation (KOSEF) for financial support through Hyperstructured Organic Materials Research Center (HOMRC). M. B. Ko and M. S. Lee thank the Ministry of Education for the support through the Brain Korea 21 Program.

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