Nonisothermal Crystallization Behavior of Exfoliated Poly(ethylene terephthalate)-Layered Silicate Nanocomposites in the Presence and Absence of Organic Modifier

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ABSTRACT: Exfoliated poly(ethylene terephthalate) (PET)-layered silicate nanocomposites (PETLSNs) excluding (PETLSNeom) and including (PETLSNiom) organic modifiers were obtained by solution methods with and without solvent-nonsolvent system, respectively. From wide angle X-ray diffraction and high resolution transmission electron microscopy, both PETLSNs were found to have exfoliated structure attributed to sufficient dispersion of silicate in prepared solvents, regardless of sample preparation method. However, organic modifier in PETLSNeom was confirmed to be well removed by elemental analysis, whereas organic modifier was still remained in PETLSNiom. Thus, the effect of the presence and absence of organic modifiers in PETLSNs on the nonisothermal crystallization behavior was investigated by differential scanning calorimetry (DSC) on the basis of a modified Avrami analysis and polarized optical microscopy (POM). From DSC results, it was found that both PETLSNs had higher degrees of crystallinity and shorter crystallization half-times than neat PET, because of the dispersed silicate layers acted as nucleating agents in both PETLSNs. However, PETLSNiom exhibited a lower degree of crystallinity and longer half-time of crystallization than PETLSNeom. Difference of crystallization behavior between PETLSNeom and PETLSNiom was ascribed to organic modifier in PETLSNiom, which may act as crystallization inhibitors. POM measurements also revealed the results which were in good agreement with crystallization behavior observed from DSC measurement. © 2008 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 46: 989–999, 2008

Keywords: crystallization; exfoliation; nanocomposites; organic modifier; poly(ethylene terephthalate) (PET)

INTRODUCTION

Recently, polymer-layered silicate nanocomposites (PLSNs) have been widely used in various industrial products due to their enhanced properties provided from the combination of a polymer matrix and layered silicate. In particular, compared with conventional composites, PLSNs exhibit extremely low gas permeabilities, high moduli, and heat resistance derived from their unique features (a high aspect ratio and a layered structure), even at low silicate loadings.1-5 The distinctive features of the layered silicates result in the nanocomposites having two possible structures, namely intercalated or exfoliated structures, which are attributed to the insertion of matrix polymer into the gallery between silicate layers. The intercalated nanocomposites...
show regularly alternating silicate and polymer layers with a repeat distance of a few nanometers, whereas the individual layers in the exfoliated nanocomposites are irregularly delaminated and dispersed in a continuous polymer matrix. Such structural differences play a key role in the enhancement of the nanocomposite properties. However, since the substrates of natural silicate are hydrophilic and the gallery height is very narrow ($\sim 1.0$ nm), it is difficult for the hydrophobic matrix polymer to penetrate into the galleries of silicate layers. Thus, organic modifiers have been introduced on the surface of the layered silicates to increase the hydrophobicity of the natural silicate, then various reports have been published on the fact that organic modifier provides a favorable insertion of matrix polymer into gallery of silicate.\textsuperscript{6–9} Recently, attention has been paid to the influence of organically modified layered silicates (OLS) on the properties of PLSNs, and then it was found that organic modifiers unavoidably lead thermal decomposition of PLSNs at high processing temperatures, which cause a deterioration of the physical properties of the PLSNs.\textsuperscript{10–17} Xie et al.\textsuperscript{10,11} reported that the thermal decomposition of organic modifiers in PLSNs was correlated with the processing residence time, the processing temperature, and the type of ammonium organic modifiers used. Davis et al.\textsuperscript{12} studied the degradation pathways of the PLSNs, with particular focus on the degradation mechanism of organic modifiers in PLSNs at high processing temperatures. Zhang et al.\textsuperscript{16,17} reported that poly(ethylene terephthalate) (PET) nanocomposite (P$_e$LSN) had poor optical properties ascribed to thermal decomposition of organic modifier. These results show that organic modifier as well as silicate structure is one of the critical factors to determine the physical properties of PLSNs.

PET is semicrystalline polymer extensively used for packaging films, beverage bottles, engineering components, and fibers for apparel on account of its excellent chemical resistance, thermal stability, and mechanical properties. Recently, the use of PET under more severe conditions requires that its various physical properties, such as its optical, thermal, mechanical, and barrier properties, should be much enhanced. Hence, the commercial importance of PET in industrial fields has driven intensive investigation into (PET)-layered silicate nanocomposites (P$_e$LSNs), because these composite materials exhibit far superior physical properties to PET blends with micro-sized additives. However, PET requires a high processing temperature for producing the various end-products. Thus, most investigations have focused on the thermal decomposition of organic modifier in P$_e$LSNs at high temperature. On the other hand, it was reported that organic modifier affects the crystallization behavior of PLSNs, which is another important factor governing the physical properties of PLSNs.\textsuperscript{18} However, there have been few studies on the effect of organic modifiers on the crystallization behaviors of P$_e$LSNs, compared with investigations on the thermal decomposition of organic modifier in P$_e$LSNs. Hence, we examined the detailed effect of organic modifiers on the nonisothermal crystallization behaviors of P$_e$LSNs with an exfoliated structure in the present study. For this purpose, PET-layered silicate nanocomposites with an exfoliated structure either excluding (P$_e$LSN$_{exom}$) and including organic modifiers (P$_e$LSN$_{iom}$) were prepared by solution methods with and without solvent–nonsolvent system, respectively, and then the nanostructure of the silicate layers was evaluated by wide angle X-ray diffraction (WXRD) and high resolution transmission electron microscopy (HR-TEM). To monitor the crystallization behaviors, we employed nonisothermal crystallization by differential scanning calorimetry (DSC) with various cooling rates and applied a modified Avrami analysis. In addition, the effect of organic modifiers on the morphological behaviors of spherulites in the P$_e$LSNs was investigated using polarized optical microscopy (POM).

**EXPERIMENTAL**

**Materials**

PET with an intrinsic viscosity of 0.64 ± 0.01 and a melting point of 255 °C was obtained from the Huvis Chemical Company. OLS with polyoxypropylene methyl diethyl ammonium cation were kindly supplied by Co-op Chemical Co. The OLS had ~4.4 nm of gallery height and 50 of aspect ratio. The weight ratio of layered silicates/organic modifiers in the OLS was verified to be about 0.4/0.6 by thermogravimetric analysis. Chloroform and trifluoroacetic acid (TFA) used for removing the organic modifier ionically attached on the layered silicate were purchased.
from Sigma-Aldrich Co., and used without any additional purification.

Sample Preparation
OLS was added in excess chloroform and stirred at 25 °C for 1 h. TFA was poured in OLS/chloroform solution and stirred for 5 min, and then neat PET was added to OLS/chloroform/TFA solution, and dissolved by stirring for an additional 1 h (neat PET/OLS = 92/8, w/w%). PET/OLS/chloroform/TFA solution was added dropwise to the cold methanol to obtain PET nanocomposite excluding organic modifier (PetLSNeom), as shown in Scheme 1. Then, precipitated materials were collected by filtering and dried in a vacuum oven at 80 °C for 12 h. On the other hand, PET nanocomposite including organic modifier (PetLSNiom) was prepared by removing both solvent from prepared PET/OLS/chloroform/TFA solution at 30 °C for 48 h. The remaining white powder was collected and dried in a vacuum oven at 80 °C for 12 h.

General Characterizations
The removal of organic modifiers in the PetLSNs was confirmed using an EA1110 elemental analyzer (EA). The nano-structure of silicate layers in the PET matrix was evaluated using WXRD on a Mac Science M18XHF at 2 ~ 10°, and Bragg’s Law was used to calculate the gallery height of the PetLSNs. Additionally, the morphological nano-structure of the delaminated and disordered silicate layers in the PetLSNs was characterized by HR-TEM.

Crystallization Behaviors
DSC 2920 (TA instruments) was used to investigate the overall kinetics of nonisothermal crystallization of the neat PET and PetLSNs. The samples were heated to 300 °C under nitrogen gas to suppress the thermal oxidation and kept for 3 min to eliminate thermal history. Nonisothermal experiments were performed by the cooling of the aforementioned molten samples at different cooling rates (2, 4, 6, 8, and 10 °C min⁻¹). The crystallization peak temperature, T_p, was estimated from the peak maximum of the DSC thermogram. In addition, the weight fraction of crystallized materials at time t, X_t, was calculated using the ratio of the crystallization enthalpy generated at time t to the crystallization enthalpy of a completely crystallized sample as follows:

\[
X_t = \frac{\int_{T_0}^{T_p} \left(\frac{dT}{dt}\right) dT}{\int_{T_0}^{T_c} \left(\frac{dT}{dt}\right) dT}
\]

where T_0 and T_c represent the onset and end temperatures of the exothermal crystallization thermograms, respectively. According to the Avrami equation, X_t can be expressed as a function of crystallization time:\(^{19,20}\):

\[
X_t = 1 - \exp\left(-k t^n\right)
\]

where k and n are the crystallization rate constant and the Avrami exponent, respectively.
\( 1 - X_t = \exp(-kt^n) \) \hspace{1cm} (2)

where \( n \) is the Avrami exponent, which depends on the shape of the growing spherulites, and \( k \) is the crystallization rate constant. Equation 2 can be transformed to the double-logarithmic form as follows:

\[
\log[-\ln(1 - X_t)] = \log k - n \log t \hspace{1cm} (3)
\]

Cebe\(^{21}\) and Herreo\(^{22}\) tried to modify the Avrami equation to nonisothermal crystallization conditions using the relationship between crystallization time, \( t \), and cooling rate, \( R \), as follows:

\[
t = \frac{T_0 - T}{R} \hspace{1cm} (4)
\]

where \( T \) is the temperature at time \( t \), and \( T_0 \) is the temperature at the initiation of crystallization, \( t = 0 \). By plotting \( \log[-\ln(1 - X_t)] \) against \( \log t \) at a given temperature, \( n \) and \( k \) can be obtained from the intercept and slope, respectively. The rate of nonisothermal crystallization depends on the cooling rate; hence, the crystallization rate constant \( k \) should be altered to account for this. The corrected crystallization rate constant, \( k' \), is given as\(^{23}\):

\[
\log k' = \frac{\log k}{R} \hspace{1cm} (5)
\]

The half-time of crystallization, \( t_{1/2} \), which is the time required for 50% of the sample to be crystalline, is calculated from the measured parameters, \( n \) and \( k' \), as follows:

\[
t_{1/2} = \left( \frac{\ln 2}{k'} \right)^{1/n} \hspace{1cm} (6)
\]

### Morphology of Spherulites

To observe the spherulite morphology in the neat PET and PETLSNs, a polarized optical microscope equipped with a hot stage (Leica Co. Germany) was employed. The molten specimens were kept at 280 °C for 1 min to eliminate the thermal history, and then cooled to the desired isothermal crystallization temperature (230 °C) at a rate of 20 °C min\(^{-1}\), and then they were maintained for 150 s and 240 s.

### RESULTS AND DISCUSSION

#### Preparation of Exfoliated PETLSNs Excluding (PETLSNeom) and Including (PETLSNiom) Organic Modifiers

To verify the existence and absence of organic modifiers in PETLSNs, the detection of nitrogen in PETLSNeom and PETLSNiom was performed using EA because the organic modifiers (polyoxymethylene methyldiethylammonium cations) contained ammonium groups. As shown in Table 1, PETLSNiom contained 0.3 wt % of nitrogen, whereas no nitrogen was detected in PETLSNeom, indicating that the organic modifiers in PETLSNiom were completely removed during the preparation procedure. Lee et al.\(^{24}\) reported that the detachment of the organic modifiers from the layered silicates was affected by the solvent acidity, and that the detachment occurred to a greater extent in more strongly acidic solvents. Thus, it is considered that the detachment of organic modifiers in this study was induced by the strong acid (TFA) to break a strong ionic bonding between the organic modifiers and the silicate layers. The structure of silicate layer in PETLSNs was characterized using WXRD and HR-TEM. In the WXRD patterns (Fig. 1), two peaks for the OLS appeared at 2\( \theta \) = 2.27° and 4.56°, which corresponded to 4.4 nm and 2.8 nm of gallery heights, respectively. However, no peak was observed in the WXRD patterns for both PETLSNs, indicating formation of exfoliated silicate structure. Furthermore, it was observed by HR-TEM images (Fig. 2) that the silicate layers in both PETLSNs were randomly disordered and delaminated in the PET matrix, being consistent with WXRD results. Generally, it was well known that the chemical or structural nature of the organic modifier attached on the surface of silicate layer can affect the penetration of polymeric chains into the layered silicate gallery. In this study, however, organic modifier was detached from the layered silicate surface by TFA, which is strong acid used for solving PET. This implies that the organic modifier does

#### Table 1. Nitrogen Content of PETLSNeom and PETLSNiom

<table>
<thead>
<tr>
<th>Samples</th>
<th>Silicate Loading (wt %)</th>
<th>Nitrogen Content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETLSNeom</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>PETLSNiom</td>
<td>8</td>
<td>0.3</td>
</tr>
</tbody>
</table>

not play a role to draw polymeric chain into the layered silicate gallery. In fact, we employed the solution mixing method using chloroform/TFA cosolvent to obtain the exfoliated PET nanocomposite. Chloroform has been known as a solvent leading to the well-dispersed OLS suspension, and TFA is the solvent to dissolve PET and miscible with chloroform. Thus, OLS can be well mixed with PET in the chloroform/TFA cosolvent, and it seems that PET molecular chains can be easily penetrated into the gallery of silicate layer by miscibility effect between both solvents even though organic modifier can not affect the formation of the exfoliation structure of PetLSNs. Therefore, PetLSNs are considered to have the exfoliated structure, regardless of the presence and absence of organic modifier in the nanocomposite.

Nonisothermal Crystallization Behaviors

Nonisothermal crystallization behaviors were evaluated by DSC with cooling rates of 2, 4, 6, 8, and 10 °C min⁻¹ from the molten state. The resulting DSC thermograms of neat PET, PetLSN=com, and PetLSN=hom are shown in Figure 3. These thermograms provide useful information on the nonisothermal crystallization behaviors, including the exothermic crystallization temperature ($T_p$), the enthalpy of crystallization ($\Delta H_c$), and the degree of crystallinity ($X_c$) (see Table 2). The $T_p$ values of neat PET, PetLSN=com, and PetLSN=hom shifted to lower temperature as the cooling rate was increased, since a shorter crystallization time was applied to the neat PET, PetLSN=com, and PetLSN=hom; that is, during crystallization at high cooling rates, the neat PET, PetLSN=com, and PetLSN=hom had insufficient time to form nuclei and grow spherulites, and hence the nonisothermal crystallization thermograms were shifted to the low temperature region. The values of $X_c$ for the neat PET, PetLSN=com, and PetLSN=hom were determined from the enthalpy evolved in crystallization using the following equation:

$$X_c = \frac{\Delta H_c}{(1-\phi)\Delta H_m^0} \times 100$$

where, $\Delta H_m^0$ (an average value of 117.6 J g⁻¹ for PET) is the inferred enthalpy value correspond-

![Figure 1. WXRD patterns of OLS, PetLSN=com, and PetLSN=hom.](image)

![Figure 2. TEM images of (a) PetLSN=com and (b) PetLSN=hom.](image)
ing to the melting of a 100% crystalline sample, and \( \phi \) is the weight fraction of the silicate layers in the \( \text{PetLSN}\). The \( X_c \) of neat PET decreased with increasing cooling rate, because the higher cooling rate indicates less time for the conformational changes required in the crystallization. For \( \text{PetLSN}_{\text{com}} \) and \( \text{PetLSN}_{\text{iom}} \), by contrast, \( X_c \) increased with increasing cooling rate. Similar unusual crystallization behavior with \( \text{PetLSN}_{\text{com}} \) and \( \text{PetLSN}_{\text{iom}} \) was reported by Xu et al.\(^{28}\) and Liu et al.\(^{29}\) In addition, Figure 4 shows the DSC thermograms of neat PET, \( \text{PetLSN}_{\text{com}} \), and \( \text{PetLSN}_{\text{iom}} \) obtained with a cooling rate of 2 °C min\(^{-1}\).

As shown in Figure 4, the nonisothermal crystallization thermograms of \( \text{PetLSN}_{\text{com}} \) and \( \text{PetLSN}_{\text{iom}} \) appeared to have a narrower width than that of neat PET, indicating fast crystalline growth. This may ascribe to the delaminated and dispersed silicate layers in PetLSNs acted as nucleating agents. According to Lu et al.,\(^{30}\) some polymer chain segments gain relatively straight conformation at the crystallization temperature. If such chain segments are next to a layered silicate surface, they may sit down on it in an ordered manner, which initializes lamellae from the melt in the first place. The lamellae initially may grow one-dimensionally, and when the lamellae grow to a certain stage, their surfaces can act as substrates to initialize more lamellae, and they can grow three-dimensionally because the nuclei are now not under the geometric constraint imposed by the silicate layer. Therefore, the crystallization of PET can be readily induced by the presence of the silicate layers, and hence the nonisothermal crystallization thermograms shifted to a higher temperature region, that is, the order of \( T_p \) was \( \text{PetLSN}_{\text{com}} \) > \( \text{PetLSN}_{\text{iom}} \) > neat PET. Chen et al.\(^{31}\) reported that the nonisothermal crystallization parameters, such as the initial slope \( (|S_i|) \) and the width at half-height of the exothermal DSC thermograms \( (\Delta W) \), can be determined from exothermal DSC thermograms. The values of \( |S_i| \) and \( \Delta W \) represent the degree of nucleation and the crystallite size distribution during the nonisothermal crystallization process. To estimate the effect of organic modifiers and silicate layers in \( \text{PetLSN} \) on the crystallization behaviors, we calculated the \( |S_i| \) and \( \Delta W \) values of neat PET, \( \text{PetLSN}_{\text{com}} \), and \( \text{PetLSN}_{\text{iom}} \) (Table 3). As seen in Table 3, \( \text{PetLSN}_{\text{com}} \) and \( \text{PetLSN}_{\text{iom}} \) exhibited higher \( |S_i| \) and lower \( \Delta W \) values than neat PET, meaning that \( \text{PetLSN}_{\text{com}} \) and \( \text{PetLSN}_{\text{iom}} \) exhibited faster nucleation, and a more uniform crystallite size distri-

**Figure 3.** DSC thermograms of nonisothermal crystallization at different cooling rates for (a) neat PET, (b) \( \text{PetLSN}_{\text{com}} \), and (c) \( \text{PetLSN}_{\text{iom}} \).
bution, in comparison with neat PET. This implies that the delaminated and dispersed silicate layers in PetLSNeom and PetLSNiom acted as nucleating agents, and led to a large $S_i$ and narrow $D_W$. On the other hand, the $S_i$ values of PetLSNeom and PetLSNiom were calculated to be 0.058 and 0.039, respectively, and the $D_W$ values of PetLSNeom and PetLSNiom were calculated to be 5.40 and 6.78, respectively. This is due to the fact that the organic modifiers in PetLSNiom acted as crystallization inhibitors, and led to a small $S_i$ and broad $D_W$. Consequently, when neat PET was mixed with OLS, the crystallization kinetics were found to increase; that is, the nonisothermal crystallization thermograms of PetLSNeom and PetLSNiom were shifted to the high temperature region, and the overall size of the spherulites in the PET matrix in PetLSNeom and PetLSNiom became uniform.32–34

To accurately understand the crystallization behaviors under nonisothermal conditions, the measured nonisothermal crystallization thermograms were studied in greater detail using the modified Avrami equation. According to eq 1, the nonisothermal crystallization exotherms, as shown in Figure 3, were analyzed, and the resulting relative crystallinity variation for neat PET, PetLSNeom, and PetLSNiom are illustrated as a function of temperature in Figure 5. According to the relation between crystallization temperature and time (eq 4), Figure 5 can be transformed into a function of time. Figure 6 shows the relative crystallinity variations as a function of crystallization time for neat PET, PetLSNeom, and PetLSNiom. As can be seen from Figure 6, the lower the cooling rate, the greater the time range at which crystallization occurs. Additionally, all curves are seen to have approximately the same shape, indicating that only the retardation effect of cooling rate on the crystallization can be observed in these curves.35 On the basis of the assumption that the crystallization temperature is constant, the Avrami equation was used for describing the primary stage of the nonisothermal crystallization kinetics (eq 2). To facilitate the evaluation of the Avrami parameters ($n$ and $k$), eq 2 is often rearranged to a double logarithmic form as eq 3. Figure 7 shows the log$[-\ln(1-X_c)]$ versus log $t$ plots (so-called Avrami plots) for neat PET, PetLSNeom, and PetLSNiom. In Figure 7, some Avrami plots seem to slightly show the S-shaped curve, indicating the secondary crystallization.30 Thus, the

### Table 2. Crystallization Peak Temperatures ($T_p$), Enthalpy of Crystallization ($\Delta H_c$), and Crystallinities ($X_c$) of Neat PET, PetLSNeom, and PetLSNiom at Various Cooling Rate

<table>
<thead>
<tr>
<th>Cooling Rate (°C min⁻¹)</th>
<th>Neat PET</th>
<th>PetLSNeom</th>
<th>PetLSNiom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_p$</td>
<td>$\Delta H_c$</td>
<td>$X_c$</td>
</tr>
<tr>
<td>2</td>
<td>199.2</td>
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</tr>
<tr>
<td>4</td>
<td>192.1</td>
<td>43.1</td>
<td>36.6</td>
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<tr>
<td>6</td>
<td>187.1</td>
<td>42.3</td>
<td>36.0</td>
</tr>
<tr>
<td>8</td>
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<td>34.1</td>
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<tr>
<td>10</td>
<td>176.8</td>
<td>34.7</td>
<td>29.5</td>
</tr>
</tbody>
</table>

### Table 3. Various Parameters of Neat PET and PetLSNeom, and PetLSNiom Obtained From the Nonisothermal Crystallization Thermograms

| Samples            | $|S_i|$ a | $\Delta W$ b |
|--------------------|---------|--------------|
| Neat PET           | 0.005   | 17.35        |
| PetLSNeom          | 0.058   | 5.40         |
| PetLSNiom          | 0.039   | 6.78         |

* a $|S_i|$, initial slope.  
* b $\Delta W$, width at half-height.
Figure 5. Plot of amorphous fraction ($1-X_t$) as a function of temperature for (a) neat PET, (b) $P_{etLSN_{com}}$, and (c) $P_{etLSN_{ion}}$.

Figure 6. Plot of amorphous fraction ($1-X_t$) as a function of time for (a) neat PET, (b) $P_{etLSN_{com}}$, and (c) $P_{etLSN_{ion}}$. 

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Avrami plots of neat PET, PETLSNeom, and PETLSNiom were reasonably fitted by the straight lines to initial portion of the curves in Figure 7 ($\log(1-X_t) < -0.5$). Then, the modified Avrami kinetics, such as the Avrami exponent ($n$), the corrected crystallization constant rate ($k'$), and the half-time of crystallization ($t_{1/2}$) for PETLSNeom and PETLSNiom, as well as neat PET, were estimated by the slope and the intercept of the straight lines, respectively, which are listed in Table 4. From Table 4, it can be seen that the $n$ values of neat PET were calculated to be in the range of 2.7–3.2 at a given cooling rate, indicating that the nucleation growth shapes corresponded to three-dimensional spherulites. For PETLSNeom and PETLSNiom, $n$ values were determined to be in the range of 2.8–3.4, implying three-dimensional spherulitic growth. However, Lu et al. reported that most of the crystallites in polymer nanocomposite cannot complete their three-dimensional growth in all directions, because many branches will be terminated by the presence of the dispersed silicate layers in their growth path. Thus, it may be considered that PETLSNs have a relatively irregular three-dimensional spherulitic crystallites interlocked together, compared to neat PET. In case of the crystallization kinetic parameters, $k'$ and $t_{1/2}$, both PETLSNeom and PETLSNiom showed a higher $k'$ and a lower $t_{1/2}$ than neat PET at a given cooling rate, it is believed that greatly increased crystallization rate was due to the heterogeneous nucleation by the silicate layers. On the other hand, PETLSNiom exhibited a lower $k'$ and a higher $t_{1/2}$ than PETLSNeom due to the physical hindrance of the organic modifiers in PETLSNiom, that is, organic modifiers hinder the packing of the PET chains in a regular manner and interrupt the lamellar pathways. Therefore, it was considered that the silicate layers in PETLSNeom and PETLSNiom effectively prompted crystallization by playing the role of nucleating agents, and organic modifiers in PETLSNiom inhibited crystallization. These crystallization kinetic trends of neat PET, PETLSNeom, and PETLSNiom were good agreement with the $|S_i|$ and $\Delta W$ results.

**Morphology of Spherulites**

POM was used to compare the morphologies of the spherulites. Figure 8 shows the POM images of neat PET, PETLSNeom, and PETLSNiom, which were crystallized at 230 °C for 150 s and 240 s,
respectively. As inferred from the nonisothermal crystallization kinetics using DSC, both $P_{etLSN_{com}}$ and $P_{etLSN_{iom}}$ show a faster spherulite growth rate and a higher density of spherulites than neat PET. On the other hand, $P_{etLSN_{com}}$ appears to show a faster spherulite growth rate and a higher density of spherulites in $P_{etLSN_{iom}}$ under the same conditions. In fact, the POM images of $P_{etLSN_{iom}}$ at 240 s, although the crystallization was complete, a number of black

<table>
<thead>
<tr>
<th>Cooling Rate ($^\circ$C min$^{-1}$)</th>
<th>Neat PET</th>
<th>$P_{etLSN_{com}}$</th>
<th>$P_{etLSN_{iom}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>$k'$</td>
<td>$t_{1/2}$</td>
</tr>
<tr>
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</tbody>
</table>

Figure 8. POM images of (a) neat PET, (b) $P_{etLSN_{com}}$, and (c) $P_{etLSN_{iom}}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 4. Modified Avrami Parameters of Neat PET, $P_{etLSN_{com}}$, and $P_{etLSN_{iom}}$
spots were observed, indicating noncrystallizable regions. It was considered that these black spots were attributed to the organic modifiers in PetLSNiom, which act as crystallization inhibitors.27,29,39 These results were good agreement with above crystallization behavior observed from DSC thermograms.

CONCLUSIONS

PET nanocomposites with an exfoliated structure excluding (PetLSNeom) and including (PetLSNiom) organic modifiers were prepared by solution methods with and without solvent–non-solvent system, respectively. Then, the effect of organic modifiers in the PetLSNs on the nonisothermal crystallization behaviors was investigated by DSC on the basis of a modified Avrami analysis and POM, and the results were compared with those for neat PET. Both PetLSNeom and PetLSNiom exhibited a higher degree of crystallinity and a faster crystallization rate than neat PET, because the silicates in both nanocomposites acted as nucleating agents for generation of crystalline. On the other hand, PetLSNiom showed a lower degree of crystallinity and slower crystallization kinetics than PetLSNeom. This result is due to organic modifier which acted as crystallization inhibitor in PetLSNiom. Spherulite morphology observed from POM measurements also revealed that delaminated and dispersed silicate layer acted as nucleating agents, and that the organic modifier in PetLSNiom acted as crystallization inhibitor.

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REFERENCES AND NOTES

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