

# Nanocomposites Based on Poly( $\epsilon$ -caprolactone) and the Montmorillonite Treated with Dibutylamine-Terminated $\epsilon$ -Caprolactone Oligomer

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**ABSTRACT:** Dibutylamine-terminated  $\epsilon$ -caprolactone oligomers (CLOs: CLOL, CLOM, and CLOH) with number-averaged molecular weight ( $M_n$ ), 500, 1300, and 2200, respectively, were synthesized by the ring-opening polymerization of  $\epsilon$ -caprolactone initiated by 2-(dibutylamino)ethanol in the presence of tin(II) 2-ethylhexanoate. Nanocomposites based on poly( $\epsilon$ -caprolactone) (PCL) and the caprolactone oligomer-treated montmorillonites (CLO-Ms: CLOL-M, CLOM-M, and CLOH-M) were prepared by melt intercalation method. The XRD and TEM analyses of the PCL composites revealed that the extent of exfoliation of the clay platelets increased with increasing molecular weight of the used CLOs. Tensile

strength and modulus of the PCL/CLO-M composites increased with increasing molecular weight of the CLO and increasing inorganic content. The tensile modulus of the PCL/CLOH-M nanocomposite with inorganic content 5.0 wt % was three times higher than that of control PCL. Among the PCL/CLO-M composites, the PCL/CLOM-M composite had the highest crystallization temperature and melting temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3112–3119, 2007

**Key words:** nanocomposites; polyesters; mechanical properties; thermal properties

## INTRODUCTION

Nanocomposites based on biodegradable polyesters and layered silicate have attracted much attention because the layered clay is environmentally friendly, naturally abundant, and economic, and the improvement of various properties in comparison with control biodegradable polymers can enlarge the application fields of the polymers. In general, polymer-layered silicate nanocomposites can be prepared by four different methods: solution intercalation, *in situ* intercalative polymerization, polymer melt intercalation, and template synthesis.<sup>1</sup> Polymer melt intercalation has been proven to be an excellent technique because of its versatility, its compatibility with current polymer processing techniques, and its environmentally benign character because of the absence of solvent.<sup>2</sup> There have been many literatures regarding the layered silicate nanocomposites prepared by the polymer melt intercalation method using biodegradable polyesters, such as poly(L-lactide)<sup>3–14</sup> and poly(butylene succinate).<sup>15–22</sup>

Regarding the biodegradable poly( $\epsilon$ -caprolactone) (PCL) nanocomposites, there have been several litera-

tures on the formation of exfoliated nanocomposites by *in situ* ring-opening polymerization method,<sup>23–27</sup> few literatures are reported on the formation of exfoliated nanocomposite by polymer melt intercalation method, which is industrially useful. It was reported that melt mixing of PCL and methyl tallow bis(2-hydroxyethyl)ammonium-treated montmorillonite (Cloisite® 30B) or dimethyl hydrogenated tallow (2-ethylhexyl)ammonium-treated montmorillonite (Cloisite® 25A) produced by Southern Clay Products affords exfoliated/intercalated nanocomposites.<sup>28–29</sup> It was also reported that the use of dimethyl dioctadecylammonium-treated montmorillonite (Cloisite® 15A) affords intercalated nanocomposites.<sup>30</sup>

The present article describes the preparation of exfoliated PCL nanocomposites by melt intercalation method using the montmorillonite treated with dibutylamine-terminated  $\epsilon$ -caprolactone oligomer (CLO). Our attention is focused on the influence of molecular weight of CLO on the extent of intercalation/exfoliation, tensile properties, and crystallization behavior of the PCL nanocomposites.

## EXPERIMENTAL

### Materials

PCL (CelGreen P-H7®, density 1.14 g/cm<sup>3</sup>, melt flow rate (190°C, 2.16 kg) 1.7 g per 10 min) was supplied

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from Daicel (Japan). Sodium ( $\text{Na}^+$ ) montmorillonite (MMT, Kunipia F, cation exchange capacity (CEC): 115 mequiv per 100 g) was supplied by Kunimine Industries (Tokyo, Japan). The reagents for the preparation of CLO, 2-butylaminoethanol,  $\epsilon$ -caprolactone, tin (II) 2-ethylhexanoate were supplied from Tokyo Kasei Kogyo, Sigma Aldrich, and Wako Chemical, respectively. All the other chemicals used in this work were reagent grade and used without further purification.

### Preparation of CLOs

The dibutylamino-terminated caprolactone oligomers (CLOL, CLOM, and CLOH) with theo.  $M_n$  500, 2000, and 4000 were prepared by the ring-opening polymerization of  $\epsilon$ -caprolactone initiated with 2-(dibutylamino)ethanol. A typical procedure for the preparation of CLOL is as follows: To a 300-mL three-neck round-bottomed flask equipped with a nitrogen inlet tube and a reflux condenser were placed 100.0 g (0.876 mol) of  $\epsilon$ -caprolactone and 52.4 g (0.302 mol) of 2-(dibutylamino)ethanol. The mixture was heated slowly to 120°C with nitrogen bubbling for 1 h, and 80 mg (0.05 wt %) of tin (II) 2-ethylhexanoate was added, followed by heating slowly to 150°C for 1 h with a continuous nitrogen stream. The resulting mixture was stirred and kept at 150°C for 23 h at a reduced pressure of 50 mmHg to yield 142 g of CLOL as a pale brown solid in 96.6% yield. In a similar manner except for the use of 9.50 g (54.8 mmol) and 4.50 g (26.0 mmol) of 2-(dibutylamino)ethanol, and 55 and 52 mg (0.05 wt %) of tin (II) 2-ethylhexanoate, CLOM and CLOH were synthesized in 96.6% and 94.8% yield, respectively. The obtained CLOL, CLOM, and CLOH were used without any purification in the preparation of the following organo-modified clays. The  $M_n$  of the CLOL, CLOM, and CLOH measured by  $^1\text{H}$  NMR method were  $\sim$ 500, 1300, and 2200, respectively. As compared with the result of  $^1\text{H}$  NMR, the  $M_n$  and weight average molecular weight ( $M_w$ ) measured by GPC method were 600 and 1800 for CLOL, 1900 and 3900 for CLOM, and 3500 and 8000 for CLOH. Because the  $M_n$  of the amine-terminated CLO measured by GPC is a relative value to a nonpolar polystyrene standard, the  $M_n$  obtained by  $^1\text{H}$  NMR method was adopted for the calculation of feed mole of CLO in the organo-modification.

### Preparation of CLO-Ms

Organoclay (CLO-Ms) were prepared by cation exchange of natural counterions with protonated ammonium ions of dibutylamino-terminated CLOs. In all cases, molar ratio of exchangeable cation calculated from CEC value, the CLO, and hydrochloric acid is 1.00 : 3.00 : 4.50. A typical procedure in case of CLOH-

M is as follows: MMT (10.0 g, exchangeable cation 11.5 mmol) was dispersed in 1000 mL of deionized water at room temperature. The CLOH (75.9 g, 34.5 mmol) was dissolved in 200 mL of ethanol, and then concentrated hydrochloric acid (4.44 mL, 51.8 mmol) was slowly added. The obtained solution was poured into the clay suspension, and stirred for 1 h at 80°C. The exchanged clay was filtered, washed with a 1 : 1 mixture of water and ethanol, and redispersed in a 1 : 1 mixture of ethanol and deionized water. This procedure was repeated three times. The obtained filter cake was freeze-dried, crushed into powder using mortar and pestle, and screened with a 280-mesh sieve to give CLOH-modified MMT (CLOH-M) as an off-white powder. In a similar manner, CLOL- and CLOM-modified MMT (CLOL-M and CLOM-M) were prepared. The organic fractions of CLOL-M, CLOM-M, and CLOH-M were 40.5, 77.9, and 82.7 wt %, respectively. Their cation exchange rates were 96.0, 171.6, and 171.9%, respectively. Their 5% weight loss temperatures were 323, 328, and 316°C, respectively.

### Preparation of PCL/CLO-M composites

The clay (MMT and CLO-Ms) particles and PCL pellets were dried under vacuum at 40°C for at least 24 h before use. Melt mixing of PCL with the clay particles was performed on a Laboplasto-Mill with a twin rotary roller-mixer (Toyo Seiki, Japan). The inorganic content of the blends was 3.0 and 5.0 wt %. The mixing was carried out for 5 min with a rotary speed 50 rpm at 120°C. The mixture was crushed to small pieces after its immersion in liquid nitrogen, and it was dried at 40°C *in vacuo* for at least 24 h prior to injection molding. The dumbbell-shaped specimen (width 5 mm, thickness 2 mm, length of parallel part 32 mm, total length 72 mm) was molded using a desktop injection molding machine (Little-Ace I Type, Tsubako, Japan). The cylinder temperature and molding temperatures during the injection molding were 150 and 20°C, respectively.

### Measurements

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker AV-400 (400 MHz) using  $\text{CDCl}_3$  as a solvent.

GPC analysis was performed at 40°C using a Shimadzu LC9A equipped with two linear PLgel 5  $\mu\text{m}$  MIXED-D columns (Polymer Laboratories), using THF as the eluent, the elution rate was 0.5 mL/min and the detector was the refractive index type. Polystyrene standards were used to generate a calibration curve for the molecular weight determination.

Cation exchange rate (CER) of organoclay was calculated from cation exchange capacity (CEC : 115 mequiv per 100 g) of Kunipia F, and the weight

decrease [ $W_1$  (g)] and remaining weight [ $W_2$  (g)] measured by thermogravimetric analysis (TGA) on a Perkin–Elmer TGA-7 instrument when the organoclay was heated from room temperature to 700°C with a heating rate of 20°C/min in a nitrogen atmosphere. CER is calculated from the following equation:  $\text{CER (\%)} = 100 (W_1/\text{MW})/[10^{-5}\text{CEC} (W_2 + 23.0W_1/\text{MW})]$ , where MW is obsd.  $M_n$  of ammonium cation of CLO. Organic fraction (wt %) of organoclay is  $100W_1/(W_1 + W_2)$ .

Tensile tests of the composites were performed using an Autograph AG-I (Shimadzu, Japan) based on the standard method for testing the flexural and tensile properties of plastics [JIS K7113 (1995)]. Span length was 50 mm and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and the standard deviation ( $\sigma$ ) were calculated.

X-ray diffraction (XRD) analysis was performed at ambient temperature on a Rigaku RINT-2100 X-ray diffractometer at a scanning rate of  $2.0^\circ \text{ min}^{-1}$ , using Cu K $\alpha$  radiation (wavelength,  $\lambda = 0.154 \text{ nm}$ ) at 40 kV and 14 mA. Sodium montmorillonite and the freeze-dried organoclay were studied as powders. The blended materials were prepared in films of 0.40-mm thickness by compression molding.

Dynamic viscoelastic measurements of the rectangular plates (length 30 mm, width 5 mm, thickness 2 mm) cut from the dumbbell-shaped composites were performed on a Rheograph Solid (Toyo Seiki, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz and a heating rate of 2°C/min.

The differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC Pyris 1 DSC in a nitrogen atmosphere. The PCL composite samples were heated to 120°C, and held at 120°C for 5 min, cooled to  $-100^\circ\text{C}$  at a rate of  $-20^\circ\text{C/min}$ , and then again heated at a rate of 20°C/min. The crystallization temperature ( $T_c$ ) and heat of crystallization ( $\Delta H_c$ )

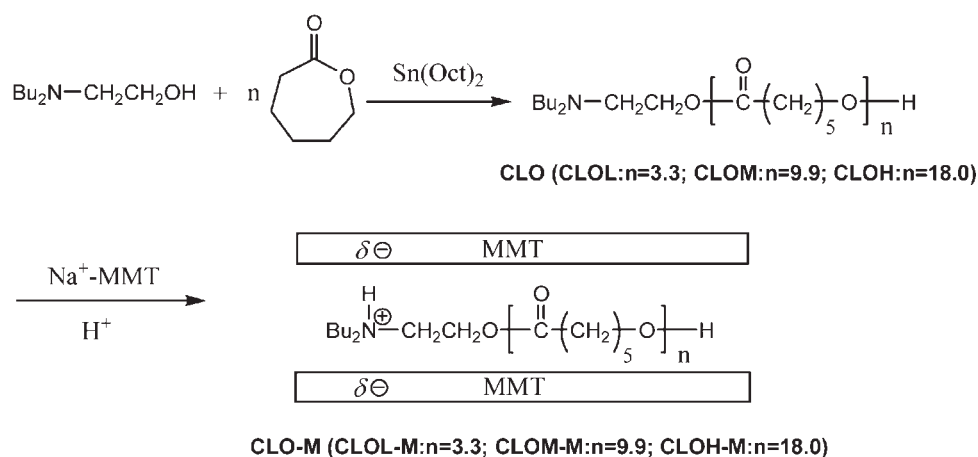
were determined from the cooling thermograms. Melting temperature ( $T_m$ ) and heat of melting ( $\Delta H_m$ ) were determined from the second heating thermograms, because there is the influence of thermal history on the first heating thermograms. A clear glass transition temperature was not observed for the heating and cooling processes.

Transmission electron microscopy (TEM) was performed on a JEOL model JEM-2200FS instrument with a 200 kV accelerating voltage. The TEM specimens were about 100-nm thick. Their specimens were prepared by ultramicrotoming the PBSAL composites encapsulated in a UV-cured resin with a diamond knife.

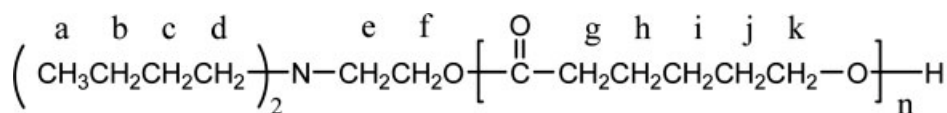
## RESULTS AND DISCUSSION

### Synthesis and characterization of CLOs

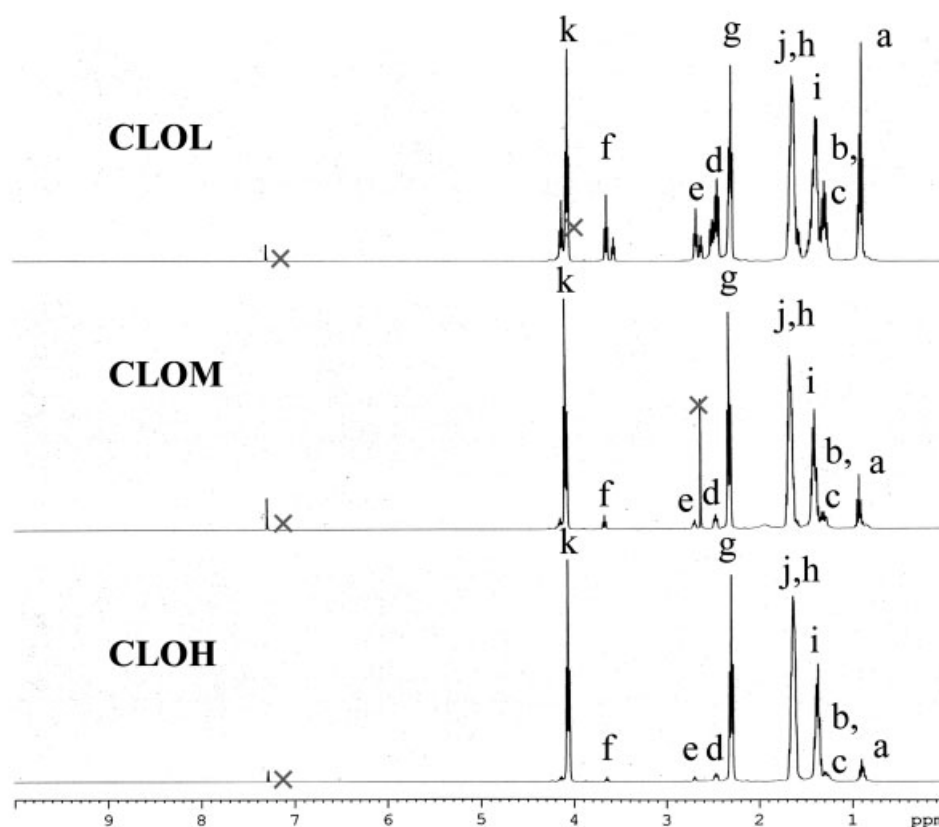
Dibutylaminoethyl-terminated  $\epsilon$ -caprolactone oligomers (CLOs: CPOL, CLOM, and CLOH) with theo.  $M_n$  500, 2000, and 4000 as organophilic modifiers of sodium montmorillonite were prepared by the ring-opening polymerization of  $\epsilon$ -caprolactone initiated by 2-(dibutylamino)ethanol in the presence of tin (II) 2-ethylhexanoate as shown in Figure 1. The  $^1\text{H}$  NMR spectra of CLOs are shown in Figure 2. Terminal methyl protons (a, 6H) of the dibutylamino group are observed at 0.9 ppm. The methylene protons (g,  $2\text{H} \times n$ ) adjacent to carbonyl group of the repeating unit of the CLO are observed at 2.3 ppm. The number-averaged degree of polymerization ( $P_n$ ) of CLOL, CLOM, and CLOH was calculated to be 3.3, 9.9, and 18.0 from the ratio of integral values of their two kinds of proton signals, respectively. Their  $P_n$ s correspond to  $M_n$  500, 1300, and 2200, respectively. Although, the observed  $M_n$  increased with increasing molar ratio of  $\epsilon$ -caprolactone/2-dibutylaminoethanol, CLOH had a lower obsd.  $M_n$  (2200) than the theo.  $M_n$  (4000).



**Figure 1** Synthetic scheme of CLOs and CLO-Ms.



CLO

Figure 2  $^1\text{H}$  NMR spectra of CLOs in  $\text{CDCl}_3$ .

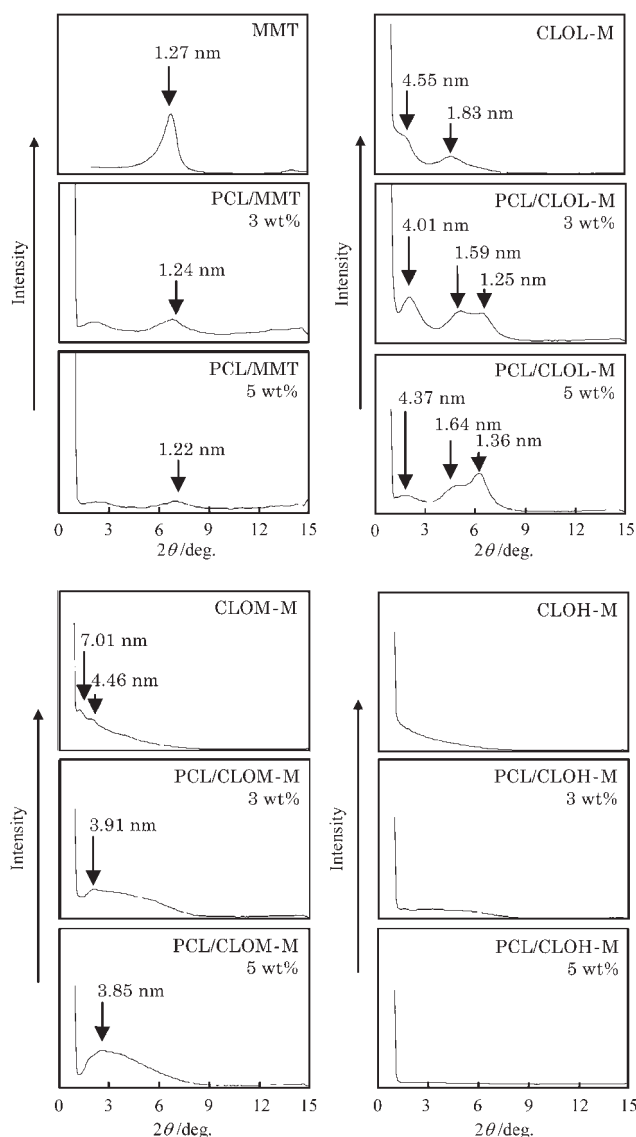
#### Preparation and characterization of CLO-M and PCL/CLO-M composites

Sodium montmorillonite was treated with the CLOL, CLOM, and CLOH protonated with hydrochloric acid in ethanol to give CLO-modified montmorillonites (CLO-Ms: CLOL-M, CLOM-M, and CLOH-M) as off-white powder. Although the ion exchange rate of CLOL-M (96.0%) calculated from the weight-loss after heating was almost quantitative, those of CLOM-M and CLOH-M (172%) were significantly higher than 100%, suggesting that excess CLOs are intercalated into the silicate gallery. Figure 3 shows the XRD patterns of clays and PCL/clay composites. The peaks correspond to the [001] basal reflection of the montmorillonite aluminosilicate. From the angular location of the peaks and the Bragg condition, the interlayer spacing of each of the clays was determined. For all the CLO-Ms, no peak corresponding to the [001] basal

reflection of MMT at  $7.02^\circ$  (1.27 nm) was observed. In case of CLOL-M and CLOM-M, the peaks corresponding to the CLO-intercalated interlayer spacing are observed at  $1.94^\circ$  (4.55 nm) and  $4.82^\circ$  (1.83 nm) for CLOL-M and at  $1.26^\circ$  (7.01 nm) and  $1.98^\circ$  (4.46 nm) for CLOM-M, respectively. The interlayer spacing of CLOM-M was higher than that of CLOL-M, in agreement with the order of the molecular weight of the CLO. In contrast, CLOH-M exhibited no clear peak except for a broad shoulder peak around  $1^\circ$ – $2^\circ$ , thus indicating the existence of interlayer distances larger than 7 nm.

The PCL/MMT (3 and 5 wt %) composites showed a relatively weak peak at the position almost near to MMT itself, indicating that no intercalation occurs and the sample is heterogeneous due to poor dispersion of the clay. The XRD pattern of the PCL/CLOL-M (3 and 5 wt %) composites is composed of mainly three peaks, two of which are relatively close to those





**Figure 3** XRD patterns of CLO-Ms and PCL/CLO-M composites.

of CLOL-M itself, one of which is not seen for CLOL-M. The peak position ( $6.50^{\circ}$ – $7.06^{\circ}$ , 1.25–1.36 nm) of a new peak is close to that of MMT, suggesting that the intercalated CLOL again comes out from the interlayer, and reaggregation of clay platelet occurs. Therefore, the PCL/CLOL-M composites are composed of the intercalated and aggregated clay platelets. In case of PCL/CLOM-M (3 and 5 wt %), a broad peak around  $2.3^{\circ}$  (3.9 nm) is observed, thus indicating the formation of intercalated nanocomposite. In contrast, no peak was observed for PCL/CLOH-M (3 and 5 wt %), suggesting the formation of highly intercalated or exfoliated nanocomposite.

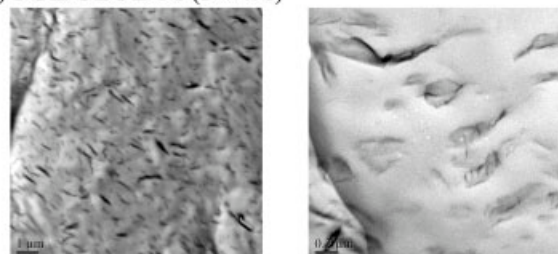
Figure 4 shows the TEM images of PCL/CLO-M composites with inorganic content 3 wt %. It is obvious that the order of a finer dispersion of the clay platelets in the matrix is CLOH-M > CLOM-M

> CLOL-M. The PCL/CLOL-M composite contained large particle agglomerates, and the dispersion of the clay platelets is not so good as compared with the other composites. In case of the PCL/CLOM-M composite, the size and shape of the dark lines in the micrographs thus supported the view of intercalated stacks, in agreement with the result of the XRD. The PCL/CLOH-M composite shows the finest dispersion of the silicate particles in the PCL matrix, based on the TEM images with lower magnification. However, in the TEM images with higher magnification, the silicate layers are not fully exfoliated into individual layers and small stacks of intercalated silicate layers are observed. Although we adopted a fixed melt mixing condition ( $120^{\circ}\text{C}$ , 5 min, twin rotary mixer, 50 rpm), the mixing condition should be optimized during further investigation to obtain completely exfoliated structures.

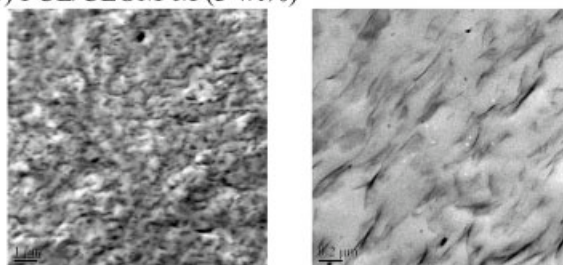
### Mechanical properties of PCL/CLO-M composites

Figure 5 shows the tensile properties of PCL/CLO-M composites. The tensile strength and modulus of the

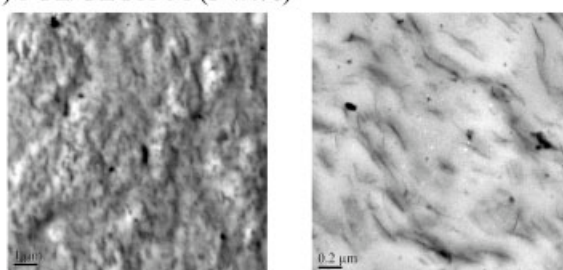
**(a) PCL/CLOL-M (3 wt%)**



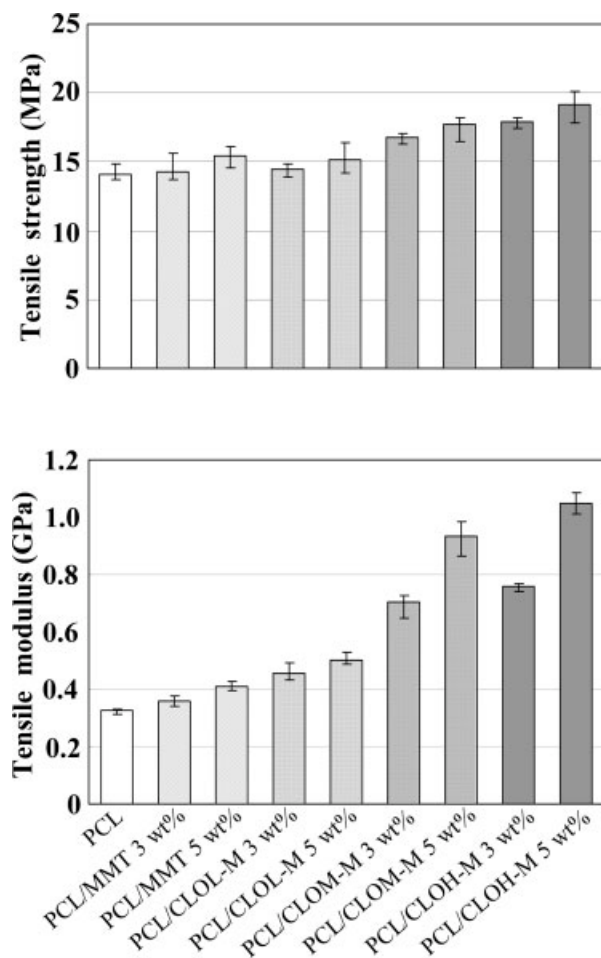
**(b) PCL/CLOM-M (3 wt%)**



**(c) PCL/CLOH-M (3 wt%)**



**Figure 4** TEM images (10,000 power) of PCL/CLO composites with inorganic content 3 wt %: (a) PCL/CLOL-M, (b) PCL/CLOM-M, and (c) PCL/CLOH-M.



**Figure 5** Tensile properties of PCL and PCL/CLO-M composites.

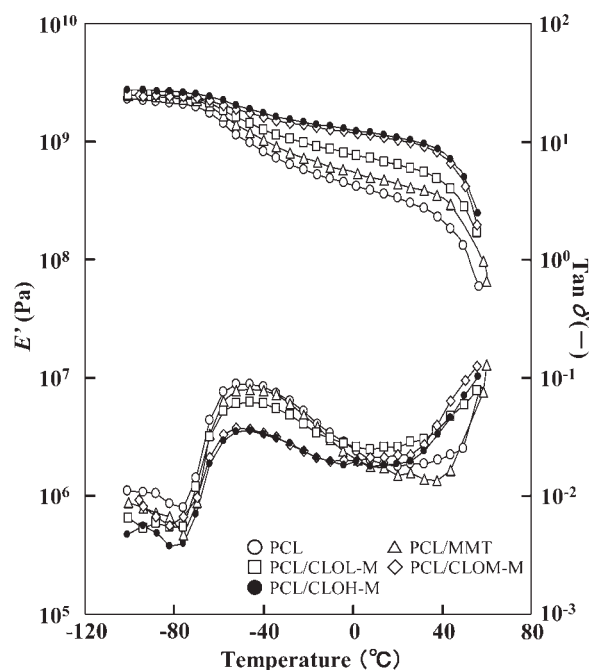
PCL/CLO-M composites increased with increasing molecular weight of the CLO used. The PCL composites with inorganic content 5 wt % also had higher tensile strength and modulus than the corresponding 3 wt % composites. It is noteworthy that the tensile modulus of PCL/CLOH-M (5 wt %) is three times higher than that of control PCL. The elongation at break for the PCL/CLOM-M and PCL/CLOH-M composites with inorganic content 5 wt % is 357 and 287%, respectively, indicating a more brittle character than control PCL (>400%). All the other PCL/clay (3 and 5 wt %) composites did not break until elongation of 400% during the tensile test.

Figure 6 shows dynamic viscoelastic curves of PCL and PCL/clay composites with inorganic content 5 wt %. All the samples showed a primary dispersion around  $-40^{\circ}\text{C}$  in the  $\tan \delta$  curves. The temperature at the maximal  $\tan \delta$  peak corresponds to glass transition temperature ( $T_g$ ) of the PCL component of PCL/clay composite. There was little change of the  $T_g$  for all the samples, indicating that  $T_g$  does not increase by the formation of intercalated/exfoliated nanocomposite. In agreement with the result of tensile modulus, the

storage modulus ( $E'$ ) of PCL/CLO-M composites around the temperature range of  $-20$  to  $40^{\circ}\text{C}$  was much higher than that of control PCL and PCL/MMT. When materials become soft above  $T_g$ , the reinforcement effect of the clay particles becomes prominent, due to restricted movement of the polymer chains, and hence strong enhancement of modulus appears. There was no significant improvement of storage modulus in the glassy state where the temperature is lower than  $-70^{\circ}\text{C}$ . Although PCL/CLOH-M and PCL/CLOM-M had a considerably higher storage modulus at the rubbery state than PCL/CLOL-M, there was little difference between PCL/CLOH-M and PCL/CLOM-M. The fact that CLOH-M (organic fraction: 82.7%) has a higher oligomer content than CLOM-M (77.9%) affects a lowering of  $E'$  for PCL/CLOH-M.

### Thermal properties of PCL/CLO-M composites

The thermal properties of the PCL composites determined by DSC measurements are summarized in Table I. All the PCL/clay composites showed a higher  $T_c$  than the control PCL. Also the PCL/CLOL-M and PCL/CLOH-M composites with inorganic content 5 wt % showed a little higher  $T_c$  than the composites with 3 wt %. These behaviors can be explained by the assumption that the silicate layers act as nucleating agents for the PCL crystallization, causing a crystallization rate higher than that of control PCL. Although there is no difference in  $T_c$  between the PCL/CLOM-M composites with inorganic content 3 and 5 wt %, the



**Figure 6** Dynamic viscoelastic curves of PCL and PCL/CLO-M composites with inorganic content 5 wt %.

TABLE I  
DSC Parameters of PCL and PCL Composites

Sample	Inorganic content (wt %)	$T_c$ (°C)	$\Delta H_c$ (J/g) <sup>a</sup>	$T_m$ (°C)	$\Delta H_m$ (J/g) <sup>a</sup>
CLOL	0	0.44	48.2	15.3–32.5 <sup>b</sup>	51.0
CLOM	0	26.1	79.5	48.9–56.5 <sup>b</sup>	84.5
CLOH	0	23.0	75.8	48.1–52.9 <sup>b</sup>	79.8
PCL	0	23.0	66.5	52.5	69.5
PCL/MMT	3	26.7	49.5	53.9	52.4
PCL/MMT	5	26.4	53.1	53.9	51.9
PCL/CLOL-M	3	24.3	54.6	53.6	64.4
PCL/CLOL-M	5	25.5	50.1	53.5	60.7
PCL/CLOM-M	3	33.2	57.3	62.3	64.1
PCL/CLOM-M	5	33.2	54.6	62.3	62.7
PCL/CLOH-M	3	25.9	49.1	53.9	55.3
PCL/CLOH-M	5	26.6	57.8	53.9	62.7

<sup>a</sup>  $\Delta H_c$  and  $\Delta H_m$  are the heat of crystallization and heat of melting per 1 g of PCL + CLO in the PCL/CLO-M composite, respectively.

<sup>b</sup> Double melting peaks were observed.

the PCL/CLOM-M composites had significantly higher  $T_c$  than the PCL/CLOL-M composites. This result is in accordance with finer clay dispersion of the former composites, and suggests that the nucleating effect of the clay platelets is already saturated at the inorganic content 3 wt %. The crystallization of PCL/CLO-M composites should contain both the crystallization of the matrix PCL and the organo-modifier CLO. Therefore, the fact that CLOM itself has a higher  $T_c$  than PCL should be also related to the increase of  $T_c$  of the PCL/CLOM-M composites. The PCL/CLOH-M composites show considerably lower  $T_c$  than the PCL/CLOM-M composites, though the former composites have finer clay dispersion. The overall crystallization rate is proportional to both the primary nucleation rate and the crystal/spherulite growth. In case of the PCL/CLOH-M composites, an increase of interface area by a much finer dispersion of exfoliated clay platelets will result in more interacting sites, which cause reductions in the mobility of the PCL molecules and, therefore the crystallization temperature.<sup>30</sup> The  $\Delta H_c$  of all the PCL/CLO-M composites was lower than that of control PCL, suggesting that the presence of organoclay retards the crystal/spherulite growth at the late stage of crystallization.

Figure 7 shows the second heating thermograms of CLOs, PCL, and PCL/clay composites. The amine-terminated CL oligomers, CLOM and CLOH showed a double melting peak in contrast to a single melting peak of PCL. In case of CLOM, the temperature of a higher melting peak was higher than  $T_m$  of PCL. In addition, the total  $\Delta H_m$  of CLOM is the highest among those of PCL and CLOs, indicating that CLOM has the highest degree of crystallinity (Table I). When the molecular weight of CLO is higher than that of CLOM ( $\sim 1300$ ), the crystallinity of the CLO is thought to decrease with increasing molecular weight and gradually approach to that of PCL. The PCL/CLOM-M

composites also showed a considerably higher  $T_m$  than the other PCL/clay composites, although the other composites showed almost the same  $T_m$ . Figure 8 shows the XRD patterns at around 20–25° for CLOs, PCL, and PCL/clay composites. All the samples had a similar XRD pattern, indicating that all the samples have the same crystalline forms. In accordance with the trend of  $\Delta H_m$  by DSC analysis, CLOM showed much stronger crystalline peaks than CLOL, CLOH, and PCL. Also, the PCL/CLOM-M 3 wt % composite had relatively higher intensity of the crystalline peaks

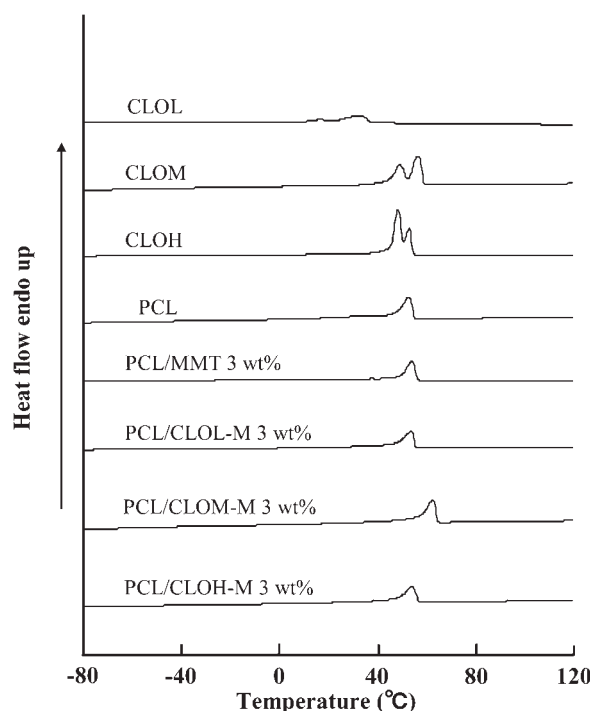
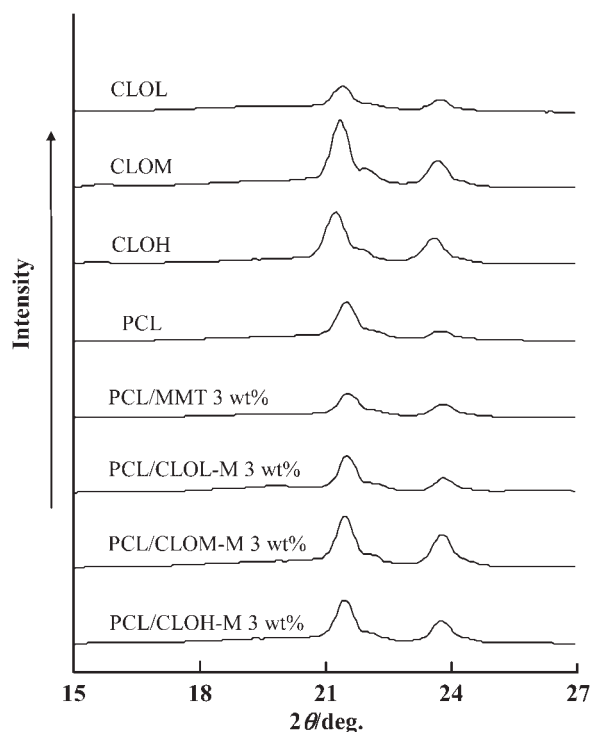


Figure 7 The second heating DSC thermograms of CLOs, PCL, and the PCL/clay composites with inorganic content 3 wt %.



**Figure 8** The XRD patterns of CLOs, PCL, and the PCL/clay composites with inorganic content 3 wt %.

among the PCL/clay composites. The presence of CLOM in PCL/CLOM-M composite contributes to an increase of the crystallinity of PCL/CLO component. Consequently, the observation of relatively high  $T_c$  and  $T_m$  for PCL/CLOM-M composite is related to superior nucleation effect of CLOM-M and high crystallinity of CLOM.

## CONCLUSIONS

Morphology, and mechanical and thermal properties of the nanocomposites prepared by melt intercalation of PCL and the montmorillonites (CLO-Ms: CLOL-M, CLOM-M, and CLOH-M) treated with dibutylamine-terminated  $\epsilon$ -caprolactone oligomers (CLOs: CLOL, CLOM, and CLOH) were investigated. The XRD and TEM analyses of the PCL composites revealed that the extent of exfoliation of the clay platelets increased with increasing molecular weight of the used CLOs. Tensile strength and modulus of the PCL/CLO-M composites increased with molecular weight of CLO and inorganic content. The tensile modulus of the PCL/CLOH-M nanocomposite with inorganic content 5.0 wt % was three times higher than that of control PCL. The addition of CLO-M to PCL matrix, in addition to a nucleation effect, can act as a retardant of crystallization if there a strong interaction exists between the polymer matrix and organoclay. The former effect is pronounced for the highly intercalated PCL/CLOM-M composites, and the latter effect

becomes dominant for highly exfoliated PCL/CLOH-M composites. Among the PCL/clay composites, the PCL/CLOM-M composite had the highest  $T_c$  and  $T_m$  because of the superior nucleation effect of CLOM-M and high crystallinity of CLOM.

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