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Effect of Organoclays on Silicate Layer Structures and Thermal Stabilities of *in-situ* Polymerized Poly(D-lactide)/Clay Nanocomposites

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Six kinds of organoclays were prepared through three kinds of polyols (PTMG, PEA and PCL) to investigate the effects of molecular weight and the chemical structure of organifiers. PTMG based organoclays showed higher ion-exchanged fraction than other organoclays and long chain organifier showed better efficiency in ion-exchanged fraction in the case of PTMG based organifiers. From WAXD and TEM analysis, it was confirmed that PTMG based organoclays formed partially exfoliated or fully exfoliated silicate layer structures. PDLA/clay nanocomposites were prepared by *in-situ* ring-opening polymerization of D-lactide with PTMG based organoclays as macro-initiators in the presence of equimolar $Sn(Oct)_2/PPh_3$ complex catalysts. The molecular weight of PDLA/clay nanocomposite decreased as increasing the feeding amount of organoclay because organoclay had hydroxyl terminal groups which can initiate the ring-opening polymerization of D-lactide. From TGA analysis, thermal stabilities of PDLA/clay nanocomposites improved with increasing organoclay content. From WAXD and TEM analysis, organoclay which was prepared by high molecular weight of PTMG based organifier was effective on the exfoliation of silicate layers in the *in-situ* polymerized PDLA/clay nanocomposite.

Keywords: PLA, poly(D-lactide), organoclay, nanocomposite, exfoliation

1 Introduction

Petrochemical-based synthetic polymers have brought extensive benefits to mankind in many aspects. But the ecosystem and environment are considerably disturbed and polluted as the result of the accumulation of petroleum-based disposable waste. For this reason, there is an urgent need to develop renewable source based environmentally benign plastic materials. For now, one of the most promising polymers in this direction is polylactide (PLA) because it is derived from 100% annually renewable resources and is readily biodegradable (1). PLA has comparable mechanical performance to those petroleum-based polyesters, especially high elastic modulus, high stiffness and biocompatibility (2, 3). However, application of PLA is restricted due to some of demerits such as brittleness, low heat distortion temperature and high gas permeability (4). In order to improve the drawbacks of PLA, PLA/clay nanocomposites are of great concern because the nanoscale dispersion of high aspect ratio filler in the polymer matrix can achieve the improvements in thermal, mechanical, gas-barrier and flame-retardant properties, even at low filler content in comparison with conventional micro- and macrocomposites (5, 6). In this reason, many research groups have studied PLA/clay nanocomposites and some of researches about PLA/clay nanocomposites are summarized in Table 1 (2, 7–12).

In this study, for the preparation of poly(D-lactide) (PDLA)/clay nanocomposites, six kinds of organifiers having reactive hydroxyl terminal groups and different polyols such as poly(tetramethylene ether glycol) (PTMG), poly(ethylene adipate) diol (PEA) and polycaprolactone diol (PCL) were synthesized. The organoclays were prepared by cation exchange reaction of pristine montmorillonite (Cloisite® Na^+) with six kinds of organifiers. The effects of the molecular weight and the chemical structure of the organifiers on the properties of the organoclays such as d-spacing, ion-exchanged fraction and morphology were investigated. Also, PDLA/clay nanocomposites

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Table 1. Summary of some researches about PLA/clay nanocomposites

Researchers	*Organoclay*	*Preparation method*	*References*
Ray, S.S. *et al*	Modified clay with trimethyl octadecyl ammonium cation	Melt extrusion	(2, 7–9)
Chen, G.X. *et al*	Modified commercial organoclay (Cloisite® 25A) with (glycidoxy propyl) trimethoxysilane	Melt extrusion	(10–11)
Paul, M.A. *et al*	Commercial organoclay (Cloisite® 30B)	*In-situ* ring-opening polymerization	(12)

were prepared by *in-situ* ring-opening polymerization of D-lactide with organoclays having organifier with hydroxyl terminal groups as macro-initiator in the presence of complex catalysts. The effects of organoclay type and organoclay content on the molecular weight, thermal stability and the silicate layer structure of PDLA/clay nanocomposites were also investigated.

2 Experimental

2.1 Materials

N-methyl diethanol amine (MDEA, 99%) was purchased from Sigma-Aldrich Co. Poly(tetramethylene ether glycol) (PTMG, Mn = 2,000) and poly(ethylene adipate) (PEA, Mn = 2,000) were received from Korea PTG Co., Ltd. and Kunsul Chemical Industrial Co., Ltd., respectively. Polycaprolactone diol (PCL, Mn = 2,000) was purchased from Sigma-Aldrich Co. MDEA and polyols (PTMG, PEA and PCL) were degassed overnight at 70°C under vacuum to remove moisture before use. Hexamethylene diisocyanate (HDI, 98%) was purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received. Dibutyltin dilaurate (T-12, Sigma-Aldrich Co.) was used as a catalyst during the synthesis of organifier. D-lactide (PURASORB® D) was purchased from PURAC Biochem and used as received. Pristine montmorillonite (Cloisite® Na^+) was purchased from Southern Clay Products, Inc. Tin(II) 2-ethylhexanoate (~95%, $Sn(Oct)_2$) and triphenylphosphine (PPh_3) as catalysts for the ring-opening polymerization of D-lactide were purchased from Sigma-Aldrich Co. All other chemicals were reagent grade and used without further purification.

2.2 Synthesis of Organifiers

Two kinds of reactive organifiers having urethane groups and hydroxyl end groups for each polyol (PTMG, PEA and PCL) were synthesized. First, isocyanate-terminated MDEA (OCN-MDEA-NCO) was synthesized by dropping 2 equiv. of HDI into 1 equiv. of MDEA at 40°C (first step in Fig. 1) until the theoretical isocyanate content (as determined by the di-n-butylamine titration method (13)) was reached. Second, chain-extended polyol for each polyol was synthesized by dropping 1 equiv. of HDI into 2 equiv. of each polyol at 65°C in the presence of 0.05 wt% of T-12 as a catalyst (second step in Fig. 1). Finally, low molecular weight organifier was synthesized by dropping 1 equiv. of OCN-MDEA-NCO into 2 equiv. of each polyol and high molecular weight organifier was synthesized by dropping 1 equiv. of OCN-MDEA-NCO into 2 equiv. of each chain-extended polyol at 65°C in the presence of 0.05 wt% of T-12 (third step in Fig. 1). All reactions were carried out under nitrogen atmosphere and the second and the third step were terminated when the isocyanate peak in HDI and OCN-MDEA-NCO disappeared in FT-IR analysis, respectively. The code of organifier indicated the kind of polyol and the molecular weight of polyol or chain-extended polyol used for the synthesis of organifier. In the code of organifier, 'T', 'E' and 'C' indicated PTMG, PEA and PCL, respectively, and the last number indicated the molecular weight of polyol. For example, 'T2K' means the organifier synthesized with PTMG (Mn = 2,000) and 'T4K' means the organifier synthesized with chain-extended PTMG (Mn ≅ 4,170).

2.3 Preparation of Organoclays

The organoclays for each polyol were prepared through cation exchange reaction between pristine montmorillonite (Cloisite® Na^+) and the excess amount of organifiers (1.5 times the cation-exchange capacity of Cloisite® Na^+). Each organifier was dissolved in the mixture of deionized water and isopropyl alcohol (IPA) with the volume ratio of 6:4 and then concentrated HCl (32%) was dropped into the organifier solution (HCl:organifier = 2:1 by mole) to quaternize the tertiary amine in the organifier. The Cloisite® Na^+ (15 g) was preliminarily dispersed in the mixture of deionized water (600 mL) and IPA (400 mL) at 65°C. The organifier solution was poured into the clay dispersion solution. The mixture was vigorously stirred for 24 h at 65°C for the cation exchange reaction. The cation-exchanged organoclays were collected by a centrifuge and subsequently washed with the mixture of deionized water and IPA until no further formation of AgCl by an $AgNO_3$ test to confirm the absence of halide anions. Finally, organoclays were freeze-dried for 2 days and then

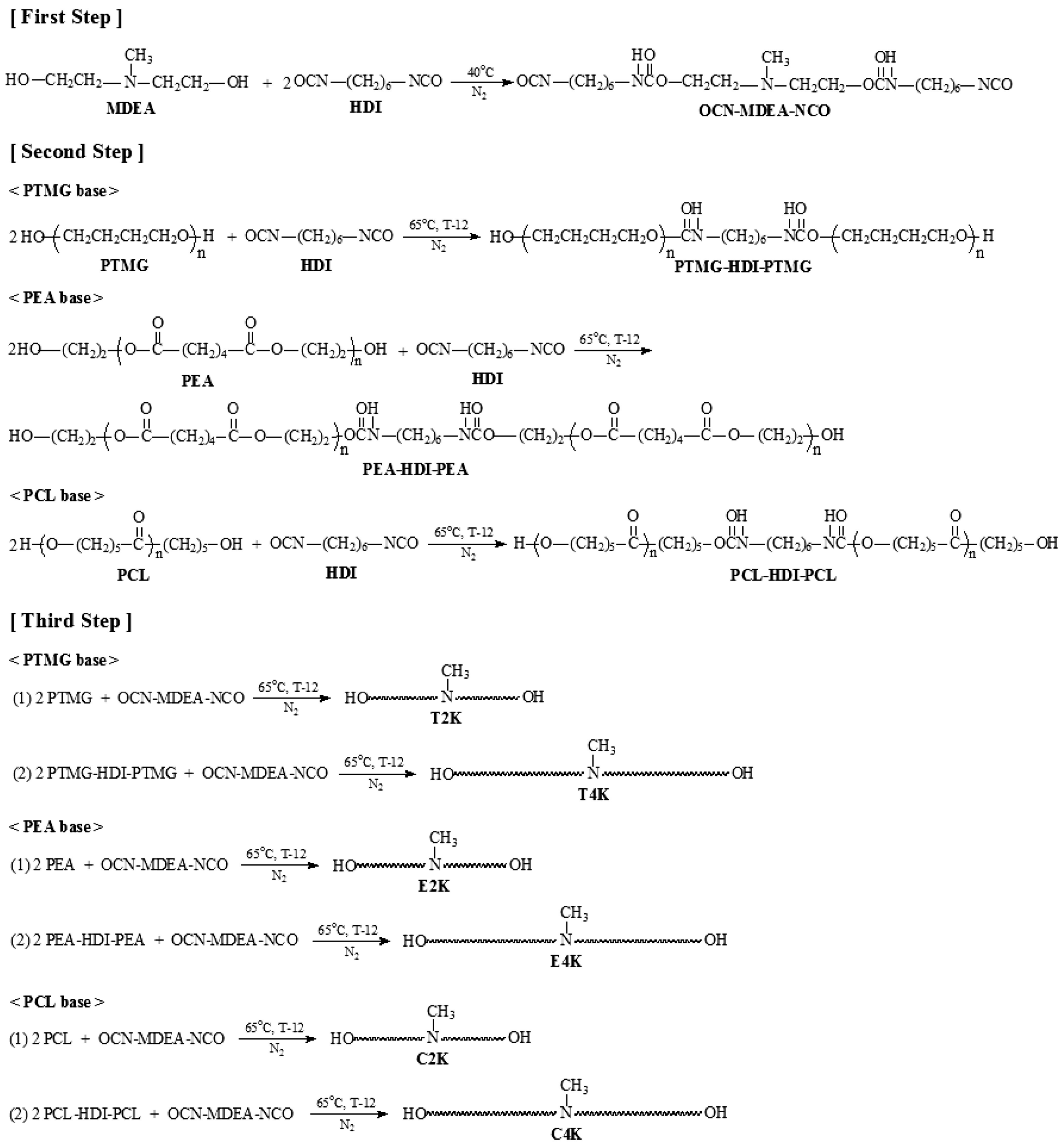

Fig. 1. Synthesis scheme of organifiers.

grounded by using IKA M20 universal cutting mill (IKA Co.) and sieved under 250 μm to obtain organoclay particles. The organoclay particles were further dried at 60°C under vacuum for 1 day. The code of organoclay was arranged as 'CL-code of organifier'. For example, 'CL-T2K' means the organoclay which was Cloisite® Na^+ treated with T2K.

2.4 Preparation of PDLA/Clay Nanocomposites

PDLA/clay nanocomposites were prepared in bulk in the Brabender counter-rotating internal mixer equipped with roller blades (Brabender GmbH & Co. KG, minimum clearance between blades was 4.0 mm). For the *in-situ* ring-opening polymerization of D-lactide onto the organoclay surface, the mixture of D-lactide, each organoclay and the pre-determined amount of 0.1M solution of the equimolar $Sn(Oct)_2/PPh_3$ in toluene (Sigma-Aldrich Co., anhydrous, 99.8%) were charged into the Brabender mixer at the same time. Polymerizations were conducted in melt at 170°C for 15 min with a constant mixing speed of 80 rpm. The monomer-catalyst molar ratio was 500 with the equimolar $Sn(Oct)_2/PPh_3$ complex. For reference, PDLA itself was polymerized by using D-lactide and poly(ethylene glycol) (Mn = 200, Sigma-Aldrich Co.) as an initiator under the same condition. The code of PDLA/clay nanocomposite was arranged as 'PD-code of organifier-inorganic content'. For example, 'PD-T2K-1' means PDLA/clay nanocomposite which contained CL-T2K as the organoclay and its overall inorganic content was 1 wt%.

2.5 Characterization

The synthesis of organifier was confirmed by using JASCO 470-plus FT-IR spectrometer.

The molecular weight and the molecular weight distribution of PDLA-organifier copolymer chains in PDLA/clay nanocomposites were determined by gel permeation chromatography (GPC, GPC 220, Polymer Laboratories) equipped with a differential refractometer detector. GPC was calibrated with PS standards. The measurement temperature was 35°C and THF was used as the eluant. Recovery of PDLA-organifier chains from PDLA/clay nanocomposites was performed by reverse cationic exchange reaction with LiCl (12).

Wide-angle X-ray diffraction (WAXD) analysis was conducted on Rigaku D/MAX-RC diffractometer with Cu K_α radiation of wavelength 1.5418Å at ambient temperature. The measurement range was from $2\theta = 1.2^\circ$ to 10° at the scan rate of 1°/min. The d-spacing of organoclay and PDLA/clay nanocomposite were calculated by using Bragg's law. For WAXD analysis, specimens with a thickness of 1.0 mm of PDLA/clay nanocomposites were prepared by compression molding at 180°C.

Thermogravimetric analysis (TGA) was performed with heating rate of 20°C/min in the temperature range from 40°C to 950°C under nitrogen atmosphere by using TA Instruments TGA Q500 to measure the inorganic content of the organoclays and to analyze the thermal stabilities of PDLA/clay nanocomposites. Before TGA measurement, organoclays were dried at 60°C under vacuum for 1 day to remove moisture and PDLA/clay nanocomposites were washed with cold methanol to remove remaining monomer and dried at 70°C under vacuum until the constant weight. The 5 wt% weight loss temperature ($T_{5\%}$) of PDLA/clay nanocomposite was obtained from TGA curve and the temperature of maximum decomposition rate (T_{max}) of PDLA/clay nanocomposite was determined as the maximum temperature in derivative TGA curve.

The ion-exchanged fraction (IEF) was calculated from the following equation (Eq. 1). The definition of IEF is the fraction of active sites on layered silicates exchanged with organifiers by cation exchange reaction.

$$\mathrm{IEF} = \frac{\text{Organifier content organoclay(mmol/100 g)}}{\text{CEC of montmorillonite(meq./100 g)}} \tag{1}$$

The inorganic content of organoclay, the molecular weight of organifier and the CEC value of pristine montmorillonite are needed to calculate IEF.

Transmission electron microscope (TEM) was used for observing the nano-structure of the organoclay and the PDLA/clay nanocomposite. TEM micrographs were obtained by using TECNAI F20 FE-TEM (Philips Electron Optics). For TEM observation of organoclay itself, pretreatment of organoclay was conducted. 1 wt% of organoclay was dispersed in ethanol and sonicated by using Sonoplus Ultrasonic Homogenizer with 70W power for 10 min. The droplet of organoclay dispersion solution was laid on the copper grid and then ethanol was dried at ambient temperature. For TEM observation of PDLA/clay nanocomposites, specimens were prepared by using RMC MT-XL microtome equipped with a diamond knife. The specimen thickness was about 40 nm.

3 Result and Discussion

3.1 Synthesis of Organifiers

The formation of urethane group and the disappearance of isocyanate group after synthesis of organifiers were confirmed by FT-IR analysis. FT-IR spectra of PTMG, chain-extended PTMG (PTMG-HDI-PTMG), OCN-MDEA-NCO and PTMG based organifiers (T2K and T4K) are shown in Fig. 2 (a). Also, FT-IR spectra of PEA, chain-extended PEA (PEA-HDI-PEA), OCN-MDEA-NCO and PEA based organifiers (E2K and E4K) are shown in Fig. 2 (b). Finally, FT-IR spectra of PCL, chain-extended PCL (PCL-HDI-PCL), OCN-MDEA-NCO and PCL based organifiers (C2K and C4K) are shown in Fig. 2 (c). As shown in Fig. 2, in the case of FT-IR spectra of final organifiers, the peak for N=C=O at 2261cm^{-1} in OCN-MDEA-NCO disappeared after reaction with polyol and chain-extended polyol in all cases. Also, the peak for C-N-H at 1527 cm^{-1} in urethane group appeared after chain extension reaction of polyol and synthesis of final organifier. In the case of PTMG based organifiers, the peak for C=O at 1716 cm^{-1} in urethane group appeared after chain extension reaction of PTMG and synthesis of final organifier. From these spectra, it was found that organifiers having urethane group were successfully synthesized.

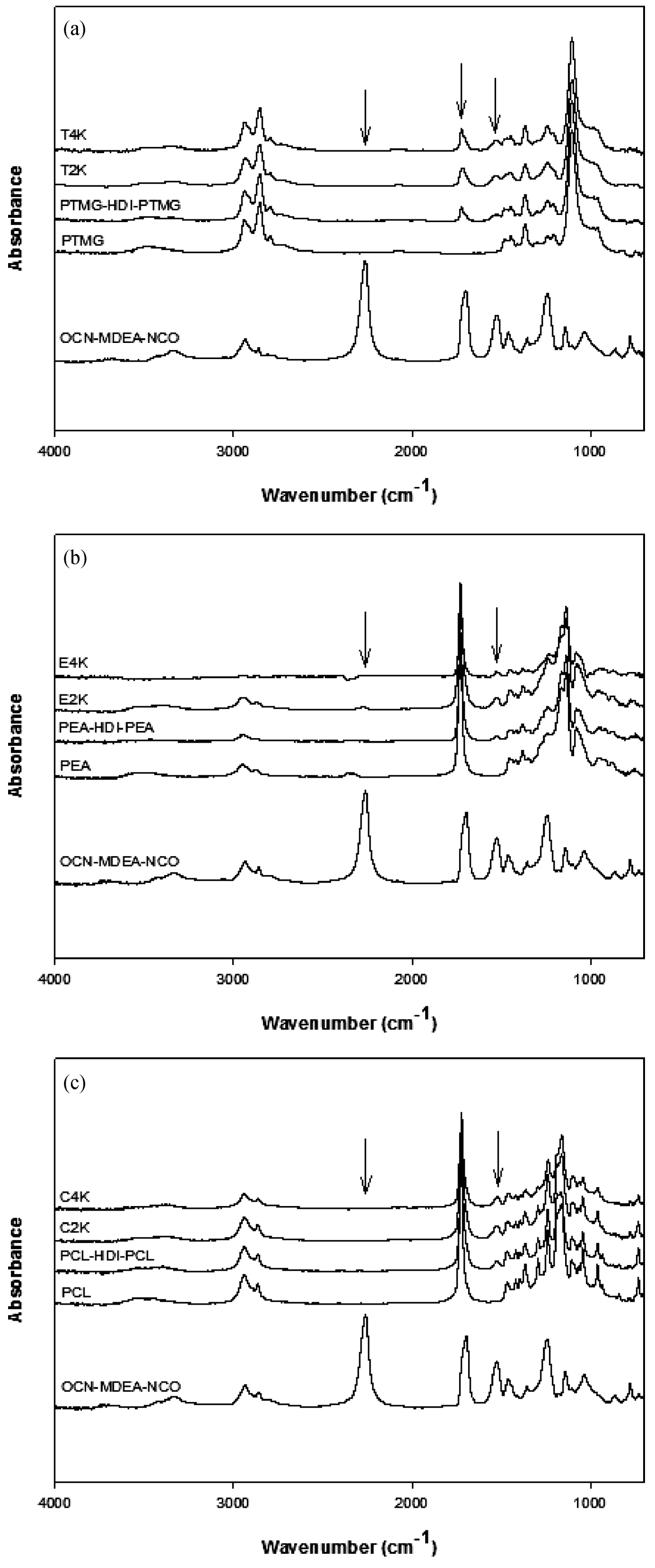

Fig. 2. FT-IR spectra of organifiers: (a) PTMG based materials, (b) PEA based materials, (c) PCL based materials.

Table 2. Inorganic contents and ion-exchanged fractions of organoclays

Organoclay	*Inorganic content*	*Ion-exchanged fraction*
	wt%	—
Cloisite® Na^+	92.4	—
CL-T2K	41.0	0.32
CL-T4K	27.2	0.31
CL-E2K	71.1	0.08
CL-E4K	71.5	0.04
CL-C2K	70.9	0.08
CL-C4K	67.1	0.05

3.2 Ion-exchanged Fraction and d-Spacing of Organoclays

Two kinds of organoclays for each polyol were prepared and their codes are as follows: CL-T2K, CL-T4K; CL-E2K, CL-E4K; CL-C2K, CL-C4K. The inorganic content of each organoclay was measured as the residual weight percent at 900°C in TGA (Table 2). From the inorganic content of each organoclay, the molecular weight of each organifier and the cationic exchange capacity (CEC) of Cloisite® Na^+ (92.6 meq./100g), the IEF of each organoclay was calculated and summarized in Table 2. From the definition, IEF means that the amount of exchanged Na^+ ion on layered silicates by the organifier via cation exchange reaction (14). As shown in Table 2, PTMG based organoclays showed lower inorganic contents than other organoclays. The inorganic contents of CL-T2K and CL-T4K were 41.0 wt% and 27.2 wt%, respectively. On the other hand, the inorganic contents of CL-E2K, CL-E4K, CL-C2K and CL-C4K were almost same as roughly about 70.0 wt%. Also, in the case of PTMG based organoclays, the inorganic content decreased as the molecular weight of organifier increased. In the case of PEA and PCL based

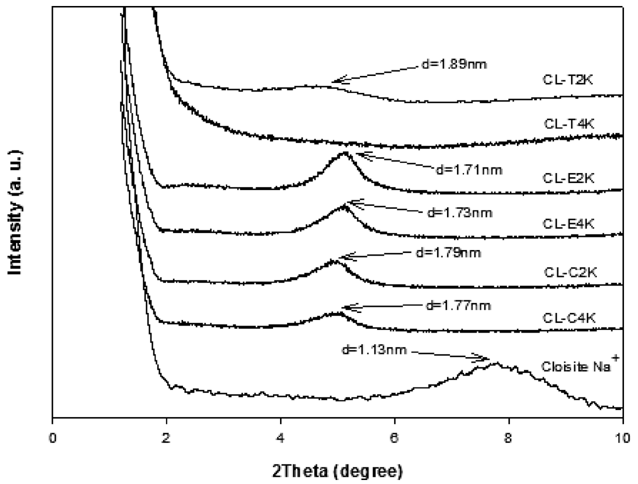

Fig. 3. WAXD patterns of organoclays.

Table 3. Feeding compositions of PDLA and PDLA/clay nanocomposites

Code	Organoclay code	*Inorganic content of organoclay*[a]	*D-lactide*	*Organoclay*	*Inorganic content of nanocomposite (Calculated)*
		wt%	*g*	*g*	*wt%*
PDLA[b]	–	–	35.00	–	–
PD-T2K-1	CL-T2K	41.0	34.15	0.85	1.0
PD-T2K-3	CL-T2K	41.0	32.44	2.56	3.0
PD-T4K-1	CL-T4K	27.2	33.71	1.29	1.0
PD-T4K-3	CL-T4K	27.2	31.14	3.86	3.0

[a] Residual wt% at 900°C in TGA analysis.

[b] 0.05 mL of poly(ethylene glycol) was used as an initiator.

Remark: $[Sn(Oct)_2]:[PPh_3] = 1:1$, $[D\text{-lactide}]/[Sn(Oct)_2] = 500$ (molar ratio).

organoclays, there were nearly no differences in inorganic content according to the molecular weight of organifier. These inorganic contents affected the IEFs of organoclays. IEFs of CL-T2K and CL-T4K were 0.32 and 0.31, respectively. On the other hand, IEFs of CL-E2K, CL-E4K, CL-C2K and CL-C4K were 0.08, 0.04, 0.08 and 0.05, respectively. IEFs of organoclays treated with PTMG based organifiers were higher than those of organoclays treated with PEA and PCL based organifiers. From these results, it was expected that PTMG based organifiers were more effectively cation-exchanged than other organifiers. Also, it was found that IEF of CL-T4K was similar to that of CL-T2K in spite of higher molecular weight of organifier. In the case of PEA and PCL based organifiers, the extents of exchanges were similar according to the base materials, therefore, IEFs decreased as the molecular weight of organifiers increased. These differences in IEFs according to the base materials of organifiers result from the specific interactions between organifier and layered silicates. In the case of PEA and PCL based organifiers, chains having hydrophilic C=O groups in organifiers and layered silicates experience attractive interactions due to their hydrophilic characteristics. Therefore, the overall conformation of each organifier is rather flat and the organifier is laid on the surface of the layered silicates. This behavior of organifier can interrupt the penetration of other organifiers during the cation exchange reaction. For this reason, the IEFs of PEA and PCL based organoclays were low compared to the PTMG based organoclays. However, in the case of PTMG based organifiers, there are no attractive interactions between the hydrophobic PTMG chains and hydrophilic layered silicates, so the PTMG chains try to retain their coil-like conformations between the inter-layers of layered silicates (14). This behavior can expand the gallery of layered silicates and help the penetration of organifiers. This behavior becomes more effective in the case of long chain organifier. Therefore, PTMG based organoclays showed relatively high IEFs and the IEF of CL-T4K was similar to that of CL-T2K in spite of its higher molecular weight of the organifier.

To confirm the effect of organifiers on d-spacing of layered silicates, WAXD analysis was conducted. XRD analysis shows the gallery spacing of silicate layers and indirectly provides information on the degree of dispersion of silicate layers in submicron level. The WAXD patterns of Cloisite® Na$^+$ and organoclays are shown in Fig. 3. Also, the d-spacing values of Cloisite® Na$^+$ and organoclays from the WAXD patterns are marked in Fig. 3. From the WAXD patterns, the d-spacing values of Cloisite® Na$^+$, CL-T2K, CL-E2K, CL-E4K, CL-C2K and CL-C4K were 1.13 nm, 1.89 nm, 1.71 nm, 1.73 nm, 1.79 nm and 1.77 nm, respectively. Except for CL-T4K, all organoclays showed intercalated silicate layer structures after cation exchange reaction and CL-T2K represented better intercalation than others. In the case of CL-T4K, no diffraction peak was detected, so the information on the d-spacing could not be obtained. This absence of the characteristic diffraction peak of CL-T4K was the strong evidence for the formation of exfoliated and disordered silicate layer structure. From these results, the gallery spacing of pristine montmorillonite was enlarged by cation-exchanged organifier. Also, PTMG based organoclays were more effective in delaminating of silicate layers than others because CL-T4K showed no diffraction peak and CL-T2K showed a diffraction peak with weak intensity. From the WAXD patterns, it can be assumed that CL-T2K had intercalated/partially exfoliated silicate layer structure and CL-T4K had exfoliated silicate layer structure. Therefore, in the case of PTMG based organoclays, the d-spacing was intensively affected by the chain length of organifier.

Table 4. GPC results and product yields of PDLA and PDLA/clay nanocomposites

Code	*Mn*	*Mw*	*PDI*	*Product yield*
	g/mol	*g/mol*	–	%
PDLA	68,000	120,000	1.8	96.5
PD-T2K-1	71,000	148,000	2.1	97.2
PD-T2K-3	31,000	65,000	2.1	93.3
PD-T4K-1	66,000	122,000	1.9	97.9
PD-T4K-3	40,000	73,000	1.8	95.1

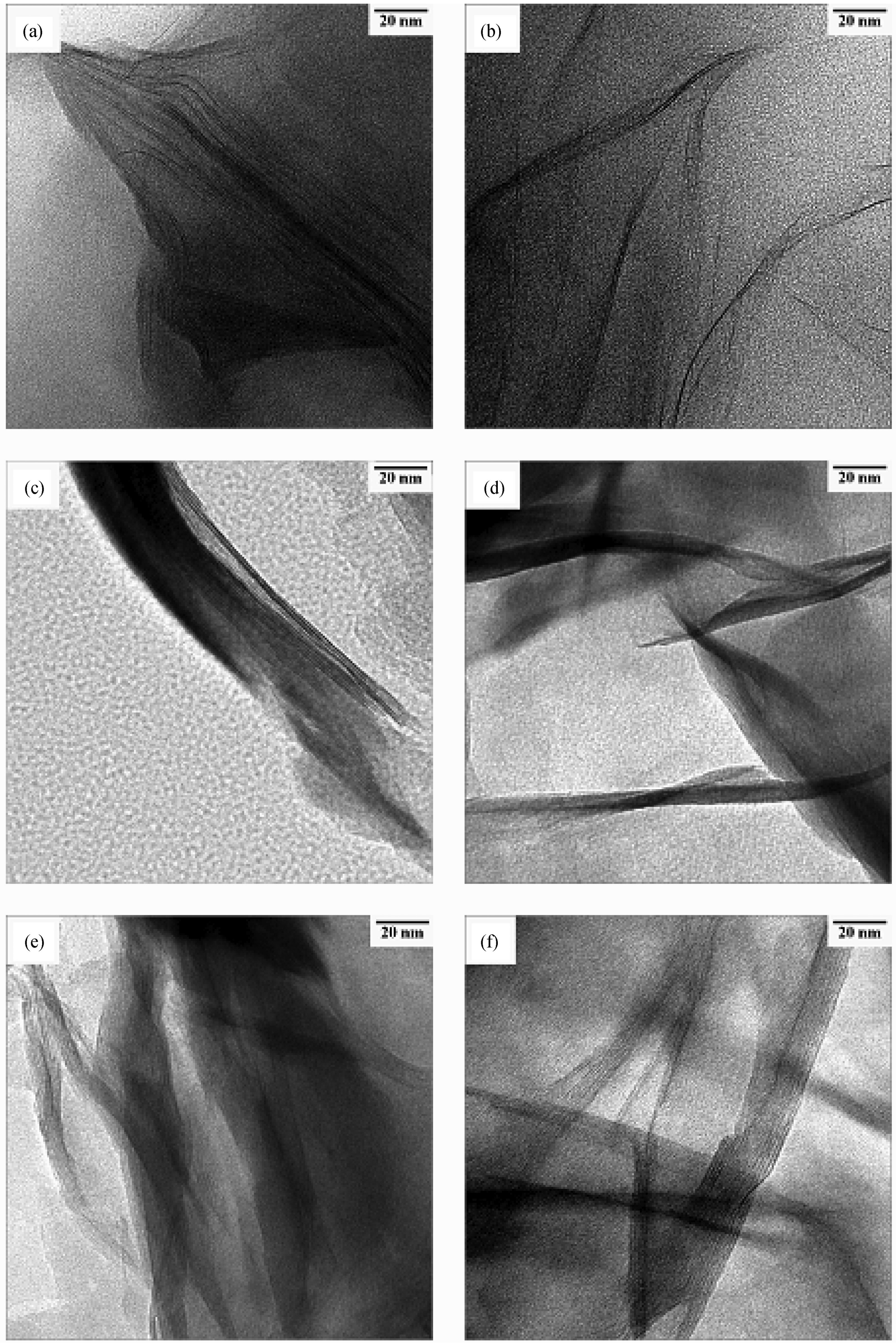

Fig. 4. TEM micrographs of organoclays: (a) CL-T2K, (b) CL-T4K, (c) CL-E2K, (d) CL-E4K, (e) CL-C2K, (f) CL-C4K.

3.3 Morphology of Organoclays

To make sure WAXD results and to observe silicate layer structures of organoclays in submicron level, TEM observations of orgnaoclays were conducted. Since XRD analysis only detects periodic stacked d-spacing, TEM micrographs provide understanding of the degree of dispersion of silicate layers. In Figure 4, TEM micrographs of organoclays are shown. In the case of CL-T2K, some of stacked silicate layers and partially exfoliated silicate layers were observed together. In the case of CL-T4K, it was seen that silicate layers were exfoliated to individual platelets or some of stacked platelets. However, PEA and PCL based organoclays formed relatively thick well-stacked silicate

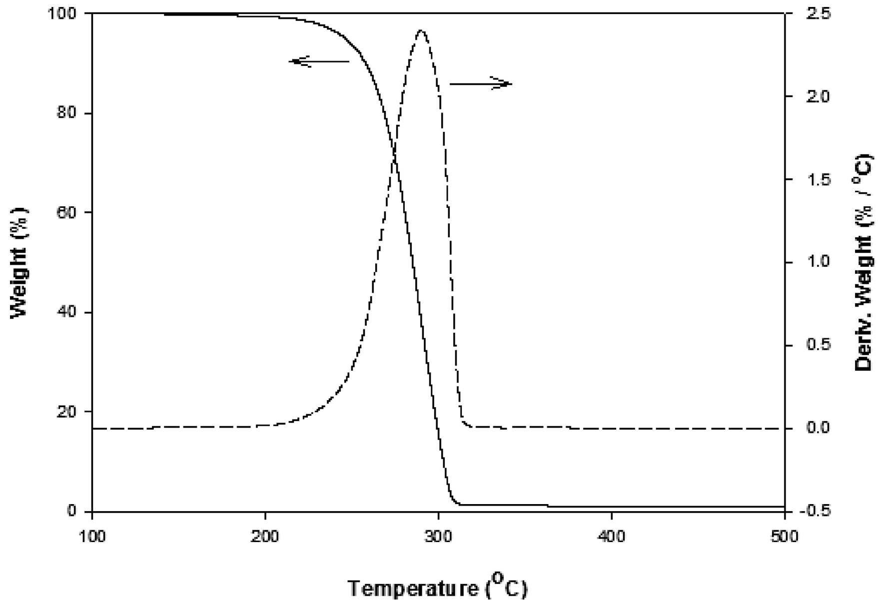

Fig. 5. TGA and derivative TGA curves of PDLA.

layers. These silicate layer structures of organoclays from TEM observations were in good agreement with WAXD results. From WAXD and TEM results, it was confirmed that PTMG based organoclays formed partially exfoliated or fully exfoliated silicate layer structures by the expansion effect of coil-like conformations of PTMG chains between the inter-layers of layered silicates due to the repulsive interaction between the hydrophobic PTMG chains in the organifier and the hydrophilic silicate surface in the silicate gallery. Also, it was clear that the silicate layer structures were highly dependent on the molecular weight of PTMG chains in the organifier.

3.4 Preparation of PDLA/Clay Nanocomposites

PDLA/clay nanocomposites were prepared by *in-situ* ring-opening polymerization of D-lactide with reactive hydroxyl terminal groups of organifiers which were attached on the surface of organoclays as macro-initiators. PTMG based organoclays (CL-T2K and CL-T4K) which showed better exfoliation of the silicates than PEA and PCL based organoclays were used as organoclays. Polymerization was conducted in the Brabender mixer in melt state at 170°C for 15 min with a constant mixing speed of 80 rpm. The feeding amount of each organoclay was regulated as the overall inorganic content of PDLA/clay nanocomposite as 1 wt% and 3 wt%. Also, the feeding amount of the equimolar $Sn(Oct)_2/PPh_3$ catalysts was determined to have monomer-catalyst molar ratio as 500:1. For reference, PDLA without clay was polymerized by using D-lactide and poly(ethylene glycol) (initiator) under the same condition. The feeding compositions for the preparation of PDLA and PDLA/clay nanocomposites are summarized in Table 3.

Molecular weight and molecular weight distribution of polymerized PDLA-organifier chains were determined by GPC after eliminating clays from PDLA/clay nanocomposites and are given in Table 4. The product

Table 5. $T_{5\%}$ and T_{max} of PDLA and PDLA/clay nanocomposites

Code	*$T_{5\%}$*	*T_{max}*
	°C	*°C*
PDLA	246	290
PD-T2K-1	254	310
PD-T2K-3	256	316
PD-T4K-1	245	304
PD-T4K-3	258	310

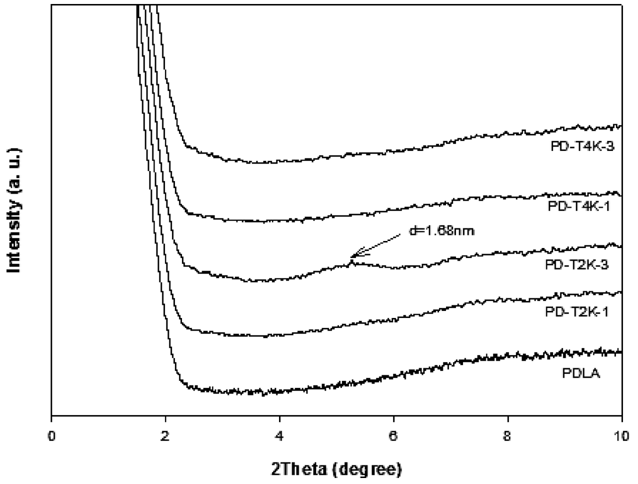

Fig. 6. WAXD patterns of PDLA and PDLA/clay nanocomposites.

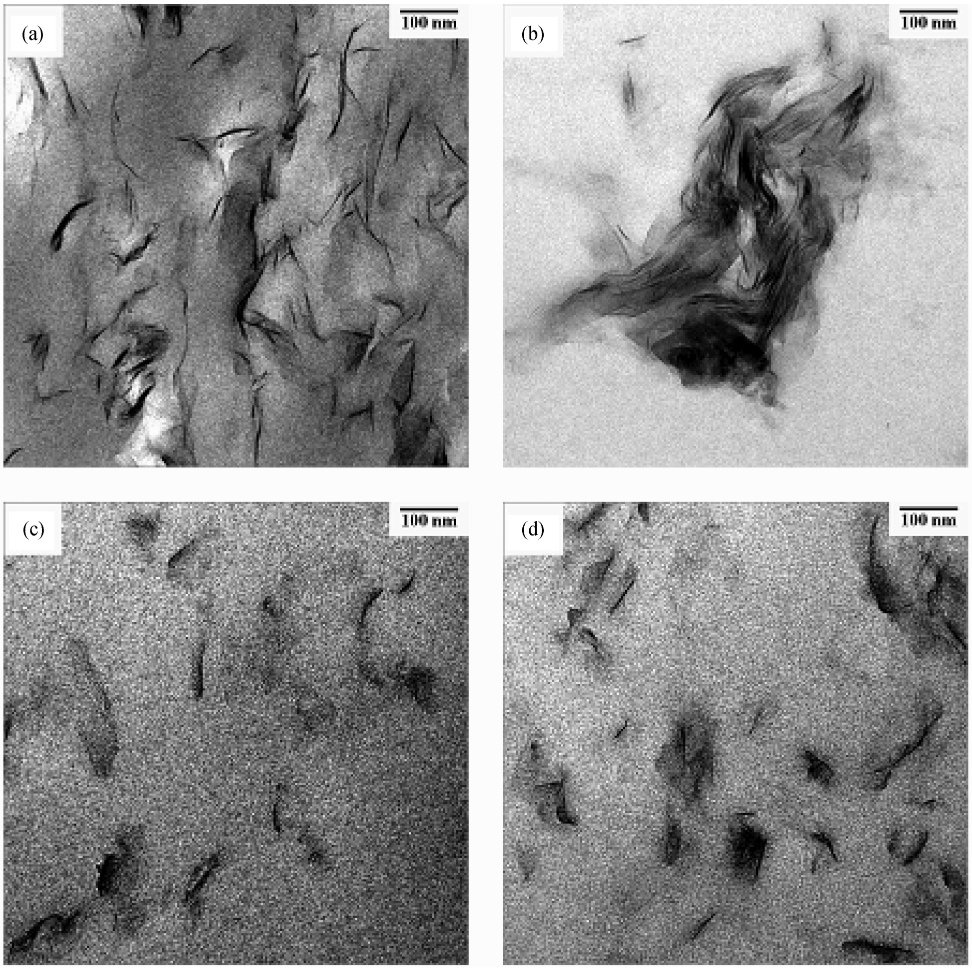

Fig. 7. TEM micrographs of PDLA/clay nanocomposites (Low magnification): (a) PD-T2K-1, (b) PD-T2K-3, (c) PD-T4K-1, (d) PD-T4K-3.

yields of PDLA/clay nanocomposites are also shown in Table 4 and calculated through the weight differences before and after removing un-reacted monomers by washing with cold methanol and then drying at 70°C under vacuum. From the GPC results, the molecular weight of PDLA-organifier chains decreased as increasing the feeding amount of organoclay because organoclay had hydroxyl terminal groups to initiate the ring-opening polymerization of D-lactide. The Mn of PD-T4K-1 which contained lower amount of CL-T4K than PD-T4K-3 was 66,000. On the other hand, the Mn of PD-T4K-3 was 40,000. The ring-opening polymerization of lactide monomer is known to follow the 'coordination-insertion' mechanism involving the selective oxygen-acyl cleavage of the cyclic ester monomer (15). At this time, lactide monomer is initiated by the tin-alkoxide which is formed by the reaction of alcohol and the tin(II) dicarboxylate (15). Therefore, the molecular weight of PLA can be tunable by the addition of alcohol. Similarly, the molecular weight of PDLA/clay nanocomposite differed from the feeding amount of organoclay having reactive hydroxyl terminal groups. Also, as shown in Table 4, the product yields of PDLA/clay nanocompsites were over 90%. It means that D-lactide monomers were almost converted to PDLA by growing PDLA chains onto the clay surface even though reaction time was as short as 15 min in the mixer. It can be explained that equimolar complex with $Sn(Oct)_2$ and PPh_3 had a favorable effect on polymerization rate and delayed the occurrence of undesirable back-biting reactions (16).

3.5 Thermal Stability of PDLA/Clay Nanocomposites

Thermal stabilities of PDLA and PDLA/clay nanocomposites were investigated by using TGA. The 5 wt% weight loss temperature ($T_{5\%}$) and the temperature of maximum decomposition rate (T_{max}) of PDLA and PDLA/clay nanocomposites are summarized in Table 5. Also, typical TGA and derivative TGA curves of PDLA sample were shown in Figure 5. As shown in Table 5, TGA performed under nitrogen flow revealed that $T_{5\%}$ and T_{max} of PDLA/clay nanocomposite were shifted toward higher

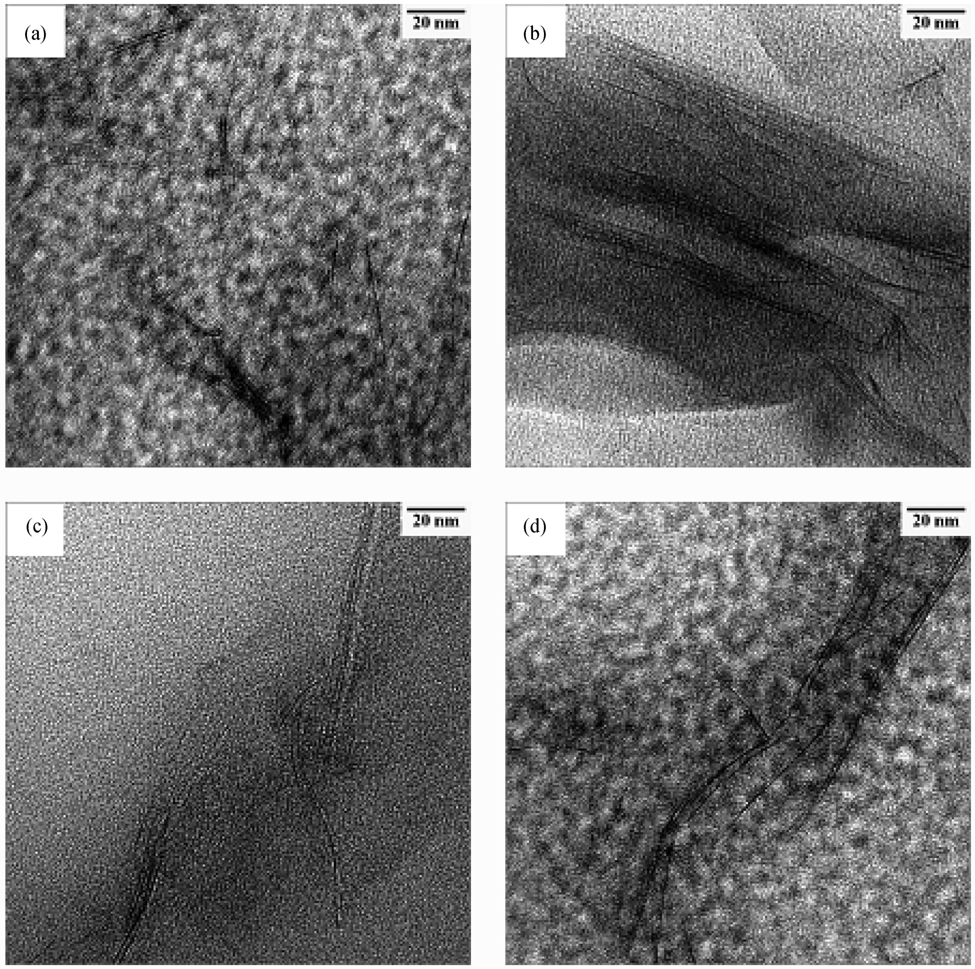

Fig. 8. TEM micrographs of PDLA/clay nanocomposites (High magnification): (a) PD-T2K-1, (b) PD-T2K-3, (c) PD-T4K-1, (d) PD-T4K-3.

temperature with increasing the organoclay content. As comparing $T_{5\%}$ and T_{max} of PDLA with those of PD-T4K-3, 12°C of $T_{5\%}$ and 20°C of T_{max} increased. This improvement in thermal stability can be explained by the fact that the finely dispersed silicate layers in polymer matrix can enhance the thermal stability of polymer by acting as thermal insulator (17) and mass transport barriers (18) to the volatile products generated during decomposition. In other words, the silicate layers acted as heat barriers, which enhanced the overall thermal stability of PDLA/clay nanocomposites (19).

3.6 d-Spacing and Morphology of PDLA/Clay Nanocomposites

Figure 6 shows the WAXD patterns of PDLA and PDLA/clay nanocomposites. Since PDLA itself contained no organoclay, there was no diffraction peak in the range of 2θ from 1.2° to 10°. Also, there were no appearances of diffraction peak for PDLA/clay nanocomposites having inorganic content of 1 wt%. This absence of diffraction peak meant that PDLA/clay nanocomposite had exfoliated silicate layer structure. In the case of PDLA/clay nanocomposites having inorganic content of 3 wt%, weak diffraction peak only appeared in PD-T2K-3 and the corresponding d-spacing was found to be 1.68 nm ($2\theta = 5.26°$). This d-spacing value was slightly smaller than the d-spacing of CL-T2K organoclay. From the WAXD patterns, it was expected that PDLA/clay nanocomposites having CL-T4K which already had exfoliated structure showed exfoliated silicate layer structure. However, PDLA/clay nanocomposites having CL-T2K which had intercalated/partially exfoliated structure showed different silicate layer structure according to the content of organoclay. In the case of PD-T2K-1, the growing PDLA chains from the hydroxyl groups of organifier covering the surface of organoclay pushed the platelets away from each other during the *in-situ* ring-opening polymerization, therefore, some of intercalated silicate layers in organoclays were changed into exfoliated silicate layers. However, in the case of PD-T2K-3, it might be difficult that some of aggregated organoclays could be exfoliated into individual platelets during the polymerization in the Brabender mixer because organoclay content was quite high.

TEM micrographs of PDLA/clay nanocomposites are shown in Figure 7 and Figure 8. Low and high magnification of TEM observations were conducted to investigate the overall dispersion of silicate layers and to confirm the structures of individual platelets. In Figure 7 and Figure 8, both of PDLA/clay nanocomposites, having CL-T4K, showed fine dispersion of silicate layers in the PDLA matrix and showed exfoliated silicate layer structure. In the case of PD-T4K-1 and PD-T4K-3, there were nearly no stacked platelets. However, PDLA/clay nanocomposites having CL-T2K showed different silicate layer structures. In the case of PD-T2K-1, silicate layers were well dispersed in PDLA matrix and partially exfoliated silicate layers were observed. On the other hand, in the case of PD-T2K-3, aggregated clays remained in PDLA matrix and stacked intercalated silicate layers were observed. From these WAXD and TEM results, organoclay which was prepared by high molecular weight of PTMG based organifier was effective on the exfoliation of silicate layers in the *in-situ* polymerized PDLA/clay nanocomposite.

4 Conclusions

In this study, six kinds of organoclays were prepared through three kinds of polyols (PTMG, PEA and PCL) to investigate the effects of molecular weight and the chemical structures of organifiers. From TGA analysis, PTMG based organoclays showed higher ion-exchanged fraction than the other organoclays and long chain organifier showed better efficiency in ion-exchanged fraction in the case of PTMG based organifiers. From WAXD and TEM analysis, it was confirmed that PTMG based organoclays formed partially exfoliated or fully exfoliated silicate layer structures by the expansion effect of coil-like conformations of PTMG chains between the inter-layers of layered silicates. Also, it was found that the silicate layer structures were highly dependent on the molecular weight of PTMG chains in the organifier.

Based on these results, PTMG based organoclays, CL-T2K and CL-T4K, were used for the preparation of PDLA/clay nanocomposites. PDLA/clay nanocomposites were prepared by *in-situ* ring-opening polymerization of D-lactide with reactive hydroxyl terminal groups of organifiers which were attached on the surface of organoclays as macro-initiators in the presence of equimolar $Sn(Oct)_2/PPh_3$ complex catalysts. The molecular weight of PDLA-organifier chains decreased as increasing the feeding amount of organoclay because organoclay had hydroxyl terminal groups which can initiate the ring-opening polymerization of D-lactide. From TGA analysis, thermal stabilities of PDLA/clay nanocomposites improved with increasing clay content. Because silicate layers dispersed in PDLA/clay nanocomposites acted as heat barriers. From WAXD and TEM analysis, organoclay which was prepared by high molecular weight of PTMG based organifier was effective on the exfoliation of silicate layers in the *in-situ* polymerized PDLA/clay nanocomposite.

In the next study, to induce the stereocomplex formation, the PDLA/clay nanocomposites will be used as master batches for the preparation of PLLA/clay nanocomposites by blending with PLLA.

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