Exfoliation of layered silicate facilitated by ring-opening reaction of cyclic oligomers in PET–clay nanocomposites

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Abstract

Ethylene terephthalate cyclic oligomers (ETCs) have been successfully polymerized to a high molecular weight poly(ethylene terephthalate) (PET) employing the advantages of the low viscosity of cyclic oligomers and lack of chemical emissions during polymerization. Using ring-opening polymerization of ETCs with organically modified montmorillonite (OMMT), we intend to ascertain the possibility of preparing high performance PET/clay nanocomposites. Due to the low molecular weight and viscosity, ETCs are successfully intercalated to the clay gallerys, what is evidenced by XRD showing a down-shift of basal plane peak of layered silicate along with TEM investigation. Subsequent ring-opening polymerization of ETCs in-between silicate layers yielded a PET matrix of high molecular weight along with high disruption of layered silicate structure and homogeneous dispersion of the latter in the matrix. Although co-existence of exfoliation and intercalation states of silicate layers after polymerization of ETCs rather than perfect exfoliation was observed, a dramatic increase in d-spacing along with fast polymerization presents us a great potential of cyclic oligomer process in producing a thermoplastic polymer–clay nanocomposites of extremely well-dispersed silicate nanoplatelets and the corresponding high performances.
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1. Introduction

Poly(ethylene terephthalate) (PET) has found a variety of applications such as fibers, bottles, films, and engineering plastics for automobiles and electronics due to its low cost and high performance [1]. The primary objective of the development of PET/clay nanocomposites was to improve the gas barrier property that is required for beverage and food packagings [2]. Another expectation for PET/clay nanocomposites is to be an alternative to the glass–fiber reinforced PET. Recently, several researchers reported the preparation and properties changes of PET/clay nanocomposites. For organically modified montmorillonite (OMMT) dispersed PET [3–5], complete delamination was not achieved, but the tensile modulus of the nanocomposites increased as much as 3 times over that of pure PET. Tsai et al. reported the synthesis of PET/clay nanocomposites by utilizing an amphoteric surfactant and an antimony acetate catalyst [3]. Their nanocomposites showed higher flexural strength and modulus than pure PET with 3 wt% loading of the silicate. However, the endeavors to prepare PET/clay nanocomposites through melt intercalation method have resulted in very limited intercalation of guest molecules presumably due to the high viscosity of PET polymer [2–5].

Preparation of an exfoliated nanocomposite of layered silicates such as clay requires that the layers of silicates be dissociated by transport of molecules from the bulk or solution into the interlayer between the silicate sheets. In general, the equilibrium interlayer spacing of the intercalated polymers is associated with a balance of free energy gain caused by increased configurational freedom of the surfactant and free energy loss provoked by confinement of the polymer. If thermodynamically favored [6,7], the

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dispersion of silicate layers and the corresponding mass transport of polymer will be strongly related to the viscosity of the medium.

Alternative method to prepare PET/clay nanocomposites using direct condensation polymerization of diol and diacid in-between silicate layers imparted formation of oligomers with significantly low molecular weight due to the ineffective control of stoichiometry and thus, a large increase in intra-gallery distance showing noticeable intercalation in silicate layers was hard to obtain [2,3,5] (Scheme 1).

There is a growing interest in preparing macrocyclic oligomers of commercially important polymers and their ring-opening polymerizations [8], such as the preparation and polymerization of aryl esters [9], poly(ether imides) [10], poly(ether sulfones) [11], poly(ether ketones) [12], cyclic aramides [13], and cyclic phenylene disulfides [14], cyclic polycarbonates [15,16] and cyclic alkylene terephthalates [17–30], because the low melt viscosities of reactive cyclic oligomers provide an opportunity for reactive processing such as reaction injection molding [26–28]. Applications of the composites were particularly appealing, since the low molecular weight cyclic oligomers are advantageous in wetting of reinforcing elements than polymers of high molecular weight, and because ring-opening polymerization of such oligomers should afford extremely high molecular weights without formation of byproduct volatiles. Other advantages include better control of molecular weight, fast polymerization cycles, and the potential to prepare functional or block polymers.

Because of low molecular weight and cyclic molecular architecture, cyclic oligomers of PET have much lower solution and melt viscosities compared to the corresponding polymer, expecting that, when clay intercalation is intended by mixing with cyclic oligomer instead of linear polymer, easier diffusion along with higher degree of intercalation or exfoliation would be obtained. Furthermore, the difference in molecular architecture (cyclic vs. linear) and the presence of end groups may alter the relative clay–polymer interaction, changing the free energy of formation. In addition, the problems such as precise control of stoichio-metric balance and high vacuum requirements, extremely required in preparation of PET by conventional conden-sation polymerization of difunctional monomers, can be effectively avoided through ring-opening reaction of cyclic oligomers. Recently, Huang et al have reported that macrocyclic polycarbonate (PC) oligomers are capable of forming a intercalated-exfoliated polycarbonate/layered silicate nanocomposites via ring-opening polymerization of cyclic oligomers [16]. A report by Tripathy et al. concerning the preparation of poly(butylenes terephthalate) (PBT)/clay nanocomposites has showed that cyclic PBT oligomers are successfully intercalated in the clay layers because of their low molecular weight and subsequent polymerization could result in an exfoliated or intercalated-exfoliated PBT/clay nanocomposite [30]. In the light of the fact that PET, PBT and PC share a large similarity in

chemical and physical natures, the low viscosity of cyclic oligomers along with the self-consistent stoichiometry prerequisite to polymer of high molecular weight should offer unique opportunities for the preparation of an exfoliated PET/clay nanocomposites. PET–clay nanocom-posite, if extremely even dispersion of silicate nanoplatelets is obtainable, has been thought to present a strong impact on wide spectrum of application fields; from a biomedical container of extremely low gas permeability along with high hydrothermal stability to a packaging material of low dielectric constant and thermal conductivity for microelec-tronic devices. Therefore, it is thought that our study on the synthesis of exfoliated PET–clay nanocomposites via ring-opening reaction of cyclic oligomers would be highly meaningful and receive a great attention.

For the purpose to obtain PET/clay nanocomposites of exfoliated silicate layers we varied conditions of ring-opening polymerization of ethylene terephthalate cyclic oligomers (ETCs) in the presence of organically modified clays, and examined the corresponding change of intercala-tion behavior.

2. Experimental

2.1. Materials

Organically modified montmorillonite (OMMT) was prepared through cation exchange reaction of Na-montmor-illonite (Na-MMT, cation exchange capacity = 98 mequiv./100 g from Southern Clay) with N,N,N-tri-methyloctadecylammonium bromide (99 + % purity from Daejung Chemical, used as received) as follows. 10 g (9.8 mequiv.) Na-MMT was stirred in 200 ml deionized water at 70 °C for 12 h. A solution of 7.69 g (19.6 mequiv.) N,N,N-trimethyloctadecylammonium bromide in 50 ml deionized water was slowly added with vigorous stirring to the MMT suspension at 70 °C. After mixing, the mixture was stirred at 70 °C for 12 h. The OMMT recovered by filtering the solution was washed with 70 °C deionized water several times to remove freely existing excess amount of ionic intercalants and impurities; this was followed by centrifugation and vacuum drying at 70 °C for 24 h.

Terephthaloyl chloride (TPC, 99 + % purity from Aldrich) was dissolved in hot n-hexane, from which insoluble impurity of acid was removed by filtration. Slow cooling of the solution after filtration resulted in needle-like fine crystal, which presented no trace of carboxylic acid on FT-IR and elemental analysis. Ethylene glycol (EG, 99 + % purity from Aldrich) was purified by vacuum distillation and stored with molecular sieve. Triethylamine (TEA, 99.5% purity from Aldrich) was refluxed with ninhydrin to remove protic impurity and stored with molecular sieve. 1,4-Diazabicyclo[2.2.2]-octane (DABCO, 98% purity from Aldrich) was sublimed before use, and dichloromethane (DCM, Aldrich) of reagent grade was refluxed with NaH
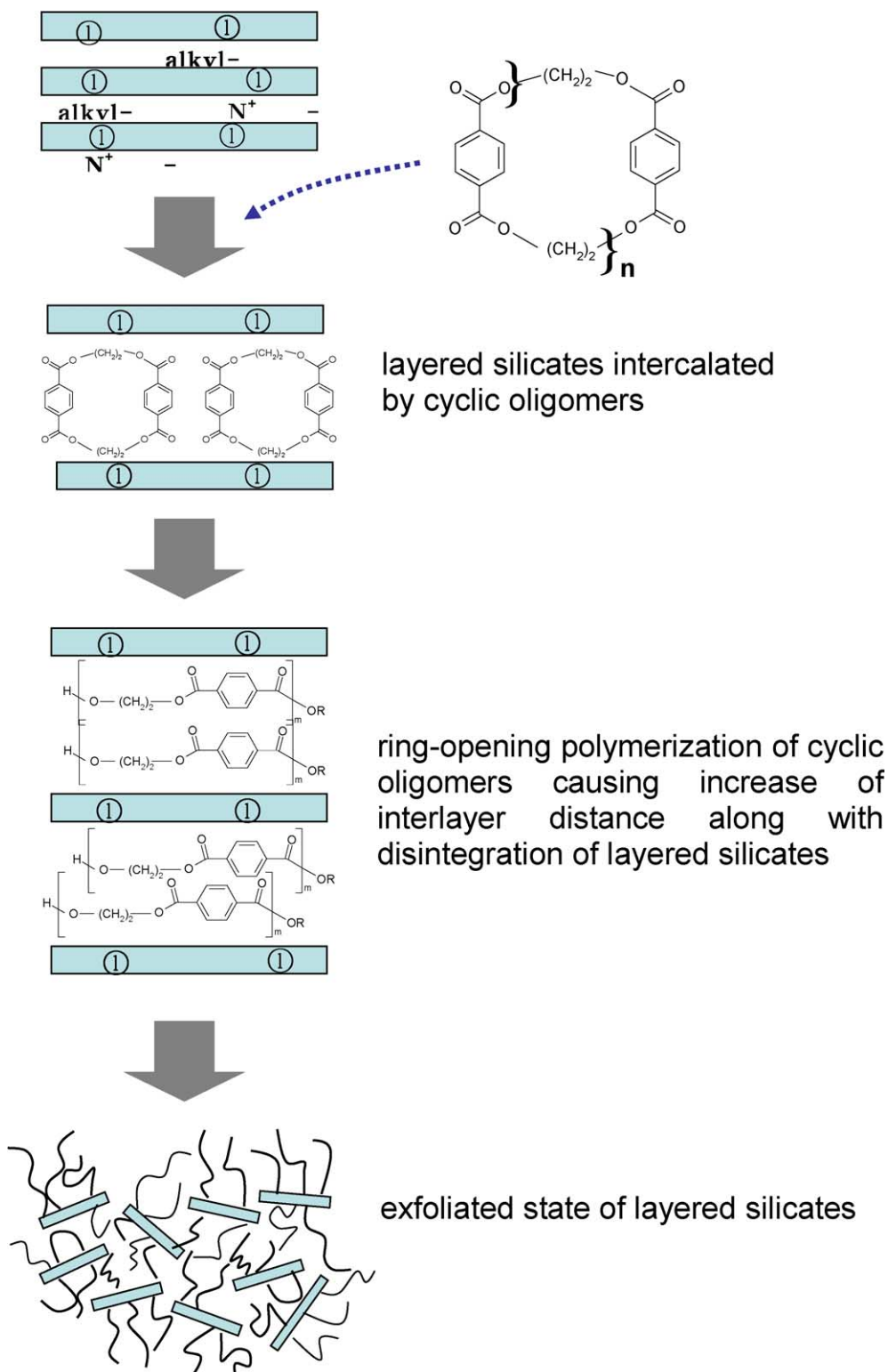
Scheme 1. Schematic representation of nanocomposite formation by ring-opening reaction of cyclic oligomers in-between silicate layers.

overnight and collected before use. Ti(O-i-C$_3$H$_7$)$_4$ (Aldrich) was used as received.

2,5-Dihydroxybenzoic acid of analytical grade, the MALDI-TOF matrix, was purchased from Aldrich, and used as supplied.

2.2. Preparation of cyclic oligomers

The direct synthesis of ETC from TPC and EG was carried out via a method of Brunelle [18,26]. In a three-necked 2 l reactor containing 1.1 mol of TEA (111.3 g) and

25 mmol of DABCO (2.8 g) dissolved in DCM 500 ml, 0.5 mol of TPC (101.5 g) in dry DCM 500 ml and neat EG of 0.8 mol (49.7 g) were added at a constant rate over 1 h, using a metering pump to maintain stoichiometry in the reactor. After the completion of reaction, 10 ml of aqueous NH_4OH (28% from Junsei Chemicals) was added to kill the reaction. Polymers and linear oligomers were removed by filtration through Celite (Celite521 from Aldrich) and the DCM solution was worked up by washing sequentially with 10 ml 3 N, 10 ml 1 N aq. HCl solution and large amount of deionized water several times. Filtration and evaporation imparted the crude ETCs of 68 g in 70% yield.

2.3. Preparation of nanocomposites

To prepare poly(ETC)/OMMT nanocomposite, polymerization of ETC in the presence of OMMT was performed with varying polymerization temperature. It is usual to use an antioxidant in polyester synthesis due to the high reaction temperature. Tripathy et al. also used an Irganox 1010 as an antioxidant when preparing the PBT/clay nanocomposites [30]. Even though the amount of antioxidant may be copious, it is desirable to avoid any impurities that are likely to affect clay intercalation, and thus, several times of extensive nitrogen purging of solutions and a high vacuum condition during polymerization were given. 2.61×10^{-3} mg of $Ti(O-i-C_3H_7)_4$ (9.2×10^{-3} mmol) dissolved in 2 ml DCM was mixed with 0.1 g OMMT (previously vacuum-dried at 70 °C for 24 h) swollen in 20 ml of DCM, followed by vigorous stirring for 12 h. The resulting mixture was added to 20 ml DCM containing 2 g of ETC (10.4 mmol) under vigorous stirring. After 12 h at room temperature, the solvent was removed under reduced pressure. The mixture of ETC/OMMT dried under vacuum at 60 °C for 12 h, was added to a reactor sealed under high vacuum and heated for 10 min at various temperatures from 240 to 310 °C. The content of OMMT was fixed at 5 wt%.

2.4. Characterization

In order to identify cyclic oligomers, MALDI-TOF (matrix assisted laser desorption ionization-time of flight) analysis was conducted. MALDI-TOF mass spectra were recorded in linear and in reflection mode, using a Voyager-DE STR mass spectrometer (Perceptive Biosystem), equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse width, and working in positive ion mode. The accelerating voltage of 25 kV and 2,5-dihydroxybenzoic acid as matrix were applied for measurements.

To confirm the polymerization of ETC, the DSC measurement was performed on Perkin–Elmer DSC7 at a heating rate of 10 °C/min from 30 to 300 °C, measuring glass transition temperature (T_g) and melting temperature (T_m). To observe a crystallization behavior (T_c), a specimen was placed on the DSC chamber preheated at 300 °C for 30 s to obtain thermal equilibrium, and subsequently, cooled

to room temperature with a rate of 10 °C/min. In addition, thermogravimetric analysis (TGA) on a TA model 2010 was conducted at a rate of 5 °C/min under nitrogen atmosphere for examining the thermal degradation behavior of organic components along with the content of inorganics in the nanocomposites.

The number-averaged molecular weight (M_n) of the polymerized ETCs during the ring-opening reaction was calculated from values of intrinsic viscosity [η] using the Berkowitz [31] equation, $M_n = 3.29 \times 10^4 [\eta]^{1.54}$. The intrinsic viscosity measurement was done at 25.0 ± 0.01 °C and a polymer concentration of 0.25% in 60/40 w/w phenol/1,1,2,2-tetrachloroethane.

The FT-IR experiment was conducted on Perkin–Elmer FT-IR 1725X (spectral resolution limit: 2 cm^{-1}) at room temperature. For a specimen of KBr-mixed disk of 0.1 mm thickness, data of 500 scans were collected and averaged. Furthermore, ^1H NMR experiment was tried on Bruker WM-360 FT-NMR spectroscopy at 360 MHz, and deuterated chloroform as solvent.

The changes of gallery height of OMMT by polymer invasion were elucidated on a wide-angle X-ray spectroscopy (MacScience MXP18) with reflection mode. X-ray generator was run at 18 kW and the target was Cu standard ($\lambda = 1.5405$ Å). Scanning was performed from 0 to 10° with a rate of 1°/min. For correction of scattering angle, a pure silicone standard was used. The basal spacing of the layered silicates, d_{100} was calculated using the Bragg's law, $\lambda = 2d \sin \vartheta$ from the position of the (100) plane peak in XRD spectrum.

Transmission electron micrographs were taken from 100 to 120 nm thick, cryo-microtomed section using JEOL JEM-2000FX TEM with accelerating voltage of 100 kV.

3. Results and discussion

Application of ring-opening polymerization is usually hindered by the limited efficiencies for synthesizing and isolating cyclic oligomers. Therefore, great endeavors have been poured in developing a practical pathway of highest efficiency in the preparation of cyclic oligomers, reporting various kinds of preparation method such as pseudo-dilution method, cyclodepolymerization, etc. [8–29]. Among them, cyclic oligomers can be easily produced through direct reaction of their monomeric components. Direct reaction of acid chlorides with glycols in dilute solution gives high yields of ETCs [22–24]. Since thin layer chromatography (TLC) analysis showed a small amount of material that did not elute from the origin in crude samples, as suggested in the literature [16,26], simple mixing cyclics with silica gel in DCM, followed by filtration and evaporation were performed to remove all the insoluble polar linear oligomers. As shown in Fig. 1, MALDI-TOF analysis indicated the level of linear oligomers in typical reactions to be less than 0.5%, testifying to the selective formation of

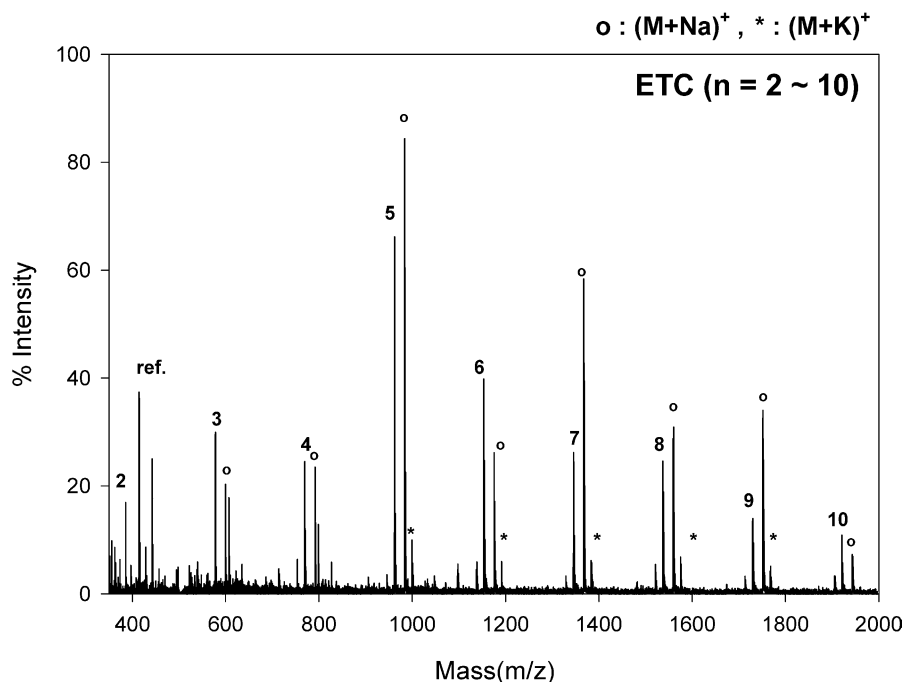o : (M+Na)$^+$, * : (M+K)$^+$

ETC (n = 2 ~ 10)

Fig. 1. MALDI-TOF trace of ETCs showing presence of cyclic oligomers without linear impurities.

cyclic oligomers over linears. The identity of the ETCs was confirmed by separation of the cyclic oligomers into individual and comparison with those reported in the literatures [24,26–29]. Additionally, hydroxyl or carboxylic acid groups dangled on both ends of linears, which were typically detected as strong stretching peak above 3000 cm^{-1}, were not detected in the FT-IR spectrum of Fig. 2(a), and all the chemical shifts in ^{1}H NMR measurement of Fig. 2(b) were assigned and clearly demonstrated successful preparation of cyclic oligomers without linear oligomers or polymeric impurities.

For the ETCs collected after purification, ring-opening polymerization was conducted around melting temperature of cyclic oligomers. When heated at 310 °C for 10 min, the melted ETCs of very low viscosity was readily solidified in ivory color, and no more stirring could be made. The fast polymerization reaction of cyclic oligomers has been known in the literatures, which suggested that crude products collected after the reaction showed a typical DSC thermogram of PET of T_g around 67 °C and T_m at 248 °C with large suppression of peaks associated with cyclic oligomers [26–29], representing ring-opening reaction of ETCs to polymer. It is known that [29] polymeric PET contains a few % of cyclic oligomers that are in equilibrium with the polymer melt, and the thermograms does not always exhibit an endotherm associated with the residual cyclics due to the accuracy limit of DSC. In order to find an evidence of conversion to polymer, a viscosity measurement for the polymerized ETCs (poly(ETC)) was conducted using the mixture solvent of phenol/1,1,2,2-tetrachloroethane, obtaining the number-averaged molecular weight (M_n) of 13,000. At the previous studies about the polymerization of ETCs,

the molecular weight of poly(ETC) has been reported to highly depend on the reaction environments such as temperature, chemical structure and concentration of catalyst, etc. [17–29]. Even though the molecular weight of poly(ETC) in this study was not as high as that of commercial PET, our aim is to examine the opportunities of polymerization-induced nanocomposite preparation, which does not require extremely high molecular weight and thus, additional endeavor to obtain PET of higher molecular weight was not given.

Before investigating the effect of ring-opening reaction of cyclic oligomers on the exfoliation of silicate layers, XRD measurements were conducted to ascertain intercalation behavior of silicate layers for the mixture of OMMT with ETCs. A mixture of OMMT with ETCs in DCM solution was prepared under vigorous stirring, and then, solvent was removed by evaporation to obtain a fine powder. As shown in Fig. 3, when cyclic oligomers was mixed with OMMT, the characteristic (100) peak of pristine OMMT detected at 4.9° of 2ϑ was dramatically shifted to a very broad peak below 2.7°. This change of basal plane evidenced that cyclic oligomers extensively participated in intercalation of silicates layers, yielding large increase in intra-gallery distance of silicate layers.

For the fine powdery mixture of ETC/OMMT, polymerization was conducted with varying reaction temperature from 240 to 310 °C. As observed in the DSC thermograms of Fig. 4(a), the mixture of ETC and OMMT prepared in DCM solution showed multiple endothermic peaks corresponding to the size distribution of ETCs which represent melting-like order–disorder transition. When a mixture of ETCs and OMMT with catalysis of Ti(O-i-C$_3$H$_7$)$_4$ was
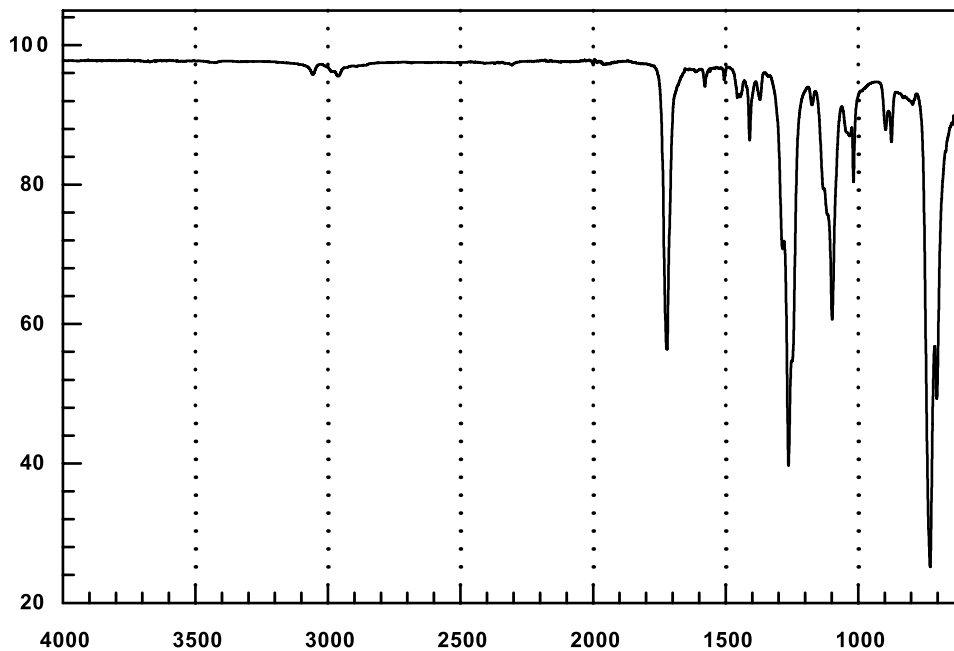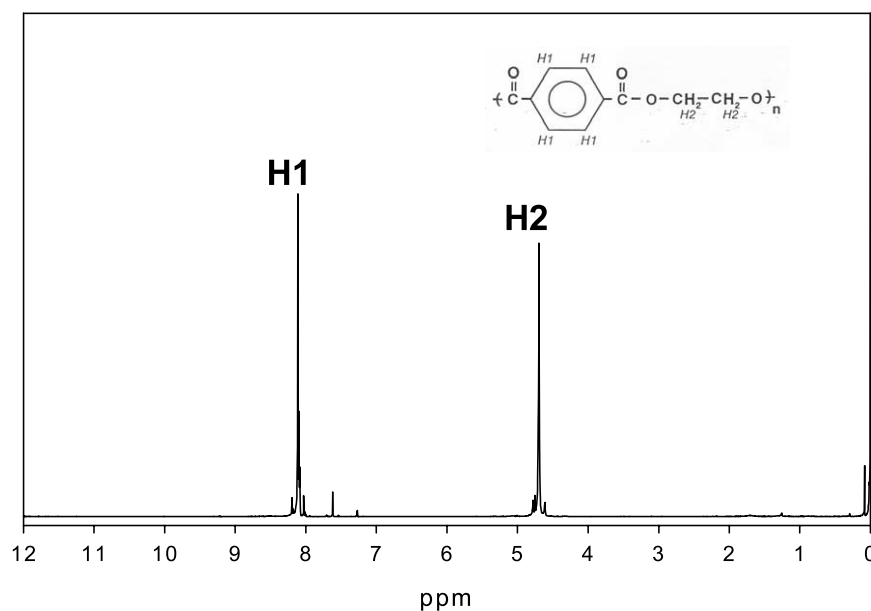
(a) FT-IR spectrum

(b) ^{1}H-NMR spectrum

Fig. 2. (a) FT-IR and (b) ^{1}H NMR spectra of ETCs. Note no detection of end-functional groups such as hydroxyl or carboxylic acid, which is associated with linear impurities, implying successful preparation of cyclic ester oligomers

heated at 240 °C, disappearance of cyclic oligomers melted below reaction temperature and increase in viscosity were observed to indicate that ring opening reaction of ETCs started. However, the increase in viscosity was very sluggish and the molecular weight obtained from intrinsic viscosity was as low as 2000. When the reaction temperature reached to the melting point of cyclic trimer or tetramer (310 °C) [32], complete disappearance of melting endotherms of ETCs except that of PET crystalline phase was observed along with much higher molecular weight; $M_n = 11000$ for poly(ETC)/OMMT-310, 8500 for poly(ETC)/OMMT-280 and 5000 poly(ETC)/OMMT-260,
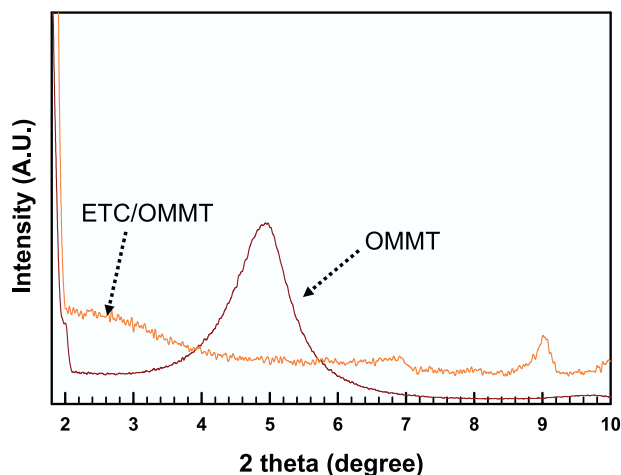
Fig. 3. XRD spectra featuring change of *d*-spacing of OMMT indicating the presence of intercalated silicate layers of OMMT dispersed in the ETCs matrix. Note that ETC/OMMT mixture showed a small peak at 2θ of 9° presenting loosely ordered state of cyclic oligomers.

respectively. The cooling thermograms in Fig. 4(b) showed a change of exothermic peak representing a crystallization of poly(ETC) in terms of polymerization temperature. The peak point was shifted to lower temperature with increase in reaction temperature from poly(ETC)/OMMT-240 to poly(ETC)/OMMT-310, while the onset temperature was not varied significantly among poly(ETC)/OMMT-240, 260 and 280. Since onset point of exothermic peak is sensitive to the presence of species of higher crystallization tendency, it is presumed that not a little amount of cyclic oligomers remained unreacted when polymerized at 240, 260 and 280 °C. For a clearer insight on the crystallization behavior, the amount of supercooling ($\Delta T = T_m - T_c$) was evaluated in Table 1, which showed increase in ΔT with polymerization temperature of cyclic oligomers. The supercooling, ΔT has been known to be highly affected by molecular weight of crystallizing species, the presence of heterogeneous phases possibly acting as crystallization nuclei, chemical structure of repeating units, etc [33]. Since the content of OMMT was fixed at 5 wt% for all the specimens, increase in super-cooling along with shift of crystallization peak to lower temperature and increase in T_m with reaction temperature implied that a temperature condition as high as 300 °C should be provided to obtain a poly(ETC) of high molecular weight, since a large amount of ETCs appeared not to

Table 1
Supercooling ($\Delta T = T_m - T_c$) changes in a function of polymerization temperature

Designation	T_m (°C)	T_c (°C)	ΔT (°C)
Poly(ETC)/OMMT-240	NA[a]	184	N.A
Poly(ETC)/OMMT-260	235	180	55
Poly(ETC)/OMMT-280	246	183	63
Poly(ETC)/OMMT-310	247	178	69

[a] For the specimen polymerized at 240 °C, melting peak of polymeric crystalline phase could not be firmly distinguished.
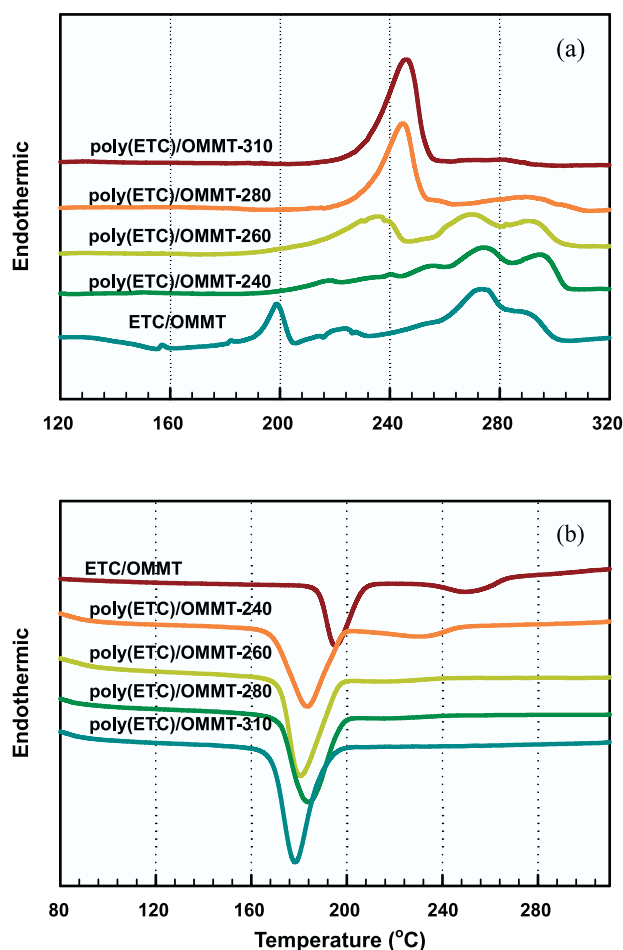

Fig. 4. DSC thermograms of the ETCs/OMMT mixtures after polymerization with varying polymerization temperature; (a) heating and (b) cooling runs to present melting endotherms and crystallization exotherms, respectively. The number after poly(ETC)/OMMT means the polymerization temperature. Note the gradual disappearance of melting endotherms of cyclic oligomers along with decrease in crystallization temperature as reaction temperature increased. ETC/OMMT means a mixture of ETC/OMMT/initiator prepared in DCM solution without polymerization.

participate in polymerization due to lack of mass transfer at the temperature below their melting point. XRD measurements showed that the broad diffraction peak of layered silicates in ETC/OMMT mixture before polymerization was highly diminished after polymerization at 310 °C as shown in Fig. 5, implying disruption of layered structure of clay effectively occurred to impart better dispersion of silicate layers in the matrix.

The thermogravimetric analysis of nanocomposites in Fig. 6 indicates better thermal stability of poly(ETC)/OMMT than its corresponding polymer without clay. For the poly(ETC) specimen without clay, it was found that the degradation was initiated at 300 °C, while the onset temperature of degradation of poly(ETC)/OMMT-310, which was polymerized at 310 °C, was well above 360 °C, yielding a noticeable increment of onset temperature of degradation by the presence of OMMT of 5 wt% (Fig. 6(a)).
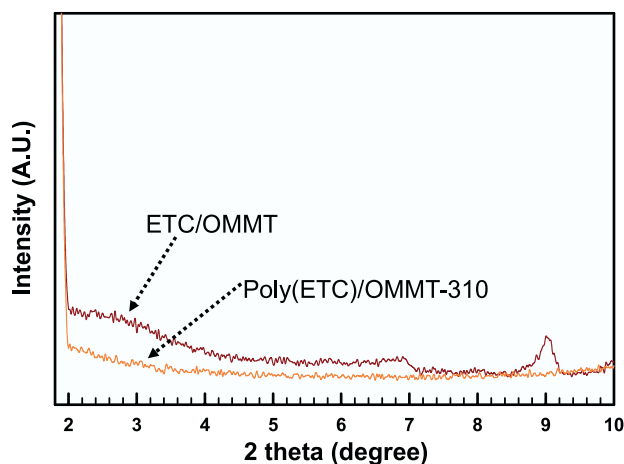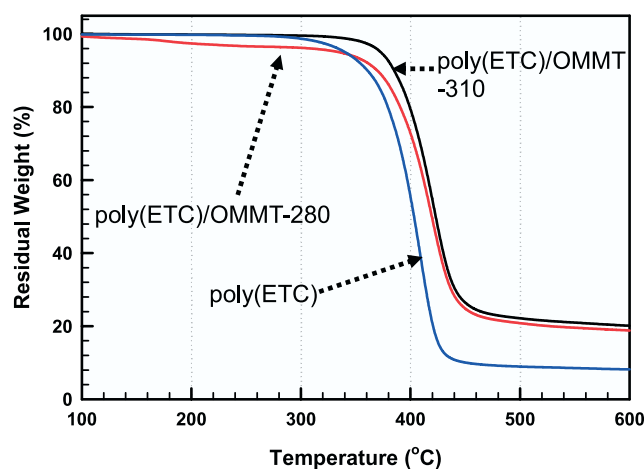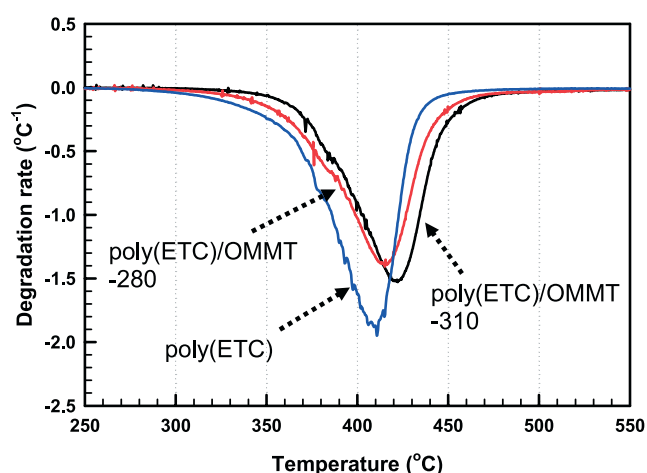
Fig. 5. XRD spectra featuring change of *d*-spacing of OMMT affected by the polymerization of cyclic oligomers at 310 °C.


Fig. 6. TGA thermograms (a) of the nanocomposites of poly(ETC)/OMMT along with neat poly(ETC) and (b) their differential curves, presenting an thermal stability and high retardation of thermal degradation of organic phase. The number after poly(ETC)/OMMT means the polymerization temperature.

In case of poly(ETC)/OMMT-280, of which poly(ETC) has a lower molecular weight than neat poly(ETC) as well as poly(ETC)/OMMT-310, the thermal degradation apparently start earlier than neat poly(ETC). However, the main featuring of degradation was similar with that of poly (ETC)/OMMT-310; there is an almost 10 °C increment in the onset temperature of degradation compared with neat poly(ETC). The differential curve of TGA thermogram in Fig. 6(b) clearly shows that thermal degradation reaction was highly retarded when clay existed. It has been well known that a thermal stability of polyester is highly affected by the concentration of end functional group which determines molecular weight, and thus, polyester of higher molecular weight is likely to show a better thermal stability. It means that tiny amount of clay is capable of improving the thermal stability of PET very effectively. Since good dispersion of clay layers is the main key to property enhancement such as better thermal stability [30,34,35], we can conclude that an extensive polymer penetration into the silicate layers of clay was obtained during ring-opening polymerization of ETCs, resulting in a nanoscale dispersion of silicate layers in the polymer matrix.

Further evidence of the nanometer-scale dispersion of silicate layers in the polymer matrix is provided by the TEM micrographs, as shown in Fig. 7. In Fig. 7(a), TEM microphotograph of cryo-microtomed section of the ETC/OMMT nanocomposites before polymerization showed that ETC with OMMT have the highly intercalated nanostructure rather than the exfoliated one. Individual layers, oriented perpendicular to the sample surface, appears as dark lines with thickness around 1 nm and width lateral size around 200–500 nm. Primary particles consist of stacks of parallel elementary sheets with an average of about 10 sheets per particle. In Fig. 7(b) for the poly(ETC)/OMMT-310 nanocomposite prepared at 310 °C, TEM bright field image of cryo-microtomed section revealed that there are mostly well-dispersed silicate layers due to significant disruption of OMMT tactoids along with some stacked silicate layers with about 10 nm thickness, consisting of about 2–10 parallel silicate layers to form morphology like thin thread. These results are reflected in XRD of the increment of the *d* spacing in comparison to the original OMMT. TEM result tells us that the ring-opening reaction of cyclic oligomers to PET in-between silicate layers can be an effective route to prepare the PET/clay nanocomposite of silicate layers of high disintegration and enhanced dispersion.

4. Conclusion

With successful conversion of cyclic oligomers of PET, nanocomposites consisting of organically modified layered silicates and PET have been obtained through ring-opening polymerization of cyclic oligomers. For the purpose to obtain PET/clay nanocomposites of exfoliated silicate
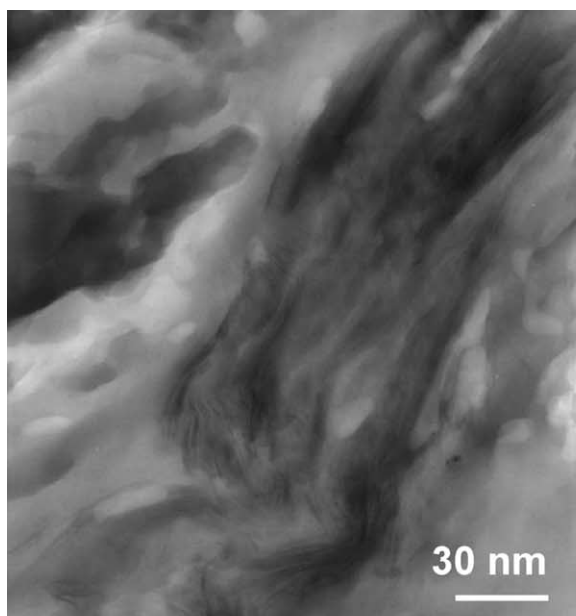
(a)
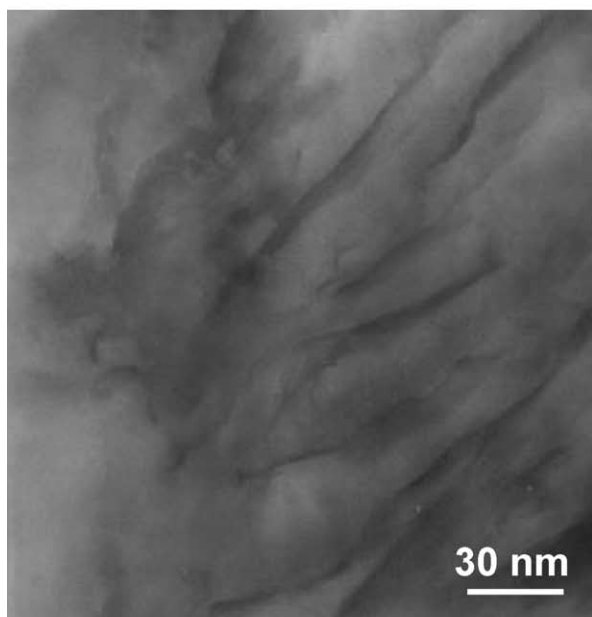
(b)

Fig. 7. TEM microphotographs of (a) the OMMT intercalated with ETCs before polymerization and (b) the poly(ETC)/OMMT-310, which was polymerized at 310 °C, presenting a high disruption of layered structure of OMMT. Note the significant disruption of stacked OMMT layers oriented perpendicular to the sample surface which is parallel to the micrograph face after polymerization of cyclic oligomers.

layers we varied a thermal condition of ring-opening polymerization of ETCs in the presence of clay, and examined the change of intercalation behavior along with the corresponding morphology and thermal properties. Because of the significantly low viscosity of cyclic

oligomers compared with the corresponding polymer, the disruption of the layered structure of silicate nanoplatelets and their dispersion in the polymer matrix has been extensively achieved. It is thought that the low viscosity of cyclic oligomers may offer unique processing opportunities for the preparation of nanocomposites, especially with respect to the enhanced mobility of the silicate layers in the polymer medium.

Acknowledgements

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