

Preparation of poly(ethylene terephthalate)/layered double hydroxide nanocomposites by *in-situ* polymerization and their thermal property

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Abstract. Terephthalate (TA) intercalated layered double hydroxides (LDHs) were synthesized using hydroxides as raw materials, and poly(ethylene terephthalate) (PET)/LDH nanocomposites with different contents of TA intercalated LDHs were prepared by *in-situ* polymerization. The structure, morphology and thermal property of PET/LDH nanocomposites were investigated. The TA intercalated LDHs were partially exfoliated and well dispersed in PET matrix. The PET/LDH nanocomposites exhibit enhanced thermal stability relative to pure PET, confirmed by the thermogravimetric analysis results. The results of differential scanning calorimetry suggest that LDH nanoparticles could effectively promote the nucleation and crystallization of PET.

Keywords: nanocomposites, poly(ethylene terephthalate), layered double hydroxides, *in situ* polymerization

1. Introduction

Layered double hydroxides (LDHs), known as a class of anionic clays, have attracted increasing interest due to their broad applications in areas such as catalysis, materials, medicine and environmental protection. LDHs can be represented by the general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{x+} \cdot A^{n-}_{x/n} \cdot zH_2O$, where the di- and trivalent cations (M^{2+} and M^{3+} , respectively) can be most metal ions. The value of x may be varied over a wide range. A^{n-} is an exchangeable anion, which can be simple inorganic species, organic anions, heteropoly acid anions, polymers [1, 2].

The polymer/LDH systems have been much less studied than the cationic clays due to the delamination difficulties of LDHs with the small gallery space and hydrophilic surface character [3]. However, the highly tunable properties, the anion exchange capacity have converted these materials into a new emerging class of layered crystals, which

seems to be better suited for the preparation of multifunctional polymer/layered crystal nanocomposites. In recent years, study on the LDH nanocomposites with various polymers such as polyimide [4], epoxy [5], poly(ethylene terephthalate) (PET) [6], polyamide 6 [7], poly(butylene terephthalate) [8], unsaturated polyester [9] and poly(vinyl alcohol) [10, 11], concerning physical properties and dispersion, has been widely reported. To apply anionic LDHs to nanocomposite system, preparation of organo-modified LDHs resulting in an increase in gallery spacing is very important because inorganic LDHs and organic polymer matrix are basically incompatible. In the past 20 years, many reports about the intercalation of organic anions into LDHs were discussed [12–17].

PET is a semicrystalline polyester with a high melting point and very good mechanical strength, due to the presence of the aromatic ring in the polymeric

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structure [18]. Recently, PET/organo-modified LDH nanocomposites have been reported and focused on their synthesis and properties. Lee and coworkers [18] prepared PET/LDH nanocomposites using anionic surfactants intercalated LDHs by a direct melt compounding method. Rives and coworkers prepared PET/LDH nanocomposites through a microwave [19] and mechanical grinding method [20]. Dodecylsulfate intercalated LDHs were used to enhance the compatibility between the PET polymer and the LDHs. Recently, Rives and coworkers [21] reported the preparation of PET/LDH nanocomposites using TA intercalated LDHs through a microwave heating route. It is found that the microwave process improves the dispersion and the thermal stability of nanocomposites due to the interaction of the microwave radiation.

However, *in situ* polymerization has become the main procedure for the preparation of nanocomposites due to its versatility and compatibility with reactive monomers [22], as well as permitting the control of the polymer and the composite structures. This method relies on the swelling of the organically modified LDHs by the monomer, followed by *in situ* polymerization initiated thermally or by addition of a suitable compound (catalyst) [19]. The chain growth in the LDH galleries accelerates exfoliation and nanocomposite formation [6]. In this work, PET/LDH nanocomposites were prepared by *in situ* polymerization. LDHs were organically modified using terephthalate (TA) as the interlamellar anion, to overcome the lack of compatibility between the polymer and LDHs containing purely inorganic anions. The chemical, thermal properties and morphology of the PET/LDH nanocomposites were studied.

2. Experimental

2.1. Materials

All the reagents were purchased from the Beijing YILI Fine Chemical Limited (Beijing, P.R. China) and used without further purification.

2.2. Preparation of TA intercalated LDHs

The preparation of TA intercalated LDHs followed a simple but efficient method that was newly developed in our laboratories [23, 24]. The key feature of this method is a reaction of freshly generated hydroxides and terephthalic acid under a hydrother-

mal condition. Compared to other methods, the terephthalate-intercalated LDHs synthesized using this method exhibit higher purity and higher crystallinity.

The freshly generated $Mg(OH)_2$ and $Al(OH)_3$ (molar ratio 2:1) were placed in 80 mL of deionized water. Terephthalic acid was added to the suspension with a vigorous stirring. Then the suspension was taken under a hydrothermal condition at 120°C for 10 h. The product was collected after filtration by vacuum pumping and washed thoroughly with deionized water several times, and dried at 80°C overnight.

2.3. Preparation of PET/LDH nanocomposites

All the samples were prepared by a conventional 2-step polycondensation [6, 25]. In a typical procedure for the preparation of PET/LDH nanocomposites, TA intercalated LDHs were previously dispersed in ethylene glycol (EG, 1 mol) using a sonicating homogenizer for 15 min. The EG slurry containing TA intercalated LDHs was then mixed with dimethyl terephthalate (DMT) (0.5 mol) and 0.020 wt% (with respect to the DMT amount) of manganese acetate and magnesium acetate as catalyst. TA intercalated LDH contents were 0, 0.5, 1.0, and 2.0 wt% with respect to the DMT amount. The ester interchange reaction was carried out at 190–230°C with a continuous removal of byproduct (methanol). Polycondensation reaction was carried out at 280°C with ethylene glycol antimony catalyst at a pressure of 0.1 Torr for 2 h. The as-synthesized nanocomposite samples were dried at vacuum oven for 1 day at 70°C.

2.4. Characterizations

The crystal structures of samples were identified using a powder X-ray diffraction (XRD) on an X'Pert Pro MPD Powder X-Ray diffractometer (PANalytical, Almelo, Holland) with $Cu K\alpha$ radiation. FT-IR spectra were recorded on a Bruker Vector 22 instrument (Bruker AXS, GmbH, Germany) after 20 scans within 4000–400 cm^{-1} at a resolution of 2 cm^{-1} . The sample was finely ground for 1 min, combined with oven dried spectroscopic grade KBr and pressed into a disc. The Scanning electron microscopy (SEM) images were recorded by a S-4800 instrument (Hitachi, Tokyo, Japan) at 15 kV. The SEM micrographs were taken from a sample fractured surface which was broken in liquid nitro-

gen and the morphology of the samples was observed on a JEM-1200EX (JEOL Ltd, Japan) transmission electron microscope (TEM) operated at 100 kV with copper mounted holey carbon grids. Thermogravimetric analysis (TGA) was carried out on a TA instrument Q5000 thermobalance (TA instruments, New Castle, DE, USA) over the range of 50 to 650°C at a heating rate of 10°C·min⁻¹ under air atmosphere (50 mL·min⁻¹). The thermal properties of the nanocomposites were examined with a Shimadzu DSC-60 instrument (Shimadzu, Kyoto, Japan). To remove previous thermal history, all samples were first heated 300°C for 5 min and then cooling run was performed at a rate of 10 °C/min. Then, second heating run was carried out at a rate of 10°C/min.

3. Results and discussion

3.1. The structure and morphology of TA intercalated LDHs

The XRD pattern of TA intercalated LDHs is shown in Figure 1. For comparison, that of the carbonate LDHs prepared by a coprecipitation reaction is also presented in Figure 1. The XRD patterns exhibit the characteristic reflections of LDH materials with a series of (00l) peaks appearing as narrow symmetric lines at low angle corresponding to the basal spacing and higher order reflections. Compared to the carbonate LDHs, the basal spacing of the TA intercalated LDHs increases from 0.76 to 1.42 nm, which suggests the terephthalate anions were successfully intercalated. Given that the thickness of the brucite-like layer of LDHs is 0.48 nm [1], the gallery height in the TA intercalated LDHs is 0.94 nm. This data is same as the diameter of the long axis of terephthalate anion, which suggests a

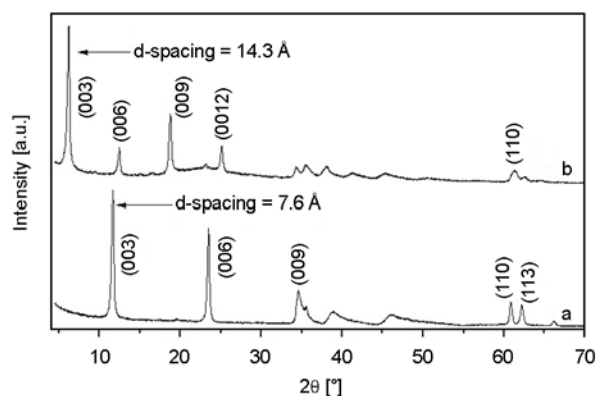


Figure 1. XRD patterns of different LDHs a) carbonate LDHs; b) TA intercalated LDHs

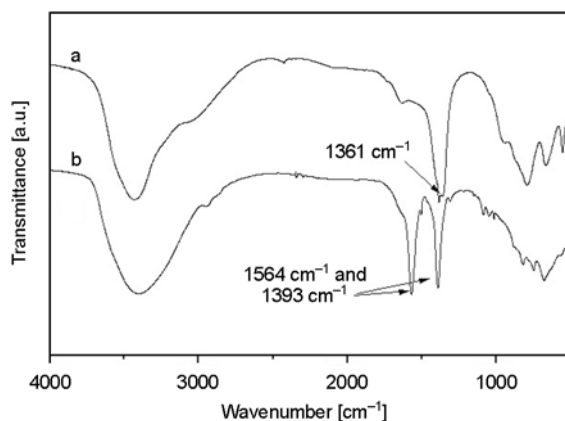


Figure 2. FT-IR spectra of different LDHs a) carbonate LDHs; b) TA intercalated LDHs

monolayer arrangement for the intercalated terephthalate anions oriented perpendicular to the LDH layers [26].

The FT-IR spectra of the carbonate LDHs and the TA intercalated LDHs are shown in Figure 2. The absorption at 1361 cm⁻¹ which is attributed to carbonate ions in the carbonate LDHs is not present in the spectrum of the TA intercalated LDHs. The spectra of carboxylate are dominated by the asymmetric and symmetric RCO²⁻ stretches of the organic guests at around 1580 and 1400 cm⁻¹ [27, 28]. As TA was incorporated into the LDH interlayers, two peaks appeared at 1564 and 1393 cm⁻¹, which are assigned to carboxylate group stretching of the terephthalate guest [23]. This confirms the existence of terephthalate anion in the interlayer of LDH sheets.

3.2. The structure and morphology of PET/LDH nanocomposites

The XRD patterns for PET and PET/LDH nanocomposites with 0.5, 1, 2 wt% of TA intercalated LDHs and 2 wt% of carbonate LDHs are shown in Figure 3. In the case of PET nanocomposites with 2 wt% of carbonate LDHs, a small (003) reflection (arrow mark) which corresponds to a basal spacing of carbonate LDHs is shown at around 11.3°. It indicates that the carbonate LDH particles were not exfoliated by the PET molecules during *in-situ* polymerization. In the cases of PET nanocomposites with TA intercalated LDHs, the characteristic peak of basal spacing for TA intercalated LDHs completely disappeared, indicating the partial exfoliation of LDHs interlayer structures in the PET matrix, in which the gallery height of intercalated

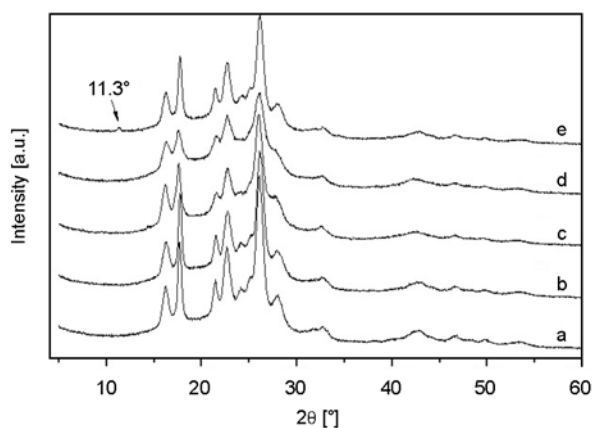


Figure 3. XRD patterns of PET (a) and PET/LDH nanocomposites with b) 0.5 wt% of TA intercalated LDHs; c) 1 wt% of TA intercalated LDHs; d) 2 wt% of TA intercalated LDHs; e) 2 wt% of carbonate LDHs

layers is large enough and the layer correlation is not detected by X-ray diffractometer. Although, XRD provides a partial picture about distribution of nanofiller and disappearance of peak corresponding to d-spacings does not always confirm the exfoliated nanocomposites [29], because XRD measure-

ments detect average diffractions came from overall sample area irradiated by X-ray. If the characteristic peak shift to the lower angle beyond the XRD scan range ($<3^\circ$) owing to increased gallery spacing resulting from the partial intercalation of PET molecules, then LDH characteristic diffractions for the gallery spacing cannot be detected by the XRD apparatus [6]. Therefore, a complete characterization of nanocomposite morphology requires to be investigated [30, 31].

The SEM images of PET nanocomposites with 2 wt% of carbonate LDHs and TA intercalated LDHs are shown in Figure 4. In Figure 4a, the particles of carbonate LDHs can be clearly seen. Some particles about 600 nm were shown, which were much bigger than the carbonate LDHs before polymerization. This is because the complete form of layered LDH aggregates. The carbonate LDHs had the least interaction with PET matrix, and were not intercalated by PET molecules during the polymerization. These layer structures can diffract the X-rays, resulting in the peak for LDH structure in XRD profiles which matches the XRD results

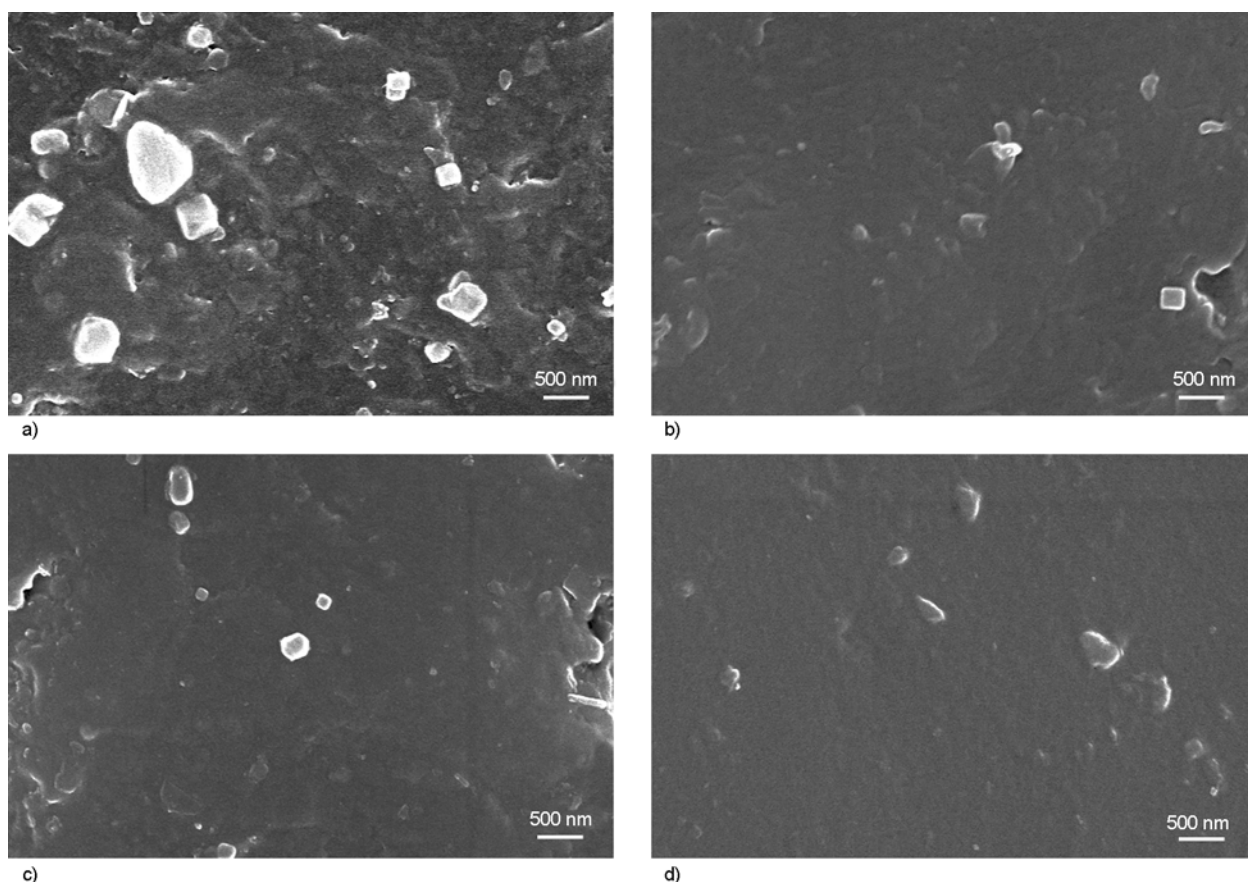


Figure 4. SEM images of the PET/LDH nanocomposites with a) 2 wt% of carbonate LDHs; b) 0.5 wt% of TA intercalated LDHs; c) 1 wt% of TA intercalated LDHs; d) 2 wt% of TA intercalated LDHs

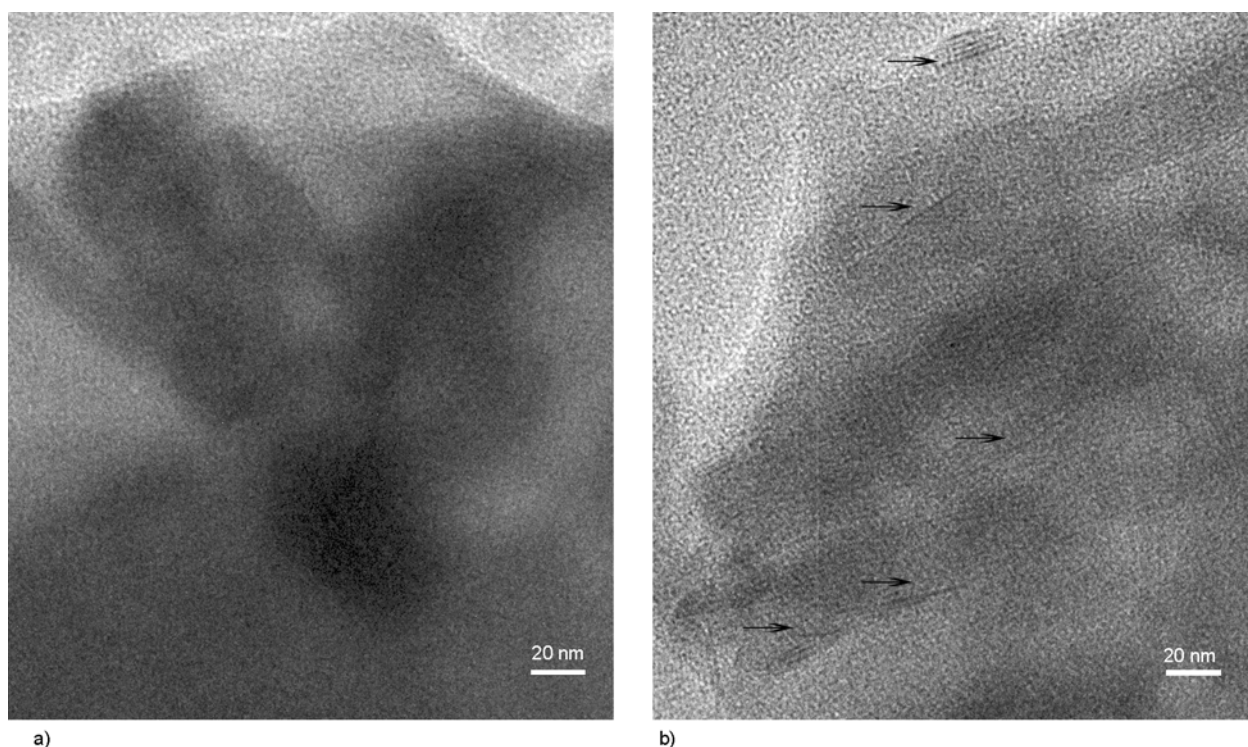


Figure 5. TEM images of the PET/LDH nanocomposites with a) 2 wt% of carbonate LDHs; b) 2 wt% of TA intercalated LDHs

shown in Figure 3. In Figure 4b, 4c and 4d, there was little agglomeration of the particles. Apparently, the particles of TA intercalated LDHs were less than that of carbonate LDHs in PET matrix with the same loading level (2%). It indicates that the TA intercalated LDHs were intercalated and/or exfoliated efficiently by PET molecules during polymerization and dispersed well in PET matrix.

TEM was used to examine exactly the state of the TA intercalated LDHs in the PET matrix. The TEM images taken from PET nanocomposites with 2 wt% of carbonate LDHs and 2 wt% TA intercalated LDHs are shown in Figure 5. The dark lines represent the LDH layers, whereas the bright areas represent PET matrix. In Figure 5a, big particles or aggregates are found because the carbonate LDHs were not intercalated by PET molecules during the in-situ polymerization. In Figure 5b, the micrograph clearly shows the lamellar structure of LDHs exfoliated by the PET macromolecular chain; the lines of the layers are well shown using the arrow marks. The thickness and lateral sizes of the exfoliated LDH layers can be calculated as being about 1~2 nm and 20~80 nm, respectively.

3.3. Thermal property and crystallization behavior of PET/LDH nanocomposites

TGA curves for PET and PET/LDH nanocomposites with 0.5, 1.0, and 2.0 wt% of TA intercalated LDHs and 2 wt% of carbonate LDHs are shown in Figure 6, and the results are summarized in Table 1. Decomposition of PET takes place in three steps [19]. The first weight loss starts at about 300°C, corresponds to removal of water. The main weight loss starts at about 400°C. This second step is attrib-

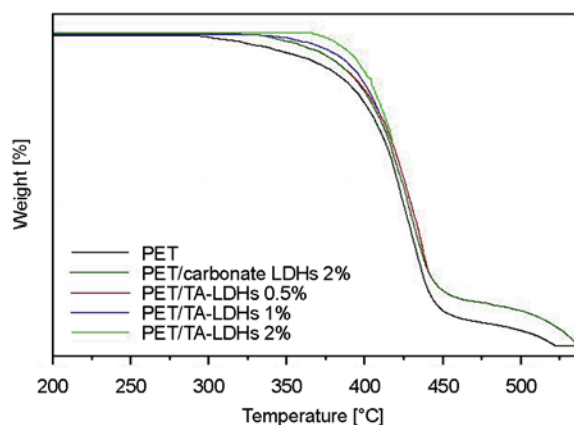


Figure 6. TGA curves of PET and PET/LDH nanocomposites with 2 wt% of carbonate LDHs and 0.5, 1, 2 wt% of TA intercalated LDHs

uted to the partial decomposition of the polymer. Finally, a new weight loss, due to oxidative elimination of the carbonaceous residue derived from the initial polymer degradation, is recorded at 470°C, and all the samples are finally lost at 520°C. In Figure 6, all the nanocomposites are more stable up to high temperature than pure PET, and show similar curves and slopes. The temperature at weight reduction of 2% (T^2_D) and 5% (T^5_D) for PET/LDH nanocomposites in Table 1 are also higher than those of pure PET. It indicates that there is a strong interaction between the TA-LDHs and polymer matrix. The exfoliated nanolayers of TA-LDHs obstructed the internal diffusion of intense heat and various gaseous substances that formed during pyrolysis of PET. Terephthalate is used to increase the basal spacing of the LDHs and overcome the lack of compatibility between the polymer and LDHs containing purely inorganic anions. The increasing of the basal spacing of the LDHs is helpful for the exfoliation of LDH layers. After polymerization, the characteristic XRD peak of basal spacing for TA intercalated LDHs completely disappeared, indicating the partial exfoliation of LDHs interlayer structures. The SEM and TEM images can show that the TA intercalated LDHs were partially exfoliated and well dispersed in PET matrix during polymerization. Thus, it is believed that the introduction of TA intercalated LDHs into the PET matrix can improve the thermal stability owing to the heat insulation effect of the LDH layers and the mass transport barrier against the volatile gases generated during thermal decomposition [6]. The thermal stability of PET/LDHs nanocomposites with 1% TA-LDHs is relatively higher than PET/LDHs nanocomposites with 2% TA-LDHs. This may be due to the dispersion of 1% TA-LDHs in the PET matrix is better than 2% according to the SEM images. The exfoliated nanolayers of PET/TA-LDHs 1% is more than that of 2%.

PET is a semicrystalline polymer and its properties are related to its morphological features such as

degree of crystallization, size (thickness and lateral dimension of lamellae) and perfection of crystallites [32]. Therefore, it is important to study the crystallization behavior of PET/LDH nanocomposites. Figures 7 and 8 are the differential scanning calorimetry (DSC) thermograms of pure PET and PET/LDH nanocomposites with 2 wt% of carbonate LDHs and 0.5, 1, 2 wt% of TA intercalated LDHs with the heating and cooling measurements, respectively. The results of DSC are summarized in Table 1. The values of the melting peaks (T_m) of the

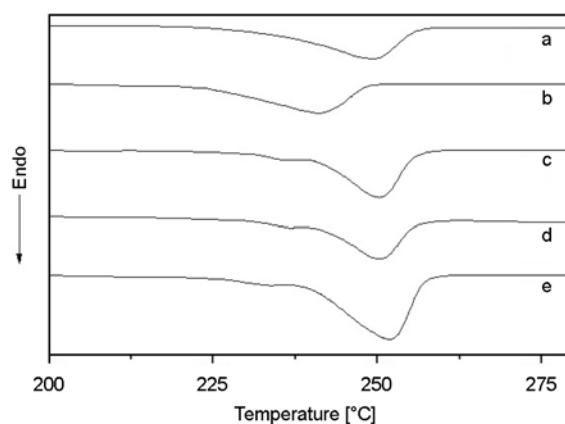


Figure 7. DSC thermograms of PET (a) and PET/LDH nanocomposites with 2 wt% of carbonate LDHs (b), 0.5 (c), 1 (d) and 2 (e) wt% TA intercalated LDHs during heating run

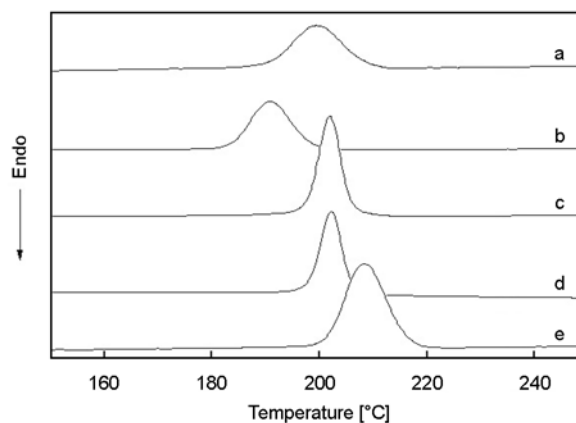


Figure 8. DSC thermograms of PET (a) and PET/LDH nanocomposites with 2 wt% of carbonate LDHs (b), 0.5 (c), 1 (d) and 2 (e) wt% TA intercalated LDHs during cooling run

Table 1. Thermal properties of PET and PET/LDH nanocomposites

Sample	T_m [°C]	ΔH_0 [J/g]	X_c [%]	T_{cc} [°C]	ΔT [°C]	T^2_D [°C]	T^5_D [°C]
PET	249.3	45.0	32	199.4	49.9	320	345
PET/carbonate LDHs 2%	241.0	38.6	28	190.7	50.3	349	368
PET/TA-LDHs 0.5%	250.2	53.4	38	201.9	48.3	329	358
PET/TA-LDHs 1%	250.3	50.0	36	202.2	48.1	377	386
PET/TA-LDHs 2%	251.8	72.7	53	208.3	43.5	354	374

nanocomposites increased from 249.3 to 251.8°C when the TA intercalated LDH content was increased from 0 to 2 wt%. The crystallization temperature during cooling (T_{cc}) of the nanocomposites increased from 199.4 to 208.3°C with increasing TA intercalated LDH content. The crystallization temperature reflects the overall crystallization rate, attributed to the combined effects of nucleation and growth [33]. Thus the degree of super cooling ($\Delta T = T_m - T_{cc}$) can be used to represent the crystallizability of the polymer; that is, the smaller the ΔT , the higher the overall crystallization rate. As shown in Table 1, the degree of super cooling of the PET/TA intercalated LDH nanocomposites decreased.

The degree of crystallinity (X_c) of the samples were determined, which can be calculated using the Equation (1) [32]:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \cdot 100 \quad (1)$$

where ΔH_f^0 is the melting enthalpy of 100% crystalline PET ($\Delta H_f^0 = 140$ J/g [34]) and ΔH_f is the normalized melting enthalpy of the sample, as shown by Equation (2):

$$\Delta H_f = \frac{\Delta H_0}{w} \quad (2)$$

where ΔH_0 is the heat of fusion of PET/LDH nanocomposites [J/g], and w is the weight fraction of PET in the PET/LDH nanocomposite samples [wt%].

As shown in Table 1, the X_c values of the PET/TA-LDH nanocomposites are all higher than those of pure PET. These results suggest that small additions of TA intercalated LDHs increased the crystallization degree of polymer. The LDH nanofillers acted as a nucleating agent for the crystallization and accelerated the crystallization rate of the PET matrix [18]. On the other hand, The T_m and T_{cc} values of PET nanocomposites with 2 wt% of carbonate LDHs were decreased. TA-LDHs can be partially exfoliated and well dispersed in PET due to the larger interlayer space and the stronger interaction with PET matrix. The exfoliated nanolayers effectively promote the nucleation and crystallization of PET. However, the carbonate LDHs had the least interaction with polymer matrix and did not

have good compatibility with PET molecules. The carbonate LDHs were not exfoliated and agglomerated in the PET matrix. Therefore they cannot act as a nucleating agent of crystallization.

4. Conclusions

The PET/LDH nanocomposites were prepared by *in-situ* polymerization. Their structure, morphology, thermal property and crystallization behavior were investigated. To enhance the compatibility between PET matrix and LDHs, TA intercalated LDHs were prepared using hydroxides as raw materials. Compared to the agglomeration of carbonate LDHs in PET matrix, TA intercalated LDHs could be partially exfoliated by PET molecules during *in-situ* polymerization and dispersed well in the PET matrix. The nanocomposites thus obtained were thermally more stable than pure PET. The addition of LDHs which acted as a nucleating agent resulted in an increase in crystallization rate.

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