

Synthesis of Poly(ethylene terephthalate)/Clay Nanocomposites Using Aminododecanoic Acid-Modified Clay and a Bifunctional Compatibilizer

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ABSTRACT: A poly(ethylene terephthalate)/clay nanocomposite (PET/clay) was prepared via *in situ* polymerization, in which the clay was modified with 12-aminododecanoic acid (ADA). A compatibilizer containing an amino and an ester group was introduced into the PET/ADA-clay system, which can attach to ADA-clay through ionic interaction and be incorporated into PET chains through transesterification. The compatibilizer-modified ADA-clay was first formed in a pretreatment process and then participated

in polymerization. The compatibilizer, as an intermedium between organoclay and polymer, improved clay dispersion in PET matrix. The PET/clay nanocomposite prepared by this novel method possesses significantly higher storage modulus than does neat PET. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1057–1064, 2006

Key words: poly(ethylene terephthalate); clay; nanocomposites; synthesis; compatibilizer

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a polymer with relatively low cost and high performance, which is widely used in various fields such as textile fibers, films, bottles, and engineering plastics for automobiles and electronics. To improve thermal, mechanical, and gas barrier properties of PET, layered silicates, i.e., so-called clay, have been used to form PET/clay nanocomposites. Two methods are mainly employed for the preparation of PET/clay nanocomposites. One is to disperse organically modified clay (organoclay) in PET via melt compounding.^{1–5} The other involves adding organoclay into monomers or oligomers, followed by *in situ* polymerization.^{6–11} The melt compounding is a convenient and flexible process capable of producing a variety of formulations on a variety of production volume scale, and the high-shear environment in extruder may permit the incorporation of a significantly higher content of clay, while PET/clay nanocomposites prepared via *in situ* polymerization in general give higher degree of clay intercalation/

exfoliation and hence possess better physical properties, such as gas barrier property.¹²

The preparation of PET/clay nanocomposites via *in situ* polymerization has been reported by several research groups. Various clay modifiers and synthesis methods have been used aimed at improving properties of PET/clay hybrids in one or more aspects for different applications. In the pioneer work by Ke et al. ethanol amine was used as clay modifier and agglomeration of clay particles was observed in the PET/clay hybrid prepared.⁶ To improve clay dispersion, Zhang et al. prepared PET/clay hybrids using hydroxypropyl trimethylammonium iodide (HPTA) as the clay modifier.⁹ It was believed that the hydroxyethyl moiety in HPTA can react with PET monomer, bis(2-hydroxyethyl) terephthalate (BHET), to facilitate clay intercalation/exfoliation in PET. Their results showed that the tensile strength of the hybrid was significantly improved when compared with that of neat PET. Similar to Zhang et al.'s work, we reported the preparation of PET/clay hybrid via *in situ* polymerization of BHET with aminododecanoic acid-modified clay. Our results showed a great impact of finely dispersed clay on crystalline morphology of PET.¹⁰ To improve thermal stability of organoclay, Chang et al. used dodecyl triphenyl phosphonium cation to substitute sodium cation in montmorillonite and subsequently prepared PET/clay nanocomposites through *in situ* polymerization.¹¹ The nanocomposites synthesized possess both enhanced thermal stability and tensile properties. Similar strategy was used to prepare PET/expandable

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fluorine mica nanocomposites, wherein 10-[3,5-bis-(methoxy-carbonyl)phenoxy]decyltriphenylphosphonium bromide was used as a compatibilizer. The compatibilizer possesses two methyl carboxylate groups, which allow it to react with PET chains through transesterification, and a phosphonium ion, which can form stable ionic bonds with the negatively charged mica layers.^{13,14} The resultant nanocomposites showed higher modulus when compared with neat PET. Despite the intensive research in this area, the degree of clay intercalation/exfoliation achieved in PET is, however, still relatively low when compared with other successful polymer/clay systems, such as nylonclay and polypropylene/clay nanocomposites.^{15,16} Currently, improving clay dispersion in PET is still a tremendous challenge.

In the aforementioned approaches, the clay modifiers contain functional groups that can, in principle, form covalent bonds with PET. The reaction in clay galleries may, however, have a low rate because of the geometric constrain. In view of this, it is interesting to investigate whether ionic interaction between PET chains and organoclay can facilitate clay dispersion. In this study, a commercially available organoclay 12-aminododecanoic acid-modified clay (ADA-clay) was used to synthesize PET/clay nanocomposites via *in situ* polymerization. An additional bifunctional compound was introduced into the system as a compatibilizer between PET and the organoclay. The compatibilizer contains an ester group, which can covalently bond to PET chains by transesterification, and an amino group, which can form ionic complex with carboxylic acid of ADA. Our results show that adding such a compatibilizer can improve clay dispersion significantly. Thermal and mechanical properties of the hybrids obtained are also reported in this article.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT, 99%, Aldrich) was dried at 80°C overnight under vacuum prior to use. Montmorillonites modified with aminododecanoic acid (Nanomer® I.24TL) having a cation exchange capacity of 100 meq/100 g were purchased from Nanocor (Arlington Heights, IL) and dried at 120°C overnight under vacuum prior to use. Ethylene glycol (anhydrous, Merck, Whitehouse Station, NJ), ethyl 4-dimethylaminobenzoate (99%, Lancaster, UK), manganese (II) acetate (98%, Aldrich, Milwaukee, WI), triphenyl phosphate (99%, Aldrich), and antimony (III) acetate (99.99%, Aldrich) were used as received. Neat poly(ethylene terephthalate) (PET) was purchased from Aldrich and dried at 80°C for 24 h under vacuum before testing.

TABLE I
Compositions and Preparation Methods
for the PET/Clay Hybrids

Sample abbreviation	Clay loading (%)	Concentration of the compatibilizer ^a	Pretreatment of clay by the compatibilizer
PET/Clay/C4	2.0	4.0	Yes
PET/Clay/C2	2.0	2.0	Yes
PET/Clay/C0	2.0	0	NA
PET/Clay/C4N	2.0	4.0	No

^aMolar ratio based on the amount of dimethyl terephthalate.

In situ polymerization

A typical synthesis procedure is given here. 12-Aminododecanoic acid-modified clay (1.12 g, ADA-clay) was suspended in 15 mL of anhydrous ethylene glycol (EG). The mixture was stirred by a mechanical stirrer under ultrasonic environment in nitrogen atmosphere for 2–4 h. Ethyl 4-dimethylaminobenzoate (0.43 g, EDMAB) was then added into the slurry, followed by high-shear stirring for 2 h.

To a dry, 250-mL, 3-necked flask equipped with a N₂ inlet, distilling apparatus, and mechanical stirrer, 53.4 g of DMT, 33 mL of EG, 1.71 g of EDMAB, and 0.12 g of manganese (II) acetate were added. The system was heated to 190°C, with stirring, under nitrogen atmosphere and maintained for 1–1.5 h until there was no more distillation. The pretreated ADA-clay/EDMAB mixture was then added, together with 0.08 g of triphenyl phosphate and 0.06 g of antimony (III) oxide, followed by heating to 280°C slowly. The mixture was kept at 280°C for 1–1.5 h until most of EG was distilled out. Then vacuum (<0.7 mbar) was applied. The reaction was continued for 1–2 h. The PET/clay hybrid obtained is named as PET/Clay/C4 in this article, for which the clay loading is 2 wt % and the molar ratio of EDMAB to DMT is 4 : 100. Reference samples with different compatibilizer content were also synthesized using the procedure similar to the aforementioned one. The specifications of all hybrid samples synthesized are given in Table I.

Characterization

Polarizing optical microscopy

A Nikon Optiphot-pol Universal Stage polarizing optical microscope (POM) was used to examine clay particle size in the hybrids. A thin piece of sample was sandwiched between two glass cover slips and placed on the digital hotplate under nitrogen. The hotplate was rapidly heated to 300°C and kept for 5 min to ensure the complete melting of PET crystallites. The melt was gently pressed to achieve a uniform thickness of about 0.1 mm. All observations were made

under crossed polarizers. A CCD camera was used to take photographs of the optical texture image.

Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) patterns were obtained using a Bruker AXS X-ray diffraction system with Cu $K\alpha$ radiation. An acceleration voltage of 40 kV and a current of 40 mA were employed. All samples were scanned from 2° to 33° with step size of 0.02°.

Transmission electron microscopy

The hybrids were sectioned with a Leica Ultracut UCT ultramicrotome. After sectioning, the ultra thin sections (~80 nm) were collected on 200 mesh copper grids coated with carbon. A JEOL 2010 transmission electron microscopy (TEM) operating at an accelerating voltage of 200 kV was used to examine the sections.

Intrinsic viscosity

Sample (0.200 g) was dissolved in 25 mL of 1,1',2,2'-tetrachloro methane/phenol (50 : 50 by weight) mixture. Measurements of intrinsic viscosity were performed using a capillary viscometer, at 25°C.

Thermal analysis

Thermal gravimetric analysis (TGA) was performed on TA Instruments Hi-Res TGA 2950 under nitrogen flow (50 mL/min) at a heating rate of 20°C/min. Thermal degradation temperature (T_d) was measured as the temperature at maximum weight loss rate. For each sample, TGA tests were repeated three times and an average T_d was taken, with the error bar estimated to be $\pm 2^\circ\text{C}$. Differential scanning calorimetry (DSC) measurements were performed on TA Instruments DSC2920 under nitrogen flow (50 mL/min) using the following scanning cycles: quickly heating up to 300°C and isothermal at 300°C for 5 min to eliminate heat history, then cooling down to 0°C, followed by heating up to 300°C. Both the cooling and the second heating rates were 5°C/min. Crystallization temperature (T_c) was measured from the cooling curves, while melting temperature (T_m) and heat of fusion (ΔH) were measured from the second heating curves. For each sample, DSC tests were repeated three times and average T_c , T_m , and ΔH were taken. The error bar for T_c and T_m was estimated to be $\pm 1^\circ\text{C}$. Dynamic mechanical analyses (DMA) were carried out under air-flow, using a TA instruments DMA 2980 dynamic mechanical analyzer, at a heating rate of 5°C/min, with specimen size of $20.0 \times 4.0 \times 1.5 \text{ mm}^3$. The samples were molded using a microinjector at injec-

tion temperatures ranging from 265 to 280°C, as determined by the samples' melting point. The mold was preheated to 50°C.

Chemical treatment

The molded hybrid and neat PET samples were immersed in a 10 wt % NaOH aqueous solution for 30 days. The weight of each sample was measured after 1, 15, and 30 days of immersion.

RESULTS AND DISCUSSION

Dispersion of clay in PET

Using POM, no clay particles could be observed in the melt of PET/Clay/C4, as shown in Figure 1(a). This indicates that an overall good dispersion of clay, at least at submicrometer scale, has been achieved with the addition of 4 mol % EDMAB. When the content of EDMAB was 2 mol % (PET/Clay/C2), clay particles and agglomerates were significantly smaller, although still visible, as shown in Figure 1(b), whereas when no EDMAB was used (PET/Clay/C0), many large clay particles and agglomerates were observed, as shown in Figure 1(c), which indicates the incompatibility between ADA-clay and PET matrix. The comparison demonstrated the effectiveness of the compatibilizer, EDMAB, in improving ADA-clay dispersion in PET. Figure 1(d) shows that small clay particles and agglomerates were observable in PET/Clay/C4N, which was prepared by adding 4 mol % EDMAB molecules to the reaction system directly without the pretreatment of ADA-clay with EDMAB. It demonstrated the importance of the pretreatment for obtaining well dispersed polymer/clay hybrids. The underlying mechanism is discussed here.

In this study, DMT and EG, instead of BHET, were used as monomers, which resembles common industrial processes. ADA-clay was added into the system at the second stage of the polymerization to minimize degradation of the modifier. At the second stage the melt was at first a mixture of DMT, EG, 2-hydroxyethyl methyl terephthalate, BHET and PET oligomers, and later mainly PET oligomers. In comparison with our previous study on *in situ* polymerization of BHET with ADA-clay,¹⁰ the compatibility between ADA-clay and the mixture was relatively poor because the mixture had higher aromatic content than did BHET, while ADA is completely aliphatic. It is believed that during the pretreatment of clay, some EDMAB molecules have been attracted into clay galleries because of the ionic interaction between the amino group of EDMAB and the acid group of ADA. This had made the clay surface more compatible with the reaction mixture. Moreover, as the ionic interaction is weak, EDMAB molecules are relatively mobile in the galler-

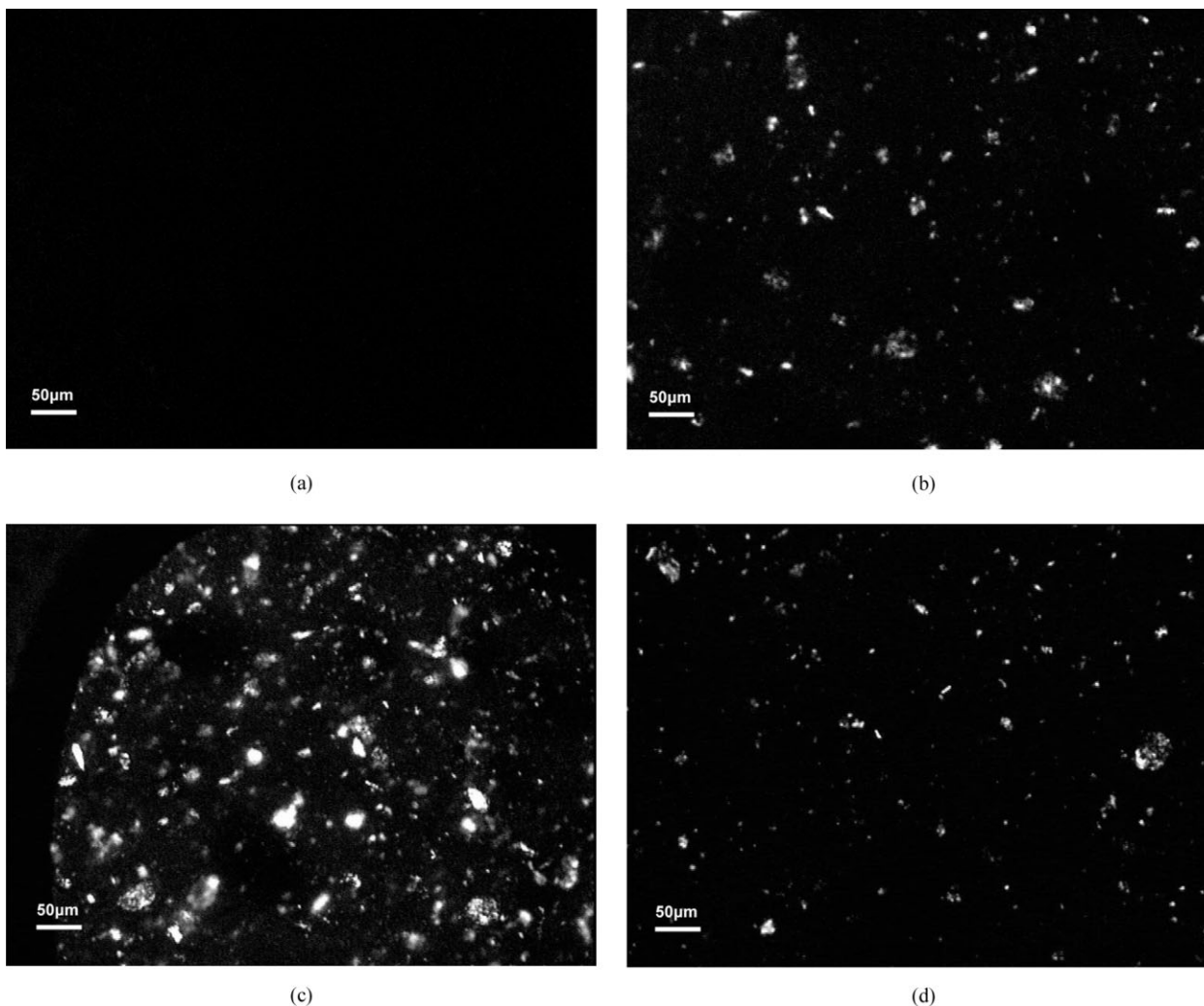


Figure 1 Polarizing optical microscopic pictures of (a) PET/Clay/C4, (b) PET/Clay/C2, (c) PET/Clay/C0, and (d) PET/Clay/C4N.

ies so that their ester groups could react with the ester groups of PET oligomers easily. On the other hand, EDMAB molecules outside of clay galleries can readily react with PET to form PET chains with amino end groups. Such chains may go into the galleries more easily as the chain ends are attracted to the acid group of ADA. Better clay dispersion can thus be achieved because tight stacks of layered silicates are easier to be broken when interlayer spacing is enlarged by the polymer chains going into the galleries. A schematic for the proposed mechanism is given in Figure 2.

Figure 3 shows WAXS patterns of ADA-clay and the PET/clay hybrids. ADA-clay has only one peak at $4.66^\circ 2\theta$ in the scanned range, which corresponds to d -spacing of about 19 Å. For the PET/clay hybrids, a weak peak is still distinct, which indicates the existence of regular stacks of layered silicates in PET matrix. The peak for the hybrids is, however, at a higher angle than that of ADA/clay, indicating that interlayer d -spacing of clay is reduced rather than ex-

panded after *in situ* polymerization. This was not a surprising result. Similar phenomenon has been observed from many other PET/clay nanocomposite systems made by *in situ* polymerization (transesterification) despite the fact that very different clay modifiers were used in these systems.^{10,11,17} The reduction in the interlayer d -spacing might be due to degradation of the modifiers induced by high vacuum or degradation of the modifiers caused by high temperature applied in the second stage of the polymerization, although experimental evidence for these has not been established. Nevertheless, experimental results^{10,11,17} have shown that clay dispersion is not greatly hindered by such a phenomenon because intercalation and exfoliation can be achieved to some extent before vacuum and high temperature are applied. In Figure 1, we have shown that clay particle size in PET/Clay/C4 is much smaller than that in the other three hybrids, which implies that EDMAB helped to introduce PET chains into clay galleries and caused breakdown of

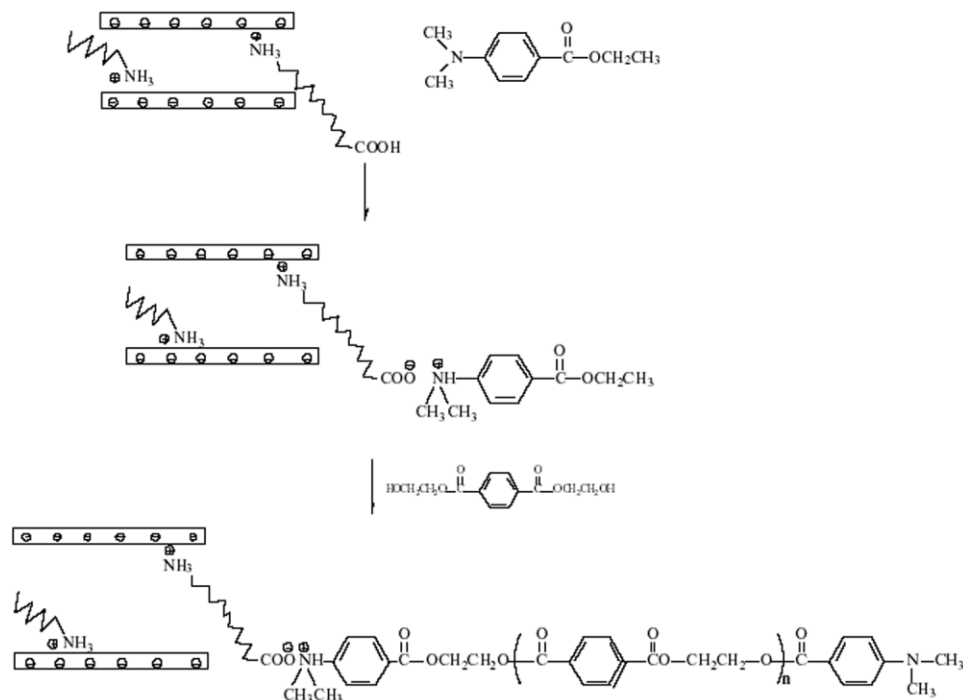


Figure 2 A schematic showing the proposed mechanism for *in situ* polymerization of PET/ADA-clay in the presence of the compatibilizer.

clay stacks. The WAXS patterns in Figure 3 confirm that PET/Clay/C4 indeed possesses a higher degree of clay intercalation when compared with PET/Clay/C2 and PET/Clay/C0. The 2θ value of the clay peak is 5.82° for PET/Clay/C4, which corresponds to an average d -spacing of 15.2 \AA , distinctively larger than that of PET/Clay/C2 and PET/Clay/C0 (14.5 \AA). It is worth noting that although the difference in d -spacing is small, it is certainly beyond experimental error and hence provided a clue for what happened during the *in situ* polymerization.

TEM micrographs of PET/clay/C4 are shown in Figure 4. It can be seen that micron-sized clay agglom-

erates still exist but their population is very small. The dispersed clay is mainly in stack rather than single layer form, while in most cases the width of the stacks is less than 50 nm . The PET/Clay/C4 synthesized in this work has, therefore, achieved nanometer-scale clay dispersion.

Effect of the compatibilizer on molecular weight

Assuming that only the ester group of EDMAB can join a PET chain while the amino group becomes an end group, the EDMAB/DMT molar ratio of 4/100 would lead to an average degree of polymerization of 52 at maximum. If a part of EDMAB molecules in the clay galleries did not take part in the polymerization or both amino and ester groups of EDMAB can react with PET, the degree of polymerization would be higher. To examine the actual effect of the compatibilizer on the molecular weight of the PET matrix, intrinsic viscosities of PET/clay/C4 as well as its references were measured. The results are summarized in Table II. When the EDMAB/DMT molar ratio was 2/100 (PET/clay/C2), the intrinsic viscosity of the hybrid was comparable to that of the sample without EDMAB (PET/clay/C0). When the EDMAB/DMT molar ratio was increased to 4/100, the intrinsic viscosity of the hybrids was significantly reduced. This verified that the addition of the compatibilizer does result in shorter polymer chains with amino end groups. It is worth noting that, in general, the PET/

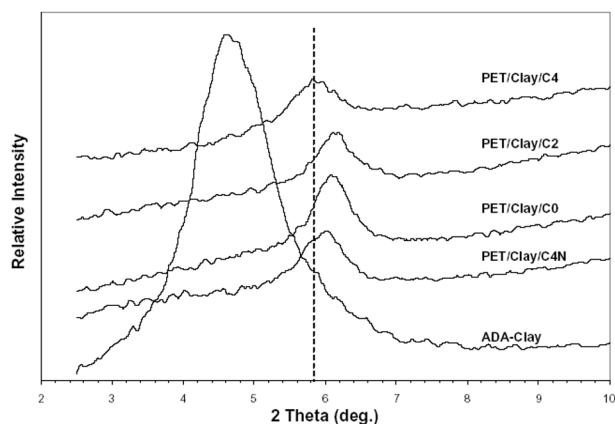
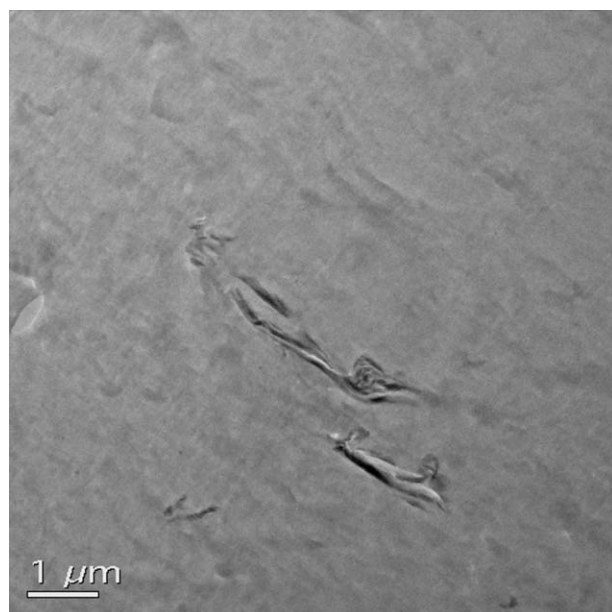
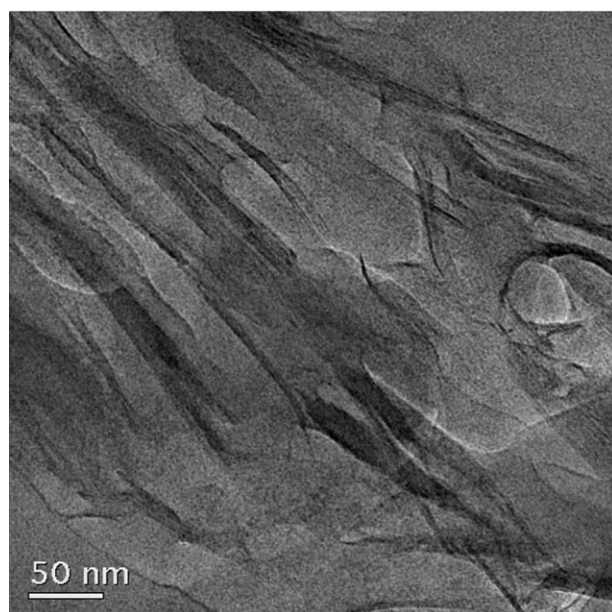


Figure 3 WAXS patterns of the PET/clay hybrids and ADA-clay.



(a)



(b)

Figure 4 TEM pictures of PET/Clay/C4.

clay hybrids made using the aforementioned procedure have a lower intrinsic viscosity than that of commercial PET. This is likely to be caused by the relatively low degree of vacuum employed. The potential impact of molecular weight variation on properties of the hybrids will be discussed in the following sections.

Thermal stability

Thermal stability of the hybrids was evaluated using TGA. Table III shows that PET/clay/C4 possesses

TABLE II
Intrinsic Viscosity (η) of PET/Clay/C4 and Its References

Sample	η (dL/g)
PET/Clay/C4	0.31
PET/Clay/C2	0.53
PET/Clay/C0	0.53
Neat PET	0.62

slightly higher thermal degradation temperature (T_d) than does PET/clay/C2 and PET/clay/C0. Considering that PET/clay/C4 has much lower intrinsic viscosity (molecular weight), which usually leads to lower T_d , the increase in T_d , although very slight, does support that the addition of the compatibilizer improved clay dispersion, and the well dispersed clay could thus act as a thermal barrier, making the composites more thermally stable.

Crystallization and melting behaviors

The cooling and the second heating DSC curves of the hybrids are shown in Figure 5. The corresponding crystallization temperature (T_c), melting temperature (T_m), and heat of fusion (ΔH) of the samples are listed in Table IV. ΔH is approximately proportional to the crystallinity of the PET matrix. Upon slow cooling at 5°C/min, PET/clay/C4 has a significantly higher crystallinity than do the other samples, which is likely to be caused by its lower molecular weight. The sharper crystallization peak of PET/clay/C4 signals the significant nucleating effect of well dispersed clay. The melting temperatures of the hybrids are lower than that of neat PET, which is mainly due to defects or reduced crystal size induced by the geometric hindering effect of clay particles.¹⁰ It is, however, intriguing that although PET/clay/C4 has the highest degree of clay dispersion and lowest molecular weight, its T_m is still higher than those of other hybrid samples. This implies that strong polymer–clay interaction may alter fine structures of spherulites. More in-depth studies need to be carried out to clarify this issue.

Dynamic thermomechanical properties

Thermomechanical properties of the PET/clay hybrids were investigated using DMA. The DMA curves

TABLE III
Thermal Degradation Temperature (T_d) of PET/Clay/C4 and Its References

Sample	T_d (°C)
PET/clay/C4	468
PET/clay/C2	463
PET/clay/C0	463
Neat PET	464

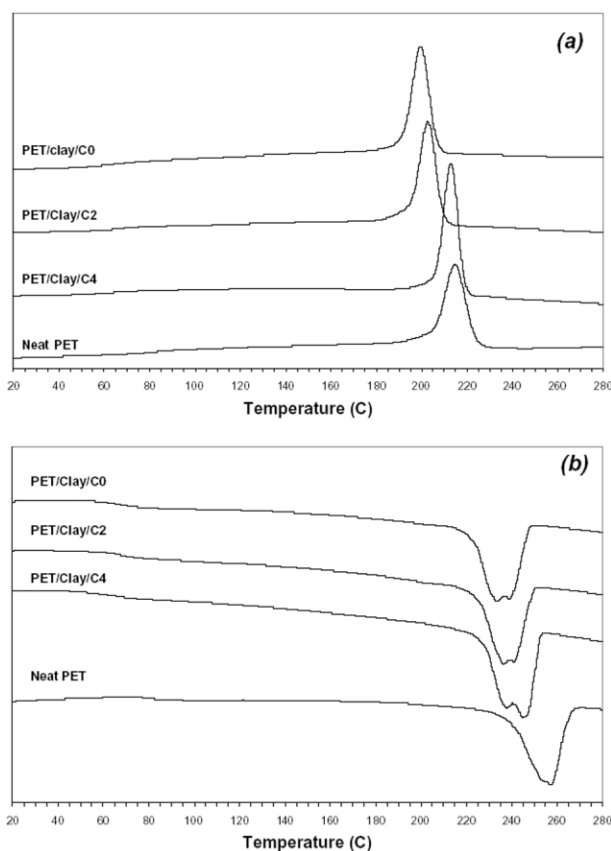


Figure 5 DSC curves of PET/Clay/C4 and its references: (a) cooling curves and (b) the second heating curves.

of PET/clay/C4 and two of its references are shown in Figure 6. At 25°C storage moduli of all the hybrids are higher than that of the neat PET, as listed in Table V. PET/clay/C4 has the highest modulus value of 3650 MPa, which was remarkably increased by nearly 30% over that of neat PET. As a comparison, the storage modulus of PET/clay/C0, which was made by *in situ* polymerization of PET and ADA-clay without the presence of the compatibilizer, is 3150 MPa, only 10% higher than that of the neat PET. The improvements were unlikely to be caused by the variation of crystallinity, as the samples were injected using a cold mold so that crystallinity is fairly low. It is well known that the mechanical properties of polymer/clay nanocom-

TABLE IV
Crystallization Temperature (T_c), Melting Temperature (T_m), and Heat of Fusion (ΔH_m) of PET/Clay/C4 and Its References

	% Wt change		
	After 1 day	After 15 days	After 30 days
PET/Clay/C4	-0.1	-2.3	-5.3
PET/Clay/C0	0.1	-4.1	-9.2
Neat PET	0.0	-4.7	-10.0

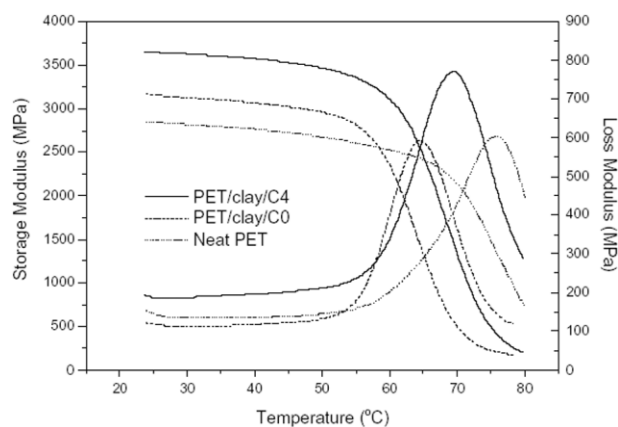


Figure 6 DMA curves showing storage and loss modulus of PET/Clay/C4 and its references, as a function of temperature.

posites depend greatly on nanometer-scale dispersion of clay. The aforementioned results demonstrated that introducing the compatibilizer into the system is helpful in improving the clay dispersion and hence enhancing the reinforcement effect of clay. To achieve a more impressive property improvement, further study is needed to combine the compatibilization approach with novel clay modifiers with better thermal stability.¹⁸

Figure 6 and Table V also show that glass transition temperatures (T_g) of the PET/clay hybrids were lower than that of the neat PET. This is likely to be accordant with their lower molecular weight. However, PET/clay/C4 shows higher T_g than does PET/clay/C0 despite the latter having much higher intrinsic viscosity than does PET/clay/C4. This fact implies that the interaction between clay and polymer chains can reduce chain mobility at interface and improve T_g , and the effect of molecular weight on T_g can be offset, to some extent, by the positive impact of clay on T_g in PET/clay/C4.

Resistance to base-catalyzed hydrolysis

Table VI shows the percentage weight loss of PET/clay/C4, PET/clay/C0, and neat PET samples after being treated with a NaOH solution. The weight losses are obviously due to base-catalyzed hydrolysis of PET.

TABLE V
Thermomechanical Properties of PET/Clay/C4 and Its References

Sample	Storage modulus (MPa) at 25°C	Glass transition temperature (°C)
PET/Clay/C4	3650	70
PET/Clay/C0	3150	66
Neat PET	2850	76

TABLE VI
Percentage Weight Loss of PET/Clay/C4 and Its
References After Treatment with a 10 wt %
NaOH Solution

	% Wt change		
	After 1 day	After 15 days	After 30 days
PET/Clay/C4	1.0–	3.2–	3.5–
PET/Clay/C0	0.1	1.4–	2.9–
Neat PET	0	7.4–	01–

Well-dispersed clay in PET/clay/C4 can effectively reduce the rate of such chemical decomposition, as the clay layers may act as physical barriers to reduce the diffusion rate of the decomposition products, which would in turn reduce the rate of the hydrolysis.

CONCLUSIONS

In this study, a compatibilizer containing an amino and an ester group was introduced into PET/ADA-clay system. The compatibilizer-modified ADA-clay was formed in a pretreating process via amine–acid interaction. The compatibilizer then participated in polymerization via its ester group through transesterification. The compatibilizer, as an intermedium between organoclay and polymer, improved clay dispersion in the polymer matrix and facilitated better intercalation of polymer chains into silicate layers. The PET/clay nanocomposite prepared by this novel

method possesses significantly higher storage modulus than does the neat PET.

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