PET-based Nanocomposites Made by Reactive and Remodified Clays

Mohammad Tarameshlou[1], Seyed-Hassan Jafari[1*], Hossein Ali Khonakdar[2], Afsane Fakhravar[3], and Madjid Farmahini-Farahani[1]

(1) School of Chemical Engineering, College of Engineering, University of Tehran,
P.O. Box: 11155-4563, Tehran, Iran
(2) Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran
(3) Department of Chemistry, Islamic Azad University,
P.O. Box: 19585-936, Tehran, Iran

A B S T R A C T

A novel modification method is used for the synthesis of reactive organoclays. A commercial organoclay (Cloisite® 30B) was therefore remodified with two kinds of acid chloride based monomers. Chlorinated diacid monomers of different chemical structures, terephthaloyl chloride (TPC) and adipoyl chloride (APC), were used as remodifying agents. The remodification process was confirmed by Fourier transform infrared (FTIR) spectroscopy. A series of poly(ethylene terephthalate) (PET)-based nanocomposites were formed by compounding the remodified clays and also the commercial organoclay with the polymer using a twin-screw extruder. The morphology of the nanocomposites was examined by transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques and their thermal stability by thermogravimetry analysis (TGA). The XRD and TEM investigations confirmed that the reactive remodified clays were much more efficiently dispersed in PET matrix compared to conventional commercial clay. The PET/virgin commercial clay nanocomposites showed a partially intercalated structure, however the PET/remodified clays showed exfoliated structure. Both remodification processes through aromatic and aliphatic moieties proved to be useful in aiding the exfoliation process, but the nanocomposites made from the remodified clays with APC monomer showed more improvement in thermal stability as compared to the samples made from TPC. This was attributed to the slightly better dispersion of APC-based clays in PET matrix. This study demonstrated the success of the reactive remodification process in more efficient dispersion of the clays in PET matrix changing the morphology from a partially intercalated to a more complete exfoliated structure and leading to an improved thermal stability.

(∗) To whom correspondence to be addressed.
E-mail: shjafari@ut.ac.ir

INTRODUCTION

There is a great interest developed in recent years on polyester/clay nanocomposites especially on poly(ethylene terephthalate) (PET) nanocomposites due to their vast range of applications [1-3]. The properties of PET/clay nanocomposites are known to be significantly dependent on the morphology and dispersion of clay particles in the PET matrix [4]. The modification of clay is normally needed for creating the desired morphology of nanocomposites and consequently resulting in enhanced thermal, mechanical and barrier properties in polymer nanocomposites [5,6]. Conventional non-reactive surfactants, alkyl- and aromatic-containing ammonium surfactants, alkyl

phosphonium surfactants, and polar structures are widely used for clay modification [7-9]. More recently some reactive surfactants such as polymerizable surfactants have also been used [10,11]. The non-reactive or conventional surfactants are suitable from the viewpoint of modification since they do not introduce any side reactions during the modification process. In most cases, the conventional surfactants change the morphology of the clay from large agglomerates into intercalated structures after mixing with polymers [12-14]. The use of reactive surfactants can improve exfoliation process in polymers having reactive functional groups. This has generally been attributed to the enhanced interaction between the polymer and the reactive surfactants which leads to extensive movement of the clay layers [15].

The polymerizable surfactants are more suitable for preparation of nanocomposites through in-situ polymerization [16]. Several reports show the effectiveness of this kind of surfactants, as compared to the conventional non-polymerizable surfactants, in dispersing clay in a polymeric matrix. But, from technological viewpoint it is clear that the in-situ polymerization is not a preferable method for preparation of polymeric nanocomposites [17]. On the other hand, due to high melt viscosity, degradation issues and thermodynamic restrictions, the melt mixing process is not inherently effective and suitable for development of a desired morphology for some polymers [18]. Some efforts have been made towards improvement of this method for having a better dispersion [12,19]. For example polymeric surfactants have been used in melt processing for preparation of polypropylene and polyethylene (PE) nanocomposites. The results showed that the high molecular weight surfactants led to an incomplete cation exchange, but promoted the nanocomposite formation [20]. Using end-functionalized oligomers was shown to be more efficient in dispersing organic modified montmorillonite (OMT) in a PE matrix [21]. In spite of all these efforts, it seems that still some efficient methods for obtaining a more complete exfoliated morphology through a simple melt mixing process is not yet completely established. Use of highly reactive surfactants might be a possible breakthrough for this problem. A simple

method to reach this goal is to make highly reactive interlayer functions through a process of remodification of conventional surfactants using suitable reactive monomers. The approach is such that the surfactants with reactive functional groups can be further modified with a compound, which reacts also with the polymer and creates strong bond between the components. To the best of our knowledge so far there are no reports on remodification of clays by reactive chlorinated monomers to use in poly(ethylene terephthalate) (PET)/clay nanocomposites.

Therefore, the aim of this work is to prepare a series of highly reactive clays through remodification of commercial clay (Cloisite® 30B) with two diacid chloride reactive monomers and to incorporate these into a PET matrix via a simple melt mixing process. The effectiveness of this approach is examined here. From economical and processing view points, remodification needs chlorinated monomers which are available with fair price and the remodification process does not demand highly technically advanced instrument and equipment. Moreover, considering the high thermal sensitivity of PET which imposes some restrictions on its compounding during melt mixing process, the remodification which enables an effective compounding with much lower shear rate might be helpful for more efficient energy consumption and optimum materials properties.

The main motivation for preparing PET/clay nanocomposites, as mentioned by several researchers, is to enhance its barrier properties especially in food and packaging industries [22]. For this purpose a good state of clay dispersion within PET matrix is essential. Our proposed remodification process of clay is an alternative approach to achieve a good state of clay dispersion which eventually could enhance the PET properties. Based on almost all published literature on polymer/clay nanocomposites, there is a major agreement on improved mechanical properties such as modulus and tensile properties and also barrier properties under 5 wt% of clay loadings if state of dispersion would be exfoliated as compared to intercalated and/or stacked morphology [22,23]. Therefore, it seems to be logical to anticipate that the mechanical and barrier properties of PET nanocomposites made from the remodified clays should be better than pure PET and/or nanocomposites based on

virgin clays due to the anticipated improved state of dispersion.

EXPERIMENTAL

Materials

The poly(ethylene terephthalate) (PET) with intrinsic viscosity of 0.8 g/dL and carboxyl end group of maximum 28.0 meq/kg, was obtained from Tongkook Co., South Korea (TexPet 874-C80). The organically modified montmorillonite (OMT grade) Cloisite® 30B was obtained from Southern Clay Products (USA). Cloisite® 30B is a type of organically modified montmorillonite with quaternary ammonium cation containing two hydroxyl groups. Adipoyl chloride (APC) monomer was purchased from Acros Organics and terephthaloyl chloride (TPC) monomer and dichloromethane solvent were obtained from Merck Company.

Remodification of Clay

The reactive remodified clays were synthesized by an esterification reaction between -OH groups of the virgin Cloisite 30B's surfactants (quaternary ammonium cation containing two hydroxyl groups) with acid chloride groups of APC and TPC monomers. A typical procedure for the preparation of reactive remodified clays was to take approximately 0.035 mol of APC and TPC to dissolve each in 150 mL dichloromethane. Then each solution was added dropwise to a suspension made from dispersion of 15 g OMT in 150 mL dichloromethane stirred under 600 rpm for 2 h. The mixture was then stirred with a reduced speed of 60 rpm with a magnetic stirrer at room temperature for 7 days. The stirring was then stopped and the suspensions were settled and washed with pure dichloromethane several times. The products (remodified clays) were dried under vacuum in order to extract the remaining solvent and/or non-reacted monomers. Finally, the products were further dried under a reduced pressure of 20 mmHg at 35°C to a constant weight. The remodified clays showed different colours compared to the virgin clay: off-gray for the one reacted with TPC monomer and brownish for the one reacted with APC monomer. The remodified clays were then characterized by FTIR.

Preparation of PET/Clay Nanocomposites

All the materials, PET and clays, were dried under vacuum for 4 h at 100°C to lower than 0.02% moisture content prior to the melt mixing process. Three sets of PET/clay nanocomposites with the remodified clays (designated as series T and A for the clays remodified with their respective TPC and APC monomers), and the virgin clay (designated as series C) were prepared by a melt-mixing process in a Brabender co-rotating twin-screw mini extruder (L/D = 25/0.8). The compositions of the prepared PET/clay nanocomposites are presented in Table 1. A screw speed of 60 rpm and the temperature profile of 245, 265, 265, 265 and 265°C (from feeding zone to die zone) were used for preparation of the samples. A dry nitrogen flow was continuously supplied to hopper and feeder to keep the materials dry and to avoid possible thermo-oxidative processes. The clay and polymer in a predetermined ratio were dry-blended

Table 1. Composition of the prepared PET/clay nanocomposites.

Sample	Clay content (wt%)	Type of monomer in remodification process
PET	0	-
C1 (PET/virgin clay)	1	-
C2 (PET/virgin clay)	2	-
T1 (PET/TPC-modified clay)	1	TPC
T2 (PET/TPC-modified clay)	2	TPC
A1 (PET/APC-modified clay)	1	APC
A2 (PET/APC-modified clay)	2	APC

prior to feeding. The extruded samples were used for different analyses.

Characterization

X-Ray diffraction (XRD) in a reflection mode was carried out with a Bruker D8 Advance diffractometer (Germany) using a Cu-K$_\alpha$ (λ = 1.54 Å) radiation at a voltage of 40 kV and a current of 30 mA. The scanning was performed at room temperature with a scattering angle (2θ) from 2 to 10 degree and a scanning rate of 0.01°/s. Background effect was removed by instrument software and the obtained patterns were analyzed. The basal spacing of the silicate layers (d) was calculated using Bragg's law, $n\lambda = 2d\sin\theta$. Microscopic images were made using a Zeiss 902A, Germany, transmission electron microscope (TEM), operating at 80 kV. Ultrathin sections were prepared on a Reichert OMU3 (Austria) microtome. The samples were first trimmed with iron knives to trapezoidal shaped faces. Subsequently, the ultrathin sections were microtomed from these faces with a diamond knife. The microtomed sections were collected in a water filled boat, attached to the diamond knife. The sections were collected out of the boat on copper TEM grids (square, 300 meshes). Thermogravimetric analysis (TGA) was used to study decomposition behaviour and thermal stability of the PET/clay nano-composites. The TGA measurements were carried out in an air atmosphere with a heating rate of 5 K/min using a Perkin-Elmer TGA instrument (USA). A Fourier transform infrared spectrometer (FTIR, Bruker Tensor 27, Germany) was used to check the reactions occurring between the diacid chlorinated monomers and hydroxyl functional groups located on the quaternary ammonium cations of the clay. The remodified clays were pressed into a thin film and then analyzed by the FTIR instrument.

RESULTS AND DISCUSSION

Remodification of Clay

The commercial organically modified clay (Cloisite 30B) contains two dangling hydroxyl groups on its modifier. The existence of these polar groups and their ability to form hydrogen bonding with PET functional groups significantly improve the compatibility between the clay and PET polymer. However, majority of the PET chains (about 70%) are terminated by OH functional groups which are not able to chemically react with OH functional groups of Cloisite 30B and only have some sort of weak intermolecular interactions. Although there are some compatibility between Cloisite 30B and PET chains but if one can change the OH functional groups of Cloisite 30B to highly reactive groups through reaction with TPC or APC monomers then its interaction with PET chain would increase significantly which improves the dispersion state of clay within PET matrix. The attached reactive monomers on clay surface can have a possibility to react with the PET chains. In this way the substituted groups can act as a coupling agent between interlayer modifiers and PET chains. This coupling improves the dispersion state of clays within PET matrix.

The remodification process can be done through an esterification reaction between the dangling -OH groups and acid chloride groups of the selected monomers. The bi-functional chlorinated monomers react from one side with functional group (-OH) of the clay modifier forming an ester bond, while the other functional group remains free to react with PET OH end-chains. In the resultant structures, the reacted monomers are situated at the end of the side group of the modifier and in this way the less reactive OH groups convert to a highly reactive -CO-Cl functional group.

The expected reactions for formation of the highly reactive modifiers were confirmed by FTIR spectroscopy. Figure 1 shows the FTIR spectra of virgin clay and the remodified clays in the region of 500-4000 cm^{-1}. Due to the presence of added functional groups, a difference is observed between the FTIR spectrum of the virgin clay and its remodified derivatives. In the FTIR spectra, presence of -C-O- stretching bands from the ester formation in the remodification process is discernible in the region of 1200-1300 cm^{-1}, which confirms the occurrence of the reactions. The -C-O- stretching bands are appeared at 1202 cm^{-1} (Figure 1c) and 1220 cm^{-1} (Figure 1b) for the remodified clays with TPC and APC monomers, respectively. In other regions, several spectroscopic stretching bands are
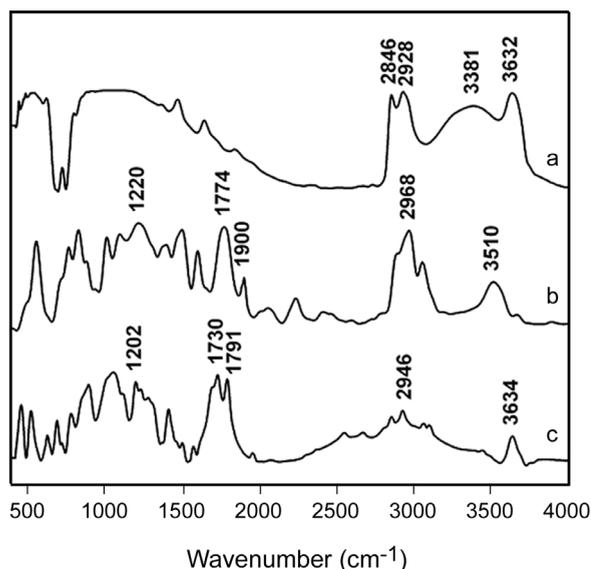
Figure 1. FTIR Spectra of (a) virgin clay, (b) APC-remodified clay and (c) TPC-remodified clay.

Figure 2. XRD Patterns of (a) virgin clay, (b) APC-remodified clay and (c) TPC-remodified clay.

discernible. For the virgin clay (Figure 1a), the bands at 3632 cm^{-1} and 3381 cm^{-1} are attributed to hydroxyl and amino (N-R) groups, respectively. The bands at 2928 cm^{-1} and 2846 cm^{-1} are attributed to amino groups as well. On the other hand, the bands at 1774 cm^{-1} and 1900 cm^{-1} are attributed to -CO-O- and -CO-Cl groups, respectively. The band at 2968 cm^{-1} is attributed to -CH groups attached to hydroxyl groups, and in the region of 1320 cm^{-1} to 1420 cm^{-1} the band is related to N-C stretching bands. A single band at 3510 cm^{-1} is related to hydroxyl group. In Figure 1c (clay remodified with TPC) the band at 2946 cm^{-1} is attributed to aromatic -CH groups. On the other hand, the bands at 1730 cm^{-1} and 1791 cm^{-1} are ascribed to -CO-O- and -CO-Cl groups, respectively. The bands in the region of 1350 cm^{-1} to 1450 cm^{-1} are related to N-C stretching bands and a single band at 3634 cm^{-1} is related to hydroxyl groups. Analyses of the remodified clays indicate the presence of both ester bond and acid chlorinated end functions. This implies that the organic structures of clay's interlayers have been remodified by the APC and TPC monomers.

Figure 2 shows the XRD patterns of the virgin clay and its remodified derivatives. The XRD pattern of the virgin clay shows a strong peak at 2θ = 4.77° corresponding to basal spacing of 18.5 Å, while both remodified clays with TPC and APC monomers show strong diffraction peaks at 2θ = 4.76° corresponding
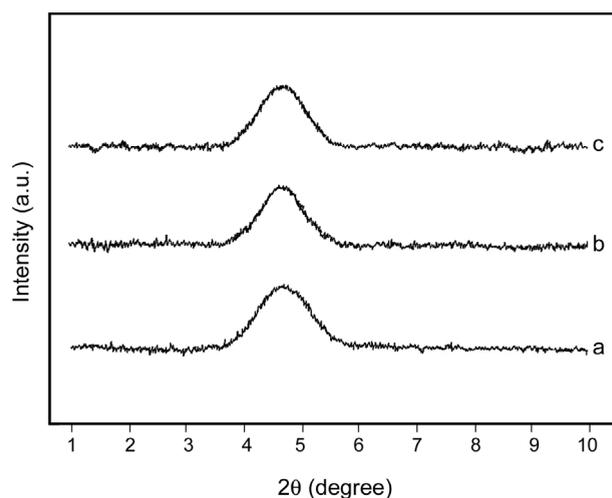
to basal spacing of 18.53 Å. Considering the broad bands shown in Figure 2, the difference between the basal spacings is nil and hence it can be stated that the structure of clay layers remains intact during the remodification process.

Properties of PET/Clay Nanocomposites
In order to check the role of remodification process on nanometric dispersion of clays in PET matrix, different sets of PET/clay nanocomposites were made
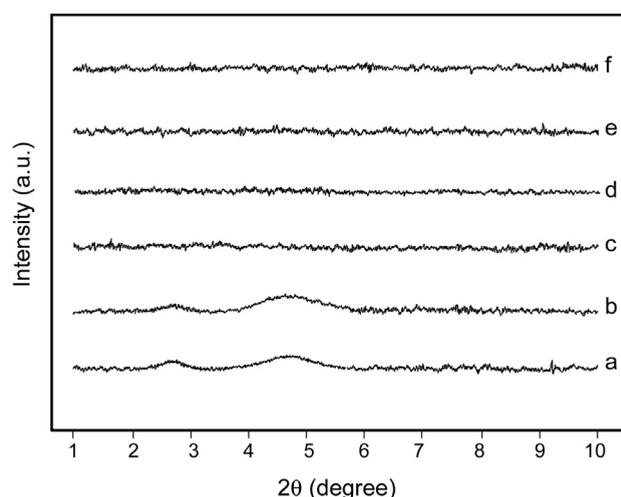

Figure 3. XRD Patterns of PET nanocomposites: made from different types of clay with varying clay loadings: (a) 1 wt% virgin clay, (b) 2 wt% virgin clay, (c) 1 wt% TPC-modified clay, (d) 2 wt% TPC-modified clay, (e) 1 wt% APC-modified clay, and (f) 2 wt% APC-modified clay.

through a melt mixing process under similar processing conditions. The performance of these nanocomposites was compared with a PET/virgin clay sample as reference.

The XRD patterns of the PET/remodified clays and PET/virgin clay nanocomposites are presented in Figure 3. Two strong diffraction peaks at 2θ = 4.77° and 2θ = 2.7° corresponding to basal spacings of 18.5 Å and 32.76 Å were displayed in the case of PET/1% virgin clay (C1) and PET/2% virgin clay (C2), respectively. The appearance of the peak at the same position similar to the virgin clay (2θ = 4.77°, as observed in Figure 2a), is a hint for ineffectiveness of

the virgin clay in proper dispersion within the PET matrix.

The XRD patterns of PET/remodified clay nanocomposites containing 1 and 2 wt% of remodified clays presented in Figure 3 (curves c and d) do not display any peaks. This might be an evidence for occurrence of effective intercalation and exfoliation processes. Although one should note that the absence of such peaks might be also due to destruction of clay structures as a result of thermal decomposition of its modifiers. Therefore, TEM investigations are necessary to corroborate the results about the dispersion state of clays within a polymer
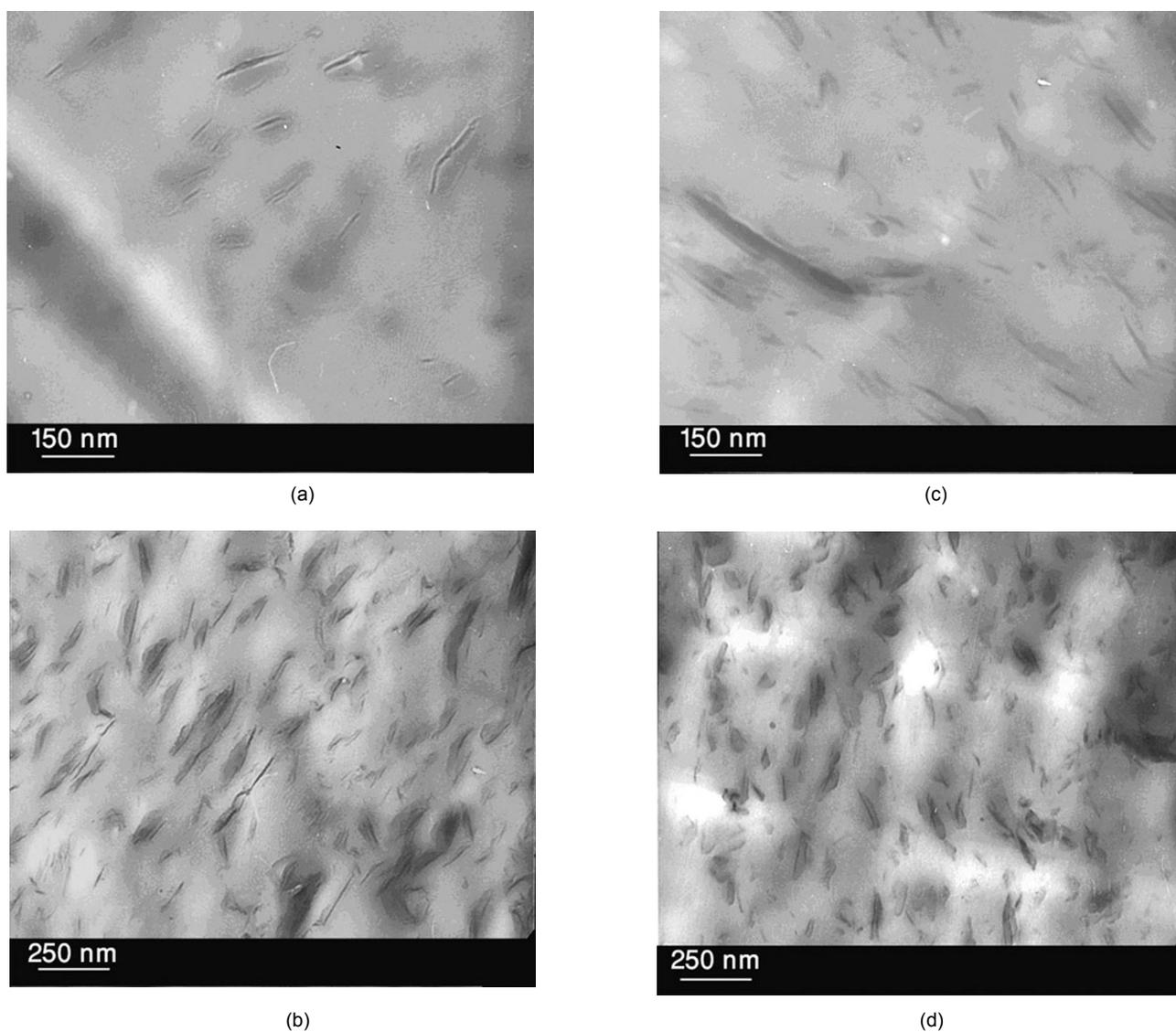

Figure 4. TEM Micrographs of PET nanocomposites loaded with: (a) 1 wt% APC-modified clay, (b) 2 wt% APC-modified clay, (c) 1 wt% TPC-modified clay, and (d) 2 wt% TPC-modified clay.

matrix.

Both the remodified clays have two dangling acid chloride functional groups which are highly prone to react with hydroxyl end groups of PET chains. This is a very fast reaction which can improve the interaction between the clay and PET matrix significantly. Therefore, the delamination and exfoliation processes in PET/remodified clays nanocomposites occur more efficiently. Direct evidence of nanometric dispersion of exfoliated montmorillonite can be found in the TEM examination of the PET/remodified clays (Figure 4). TEM Micrographs of C1 and C2 are necessary in order to be able to claim that the remodification has improved the intercalation or exfoliation process. However, since the XRD patterns of the virgin clay-PET nanocomposites did not show any evidence of highly exfoliated clay morphology; therefore, TEM investigation was not performed on the virgin clay-PET samples to examine the state of clay dispersion. It is clearly seen that generally in both systems (APC and TPC based systems) a homogeneous distribution of the clay layers exists within the PET matrix. Some instances of stacking of few layers also exist but generally the isolated layers are more prominent. The slight differences between these two series of samples might be attributed to the differences in the APC and TPC structures. It is expected that presence of a bulky and rigid aromatic group in the TPC structure makes it less prone to diffuse in between the clay layers as compared to the APC with its aliphatic structure. However, the highly reactive nature of these clays leads to development of homogeneous morphologies in these two systems.

It is expected that the difference between the morphology of the PET/virgin clay and PET/
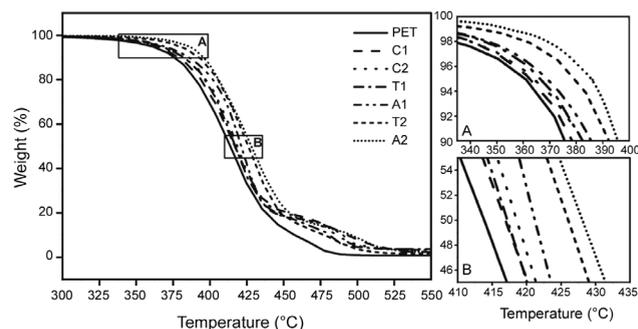

Figure 5. TGA thermograms of the virgin PET and PET/clay nanocomposites.

remodified clays nanocomposites should affect their thermal properties. The TGA thermograms of the prepared nanocomposites with different clay loadings are given in Figure 5. It can be observed from the TGA thermograms that thermal degradation characteristic temperatures of PET/remodified clays nanocomposites are higher than those of pure PET and PET/virgin clay nanocomposites. It should be noted that there is an overlap of some of TGA curves at the beginning of part A in Figure 5. However, at higher temperatures (region B) the differences between the curves become clearer. Table 2 illustrates the onset of degradation temperature (T_{onset}) and maximum degradation temperature (T_{max}) of the prepared nanocomposites. From the data presented in Table 2, it can be seen that by addition of clay and increasing the clay content the T_{onset} of PET increases. Compared to the virgin PET, the increase in T_{onset} is about 4°C for PET nanocomposites loaded with 2 wt% of virgin clay, 8°C with 2 wt% TPC-modified clay and beyond 20°C with 2 wt% APC-modified clay. The higher stability observed for APC-

Table 2. Thermal degradation characteristic of PET and PET/clay nanocomposites.

Sample	T_{onset} (°C)	T_{max} (°C)
PET	360.8	414.1
C1 (PET/virgin clay)	362.5	417.1
C2 (PET/virgin clay)	364.2	471.4
T1 (PET/TPC-modified clay)	366.2	419.1
T2 (PET/TPC-modified clay)	368.3	421.2
A1 (PET/APC-modified clay)	376.2	426.1
A2 (PET/APC-modified clay)	385.4	428.3

based remodification, as compared to the TPC-based remodification, can be attributed to the slightly better dispersion of the former in the PET matrix. Accordingly, T_{max} of PET/virgin clay nano-composites is lower than PET/remodified clays. The increase of T_{max} for T1 and T2 samples is lower than those of A1 and A2, respectively. Therefore, thermal stability of nanocomposites prepared by APC remodified clays is significantly higher than those of nanocomposites made from TPC-based remodified clays. It can be observed that the remodification process has led to about 20°C improvement in thermal stability of the PET/remodified clays as compared to the PET/virgin clay nanocomposites, at 2 wt% clay loadings. This also confirms the success of the reactive remodification process in better dispersion of clays leading to improvement of thermal stability.

CONCLUSION

We were able to synthesize two series of interlayer reactive clays by a new approach of remodifying commercial organically modified clay (Cloisite® 30B) through reaction with two kinds of diacid chloride monomers. The monomers were selected in such a way that they were able to make ester bond from one side with dangling hydroxyl groups of the clay modifier, and interact from the other side with the hydroxyl end groups of the PET. With the use of these two series of reactive remodified clays, PET/clay nanocomposites were made through a simple melt mixing process and their behaviour was compared with a conventional PET/clay nanocomposites prepared under similar processing conditions. The XRD and TEM investigations confirmed that the reactive remodified clays are much more efficiently dispersed in PET matrix than the conventional commercial clay. The PET/virgin clay nano-composites showed a partially intercalated structure. However, the PET/remodified clays showed exfoliated structure. Both remodification processes through aromatic and aliphatic moieties proved to be useful in aiding with the exfoliation process. The nanocomposites made from the remodified clays with APC monomer showed a better improvement in thermal stability as compared to nanocomposites

made from TPC. This was attributed to the slightly better dispersion of APC-based clays in PET matrix. This study demonstrated the success of the reactive remodification process in better dispersion of clays leading to improvement of thermal stability and may shed light on production of next generation of nano-composites with highly improved properties.

REFERENCES

1. Yin M, Li CC, Guan GH, Yuan XP, Zhang D, Xiao YN, In-situ synthesis of poly(ethylene terephtha-late)/clay nanocomposites using TiO_2/SiO_2 sol-intercalated montmorillonite as polycondensation catalyst, *Polym Eng Sci*, **49**, 1562-1572, 2009.

2. Chen ZJ, Luo P, Fu Q, Preparation and properties of organo-modifier free PET/MMT nanocompos-ites via monomer intercalation and in situ poly-merization, *Polym Adv Technol*, **20**, 916-925, 2009.

3. Khonakdar HA, Jafari SH, Asadinezhad A, A review on homopolymer, blends, and nanocom-posites of poly(trimethylene terephthalate) as a new addition to the aromatic polyesters class, *Iran Polym J*, **17**, 19-38, 2008.

4. Ammala A, Bell C, Dean K, Poly(ethylene tereph-thalate) clay nanocomposites: improved dispersion based on an aqueous ionomer, *Compos Sci Technol*, **68**, 1328-1337, 2008.

5. Alexandre M, Dubois P, Polymer-layered silicate nanocomposites, *Mater Sci Eng*, **28**, 3520-3569, 2000.

6. Xu XF, Ding YF, Wang F, Wen B, Zhang JH, Zhang SM, Yang MS, Effects of silane grafting on the morphology and thermal stability of poly(ethylene terephthalate)/clay nanocomposites, *Polym Compos*, **31**, 825-834, 2010.

7. Okamoto M, Morita S, Kim HY, Kotaka T, Tateyama H, Dispersed structure change of smectic clay/poly(methyl methacrylate) nano-composites by copolymerization with polar comonomers, *Polymer*, **42**, 1201-1206, 2001.

8. Zhang W, Chen D, Zhao Q, Fang Y, Effects of different kinds of clay and different vinyl acetate content on the morphology and properties of EVA/clay nanocomposites, *Polymer*, **44**, 7953-

7961, 2003.

9. Yei DR, Kuo SW, Su Y, Chang F, Enhanced thermal properties of PS nanocomposites formed from inorganic POSS-treated montmorillonite, *Polymer*, **45**, 2633-2640, 2004.

10. Fu X, Qutubuddin S, Polymer-clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene, *Polymer*, **42**, 807-813, 2001.

11. Xu M, Choi YS, Kim YK, Wang KH, Chung IJ, Synthesis and characterization of exfoliated poly(styrene-*co*-methyl methacrylate)/clay nanocomposites via emulsion polymerization with AMPS, *Polymer*, **44**, 6387-6395, 2003.

12. Wang K, Liang S, Du R, Zhang Q, Fu Q, The interplay of thermodynamics and shear on the dispersion of polymer nanocomposite, *Polymer*, **45**, 7953-7960, 2004.

13. Tyan H, Leu CM, Wei KH, Effect of reactivity of organics-modified montmorillonite on the thermal and mechanical properties of montmorillonite/polyimide nanocomposites, *Chem Mater*, **13**, 222-226, 2001.

14. Calcagno CIW, Mariani CM, Teixeira SR, Mauler RS, The effect of organic modifier of the clay on morphology and crystallization properties of PET nanocomposites, *Polymer*, **48**, 966-974, 2007.

15. Zhang WA, Chen DZ, Xu HY, Shen XF, Fang YE, Influence of four different types of organophilic clay on the morphology and thermal properties of polystyrene/clay nanocomposites prepared by using the γ-ray irradiation technique, *Eur Polym J*, **39**, 2323-2328, 2003.

16. Samakande A, Hartmann PC, Cloete V, Sanderson RD, Use of acrylic based surfmers for the preparation of exfoliated polystyrene-clay nanocomposites, *Polymer*, **48**, 1490-1499, 2007.

17. Costache MC, Heidecker MJ, Manias E, Wilkie CA, Preparation and characterization of poly(ethylene terephthalate)/clay nanocomposites by melt blending using thermally stable surfactants, *Polym Adv Technol*, **17**, 764-771, 2006.

18. Tarameshlou M, Jafari SH, Khonakdar HA, Farmahini-Farahani M, Ahmadian S, Synthesis of exfoliated polyamide 6,6/organically modified montmorillonite nanocomposite by in-situ interfacial polymerization, *Polym Compos*, **28**, 733-738, 2007.

19. Treece MA, Zhang W, Moffitt RD, Oberhauser JP, Twin-screw extrusion of polypropylene-clay nanocomposites: influence of masterbatch processing, screw rotation mode, and sequence, *Polym Eng Sci*, **47**, 898-911, 2007.

20. Zhang J, Wilkie CA, Polyethylene and polypropylene nanocomposites based on polymerically-modified clay containing alkylstyrene units, *Polymer*, **47**, 5736-5743, 2006.

21. Osman MA, Jorg EPR, Suter UW, Effect of non-ionic surfactants on the exfoliation and properties of polyethylene-layered silicate nanocomposites, *Polymer*, **46**, 8202-8209, 2005.

22. Bharadwaj RK, Modeling the barrier properties of polymer-layered silicate nanocomposites, *Macro-molecules*, **34**, 9189-9192, 2001.

23. Tjong SC, Structural and mechanical properties of polymer nanocomposites, *Mater Sci Eng R-Reports*, **53**, 73-197, 2006.