

Effects of Melt-Processing Conditions on the Quality of Poly(ethylene terephthalate) Montmorillonite Clay Nanocomposites*

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ABSTRACT: Organically modified montmorillonite was synthesized with a novel 1,2-dimethyl-3-*N*-alkyl imidazolium salt or a typical quaternary ammonium salt as a control. Poly(ethylene terephthalate) montmorillonite clay nanocomposites were compounded via melt-blending in a corotating mini twin-screw extruder operating at 285 °C. The nanocomposites were characterized with thermal analysis, X-ray diffraction, and transmission electron microscopy to determine the extent of intercalation and/or exfoliation present in the system. Nanocomposites produced with *N,N*-dimethyl-*N,N*-dioctadecylammonium treated montmorillonite (DMDODA-MMT), which has a decomposition temperature of 250 °C, were black, brittle, and tarlike resulting from DMDODA degradation under the processing conditions. Nanocomposites compounded with 1,2-dimethyl-3-*N*-hexadecyl imidazolium treated MMT, which has a decomposition temperature of 350 °C, showed high levels of dispersion and delamination. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 40: 2661–2666, 2002

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INTRODUCTION

Poly(ethylene terephthalate) (PET) is a low-cost, high-performance polymer that finds use in a

wide variety of applications. With only minor differences in molecular weight and modifications, PET is used in textiles (clothes, curtains, and furniture upholstery), reinforcement of tires and rubber goods, and food and beverage packaging (water, soft drink and isotonic beverage bottles, sauce and jam jars, etc).¹ Incorporation of nano-dispersed clay can have a significant impact on such applications, potentially imparting higher flame resistance² for textiles, to decreasing oxygen permeability in food packaging, and increasing the modulus in both reinforcement and packaging products. In each of these applications, the

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clay modification does not lead to degradation of other existing polymer properties.³

Polymer/clay nanocomposites are synthesized via melt-intercalation, common solvent mixing, or *in situ* polymerization.⁴ In the process of melt-mixing, the layered silicate is mixed with a molten polymer matrix. If the silicate surfaces are sufficiently compatible with the chosen polymer, then the polymer can enter the interlayer space and form either an intercalated or an exfoliated nanocomposite.⁵ Exfoliation, or a high level of intercalation, is important in producing a polymer/clay nanocomposite because it is only with such separation of individual clay sheets that high aspect ratios are obtained with the inorganic reinforcing materials.

Matayabas et al.⁶ prepared PET nanocomposites by melt-compounding varying amounts of Claytone APA, a commercial organoclay,⁷ with a 1,4-cyclohexanedimethanol modified PET. Physical mixtures of the organically modified (om) clay and PET copolymer (co-PET) were dried under vacuum at 120 °C before extrusion at 280 °C. The result was a decrease in the co-PET inherent viscosity, indicating degradation. This degradation increased in severity as the clay content increased from 0.36 to 6.7 wt %. In an attempt to compensate for the degradation, a higher-molecular-weight PET was used, but unfortunately this led to more severe degradation.

The synthesis of PET clay nanocomposites has not been as successful as compared with other polymers. Takekoshi et al.⁸ prepared polyester clay nanocomposites via *in situ* polymerization with quaternary ammonium salt modified clay and cyclic PET oligomers. They observed good nanoparticle dispersion and improved physical properties, such as improved impact strength and elastic modulus. A more commercially viable approach with conventional polymer processing techniques is melt-mixing of the polyester with om-clay.⁹ However, as Matayabas et al.⁶ found, this approach has been far less successful usually leading to poorly dispersed clay particles. This may be attributed to the low decomposition temperature (250 °C) of the organic modifier bound to the clay surface.

In this study, we melt-blended PET with novel organically modified montmorillonite (om-MMT) at various blending conditions to attempt to prepare nanocomposites with high MMT dispersion and delamination. The novel imidazolium-based organic modifier, 1,2-dimethyl-3-*N*-hexadecyl imidazolium, is thermally stable at PET

processing conditions^{4,10} and was used to maximize MMT and PET compatibility. Previous work¹⁰ has demonstrated that the exchange of 1,2-dimethyl-3-*N*-alkyl imidazolium ions for sodium ions in natural MMT produces an organophilic MMT with a 100 °C improvement in thermal stability (in N₂) when compared with alkylammonium-treated MMT fillers. *N,N*-dimethyl-*N,N*-dioctadecylammonium MMT was also used in this study for comparison. Various blending conditions were explored to maximize dispersion and delamination.

EXPERIMENTAL¹¹

Materials

All reagents were used as received from Aldrich Chemical Co. unless otherwise indicated. Sodium-treated montmorillonite clay (Na-MMT) was provided by Southern Clay Products as a 2.95 wt % Na-MMT aqueous slurry [trade name sodium Cloisite, cation-exchange capacity (CEC) value of 92 mmol of exchangeable sites per 100 g of Na-MMT, specific gravity 2.6]. Imidazolium salts were used as received from the Naval Research Laboratory.¹² All PET polymers and copolymers were provided by KoSa.¹³

Synthesis

om-MMT

The om-clays were prepared by ion exchange of Na-MMT (CEC = 92 mmol/100 g, Southern Clay Products) with either 1,2-dimethyl-3-*N*-hexadecyl imidazolium tetrafluoroborate^{10,14} (hexadecyl-BF₄, Fig. 1) or *N,N*-dimethyl-*N,N*-dioctadecylammonium bromide (DMDODA-Br, Aldrich). The ion-exchange procedure used in this work was a slight modification from that in the literature;¹⁵ 1.2 equiv of organic modifier, with respect to the clay CEC value, was used instead of the usual 2 equiv. This change reduced the "soapiness" of so-

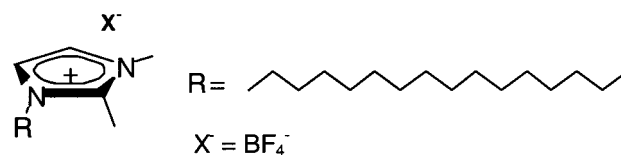


Figure 1. Structure of 1,2-dimethyl-3-*N*-hexadecyl imidazolium tetrafluoroborate used to organically modify Na-MMT.

lutions and helped facilitate their filtration. Na-MMT slurry (101.7 g) was agitated at 60 °C in a 250-mL Erlenmeyer flask fitted with a thermometer. In a separate 250-mL Erlenmeyer flask, 1,2-dimethyl-3-*N*-hexadecylimiazolium-BF₄ (1.35 g, 3.31 mmol) was dissolved in a 60 °C water/ethanol (EtOH) solution (~10 mL). This was then added to the heated Na-MMT slurry. The om-MMT immediately precipitated; however, the 60 °C reaction mixture was agitated with a magnetic stirrer for an additional 5 h and then stirred overnight at room temperature. om-MMT was filtered with a medium frit ceramic filter (15 μm) and washed 15 times (100 mL each) with distilled water. The crumbly solid (mustard yellow) was Soxhlet extracted with EtOH for 10 h and then dried at 90 °C for 1 h, and then at 150 °C for 2 h in a convection oven. It was ground to a fine powder with a mortar and pestle and dried overnight at 150 °C in a vacuum oven (533 Pa). The mustard yellow solid (3.56 g, 85.7% yield, 88.1% om) was cooled to room temperature under vacuum before characterization.

MMT/PET Nanocomposites

MMT/PET nanocomposites (2.85 g PET, nominally a mass fraction of 5% om-MMT) were compounded via melt-blending in a corotating mini twin-screw extruder operating at 285 °C in a nitrogen atmosphere at 21 rad/s (200 rpm) and 31 rad/s (300 rpm) screw speeds as well as residence times of 2, 5, and 7 min. Before processing, PET pellets (KoSa) and om-MMT were dried overnight under high vacuum (533 Pa) at 120 and 150 °C, respectively.

Characterization

Before characterization, pellets of commercial PET polymer (0.76 dL/g intrinsic viscosity, measured in a 1% mass fraction dichloroacetic acid solution; number-average molecular weight: 25,000 g/mol) produced from dimethyl terephthalate and ethylene glycol with a manganese acetate/antimony oxide catalyst system, provided by KoSa, and MMT/PET nanocomposites were dried overnight at 120 °C. om-MMT was dried overnight at 150 °C under high vacuum (533 Pa) and cooled to room temperature before removing from the vacuum oven.

Thermogravimetric analysis (TGA) experiments were conducted on a thermal analysis SDT-2960 simultaneous TGA/differential ther-

mal analysis instrument. Samples were heated at 10 °C/min to 800 °C in a nitrogen or air atmosphere. The standard uncertainty of decomposition temperatures reported is ±1 °C.

X-ray diffractions (XRDs) were obtained with a Philips diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm), a step size of 0.02° 2θ, and count times of 2 s. *d*-Spacing experimental standard uncertainty was ±1.2 Å. Before analysis, om-MMT and Na-MMT were ground to particle sizes less than 40 μm, and polymers were melt-pressed into 1-mm sheets.

Transmission electron microscopy (TEM) samples of PET nanocomposites were prepared with ultramicrotomy at -110 °C to cut 70-nm-thick sections. The sections were transferred onto carbon-coated Cu grids of 200 mesh. Bright-field TEM images of the PET nanocomposites were obtained at 120 kV under low-dose conditions with a Philips 400T electron microscope with Kodak SO-161 film at magnifications of 20,000, 56,000, and 160,000.

RESULTS AND DISCUSSION

om-MMT

MMT was organically treated with either a conventional melt-extrusion organic modifier (DMDODA-Br) or a novel imidazolium salt (hexadecyl-BF₄). Typical melt-processing temperatures for PET [melting temperature (T_m): 254 °C] were 285–290 °C. Nanocomposites produced with DMDODA-MMT^{16,17} were black and brittle resulting from DMDODA degradation at PET processing conditions and therefore were not of interest for full characterization and testing. The imidazolium-based organic modifiers were thermally stable at the processing conditions.

Results from TGA and XRD analyses of Na-MMT and the two om-MMT fillers are provided in Table 1. The decomposition temperatures (T_{dec} 's) in air and nitrogen on the basis of the 5 wt % loss are well above the PET processing temperature. In addition, isothermal TGA of hexadecyl-MMT (and hexadecyl-MMT/PET) at 285 °C for 10 min in air showed no mass loss, thus supporting the observations that hexadecyl-MMT is thermally stable under the processing conditions. TGA mass loss up to 800 °C in air (minus water from hydrated unexchanged sodium ions and dehydroxylation, total of 6.1 mass %) yields the percentage

Table 1. Organically Modified Clay Properties Observed from TGA and XRD

Modified Cloisite Clay	TGA		XRD	
	T_{dec} (°C) N ₂	T_{dec} (°C) Air	CEC Exchange (%)	Gallery Spacing (Å)
Na-MMT	—	—	—	11.9
Hexadecyl-MMT	392	323	88.1	18.2
DMDODA-MMT	304	285	93.8	25.0

of organic mass content of om-MMT. The organic content is reported (Table 1) as the percentage of the theoretical mass calculated from the CEC content (percentage of CEC exchange). Generally, 90% exchange is observed, and as shown in Table 1, we observed similar values.

The distance between MMT sheets after organic treatment, the *d*-spacing or gallery spacing, was determined by XRD. The increase in gallery spacing, as observed by XRD and compared to Na-MMT, confirmed the synthesis of the imidazolium-based MMT. Larger gallery spacings normally translate into increased dispersion and delamination in the polymer.

MMT/PET Nanocomposites

MMT/PET nanocomposites were melt-blended (3-g scale) at various mixing times and screw speeds; the conditions and samples are described in Table 2. These nanocomposites were analyzed with conventional nanocomposite characterization techniques (TGA, XRD, and TEM).

XRD of the nanocomposites indicates a shift in the major peak of hexadecyl-MMT from $4.8^\circ 2\theta$ to a weaker, broader peak ranging from 2.8 to $3.2^\circ 2\theta$. XRD spectra of nanocomposites CD 5 and CD 13 (Fig. 2) contained no major peaks.

TEM images of selected nanocomposites are provided in Figures 3 and 4. The TEM images showed varying levels of om-MMT dispersion and

delamination in hexadecyl-MMT/PET nanocomposites (CD 5, 9, 12, and 13). TEM images of nanocomposite CD 12 (Fig. 3) demonstrate that this nanocomposite has the highest degree of om-MMT delamination and dispersion obtained in this study (nominally less than $0.1 \mu\text{m}$ between clay layers; hexadecyl-MMT/PET melt-mixed at 21 rad/s for 2 min in nitrogen atmosphere). The hexadecyl-MMT in nanocomposite CD 12 appears homogeneously distributed throughout the PET matrix (four separate sections were analyzed) with tactoids rarely larger than three clay sheets. A tactoid is defined as a clay particle consisting of intercalated clay sheets. This nanocomposite is considered to be a mixed delaminated/intercalated system because complete delamination was not achieved. Hexadecyl-MMT/PET nanocomposites CD 5(not shown), CD 9 (not shown), and CD 13 (TEM images provided in Fig. 4) contained lower levels of om-MMT dispersion and delamination, with larger tactoids of nominally seven sheets and no single sheets.

The restrictions of XRD are depicted in the analysis of the samples (Fig. 2). XRD has a rather sharp and large peak (considering the om-MMT concentration) at $3^\circ 2\theta$ for intercalated MMT sheets. This generally indicates poor clay delamination, and because of the sharpness, a large amount of well-defined tactoids. However, TEM leads to a contrary conclusion showing a high level of dispersion and delamination in the sam-

Table 2. Composition and Extrusion Conditions of PET Nanocomposites

Sample	Sample Composition (5 wt % Clay)	Screw Speed (rad/s)	Residence Time (min)
CD 12	PET + hexadecyl-MMT	21	2
CD 5	PET + hexadecyl-MMT	21	5
CD 9	PET + hexadecyl-MMT	21	7
CD 13	PET + hexadecyl-MMT	31	5

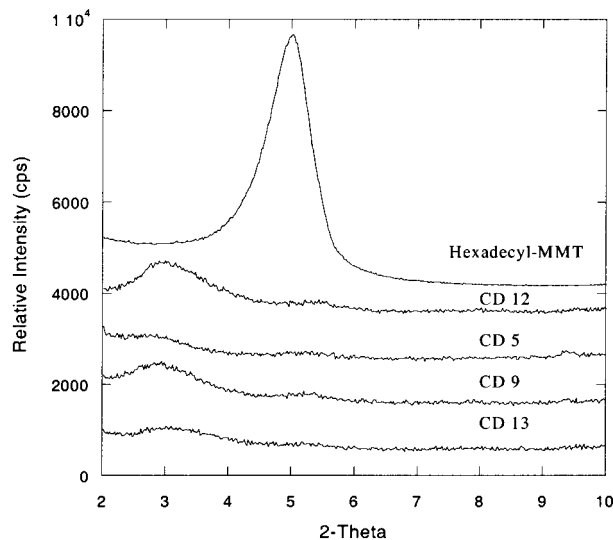


Figure 2. XRD data of hexadecyl-MMT/PET nanocomposites that were melt-blended at 285 °C for 2, 5, and 7 min at screw speeds of 21 and 31 rad/s.

ples. The reason for this discrepancy likely stems from the fact that XRD does not indicate anything about the level of dispersion and contains no peak representing delaminated MMT; only the intercalated peaks are observed by XRD. Because the tactoids in the samples are few but very well defined, most of the intercalated MMTs have similar spacing, resulting in a narrow peak that is easier to see at low concentration. This peak would then correspond to a broad distribution of gallery spacings because of a greater distribution of tactoid sizes that are at higher concentrations. This results in a broader peak that is easily lost in the baseline curvature, such as CD 5 in Figure 2.

All hexadecyl-MMT/PET nanocomposites revealed a high degree of dispersion and delamination with no micron-sized particles and tactoids containing less than seven MMT sheets. However, the highest level of exfoliation was observed

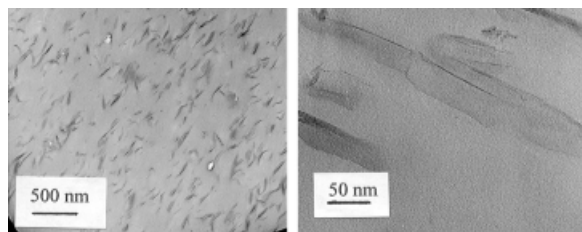


Figure 3. TEM images of CD 12 showing high levels of dispersion and exfoliation, average tactoids of four sheets per stack.

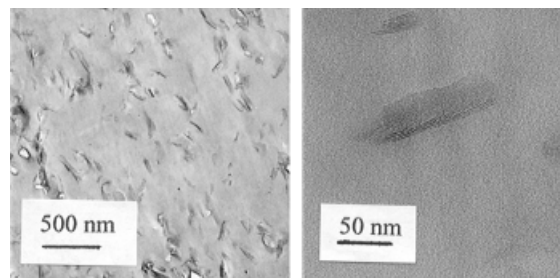


Figure 4. TEM images of CD 13 showing similar levels of dispersion and delamination as compared to CD 12. Similar levels of om-MMT dispersion and delamination were also observed in CD 5 and CD 9.

in CD 12 that exhibited the lowest tactoid content and tactoids usually no more than two sheets. TEM images of samples CD 5, 9 (not provided), and 13 (Fig. 4) appeared similar to that of CD 12—no micron-sized particles, high levels of dispersion, and white holes (because of the sample tearing during microtoming)—but contained more tactoids than CD 12 (the tactoids were normally two to three sheets, up to seven sheets).

TGA thermograms of all sets of samples tested were similar to one another, as were the 5 mass % T_{dec} 's. Within the standard uncertainty of TGA 5 mass % T_{dec} (± 1 °C), all materials decomposed at 390 °C (including as-received and processed virgin PET and nanocomposites). Therefore, processing and incorporation of imidazolium-MMT does not change the inherent thermal stability of PET. This is in contrast with the results for quaternary alkyl ammonium MMT, where degradation was extensive. This is the first report of successful direct melt-intercalation of PET with imidazolium-MMT.

CONCLUSIONS

Within the samples tested, the highest level of MMT dispersion in PET was achieved with hexadecyl imidazolium treated MMT melt-blended with virgin PET. The more conventional organic modifier, DMDODA led to black PET nanocomposites because of DMDODA degradation under the processing conditions. The most dispersed, exfoliated PET nanocomposite was achieved by melt-mixing at 21 rad/s for 2 min in a nitrogen atmosphere after drying the polymer at 120 °C and the clay at 150 °C. Alternative mixing conditions, longer residence times, and higher screw speeds

resulted in lower quality nanocomposites. Physical property evaluations of these well-exfoliated PET-clay nanocomposites will follow in future work.

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