

Morphology and Thermomechanical Properties of Recycled PET–Organoclay Nanocomposites

Maria T. M. Bizarria,¹ André L. F. de M. Giralardi,¹ Cesar M. de Carvalho,² Jose I. Velasco,³ Marcos A. d'Ávila,⁴ Lucia H. I. Mei¹

¹Departamento de Tecnologia de Polímeros da Faculdade de Engenharia Química da Unicamp, Campinas, SP, Brazil

²M&G Fibras e Resinas Ltda, Brazil

³Centre Catala del Plastic (CCP), Universitat Politècnica de Catalunya (UPC), Colom 114, 08222 Terrassa, Spain

⁴Departamento de Processos Químicos da Faculdade de Engenharia Química da Unicamp, Campinas, SP, Brazil

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ABSTRACT: Recycled PET/organoclay nanocomposites were prepared by melt intercalation process with several amounts (1, 3, and 5 wt %) of clay modified with quaternary ammonium salt (DELLITE 67G) dispersed in a recycled poly(ethylene terephthalate) (rPET) matrix. The resultant mechanical properties (modulus and yield strength) of the nanocomposites were found to be different from those of rPET. Wide angle X-ray scattering (WAXS) and Transmission Electron Microscopy (TEM) measurements have shown that although complete exfoliation was not achieved, delaminated clay platelets could be observed. Thermal anal-

ysis did not show significant changes in the thermal properties from those of recycled PET. Mechanical testing showed that nanocomposite properties were superior to the recycled PET in terms of strength and elasticity modulus. This improvement was attributed to nanoscale effects and strong interaction between the rPET matrix and the clay interface, as revealed by WAXS and TEM. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1839–1844, 2007

Key words: recycled pet; nanocomposites; thermomechanical properties

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a low cost, high performance polymer that is found in many applications, ranging from fibers to extruded parts. Traditionally, it has not been considered for applications involving high speed processing, such as injection molding, due to its high melting temperature and low crystallization rates. However, crystallization rates can be accelerated by adding nucleating agents¹ such as Al(OH)₃ which acts as an effective nucleating agent for PET cooled from the melt.² Studies using PET/mica nanocomposites³ have shown that 4 wt % of mica played a strong nucleating role by exhibiting a drastic increase in the crystallization temperature (T_c), glass transition temperature (T_g), and melting point (T_m) as compared to the pure PET.³

In filled systems, the constituents are immiscible, resulting in a coarsely blended microcomposite with chemically distinct phases. This is due to the poor miscibility between the organic and inorganic com-

ponents, leading to agglomeration of the latter, and therefore, weaker materials. The microsize fillers frequently used, e.g., glass beads, glass fibers, mica, talc, and CaCO₃, usually form microcomposites with limited improvement in properties. Nanosize fillers have attracted a great deal of interest as a method of obtaining composites with higher performance, due to the substantial increase of the contact area between matrix and fillers, affecting positively their final properties.^{4–6}

It has been reported that polymer-layered silicate nanocomposites often have superior physical and mechanical properties over their microcomposites counterparts, including improved modulus,^{7,8} reduced gas permeability,^{6,7} and flame retardancy.⁶ These enhanced properties are achieved by dispersing the layered silicate particles (e.g., montmorillonite clay) within the polymer matrix. The silicate polymer mixture is termed intercalated when, at least, one extended polymer chain is absorbed between the host platelets; the result is a well-ordered multilayer system with alternating polymer/inorganic host. When the silicate platelets are dispersed, the nanocomposite material is called exfoliated. Particularly, in the exfoliated state significant enhancements in physical properties have been observed.^{2,9} Silicate nanocomposites may be formed using several different dispersion techniques such as ultrasonic agitation,⁸ melt mixing,^{8,10–16} and solution mixing.¹⁷

Correspondence to: L. H. I. Mei (lumei@feq.unicamp.br).

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Dispersed clay particles have been found to significantly influence the crystallization and polymorphism of polyesters and polyamides.^{18–20} Ke and coworkers¹⁸ found a threefold increase in the crystallization rate of PET containing 5 wt % of dispersed clay relative to that of pure PET, attributed to the nucleation effect of the clay platelets. Similar results were also found by Liu et al.,¹¹ and Jimenez et al.¹⁹ for polyamide and polyester systems. Formes et al.^{21,22} performed an in-depth study of the organoclay structure effects on montmorillonite-based nylon 6 nanocomposites and concluded that the surfactant structural issues significantly affect the nanocomposite morphology and mechanical properties.

Although numerous patents have been issued and a number of papers have been published on PET/clay nanocomposites, no products have already entered the market.^{19,23–27} Few papers have been published on the preparation and characterization of the recycled PET/clay nanocomposites.²⁸ Brazil is one of the main countries in PET recycling. Large amounts of PET recycled from municipal wastes are currently stimulating its usage in the same demanding applications in which virgin PET is used. From the point of view of industrial application, which has made PET the main target for plastic recycling, we have prepared and characterized recycled PET/MMT nanocomposites by melt intercalation process using commercial products. The objectives of this work were to investigate (i) the crystallization characteristics, (ii) the morphology, and (iii) the mechanical properties of rPET/MMT nanocomposites containing 1, 3, and 5 wt % of clay.

MATERIALS AND COMPOUNDING

Recycled poly(ethylene terephthalate) (rPET) pellets (with intrinsic viscosity ASTM D 4603-91 = 0.69 dL/g) were produced by RECI PET - M and G (Indaiatuba-Brazil) by extruding reclaimed beverage bottles. The montmorillonite clay (DELLITE[®] 67G) was supplied by Laviosa Chimica Mineraria (Livorno, Italy) and was dried at 120°C for 16 h before its use. DELLITE[®] 67G is a nanoclay derived from a naturally occurring montmorillonite (MMT), which is purified and modified with a high content of quaternary ammonium salt (dimethyl dihydrogenated tallow ammonium). An antioxidant (Irganox B561) produced by Ciba was used in all nanocomposites to avoid as much as possible the degradation effects of hydrolysis caused by moisture. This antioxidant has a widespread use in PET composites processing to reduce degradation during extrusion. Also, pellets of recycled PET have been dried at 130°C for 6 h before the extrusion.

Composites containing 1, 3, and 5% by weight of DELLITE[®] 67G in rPET were prepared by direct melt compounding in a Theysohn twin-screw ex-

truder, with L/D ratio equal to 40. The process was carried out with the following temperature profile: 190-270-270-280-280-285°C, from the hopper to the die, with a screw speed of 250 rpm. The obtained nanocomposites were cut into pellets using a cutting machine. These pellets were used to produce the testing specimens using a Boy injection-molding machine, model 80A. The basic process parameters were: melt temperature of 270°C, nominal injection pressure of 50 bar, cooling time of 25 s and holding pressure of 40 bar for 20 s. Tensile tests were conducted according to ASTM D 638-99 with specimen dimension Type I. Samples for differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS) and transmission electron microscopy (TEM) were cut face from tensile fracture surfaces.

CHARACTERIZATION ANALYSIS

Intrinsic viscosity

Intrinsic viscosity (η) of the recycled PET with and without antioxidant was evaluated according to ASTM D 4603-91 standard using an Ubbelohde type B1 viscometer at 30°C. A mixture of phenol and 1,1,2,2-tetrachlorethane (6 : 4 wt) was used as a solvent for PET at a concentration of 0.5 g PET/dL.

Differential scanning calorimetry

Thermal analysis was carried out employing a DSC 2920 modulated-TA instrument. The samples in the weight range of 10–14 mg were submitted to the following thermal cycles: (i) first heating from room temperature to 300°C, at 10°C/min to obtain the first polymer melting patterns, and kept for 2 min to erase the crystalline nuclei; (ii) cooling from 300 to 40°C, at 10°C/min, to obtain the crystallization data; and (iii) second heating from 40 to 300°C at 10°C/min, to obtain information about the melting of the polymer crystallized from the melt. The glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), enthalpy of crystallization (ΔH_c) and melting enthalpy (ΔH_m) were determined. The crystalline fraction (χ_c) was calculated by integration of the melting endotherm referring it to theoretical data of melting enthalpy of fully crystalline PET (140 J/g),⁴ according to equations

$$\chi_c(\text{wt}\%) = \frac{\Delta H'}{\Delta H_{100\%c}} \times 100 \quad (1)$$

and

$$\Delta H' = \frac{\Delta H_{\text{exp}}}{1 - x} \quad (2)$$

Here, ΔH_{exp} is the melting enthalpy measured and x is the organoclay weight fraction.

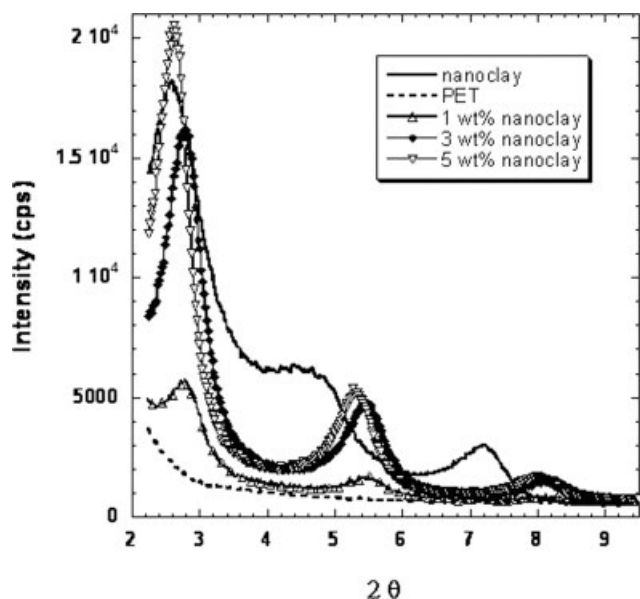


Figure 1 X-ray patterns of organoclay recycled PET nanocomposites.

Mechanical tests

Tensile tests were conducted on ASTM-D638 specimens by using a universal testing machine TestStar II, equipped with a 10-kN load cell. The tensile specimens dimensions were 3.2 mm of thickness and 13 mm of width. Yield and fracture data were evaluated at a cross-head speed of 50 mm/min at 23°C. All mechanical properties were evaluated on at least seven specimens.

Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) was used to observe the eventual interaction of rPET in the clay crystalline structure. A powder diffractometer PHILIPS (model PW 1730/10), with an area detector operating under 40 kV and 30 mA, using $\text{CuK}\alpha$ radiation ($\lambda = 0.1542$ nm) was used. Measurements were carried out on the specimen surface, which was cut perpendicular to the flow direction in the injection molding. Samples were scanned from $2\theta = 2.0^\circ$ – 15° at scanning rate of $2^\circ/\text{min}$.

Transmission electron microscopy (TEM)

Dumb-bell specimens were cut in the middle of their length in the direction perpendicular to the injection flow. Afterwards, ultra thin sections of approximately 80 nm were cut off using a Riechert-Jung ultramicrotome. The transmission electron microscope used was a Hitachi H800 TEM. It works in a range between 75 and 200 kV and has a maximum resolution of 0.27 nm.

RESULTS AND DISCUSSION

Intrinsic viscosity

The intrinsic viscosity value of the supplied recycled PET was 0.69 dL g^{-1} and that of the extruded polymer with and without antioxidant was 0.34 and 0.33 dL g^{-1} , respectively. There was a reduction of approximately 50% in the intrinsic viscosity after extrusion, indicating a high degree of degradation for both systems. This result shows that, in the present case, the antioxidant used (Irganox B561) was not effective to avoid degradation.

X-ray diffraction and TEM analysis

Figure 1 shows the WAXS patterns of both organoclay and recycled PET nanocomposites. It can be seen an intensity maximum at approximately $2\theta = 2.6^\circ$, which corresponds to the basal spacing of the (001) plane of clay, with interlamellar spacing of 3.4 nm. As expected, this peak appeared in the organoclay at lower diffraction angle than in the untreated neat clay, where typical values for montmorillonite 2θ reported in the literature range from 6° to 8° , depending on the specific characteristics of the clay.^{29,30} This indicates that intercalation occurred. The interlayer spacing of the clay was increased by the organic modification showing that complete exfoliation of the organoclay did not occur completely. Moreover, when comparing the position (001) plane peak of organoclay with PET nanocomposites, there is no evidence of further inter-

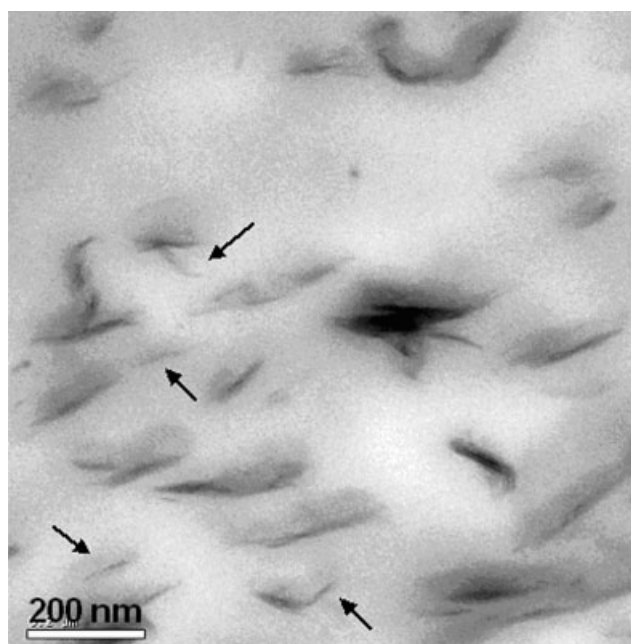


Figure 2 TEM micrograph of the nanocomposite sample (5% MMT). Arrows indicate delaminated clay platelets.

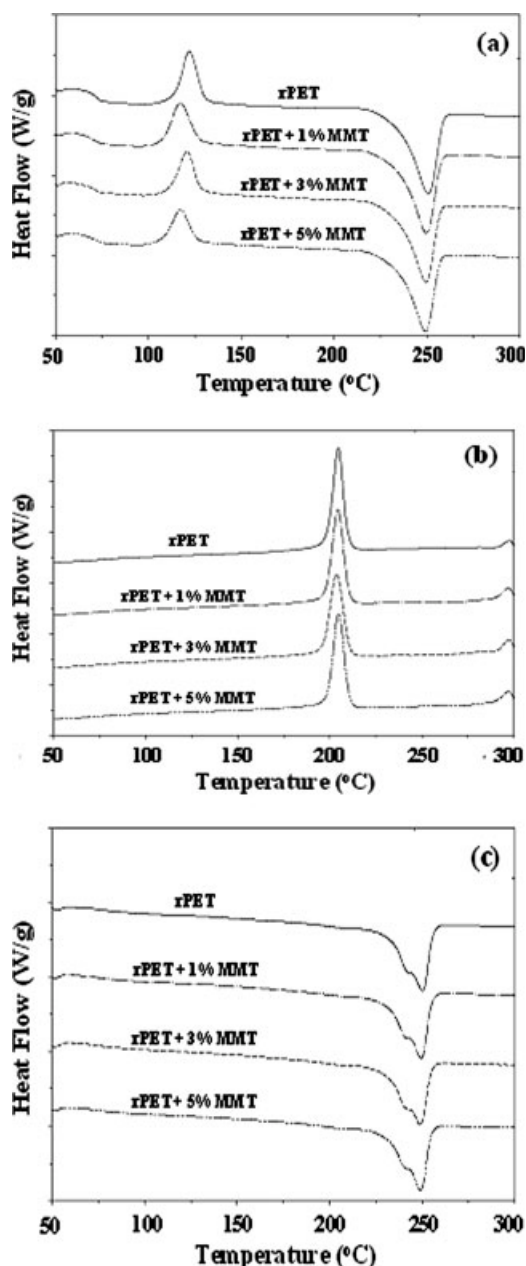


Figure 3 DSC curves of recycled PET and rPET nanocomposites: (a) heating, (b) cooling, and (c) second heating.

calation due to recycled PET molecules, since a peak shift to lower angles is not observed. Actually, it can be observed that there is a shift to higher angles, indi-

cating a decrease in the interlamellar spacing for the nanocomposites compared to the organoclay. Similar results were obtained by Junior et al. (2005) in studies of polypropylene–clay nanocomposites prepared by melt intercalation.³¹

More direct evidence of the formation of a true nanocomposite was provided by TEM analysis. From this, some extent of exfoliation was found (Fig. 2), which should be attributed to diffusion of the PET chains into the clay galleries, leading to a peeling apart of the clay platelets³² helped by application of shear forces during the melt mixing. Clay delamination due to shear-induced sliding of clay platelets has been reported, leading to both delaminates³¹ and tactoids.³³ Although WAXS results did not show significant PET chain intercalation, both clay intercalation and exfoliation was detected from TEM, showing that most of delamination might have occurred due to shear rather than diffusion. However, additional studies should be taken to understand better the exfoliation and intercalation mechanisms involved in this system.

Thermal analysis

Figure 3 shows the DSC thermograms of (a) first heating, (b) cooling, and (c) second heating for all samples.

Glass transition temperatures T_g slightly decreased with the clay presence (Table I), indicating an increase of the molecular mobility in all the nanocomposites. This decrease in T_g seems to be the result of clay agglomeration, which occurs for the addition of clay to the polymer matrix above a critical clay loading.^{34–37} According to Fornes et al.,³⁸ the presence of clay particles in nanocomposites processed from the melt promotes degradation of the polymer matrix during processing. This could also explain the decrease in T_g even though that the molecular mobility was expected to decrease due to polymer-particle interactions. This hypothesis is coherent with lower values of intrinsic viscosity obtained, and would also be supported by the fact that there was a decrease in the cold crystallization peak temperature (T_{cco}) as the organoclay percentage was increased. During the heating step, the growing of the already existent

TABLE I
DSC Data of PET or PETr/MMT Nanocomposites

Composition	(From first heating and cooling scans)						(From second scans)		
	T_g (°C)	T_{cco} (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
rPET/MMT									
100/0	77.4	121.9	250.2	48.7	204.6	44.2	77.4	250.2	40.6
99/1	72.5	120.7	249.0	44.9	203.6	42.6	72.5	249.0	38.4
97/3	74.6	117.0	249.5	46.8	204.3	42.4	74.6	249.5	39.5
95/5	73.9	117.2	249.1	44.9	204.7	41.4	73.9	249.1	38.6

TABLE II
Mechanical Properties of Nano-recycled PET

Tests	Samples					
	Recycled and processed PET					
	rPET	rPET without antioxidant	MMT (%) + antioxidant			
			0	1	3	5
Young's modulus (GPa)	1.9 ± 0.3	2.0 ± 0.5	2.0 ± 0.3	2.5 ± 0.4	2.4 ± 0.5	2.5 ± 0.6
Yield strength (MPa)	63.2 ± 7.5	18.7 ± 1.4	24.4 ± 9.0	21.8 ± 7.5	35.4 ± 13.1	42.0 ± 10.8

crystals would be slightly accelerated because of the increased molecular mobility. This could have been caused by slight molar mass reduction due to PET degradation under organoclay presence.

The melting peak temperatures of rPET slightly decreased with the addition of only 1 wt % of organoclay. This result could be explained based on the effects of nanoscale interactions between the polymer and the clay surface, which could lead to the formation of less stable crystals during the crystallization from the melt. This is supported by other studies that showed that PET melting temperature slightly decreased in the presence of nanoparticles.^{1,19} Here, concentrations of nanoclay higher than 1 wt % did not cause further reduction of T_m .

A significant effect in both melting and crystallization enthalpy (ΔH_m , ΔH_c) was not observed due to the presence of nanoclay. Also, nanoclay addition did not have an effect on the crystallization peak temperature (T_c). Thus, the organoclay did not increase the nucleation rate of rPET. According to our knowledge, all published studies on PET nanocomposites showed a gradual increase of T_c and ΔH_c values as the organoclay content was increased, indicating that nanoclay particles may increase the nucleation rate of PET.^{1,39} Probably, inorganic and/or polymeric components in the rPET could be

acting as nucleating agents for PET crystallization, being responsible for the system to achieve its maximum rate and, consequently, hiding a possible effect of the nanoclay.

Mechanical properties

Table II shows the nanocomposite mechanical properties in terms of Young's modulus and yield strength.

As a general result, rPET nanocomposites show both higher stiffness and tensile strength than the unfilled recycled PET in Figure 4. Usually, these results are those expected for virgin polymer clay nanocomposites. Ke et al.¹⁸ working with virgin PET found the following values for composites with 5 wt % of clay: $E = 3.8$ GPa and $\sigma_{\max} = 82$ MPa. Few papers have shown mechanical properties of recycled PET/clay nanocomposites. Pegoretti et al.²⁸ noted that the use of clays in recycled PET nanocomposites increased the modulus of the composites and the highest value was found for the composite with 5 wt % of clay content ($E = 2.8$ GPa and $\sigma_{\max} = 55$ MPa).

The reinforcing effects of the clays in rPET obtained in this study by melt intercalation, using a corotating twin screw extruder and a injection molding machine, can be related to a good clay dispersion. As seen in WAXS and TEM results, although a complete exfoliation was not obtained, it was found that a nanoscale dispersion was formed, leading to an effective polymer-clay interaction. These results show that the addition of small amounts of organoclay in the system can effectively increase the mechanical properties of rPET.

CONCLUSIONS

Recycled PET/MMT nanocomposites were prepared by melt intercalation. The intrinsic viscosity $[\eta]$ exhibited a large decrease after extrusion/injection processing. It can be seen that the yield strength and modulus have been improved by the addition of organoclay contents as low as 1 wt %. This reinforcement effect using small amounts of MMT implies a strong interaction between the matrix and the clay

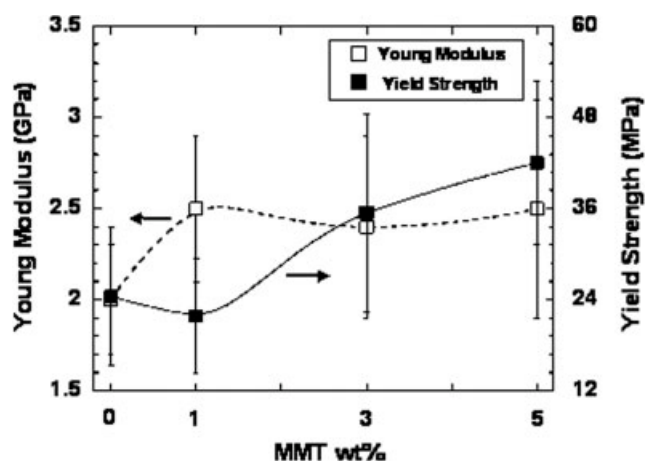


Figure 4 Mechanical properties of rPET/clay nanocomposites.

interface that can be attributed to the nanoscale and uniform dispersion of the silicate layers in the recycled PET matrix. The results of DSC analysis showed that PET did not exhibit heterogeneous nucleation in the presence of clay, which lead to the conclusion that the MMT used in this work did not act as an effective nucleating agent for the nanocomposites studied. The combined WAXS and TEM results showed that delaminated polymer nanocomposites were formed to some extent, although effective polymer intercalation was not detected.

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