Effects of Extrusion Conditions on the Properties of Recycled Poly(Ethylene Terephthalate)/Nanoclay Nanocomposites Prepared by a Twin-Screw Extruder

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ABSTRACT: The effects of extrusion conditions on the mechanical properties of recycled poly(ethylene terephthalate) (rPET)/clay nanocomposites were studied. Nanocomposites of recycled PET containing 2.5 and 5.0 wt % of montmorillonite modified with organophilic quaternary ammonium salt (DELLITE 67G) were prepared by melt compounding using a corotating twin-screw type extruder at two different screw rotation speeds: 250 and 150 rpm. The highest value of Young's modulus was found for low screw rotation speed (150 rpm). Morphological analysis using transmission electron microscopy (TEM) revealed the presence of fully exfoliated clay platelets in samples prepared at 150 rpm. It was concluded that the screw rotation speed should be optimized when preparing recycled PET/clay nanocomposites by melt compounding. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2252–2259, 2008

Key words: melt compounding; nanocomposites; organoclay; recycled poly(ethylene terephthalate); processing

INTRODUCTION

Nanocomposites refer to solid multiphase materials in which, at least, one dimension of a dispersed phase is in the nanometer range, typically 1–20 nm. Polymeric intercalation-type nanocomposites have been the subject of extensive academic and industrial researches over the past decade.[1–4] One of the challenges in producing polymer/clay nanocomposites with enhanced properties is tailoring the morphology (i.e., intercalated or exfoliated) of the system by promoting the interaction of the polymer matrix with inorganic particles. Incorporation of nanodispersed clay may lead to a broad range of applications such as imparting higher flame resistance for textiles, decreasing gas permeability in food packaging and bottles, and increasing the mechanical properties of different plastic parts.[5,6]

Polymer/clay nanocomposites are usually prepared by three main routes: melt intercalation, solvent dissolution, or *in situ* polymerization.[7] In the process of melt intercalation, the layered silicate is mixed with a polymer matrix. If the silicate surface is sufficiently compatible with the chosen polymer, then it will penetrate in the interlayer spaces and form either an intercalated or an exfoliated nanocomposite.[8] Exfoliation or high level of intercalation is desired when producing a polymer/clay nanocomposite, because the separation of individual clay sheets leads to dispersed particles of high aspect ration and large surface area, which is recognized to be very effective in mechanical properties enhancement.

In the melt intercalation route, at first, a suitable organic salt, thermodynamically favorable with the host polymer, is usually intercalated between the clay layers to promote its future dispersion.[9,10] Also, a high molecular weight polymer matrix improves clay dispersion rather than a low molecular weight, due to its larger degree of transferable shear stress to the clay.[11] Other important factors for effective clay dispersion are the processing conditions. Processing equipments that promote high shear stresses and shear rates were found to aid in the clay dispersion along with the proper organic modifier.[12,13]

Melting extrusion process is the most industrially viable route for preparing nanocomposite materials. Davis et al.[6] investigated two systems prepared via twin-screw extrusion utilizing different organic modifiers in PET/MMT. One system, using a commercial alkyl ammonium modifier, N,N-dimethyl-

N,N-dioctadecylammonium, formed black, brittle nanocomposites resulting from the modifier degradation. The second system, utilizing 1,2-dimethyl-3N-hexadecyl imidazolium tetrafluoroborate, exhibited high levels of dispersion observed by transmission electron microscopy (TEM). Pegoretti et al.[14] examined nanocomposites of recycled PET (rPET) with the sodium form of MMT (Cloisite® Na+) and an organically modified MMT (Cloisite 25A) prepared through melt compounding and injection molding. TEM clearly showed that the organically modified Cloisite 25A was easier dispersed in the rPET matrix. However, the TEM combined with XRD results demonstrated that although the lamellar periodicity of the clay evaluated through $d_{(001)}$ increased, the morphology remained intercalated. It was also found that the nanocomposite prepared with Cloisite 25A exhibited a higher tensile modulus relative to that of the Cloisite Na+. This effect was attributed to the better clay dispersion in the rPET matrix.

Matayabas et al.[15] prepared PET copolymer (co-PET) nanocomposites by melt-compounding by varying the amount of a commercial organoclay,[16] named Claytone APA, with 1,4-cyclohexanedimethanol modified PET. Physical mixtures of the organically modified clay and (co-PET) were dried under vacuum at 120°C before extrusion at 280°C. It was found a decrease in the co-PET inherent viscosity, indicating degradation, which increased in severity as the clay content increased from 0.36 to 6.7 wt %. In an attempt to compensate the effect of this degradation on the final properties of the nanocomposites, a higher-molecular weight PET was used; however, this led to a more severe degradation.

Few studies have been carried out to investigate the effects of the extrusion conditions on the mechanical properties and morphology of PET nanocomposites. Lertwimolnun and Vergnes (2006) worked with polypropylene (PP)/organoclay nanocomposites and showed that no evolution of intercalated structures occurred along the screws (using a twin-screw extruder) and that the effectiveness of the screw geometry was only observed in particular extrusion conditions.[17]

Tanoue et al. (2006) studied the effect of screw rotation speed on the mechanical and rheological properties and clay dispersion state of polystyrene (PS)/organoclay nanocomposites prepared by melt compounding with a counter-rotating type twin-screw extruder. Poly(styrene-co-vinyloxazolin) (OPS) was used as an additional material. The highest value of Young's modulus of the PS/OPS/clay was found at a screw rotation speed of 70 rpm. This implied in the existence of an optimized screw rotation speed for the melt compounding of the nanocomposite.[18]

These researches give clear evidence that the screw rotation speed could be optimized when preparing polymer/clay nanocomposites. The aim of the present work was to provide guidelines for the melt compounding of recycled PET-based nanocomposites with commercial organ-clay organoclay. The effects of two different screw rotation speeds on the morphology and mechanical properties of nanocomposites prepared with two different clay concentrations, using a corotating twin-screw extruder, were analyzed.

MATERIALS AND COMPOUNDING

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

Table I shows the composition of the nanocomposites. The organoclay contents of nanocomposites were set up at 2.5 and 5 wt %. Recycled PET pellets, antioxidant, and clay powders were melt-mixed directly by melt compounding in a Theysohn twin-screw extruder with a screw length/diameter ratio

TABLE I
Processing Conditions of Recycled PET/Organoclay Nanocomposites

Material Characteristics			
Processing conditions	Screw speed (rpm)	Antioxidant (1 wt %)	Organoclay (% wt)
1	250	Without	0
2	250	With	0
3	250	With	2.5
4	250	With	5.0
5	150	Without	0
6	150	With	0
7	150	With	2.5
8	150	With	5.0
9	(*)	Without	0

(*), this condition was tested the recycled PET as received from by RECIPET - M&G (Indaiatuba-Brazil).

of 40. The process was carried out with the following temperature profile: 190–270–270–280–280–285°C, from the hopper to the die. Nanocomposites were obtained and cut into pellets using a cutting machine. Two screw rotation speeds for each recycled PET/organoclay nanocomposite were selected: 250 and 150 rpm.

The specimens for tensile and impact tests (ASTM-D638-99, Type I) were prepared by using a Boy injection-molding machine at a temperature profile of 200–255–255–260°C. The basic process parameters were selected as follows: nominal injection pressure of 50 bar, cooling time of 30 s, and holding pressure of 50 bar for 30 s. The composites were previously dried at 120°C for at least 12 h before molding. Samples for wide angle X-ray scattering (WAXS) analysis and TEM observations were machined from the injection-molded tensile specimens.

CHARACTERIZATION ANALYSIS

Intrinsic Viscosity

Values of intrinsic viscosity [η] of the recycled PET with and without antioxidant, processed with screw rotation speeds of 250 and 150 rpm, were obtained at 30°C according to ASTM D 4603-91 standard procedure, using an Ubbelohde viscometer. A mixture of phenol and 1,1,2,2-tetrachlorethane (6 : 4 by weight) was used as a solvent for PET at 0.5 g PET/dL.

Mechanical Tests

Tensile tests were conducted on the 3.2×13 mm² standard tensile specimens by using a universal testing machine (TestStar II), equipped with a 10-kN load cell and an extensometer. After injection-molding, specimens were kept at room temperature for at least 48 h to allow elastic relaxation. Tensile data were obtained at 50 mm/min of cross-head speed and at 23°C according to ASTM D 638-95. Izod impact tests were performed on notched specimens according to ASTM D 256-93, using an impact pendulum machine Ceast 25. All mechanical properties were evaluated on at least seven specimens.

Wide-Angle X-Ray Scattering

X-ray spectra were obtained on the specimen surface to evaluate rPET/clay interactions. A powder diffractometer PHILIPS (model X'Pert), with an area detector operating under 40 kV and 30 mA (Cu Kα radiation, λ = 1.5406 Å) was employed. Samples were scanned from $2\theta = 2°$ to $2\theta = 40°$ at a scanning rate 2°/min.

Transmission Electron Microscopy

The tensile specimens were cut in the middle of their length in the direction perpendicular to the injection flow. Afterwards, ultra-thin sections of $\sim$ 80 nm were cut off using a Riechert–Jung ultramicrotone. The transmission electron microscope (TEM) used was a Hitachi H800. The equipment operates 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 values were 0.69 dL g^{-1} for the rPET as supplied, and 0.53 and 0.57 dL g^{-1} for the injection-molding polymer extruded at 250 rpm, without and with antioxidant, respectively. There was an intrinsic viscosity reduction of $\sim$ 22% after the extrusion, indicating a high degree of degradation for this system without antioxidant. On the other hand, for the system with antioxidant, the reduction was 16%. This result shows that, in the present case, the antioxidant used (Irganox B561) had some effective influence in avoiding degradation.

The formulations processed at 150 rpm screw speed displayed, after processing, a larger decrease in the intrinsic viscosity when compared with the counterpart formulations extruded at 250 rpm. Again, the antioxidant used (Irganox B561) was not effective in avoiding degradation, since a reduction of 26% was observed. These results showed clear evidences that, in the studied system, a larger residence time resulting of a lower screw speed (150 rpm) had promoted a stronger thermal degrading effect than a larger shear stress provoked by a higher screw speed (250 rpm). It is well-known[9–11,19] that degradation reactions in PET are strongly affected by high temperature and residence time in extruders and/or molding machines, reducing the material performance.

Mechanical Properties

Table II shows the mechanical properties of all rPET processed formulations in terms of Young's modulus, tensile strength, and impact strength for the two different screw rotation speeds. The Young's modulus of both neat rPET and rPET with antioxidant was found to be practically independent of the screw rotation speed. For the nanocomposite formulations, it only resulted $\sim$ 4% higher at 150 rpm than at 250 rpm, in the nanocomposite with a larger filler amount. As expected, the Young's modulus of the rPET/clay nanocomposites had increased with clay

Processing conditions	Nanocomposites properties				
	Tensile strength (MPa)	Young's modulus (GPa)	Strain at break (%)	Impact strength (J/m)	Intrinsic viscosity [η] (dL g^{-1})
1	65.5 ± 0.2	2.1 ± 0.03	9.1 ± 0.1	27.4 ± 1.8	0.53
2	65.8 ± 0.2	2.1 ± 0.03	9.1 ± 0.1	29.9 ± 1v4	0.57
3	63.5 ± 1.5	2.4 ± 0.02	7.5 ± 0.3	18.5 ± 1.2	(**)
4	61.7 ± 0.5	2.7 ± 0.03	5.0 ± 0.6	17.5 ± 0.9	(**)
5	64.2 ± 4.4	2.1 ± 0.10	7.5 ± 0.5	25.0 ± 1.6	0.46
6	66.7 ± 0.3	2.2 ± 0.02	8.0 ± 0.3	27.7 ± 1.1	0.50
7	65.3 ± 2.1	2.6 ± 0.11	6.2 ± 0.9	16.5 ± 1.8	(**)
8	41.5 ± 0.6	2.8 ± 0.05	3.0 ± 0.3	12.3 ± 1.5	(**)
9	64.8 ± 0.3	2.1 ± 0.02	9.1 ± 0.3	28.8 ± 0.9	0.69

(**), was not performed for the present condition.

concentration increase, even if one considers the standard deviations. The Young's modulus of the nanocomposites showed a maximum value at a screw rotation speed of 150 rpm with 5 wt % of clay and was 30% larger than that of neat rPETs for the same rotation speed. The stiffness increase was found to be slightly higher for the low speed condition (150 rpm) than for the high speed one (250 rpm).

Despite, the later results suggest that there could be an optimum screw rotation speed for the melt compounding of polymer/clay nanocomposites, one has to be careful before to take such conclusion, because the relatively high standard deviations have to be taken in consideration.

The tensile strength of the nanocomposites was found almost independent on the screw rotation speed (Table II). It was practically the same as that of the neat rPET. However, in the case of rPET/clay nanocomposite with 5% clay extruded at 150 rpm, it was found that the property was almost 40% smaller than that of neat rPET. Interestingly, the same behavior was not observed on the equivalent formulation processed at 250 rpm. Again, as could be observed in the intrinsic viscosity values, it appears that a larger residence time into the extruder produces a more detrimental effect on the polymeric matrix by favoring the thermal oxidative degradation than a higher shear stress at a larger screw speed. Although the processing of nanocomposite at 150 rpm with 5% of clay, decrease of molecular mass of the polymeric matrix occurred. Besides a larger residence time also a high abrasive degradation from mixing a larger amount of inorganic material (in a twin-screw extruder), the PET, which has a natural tendency thermal oxidative and hydrolytic degradation. On the other hand, the presence in the final material of relatively larger amounts of the aggregated particles, in this case on the formulations processed on both speeds (250 and 150 rpm), must have

contributed to the severe decrease of tensile properties in the later formulations.

This decrease in the tensile strength with the increase of clay content was also observed in PET/clay nanocomposites by Pegoretti et al. and Ke et al.[14,20] That was attributed to particle aggregation at higher clay concentrations [Fig. 1(a,b)] and to the polymer matrix degradation.[9–11,19]

The nanocomposite strain at break was found to be reduced with the increasing of the nanoclay concentration, especially the lower extrusion screw speed condition (Table II). Once more, a higher resident time from lower extrusion speed would had promoted higher molecular degradation, which must had been the cause of lower strain at break value. It has to be noted that both the tensile strength and the strain at break values for the nanocomposites resulted unaffected by the addition of antioxidant.

From the above results, it is clear that some of the detrimental effects are due to high clay fractions on the recycled PET nanocomposites, which is characterized by notable reduction of ductility. In this sense, large reduction of strain at break in studies on polymer/clay nanocomposites, with polymeric matrix other than recycled PET, prepared by melt-intercalation process.[14,18,21–26] The relative Young's modulus, as well as other mechanical properties, of melt-compounded thermoplastic nanocomposites containing MMT-based organoclays strongly depends on the matrix type and processing conditions.

Impact strength was measured for rPET nanocomposites. The values were dependent upon clay concentration and screw rotation. As it is shown in Table II, the impact strength values of rPET/clay nanocomposites were about 40% smaller than those of neat rPET. However, the impact strength of samples containing 5 wt % of organoclay resulted in slightly lower values than those samples with 2.5 wt %. Yet again, a higher residence time seems to
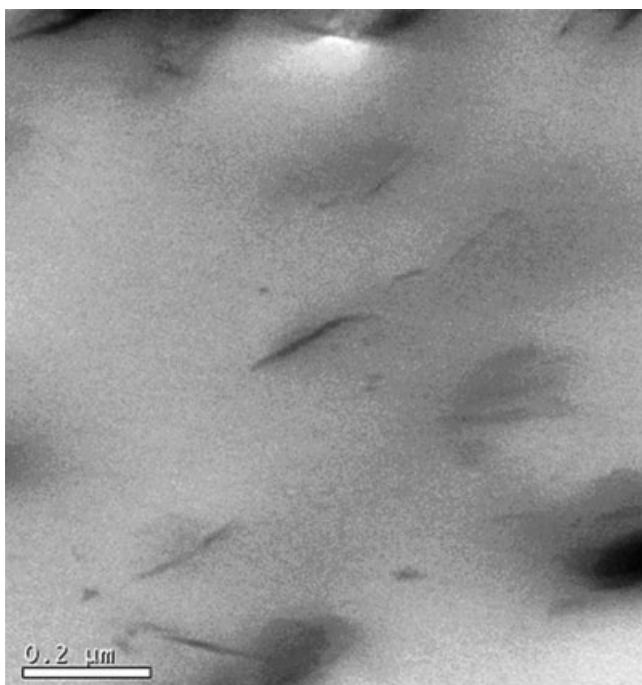
(a)
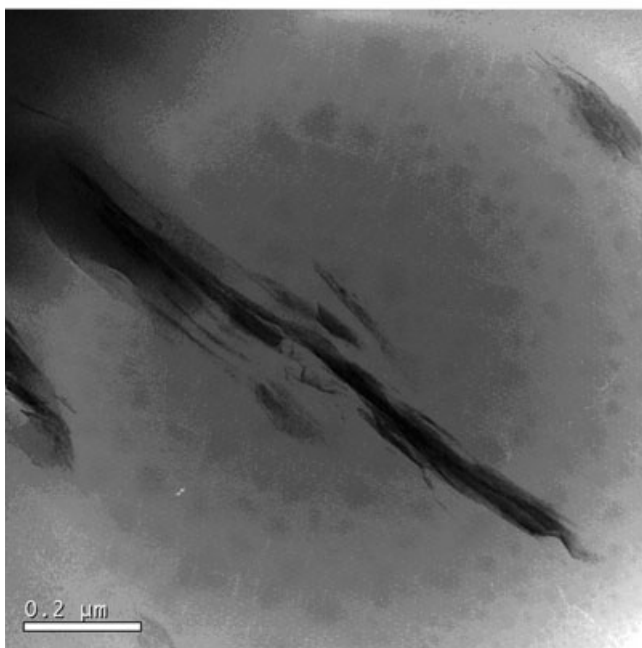
(b)

Figure 1 (a) and (b) TEM images of rPET/nanoclay nanocomposites prepared by a twin-screw extruder at a screw rotation speed of 150 rpm screw rotation speed (organoclay content 2.5 and 5.0 wt %).

be the reason of the lower impact resistance found in nanocomposites prepared at lower extrusion rate. In this sense, the impact strength values of neat rPET also resulted slightly lower than those of rPET with antioxidant.
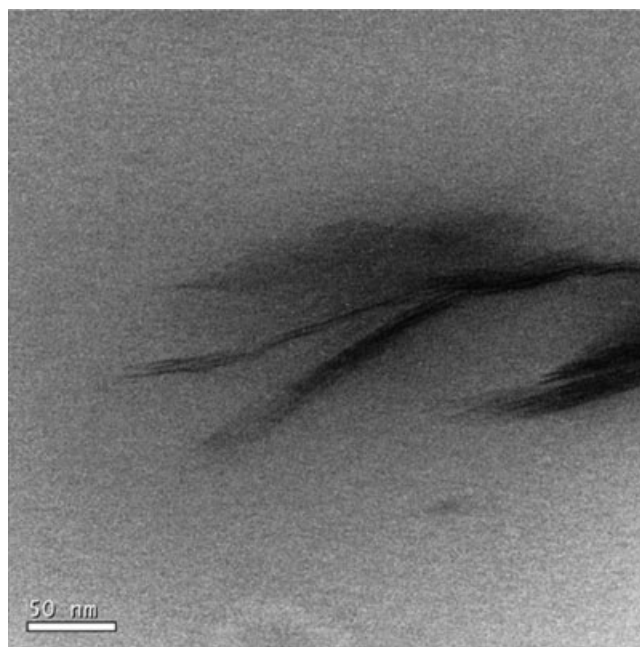
Figure 2 X-ray patterns of organoclay recycled PET nanocomposites processed at 250 rpm speed screw rotation.

Effect of Screw Speed Rotation on Final Morphology

The effects of operating conditions on the intercalation state were examined using WAXS measurements and TEM. Figures 2 and 3 display WAXS spectra of neat organoclay, rPET, and rPET/organoclay nanocomposites under study. An intensity max-
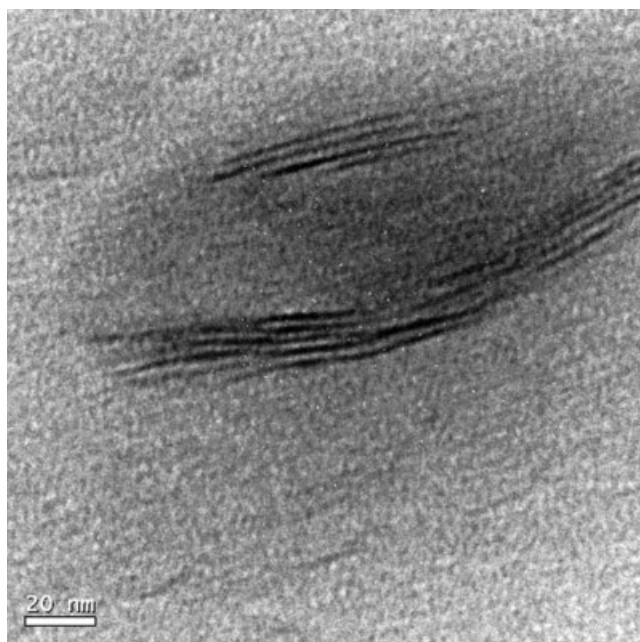
Figure 3 X-ray patterns of nanonoclay recycled PET nanocomposites processed at 150 rpm speed screw rotation.

TABLE III
Values of *d*-spacings for rPET/Nanonoclay Nanocomposites as a Function of the Processing Conditions

Processing conditions	d_{001} (nm)
Nanoclay	3.272
3	1.618
4	1.640
7	1.619
8	2.471

imum at $\sim 2\theta = 2.7°$, corresponding to the basal (001) diffraction plane of clay, may be identified on the neat organoclay spectra. As expected, the organoclay peak appeared at a lower diffraction angle than of the untreated neat clay, where typical 2θ values reported in the literature for MMT range from $9°$ to $10°$, depending on the specific characteristics of the clay.[27,28]

Since the intensity of the first peak was larger than that of the second peak, it was possible to judge that the first peak was from $d_{(001)}$ and that the second one was from $d_{(002)}$. From Bragg's formula, the spacing between clay platelets could be obtained. Table III compiles the spacing value for neat organoclay and each nanocomposite. It can be seen that the *d*-spacings of all rPET/clay nanocomposites, prepared at both rotation speeds were smaller than that of the neat organoclay. One possible explanation is that the DELLITE 67 G is a highly organically modified clay, thus, some of the organic modifier between clay platelets might have degraded due to the high temperature during the melt compounding inside the extruder, decreasing the *d*-spacing of clay, even with the additional rPET intercalation by shear and elongation during melt compounding by the twin-screw extruder.

The above tendency has not been published in precedent studies on rPET/organoclay nanocomposites.[29] However, it agrees with Xie et al. conclusions[30] who in their careful study about the thermal behavior of the MMT, with different kinds of natural organic surfactant modifiers, have found that the onset temperature of the chemical degradation for alkylammonium surfactants is around $180°C$, which is much lower than the temperatures used in PET nanocomposites processing.

The presence of diffraction peaks shows that complete exfoliation of the organoclay into recycled PET did not occur at both screw rotation speeds. Moreover, when comparing the position of organoclay (001) diffraction plane peak in PET nanocomposites for each screw rotation speed, there were no evidences of further intercalation of recycled PET molecules, since a peak shift to lower angles was not observed. Actually, it can be observed that there is a

shift to higher diffraction angles, indicating a decrease in the interlamellar spacing for the nanocomposites compared with the organoclay, for both screw rotation speeds. Similar results were obtained by Júnior et al. in studies of polypropylene-clay nanocomposites prepared by melt intercalation.[31]

The state of clay dispersion in the rPET/clay nanocomposites was analyzed by TEM. Figures 4 and 5 display TEM micrographs for of rPET/clay nanocomposites with 2.5 wt % of organoclay extruded at 250 and 150 rpm screw rotation speed, respectively.

Figures 6 and 7 display TEM micrographs of rPET/clay nanocomposites with 5 wt % of organoclay extruded at 250 and 150 rpm screw rotation speed, respectively.

In general, a mixed morphology of intercalated and exfoliated particles could be appreciated in all the samples. However, nanocomposites prepared at different screw speeds revealed different degrees of platelet exfoliation. At low screw rotation speeds (150 rpm), exfoliation of clay platelets was observed, which could be attributed to diffusion of the PET chains into the clay galleries, leading to a peeling apart of the clay platelets[28] helped by application of shear forces during the melt mixing. Some aggregates or stacks of platelets remained not exfoliated in these samples. At higher screw rotation speeds (250 rpm), smaller extent of exfoliation was observed. Even at the highest screw rotation speed it was not possible to prepare fully exfoliated rPET/
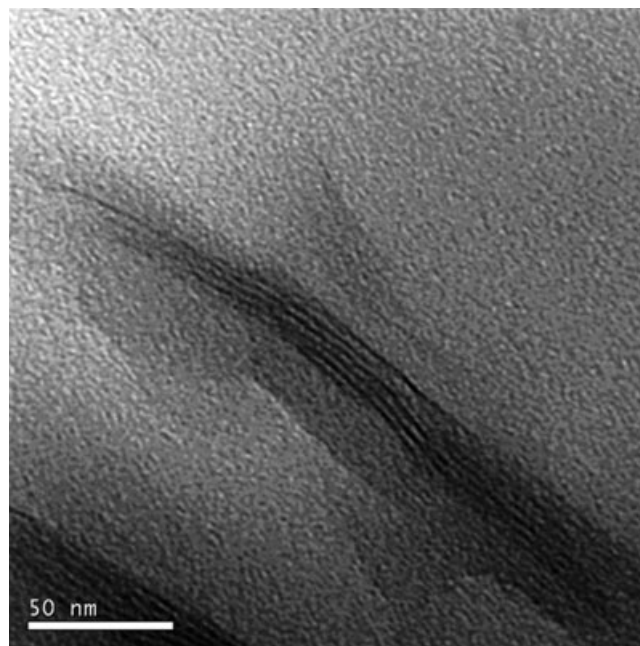
Figure 4 TEM images of rPET/nanoclay nanocomposites prepared by a twin-screw extruder at 150 rpm screw rotation speed (organoclay content 2.5 wt %).
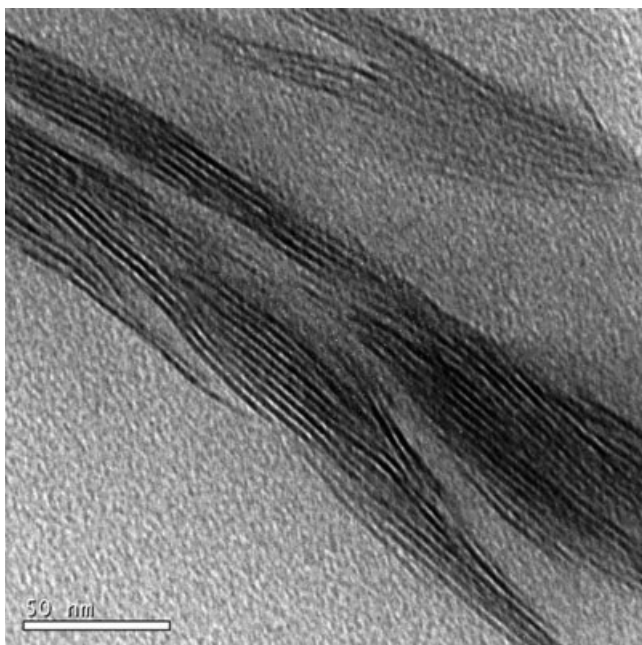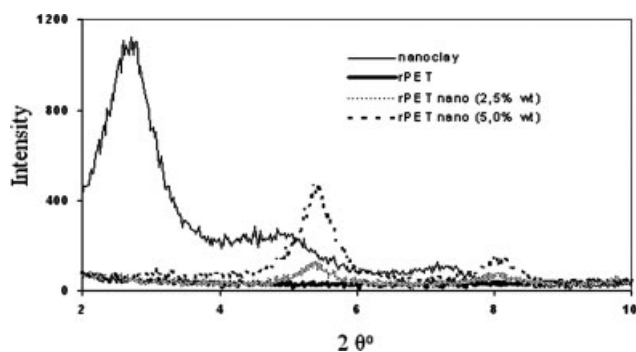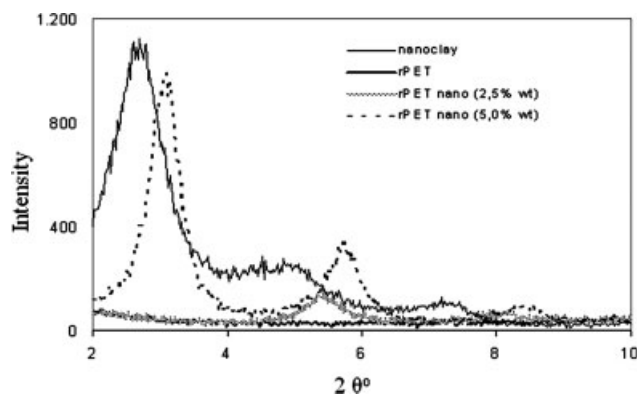
Figure 5 TEM images of rPET/nanoclay nanocomposites prepared by a twin-screw extruder at 250 rpm screw rotation speed (organoclay content 2.5 wt %).

organoclay nanocomposites. This mixed nanocomposite morphology, between exfoliated and intercalated one, has been reported for different polymer/clay systems.[13] Tanoue et al. (2006) reported a similar behavior in their study with PS/clay system prepared using the twin-screw extruder when the screw rotation speed was set up at a high value.[18]

Clay delamination due to shear-induced sliding of clay platelets, leading to both delaminates[1] and tactoids[13] is the accepted mechanism for the formation of polymer/clay nanocomposites. Although WAXS results did not give evidence of significant PET chain intercalation for both screw rotation speeds studied in this article, both clay intercalation and exfoliation was detected from TEM analysis, suggesting that the extent of delamination is due to the balance between

Figure 6 TEM images of rPET/nanoclay nanocomposites prepared by a twin-screw extruder at 150 rpm screw rotation speed (organoclay content 5.0 wt %).

Figure 7 TEM images of rPET/nanoclay nanocomposites prepared by a twin-screw extruder at 250 rpm screw rotation speed (organoclay content 5.0 wt %).

shear and residence time. However, additional studies should be conducted to understand better the exfoliation and intercalation mechanisms involved in this system.

CONCLUSIONS

The effect of twin-screw rotation speed on the mechanical properties and dispersion state of clay platelets of rPET/organoclay nanocomposites was discussed. The influence of clay concentration and antioxidant addition was also analyzed.

It was found that the Young's modulus of the rPET/clay nanocomposites prepared at low screw rotation speeds (150 rpm) was little higher than at a higher one (250 rpm). On the basis of the influence of the residence time, the existence of an optimum screw rotation speed for the preparation of rPET/ organoclay nanocomposites by the melt compounding method in a twin-screw extruder was evidenced.

The clay dispersion state was found to be dependant on the screw rotation speed applied during the melt compounding. Different clay dispersion states were confirmed by TEM analysis. In this study, the rPET/clay nanocomposite prepared at 150 rpm had a high extent of exfoliated clay platelets.

In general, the Young's modulus of the polymer/ clay nanocomposites with high extent of exfoliated clay platelets was 35% larger than that of neat matrix polymer. The tensile strength of the nanocomposites was almost the same as that of the neat matrix polymer. Further investigation concerning the screw design and extrusion conditions has to be carried out to improve the melt compounding process of rPET/clay systems.

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