

In Situ Microwave-Assisted Polymerization of Polyethylene Terephthalate in Layered Double Hydroxides

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ABSTRACT: The synthesis of poly(ethylene terephthalate) (PET)/layered double hydroxide (LDH) nanocomposites through microwave methods has been investigated. To enhance the compatibility between the PET polymer and the LDH, dodecyl sulfate was intercalated in the lamellar structure. The organo-LDH structure was confirmed by powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy (FTIR). PET nanocomposites were prepared with 0–10 wt % of LDH content by *in situ* microwave-assisted polymerization. PXRD was used to detect the formation of the exfoliated PET/LDH

nanocomposites. Transmission electron microscopy was used to observe the dispersed layers and to confirm the exfoliation process. FTIR spectroscopy confirmed that the polymerization process had occurred. TG and DTA are used to study changes in thermal stability of the nanocomposites, which resulted enhanced by well dispersed LDHs layers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1388–1394, 2008

Key words: layered double hydroxide; microwave; nanocomposite; poly(ethylene terephthalate)

INTRODUCTION

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds, find applications in different classical areas such as catalysis, adsorption processes, medicine,^{1,2} etc, although currently a new and interesting field involving the synthesis of nanocomposite materials is also being developed.^{3–6}

LDHs are generally described by the formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2](A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} is a divalent cation, M^{3+} a trivalent cation, and A^{n-} a n -charged interlamellar anion.^{7,8} Structurally, they are similar to brucite $[\text{Mg}(\text{OH})_2]$, where Mg^{2+} cations (octahedrally coordinated by hydroxide ions) share edges to form layers, where partial replacement of divalent cation by trivalent ones occurs. The resulting positive charge on the layers needs the incorporation of charge-balancing anions within the interlayer, together with water molecules.

The clay–polymer systems involving anionic clays have been much less studied than the cationic ones due to the delamination difficulties found when

using this sort of clays because of the strong interlayer electrostatic interactions, small gallery space, and hydrophilic character of the LDH surface.⁹ However, the highly tunable properties, the anion-exchange capacity (2–3 times greater than for cationic clays) and the easy synthesis of LDHs¹⁰ have converted these materials into a new emerging class of layered crystals, which seems to be better suited for the preparation of multifunctional polymer/layered crystal nanocomposites.¹¹

On the other hand, poly(ethylene terephthalate) (PET) is a semicrystalline polyester with a high melting point and very good mechanical strength, due to the presence of the aromatic ring in the polymeric structure.⁶ It is resistant to heat and virtually unattacked by many chemicals.¹² This polymer, which is of relatively low cost and high performance, is widely used in various fields such as electrical, construction, automotive, and packaging industries.¹³ Thus, any enhancement of the crystallization, mechanical, thermal, and other properties of PET is of great potential for industrial applications.

Several methods have been used to obtain nanocomposites by using clays.^{14,15} However, *in situ* polymerization has become the main procedure for the synthesis of nanocomposites, due to its versatility and compatibility with reactive monomers,¹⁶ as well as permitting the control of the polymer and the composite structures. This method relies on the swelling of the organically modified LDH by the monomer, followed by *in situ* polymerization initi-

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ated thermally or by addition of a suitable compound (catalyst). The chain growth in the LDH galleries accelerates exfoliation and nanocomposite formation.⁵

Microwave heating is rapidly developing as an alternative to conventional heating techniques used in thermally initiated polymerization. Liao et al.¹⁷ used microwaves to obtain poly- γ -caprolactone in short periods of time; Mallon and Ray¹⁸ showed that the microwave energy could induce small increases in the molecular weight of PET; Hoogenboom¹⁹ scaled up microwave-assisted processes to the cationic ring-opening polymerization of 2-ethyl-2-oxazoline. The interaction between the microwave energy and molecular dipole moments of the starting materials provides an effective, selective, clean, and fast synthetic method.²⁰ However, although many benefits of microwave radiation have been recognized, the use of this radiation in polymer chemistry is still rather unexplored.

In this work, we have prepared PET-LDH composites by an *in situ* polymerization method, using microwave radiation as an alternative to conventional heating methods. An LDH was organically modified using dodecyl sulfate as the interlamellar anion, to overcome the lack of compatibility between the polymer and LDHs containing purely inorganic anions, such as carbonate, nitrate, etc. Also, the chemical and thermal properties of the samples were studied.

EXPERIMENTAL

All chemicals were obtained from Fluka (Basel, Switzerland) and were used as received. The layered double hydroxide (LDH) was prepared by dropwise addition of an aqueous solution containing 0.1 mol sodium dodecyl sulfate 85% (DS) to an aqueous solution containing 0.1 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 98% and 0.05 mol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 98%. Nitrogen was continuously bubbled through the solution to avoid carbon dioxide absorption and pH was kept at a value of 10 by addition of aqueous (2M) NaOH 98%. The precipitate formed was aged for 24 h under the same synthesis conditions and then it was repeatedly washed with decarbonated water.

The polymer (PET) was prepared under reflux conditions, mixing 0.05 mol ethylene glycol 99% (EG), 0.25 mol dimethyl terephthalate 99% (DMT), and 0.01 g zinc acetate 99% (as a catalyst). The mixture was heated in a Milestone Ethos Plus microwave oven (Shelton, CT), where the temperature was raised from room temperature to 140°C (20°C/min), then to 200°C (12°C/min), and finally to 270°C; this final temperature was maintained for 35 min. The reaction mixture was continuously and gently stirred during heating in the oven.

The PET-LDH nanocomposites were prepared in a similar way as described for PET preparation; the only difference was that the LDH was previously dispersed for 1 h in a Fungilab ultrasonic bath (Barcelona, Spain) at 250 W in EG. The content of LDH corresponded to 1, 2, 5, and 10% (w/w) with respect to the polymer.

Once prepared, PET and the PET-LDH nanocomposites were heated in an oven at 190°C and 250 mmHg, as preliminary essays had shown that under these conditions dispersion and crystallization of PET and the nanocomposites is improved.

PET and the nanocomposites were characterized by FTIR spectroscopy in a Perkin-Elmer FTIR 1600 instrument (Waltham, MA), using the KBr pellet technique; 100 spectra (recorded with a nominal resolution of 4 cm^{-1}) were averaged to improve the signal-to-noise-ratio. Powder X-ray diffraction (PXRD) diagrams were recorded in a Siemens D-500 instrument (Erlangen, Germany), using Ni-filtered Cu K α radiation ($\lambda = 1.54050 \text{ \AA}$) with a scanning speed of 2° (2 θ)/min, equipped with Diffract AT software. Thermogravimetric (TG) and differential thermal (DTA) analyses were carried out in TGA-7 and DTA-7 instruments, respectively, from Perkin-Elmer (Waltham, MA), under flowing (30 mL/min) oxygen (from L'Air Liquide, Valladolid, Spain), at a heating rate of 10°C/min.

Transmission electron microscopy (TEM) photographs were obtained in Servicio General de Microscopía Electrónica (University of Salamanca, Spain) using a Zeiss 902 instrument (Barcelona, Spain). The samples were ultrasonically dispersed in acetone and then a drop of the suspension was deposited onto a Cu grid-coated with a holey carbon film.

RESULTS AND DISCUSSION

FTIR spectroscopy

The FTIR spectra of PET-LDH nanocomposites with LDH loadings of 1, 5, and 10% are included in Figure 1. Bands due to both the organic and inorganic components are recorded.

The intense and broad band centered around 3424 cm^{-1} is due to the stretching mode of hydroxyl groups from the brucite-like layers; the band at 1636 cm^{-1} corresponds to the bending mode of water molecules from the interlayer and also probably absorbed on the external surface of the crystallites.²¹

The weak bands at 2925 and 2854 cm^{-1} are due to the antisymmetric and symmetric modes, respectively, of the C—H bonds in the methylene groups, which originate from the aliphatic chain of dodecyl sulfate (used for swelling the interlayer of the LDH and to facilitate incorporation of the polymer), as

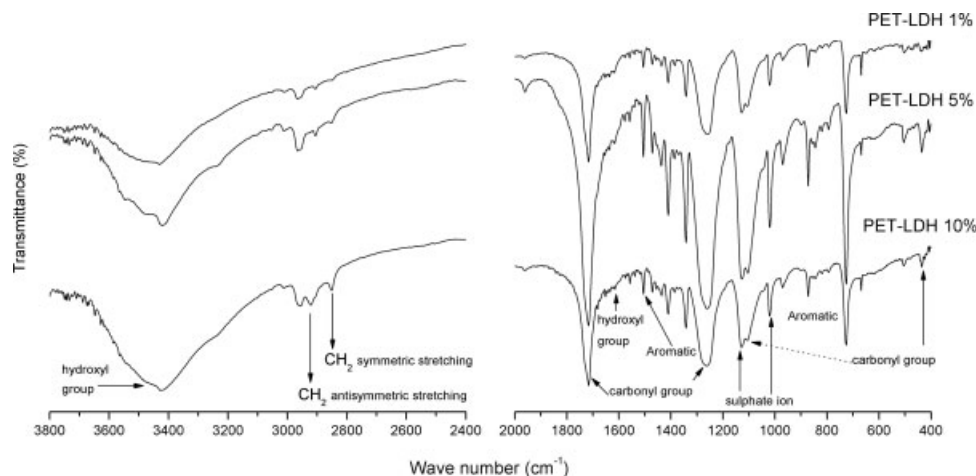


Figure 1 FTIR spectra of PET-LDH samples with 1, 5, and 10% LDH loading.

well as from the PET molecules. Other bands originated by the DS molecule are those recorded at 1178 and 1038 cm^{-1} (antisymmetric and symmetric modes of the sulfate group).²¹ Finally, bands corresponding to metal-OH translation modes within the brucite-like sheets, which should be recorded in the low wavenumber region of the spectra, are vanished due to the high dispersion of the LDHs in the polymer matrix and their low loading.

Bands associated to the PET molecule are also recorded. Six of them are characteristic of the ester group and others of the aromatic ring.²² The band at 1716 cm^{-1} is due to the stretching mode of the carbonyl group, the bands due to the C—O—C group are recorded in the 1140–1108 cm^{-1} range (symmetric mode) and in the 1280–1230 cm^{-1} range (antisymmetric mode). The band due to the bending mode of this group is recorded at $\sim 422 \text{ cm}^{-1}$. The antisymmetric and symmetric stretching vibrations of the C—H groups are recorded in the same positions as for bulk PET and for DS.

The bands due to the aromatic ring are recorded at 1505 cm^{-1} , together with several weak bands around 800 cm^{-1} , due to the 1,4-substituted aromatic ring.

Only minor differences in the bands intensity are registered when the content of LDH is increased. In the same way, as expected, all vibrations previously described are identified for PET sample and for the PET-LDH nanocomposites, because in all cases the most abundant compound is PET. Only in the PET-LDH 10% sample it could be expected that the larger amount of LDH could induce some small changes in the spectra, although no change was actually clearly seen; in the other nanocomposites, the LDH percentage is very low for giving rise to any important change in the spectra. Therefore, the spectra allowed to identify mainly one compound organic.

Powder X-ray diffraction

The structure of the LDH modified by intercalation of DS in the interlayer space is similar to that reported in previous studies.²³ Assuming a 3R stacking of the layers, the first diffraction maximum at low angles is due to planes (003) which corresponds to a spacing of 26.03 Å; this very large value (that one corresponding to a LDH with intercalated carbonate is close to 7.8 Å) demonstrates the swelling of the structure upon intercalation of the large DS anion. From the value for the thickness of the brucite-like layer, 4.8 Å,²⁴ the value calculated for the gallery height was 21.23 Å.

Consequently, incorporation of the DS molecules has a double effect: first of all, the commented swelling provides a very open, accessible interlayer space, where the polymeric molecules can be easily hosted; and second, the enhancement of the hydrophobicity due to the presence of the organic chain also makes easier the incorporation of the organic polymer. The expanded structure also facilitates ultimately the exfoliation of the structure, leading to isolated LDH sheets or stacking of very few layers.

The PXRD patterns of the loaded nanocomposites are shown in Figure 2, together with that for PET, before curing under vacuo. Only diffraction maxima due to PET are recorded. This is not unexpected for samples containing 1% of LDH, as such a percentage is too low and diffractions from solids in this order of concentration are hardly detected by PXRD; the dispersion of the inorganic filler, as well as the probable exfoliation of the layers, should give rise to extremely low particles, unable to produce a coherent diffraction strong enough to be detected. However, such a detection limit is not applicable for a sample with 5% LDH, as this percentage is large enough for permitting identification of LDH diffrac-

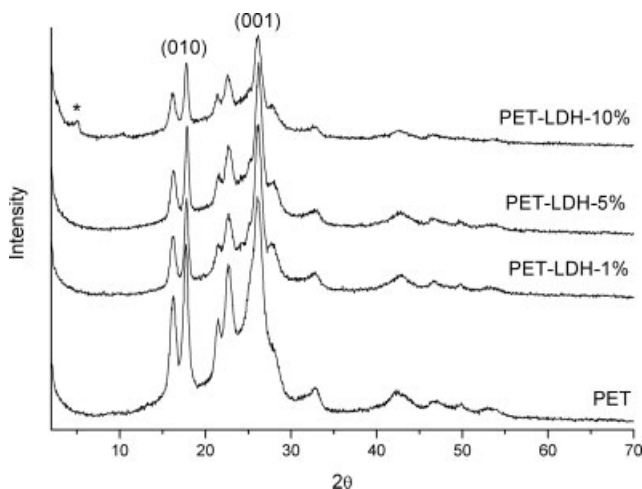


Figure 2 PXRD patterns for pristine PET and 1, 5, and 10% PET-LDH nanocomposites (* = LDH).

tion maxima. In this case, peaks due to diffraction by LDH are not detected either. This result can arise, as commented earlier, from the presence of completely or almost completely exfoliated LDH or, alternatively, from the fact that an extremely large swelling of the layers, upon incorporation of the large molecules of the organic polymer, has shifted the peak to a position below $2\theta = 2^\circ$, and therefore undetected under the experimental conditions used. However, this should not be the case, as the harmonic peaks at larger diffraction angles would have been recorded. The lack of LDH diffraction peaks confirms that even with a loading equivalent to 5% (w/w), the LDH crystallites have become completely exfoliated and well dispersed in the PET matrix. The diagrams are only very slightly modified after curing the samples, and are not shown here for the sake of brevity.

The PXRD patterns of the sample containing 10% PET (w/w) also before curing under vacuo show some changes. The diffraction maxima once again coincide with those of PET, as it can be clearly seen when PET-LDH with 1 and 5% loadings are compared. However, a weak diffraction maximum due to the LDH is recorded at $2\theta = 4.9^\circ$. The presence of this peak strongly suggests formation of small LDH aggregates. The interlayer space that corresponds to this aggregate is 17.7 Å, and for the sample before vacuo treatment is 18.1 Å, very close for the first one. However, the amount of undispersed (or unexfoliated) LDH should be still rather small, as no other diffraction peak due to the LDH is recorded. This means that the maximum amount of LDH which can be effectively dispersed in the PET matrix is between 5 and 10% (w/w). The spacing calculated from the position of the more intense peak for the PET sample on all composites, both before and after

vacuo treatment, is 3.4 Å. Consequently, treatment *in vacuo* can be skipped or not when preparing this sort of PET-LDH nanocomposites. The spacing values measured for PET are coincident within experimental error, indicating that incorporation of the LDH does not introduce any sort of appreciable distortion in the structure of the polymer, whichever the amount of LDH existing in the composite. No effect is either observed upon submitting the samples to treatment under vacuo.

On the other hand, the treatment *in vacuo* of sample indicates that it does not modify the structure of PET or that of the LDH, nor does it favor nor hinder its dispersion in the PET matrix, as no change in the positions or the relative intensities of the peaks is observed after such a treatment. Consequently, treatment under microwave radiation is enough to stabilize the polymer, the final, conventional, curing step under vacuum, first used to remove the unreacted monomers, and may be unnecessary because no changes were observed in the structure identified by PXRD.

Preliminary studies show that polymerization of PET and dispersion of the LDH under conventional reflux conditions require longer reaction times, up to 2 h; however, when using microwave heating, the same (or even better) results are attained in just 35 min. This is a consequence of the bulk heating provided by microwaves, much more efficient than conventional heating using a furnace, favored by the interaction of the microwave radiation and the dipolar properties of EG and DMT monomers.

Transmission electron microscopy

The most important results obtained by TEM studies are included in Figure 3. Micrographs correspond to two representative samples and analyze in depth the possible dispersion and exfoliation process. Figure 3(a) corresponds to sample PET-LDH 5%. The dark, almost black, zones correspond to some layered particles, oriented with their main particle plane perpendicular to the observer. The stacked layered structure is almost lost, and the layers are oriented randomly across the polymer matrix. Accordingly, the exfoliation process mentioned earlier is observed clearly in this sample also by TEM. So, it is possible to confirm the exfoliation and dispersion into the PET matrix for PET-LDH nanocomposites at 5% or lower loaded LDH. The other micrograph [Fig. 3(b)] corresponds to sample PET-LDH 10%, where agglomeration of particles is observed, confirming, as concluded from the PXRD studies, that dispersion is not so efficient as for the lower loaded samples.

Thermal analyses

DTA curves for some representative samples are shown in Figure 4. Two endothermic peaks can be

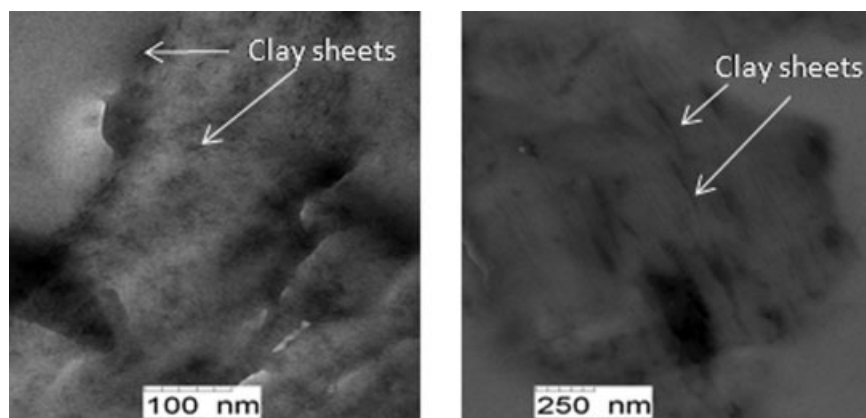


Figure 3 TEM images of PET-LDH nanocomposites with 5% (left) and 10% (right) LDH loading.

observed, the first one around 120°C, corresponding to glass-transition of the polymer (T_g), and the second one at $\sim 220^\circ\text{C}$, attributed to the melting-transition temperature (T_m); the exothermic peak, between 370 and 395°C, is due to the partial decomposition of the polymer.

T_g of PET nanocomposites increased from 102 to 132°C as the LDH loading was increased from 0 to 2 wt %. The increase in T_g of these compounds can be due to two reasons. First, the effect of small amounts of dispersed LDH layers in the PET matrix. The second factor is the interaction within the LDH galleries of the intercalated polymer chains with the inorganic matrix,¹⁵ i.e., an improvement in the adhesion between the polymer matrix and the LDH layers. The nanometric particles restricted segmental motion near the organic–inorganic interface. This is a typical effect for the inclusion of LDH in a polymer matrix.²⁵ However, when the LDH loading is increased from 2 to 5%, an opposite effect of the LDH on the T_g is observed. The T_g of nanocomposites decreased slightly from 132 to 129°C. This decrease in T_g seems to be a result of incipient LDH agglomeration. The LDH particles block end groups needed for the polymerization chains during reaction; thus the crosslink density might decrease at high clay contents and decreasing crosslink density would result in decreased T_g .

The T_m endothermic peak for PET is recorded at 216°C. This temperature is directly related to the amount of the LDH loading phase. The T_m values of the composites increased from 216 to 245°C when the LDH content was increased from 0 to 2 wt %. This suggests that small additions of LDH increased the crystallization degree of polymer in different extents; in agreement with previous reports by Cho, fillers may act as nucleating agents causing a better crystallization.²⁶ On the other hand, Desharun et al.²⁷ also mentioned such a T_m increase because the crystallinity of the polymer matrix is enhanced

and is associated to the amount of LDH added. The increase in the melting temperature can be due to an improvement in the short-range order, which is not detected by PXRD.

On the other hand, the decomposition temperature also increases when the LDH content increases up to a value of 2 wt %; this increase can be due to different factors, particularly the larger thermal stability of the LDH and the interaction between the LDH particles and the polymer matrix.

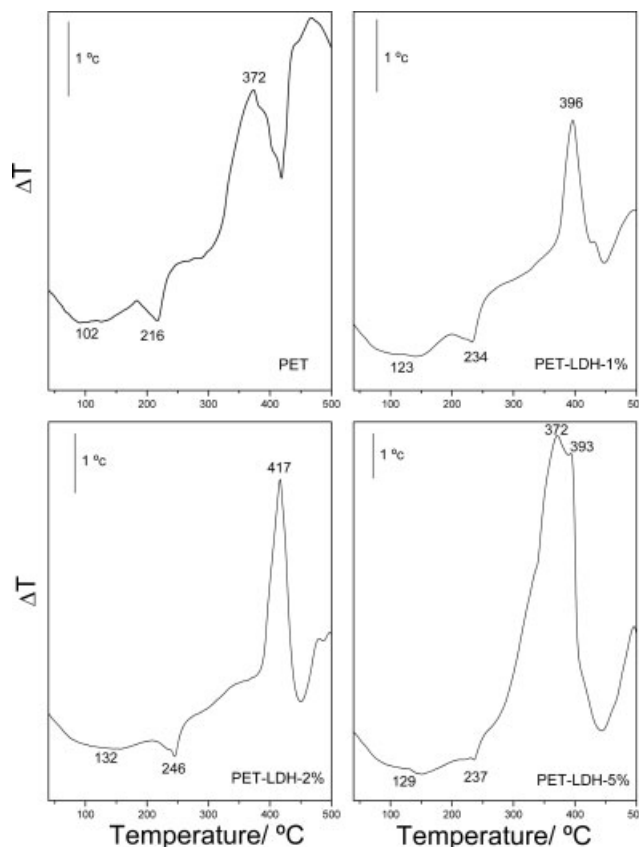


Figure 4 DTA curves for PET and PET-LDH nanocomposites with 1, 2, and 5% LDH loading.

It is expected that deagglomeration and dispersion of the inorganic filler in the polymer matrix will modify the thermal properties of the composite, in comparison to those for the pure polymer. The TG curves for the uncured nanocomposites and pure PET recorded in flowing oxygen are included in Figure 5.

Decomposition of PET takes place in three steps. The first weight loss starts at $\sim 300^\circ\text{C}$, amounting $\sim 18\%$ of the initial sample weight, and corresponds to removal of water. The main weight loss starts at $\sim 470^\circ\text{C}$ and the residue, amounting $\sim 10\%$ of the initial sample weight, is thermally stable up to $\sim 620^\circ\text{C}$. This second step is attributed to the partial decomposition of the polymer. Finally, a new weight loss, due to oxidative elimination of the carbonaceous residue derived from the initial polymer degradation,²⁸ is recorded at this temperature, and all the material is finally lost at $\sim 715^\circ\text{C}$.

Regarding the composite samples, all of them show similar curves below 500°C , but the weight loss starts smoothly around 460°C , and the first weight loss observed for the PET sample is no longer recorded. In other words, introduction of the inorganic filler somewhat stabilizes the polymer matrix. This enhancement of the thermal stability of the nanocomposite may be ascribed to a decrease in oxygen availability and volatile degradation products permeability/diffusivity deriving from the barrier effect of the exfoliated LDH in the PET matrix. However, after the main weight loss, recorded in the same temperature range as for pure PET, the plateau is not observed, and weight is lost smoothly up to $\sim 740^\circ\text{C}$. The weight of the residue obviously increases with the content of LDH in the sample. The continuous weight loss after the main weight loss step should be due to evolution of water vapor and products from decomposition of the interlayer anion. The residue, although it was not analyzed,

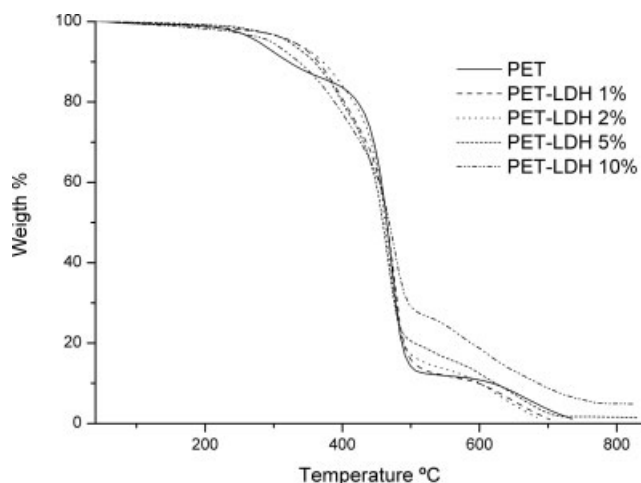


Figure 5 TG curve for PET and PET-LDH nanocomposites.

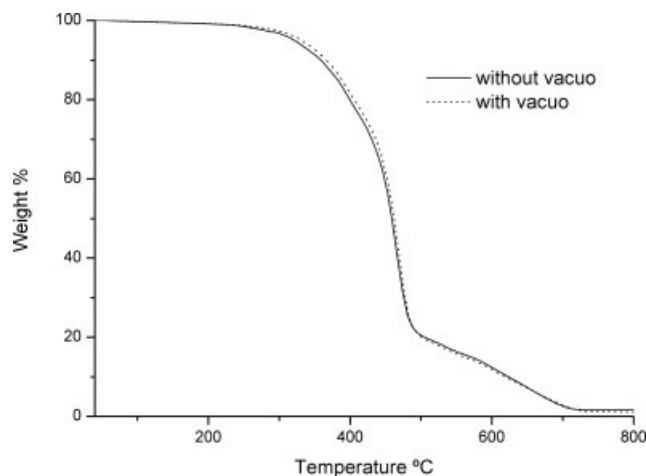


Figure 6 TG curve for PET-LDH 5% nanocomposites with and without treatment in vacuum.

should undoubtedly correspond (in agreement with the thermal decomposition patterns of LDHs) to a mixture of oxides and sulfates of the layer cations, which are only decomposed above the upper limit of the instrument used.

To determine the influence of the vacuum treatment on the thermal stability of the samples, a TG analysis of the samples submitted to vacuum was carried out. The TG curves recorded for samples with and without treatment *in vacuo* are included in Figure 6. It can be observed that vacuum treatment does not greatly affect the thermal behavior of PET-LDH nanocomposites. Therefore, this step in the samples preparation can be deleted.

CONCLUSIONS

It has been shown that *in situ* polymerization under microwave radiation constitutes an alternative method for preparing PET-LDH nanocomposites. The preparation time is considerably reduced, and the inorganic filler results well dispersed and exfoliated in the polymer matrix. The nanocomposites thus obtained are thermally more stable than original PET, especially for the low-loaded nanocomposites. Exfoliation and dispersion seems to be complete for LDH loadings up to 5% (weight); larger loadings lead to LDH aggregates in the composite.

Curing under vacuo of the composite can be skipped, as it neither modifies the structure or properties of the nanocomposites nor the thermal stability is enhanced.

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