Layered double hydroxide/polyethylene terephthalate nanocomposites. Influence of the intercalated LDH anion and the type of polymerization heating method

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ABSTRACT

Conventional and microwave heating routes have been used to prepare PET–LDH (polyethylene terephthalate–layered double hydroxide) composites with 1–10 wt% LDH by *in situ* polymerization. To enhance the compatibility between PET and the LDH, terephthalate or dodecyl sulphate had been previously intercalated in the LDH. PXRD and TEM were used to detect the degree of dispersion of the filler and the type of the polymeric composites obtained, and FTIR spectroscopy confirmed that the polymerization process had taken place. The thermal stability of these composites, as studied by thermogravimetric analysis, was enhanced when the microwave heating method was applied. Dodecyl sulphate was more effective than terephthalate to exfoliate the samples, which only occurred for the terephthalate ones under microwave irradiation.

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1. Introduction

Polyethylene terephthalate (PET) is a hydrophobic and semi-crystalline polymer possessing many excellent properties, namely, thermal stability, chemical resistance, high strength, good flexibility, low cost, etc.; it finds applications in electrical components, textiles, automobiles, rubber goods, and in food and beverage packaging [1]. To use it under more severe conditions requires to improve some properties, such as thermal, mechanical, and barrier ones. Hence considerable effort has been devoted to improve the various properties of PET for industrial applications [2,3].

Formation of inorganic/organic nanocomposites is a very active area of research because very small amounts of filler lead to a large enhancement of permeability and mechanical, thermal, electrical, optical and fire properties, as compared to the pure polymer or the conventional composites [4]. This improvement arises from the small size of the structural unit, its large surface area, the high surface-to-volume ratio, and improved adhesion between the nanoparticles and the polymer [5]. Although fillers such as alumina, silica, etc., can be added, layered plate-like particles (clay minerals or hydrotalcites) have shown the most promising results [6–14], due to its easy exfoliation, leaving layers with a thickness of the order of nanometers, [10] achieving an adequate dispersion of the lamellar nanoparticles within the polymer matrix.

Hydrotalcite-like compounds, also known as layered double hydroxides (LDHs) or anionic clays, are currently gaining attention for this purpose, as they exhibit certain specific advantages (purity, crystallinity and particle size control, easy functionalization), which are lacking in layered silicates type nanoclays [15,16]. They can be described by the empirical formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2(A^m)_{x/m} \cdot nH_2O]$, where A^{m-} is the anion balancing the net positive charge of the $M^{2+}(OH)_2$ brucite-like layers developed by a partial M^{2+}/M^{3+} isomorphic substitution. This sort of materials can host several types of anions, such as organics [16–18], polyoxometalates [19–20], bioactive molecules [21–22], metal cyano-complexes [23], etc. Functionalization switches the originally organophobic material into an organophilic one, making it more easily and homogeneously dispersible in a nonpolar polymer [24–27].

We here disclose the synthesis of LDH/PET nanocomposites by *in situ* polymerization. We have varied the thermal treatment during polymerization (conventional or microwave), and the nature of intercalated moieties in the LDH, dodecyl sulphate (DS) or terephthalate (Tph). Concerning the first parameter, microwave heating comes from direct interaction between microwaves and materials [28], the microwave radiation being first coupled to and then absorbed by the material; the electromagnetic energy is converted to thermal energy and heat is generated inside the material, in contrast with conventional heating methods, where heat is transferred from outside to inside. The reaction time and energy cost can be decreased, making easier the

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preparation of new materials; microwave irradiation heating is much faster, simpler and more efficient in energy consumption, compared to conventional methods [29]. Insertion of organic anions in the LDH interlayer improves the compatibility with the polymer [30–32]; intercalation of DS permits the sorption of different organic molecules due to its organophilic nature; the interlayer spacing increases, and intercalation and dispersion of organic molecules or polymer chains is easier. Carboxylate groups of Tph can covalently bond to PET chains by transesterification [33], and, in addition, terephthalate is a part of the PET monomer.

The degree of dispersion of the LDH particles and the type of the polymeric composites obtained were studied by transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD). The interactions between LDH and PET were discussed on the basis of the FTIR spectroscopy data and the thermal stability was determined by TGA and DTA analyses.

2. Experimental

2.1. LDH preparation

All chemicals were from Fluka and used as-received. The organo-LDH modified with terephthalate (Tph-LDH) or dodecyl sulphate (DS-LDH) were prepared by the coprecipitation method [34] in an N_2 (from L'Air Liquide, Spain; 99.995%) atmosphere to exclude carbonate from the LDHs. A salt of the anion (0.01 mol) was dissolved in 100 ml of deionized water and the pH was adjusted to 10 (2 mol/L NaOH). A solution of magnesium nitrate (0.01 mol) and aluminum nitrate (0.005 mol) in 100 mL of deionized water was then slowly dropped into the vigorously stirred organic solution. The pH of the solution was maintained at 10 by adding 2 mol/L NaOH solution. The precipitate was washed with carbonate-free water, until removal of the excess of charge balancing anions and cations in the starting salts was achieved.

2.2. Nanocomposites synthesis

Poly(ethylene terephthalate), PET, was prepared by conventional heating: a mixture of 0.05 mol ethylene glycol (EG), 0.025 mol dimethyl terephthalate (DMT) and 0.01 g zinc acetate (ZnAc) was refluxed at 220 °C for 2 h under a nitrogen stream. The change in viscosity confirmed formation of the polymer.

For preparing the polymer under microwave heating, 0.05 mol EG, 0.025 mol DMT and 0.01 g ZnAc were mixed and heated in a Milestone Ethos Plus microwave oven; the temperature was raised from room temperature to 140 °C (20 °C/min), then to 200 °C (12 °C/min) and finally set to 270 °C for 35 min. The reaction mixture was continuously gently stirred during heating.

The composites were prepared similarly, the only difference being that the LDH was previously dispersed for 1 h in a Fungilab ultrasonic bath at 250 W in EG and added to the organic mixture.

The samples prepared following the conventional heating method were named as *y-X*-PET, while those obtained under microwave irradiation were named as *y-X*-PETmw; *y* stands for the mass percentage content of LDH (1%, 2%, 5% and 10% with respect to the mass of polymer) and *X* for the anion intercalated in the LDH (*X*=DS for dodecyl sulphate or *X*=Tph for terephthalate).

2.3. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D-500 instrument equipped with Diffract AT software, using Ni filtered Cu *K*α radiation (λ=1.54050 Å) with a scanning speed of 2° (2θ)/min. The FTIR spectra were recorded in a Perkin Elmer FTIR 1600 instrument, using the KBr pellet technique;

100 spectra (with a nominal resolution of 4 cm^{-1}) were averaged to improve the signal-to-noise ratio. Thermogravimetric (TGA) and differential thermal analyses (DTA) were carried out in TGA-7 and DTA-7 instruments, respectively, from Perkin Elmer, under flowing (30 mL/min) oxygen (from L'Air Liquide, Spain), at a heating rate of 10 °C/min. Transmission electron microscopy (TEM) studies were performed in Servicio General de Microscopia Electrónica (University of Salamanca, Spain) using a Zeiss 902 apparatus. The samples were sonicated in acetone and then a drop of the suspension in acetone was deposited onto a holey carbon film deposited on a Cu grid.

3. Results and discussion

The LDH fillers have been characterized in a preceding work [18]. The lamellar materials were submitted to microwave radiation to different times and finally calcined at 225 °C. These processes were carried out in order to understand the LDHs behavior under similar conditions than those used in the nanocomposite preparation. Diffraction patterns of solids intercalated with dodecyl sulphate and terephthalate and calcined at 225 °C show that the lamellar structure is maintained. However, some differences are observed depending on the intercalated anion. In systems intercalated with dodecyl sulphate the basal spacing decreases due to grafting of anions into the brucite-like layers, and only minor differences were observed when the samples had been submitted to microwave radiation. The terephthalate series shows a partial loss of crystallinity, and, in addition and more important, the basal diffraction lines were modified, pointing to a rearrangement of the interlayer anions, showing different phases (perpendicular, parallel or interstratified), which precise nature is slightly dependent on the previous microwave treatment. The PXRD patterns of the fresh samples intercalated with dodecyl sulphate and terephtalate are included in Fig. 1 in order to observe the changes produced upon compounding.

The diffraction patterns of PET and some composites prepared are also shown in Fig. 1. All samples show the diffraction maxima characteristic of PET [35,36]; the main ones, labeled in the figure with their Miller indexes and corresponding to the (0 1 0), (1 1 0) and (0 0 1) reflections, are recorded at 2θ=17.3°, 22.5° and 25.7°, respectively. However, several differences can be observed between the PXRD patterns of the samples obtained using different LDHs.

As previously reported [12,37], only the diffraction maxima due to PET are recorded in the patterns of the low loaded ($\leq$5%) composites prepared with DS-LDH (panels A and B in Fig. 1), whichever the heating method used in the polymerization process. No reflections corresponding to the separate LDH phase were observed. This behavior is due to disordering of the layers or to a large basal spacings (2θ<2°) produced by the insertion of polymer chains in the interlayer region. Samples 10-DS-PET and 10-DS-PETmw (not shown here) exhibit a weak maximum diffraction at 2θ=4.9°, due to the LDH, indicating that the LDH crystal structure is not destroyed completely.

Samples obtained with Tph-LDH show a different behavior: The PXRD patterns display the characteristic maxima of PET, but when the samples were obtained by conventional heating (panel C), all solids show additional weak maxima close to 2θ=6.3°, 12.7° and 61° due to diffraction by planes (0 0 3), (0 0 6) and (1 1 0), respectively, of the terephthalate LDH material with a basal spacing of 14 Å (marked with an asterisk in the diagram of sample 5-Tph-PET). The intensities of the LDH reflections increased with the LDH content. This behavior indicates that the lamellar structure in the polymeric matrix has not been completely destroyed, as even at low LDH loading (1%) the characteristic maxima of the LDH can be identified.
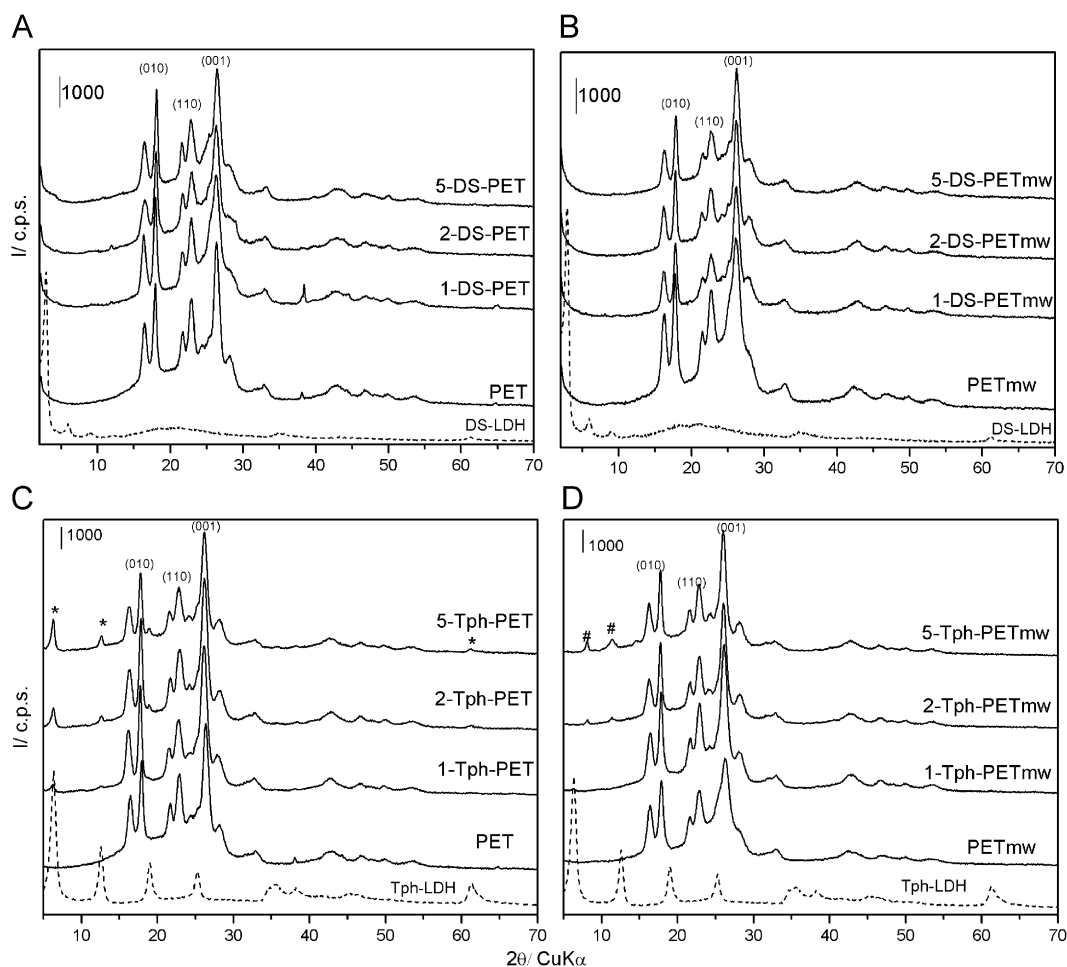
Fig. 1. PXRD patterns of pristine LDH, PET and some nanocomposites prepared.

When the polymerization was carried out under microwave radiation, the behavior was different. The pattern for sample with 1% LDH loading does not show any maximum due to the lamellar solid, probably because the LDH content is too low and LDH diffractions are hardly detected; alternatively, it can be due to the dispersion of the inorganic filler, as well as to the probable LDH delamination. On increasing the LDH content, two new reflections were developed at $2\theta=8.1°$ and $2\theta=11.5°$ (marked with # in the pattern of sample 5-Tph-PETmw), while the maximum close to $2\theta=61°$, corresponding to the (1 1 0) reflection, is not observed. Although these new reflections are not characteristic of a lamellar compound, they could be attributed to two different phases of Tph-LDH which formation is induced by the microwave treatment. However, in the preceding work [18], the possible phases formed by LDH with terephthalate, display PXRD maxima at $2\theta=5.8°$, $11.3°$ and $17.4°$ for a phase with the terephthalate anions perpendicular to the layers, at $2\theta=9.1°$ and $18.4°$ if the intercalated terephthalate anions are parallel to the layers, and at $2\theta=3.7°$, $7.6°$ and $10.3°$ in the interstratified phase. Comparing different data, it can be concluded that the new reflections cannot be assigned to any phase corresponding to the LDH. Therefore, the two new maxima at low diffraction angles are probably due to the presence of a third phase of PET, which is partially ordered [38,39].

Therefore, when the samples are prepared by conventional heating (panels A and C in Fig. 1) incorporation of DS increases the interlayer distance, ultimately leading to the probable delamination of the inorganic sheets (diffraction by basal planes are undetected), and increases the compatibility between the LDH material and the organic polymer. However, Tph does not favor

the exfoliation of the LDH sheets and their dispersion in the polymeric matrix. This difference can be due to the fact that terephthalate is a component of the monomer, and its insertion can reduce the entropy of the system, disfavoring the intercalation process [40], or more probably, it can be due to the charge density of terephthalate, higher than that of DS, and the basal spacing of the DS-intercalated LDH, much higher than that of the terephthalate-LDH samples.

Concerning the heating method, microwave heating reduces the preparation time, because of the bulk heating provided by microwaves, favored by the interaction of the microwave radiation and the dipolar properties of EG and DMT. EG has a high permanent dipole and therefore is an excellent susceptor of the microwave irradiation, taking up the energy from the microwave field and immediately heating the reaction solution at a high temperature [28,41]. Summarizing, the use of microwaves improves the dispersion of the inorganic filler in the polymer matrix of the TpH-PET samples.

The FT-IR spectra of the samples obtained from DS-LDH by *in situ* polymerization under microwave radiation are included in Fig. 2A. The spectra of the samples obtained under conventional heating are similar to those here shown. All spectra show characteristic bands due to PET [42,43] and the LDH [18].

The intense and broad band at ca. $3420\ cm^{-1}$ is due to the stretching mode of hydroxyl groups from the brucite-like layers; the very weak band at $1636\ cm^{-1}$ corresponds to the bending mode of water molecules from the interlayer. The weakness of this band should be related to the small amount of water existing in the hydrophobic interlayer. The weak bands at 2925 and
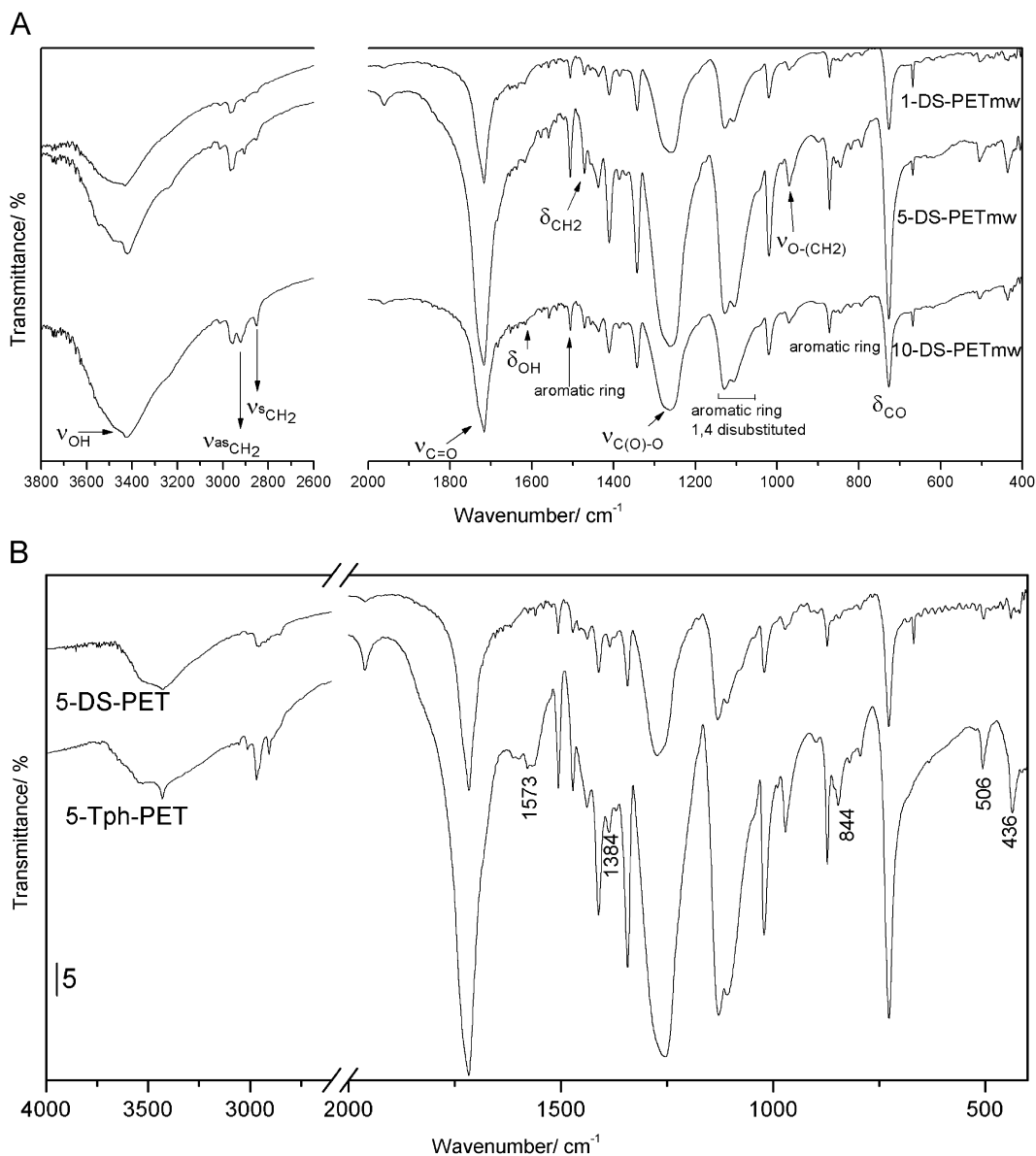
Fig. 2. FT-IR spectra of (A) nanocomposites obtained with DS-LDH and microwave heating and (B) nanocomposites 5-DS-PET and 5-Tph-PET.

2854 cm^{-1} are due to the antisymmetric and symmetric modes, respectively, of the C–H bonds in the methylene groups of the aliphatic chain of DS, as well as from the PET moieties. Other PET bands are recorded at 1716 cm^{-1} (stretching mode of the carbonyl group), 1264 cm^{-1} (C–(O)–O groups), 927 cm^{-1} (stretching vibration of the O–CH$_2$ group), and 730 cm^{-1} (bending mode of the carbonyl groups in the aromatic ring) [42].

The weak bands due to the aromatic ring are recorded close to 1580, 1400 and 850 cm^{-1}, together with two bands at 1126 and 1021 cm^{-1} due to the 1,4-substituted aromatic ring. Finally, the bands corresponding to metal–OH translation modes within the brucite-like sheets, which are expected in the low wavenumbers region of the spectra, are not recorded, due to the high dispersion and low concentration of LDH in the polymer matrix.

The spectra of the samples obtained with Tph-LDH are similar to those for the DS-PET nanocomposites, but with some of bands attributed to Tph-LDH. For an easy comparison, the spectra of both samples, prepared by conventional heating and with 5% LDH loading, are shown in Fig. 2B. The spectrum of sample 5-Tph-PET shows bands at 1573 and 1384 cm^{-1} (v_{as}(COO) and v_s(COO)

modes of the carboxylate groups), 844 cm^{-1} (benzene ring), and 506 and 436 cm^{-1} (stretching modes of the octahedra layers).

In addition, FTIR spectroscopy is able to inform about short-range order, which depends on the coupling of a vibration mode to adjacent vibrations. The IR bands of conformers *trans* and *gauche* of PET have been used to determine the structural changes taking place when LDH was added or microwave heating was used. The characteristic bands at 899 and 1042 cm^{-1} have been assigned to vibrations of the *gauche* conformer, which exists only in the amorphous phase. Two bands at 845 and 970 cm^{-1} have been assigned to vibrational modes of the combined crystalline and amorphous phases in the *trans* conformer [44,45]. The bands at 793 and 875 cm^{-1}, due to vibrations of the benzene ring, are not affected by the conformational changes and are usually used as a sort of internal reference.

The FTIR spectra of some Tph-LDH composites are included in Fig. 3; only the 1080–760 cm^{-1} range is shown. The presence of LDH in the polymer apparently has no influence on the structure of PET, except for the weak increase in the intensity of the shoulder at 899 cm^{-1}. Its intensity increases for the nanocomposites obtained
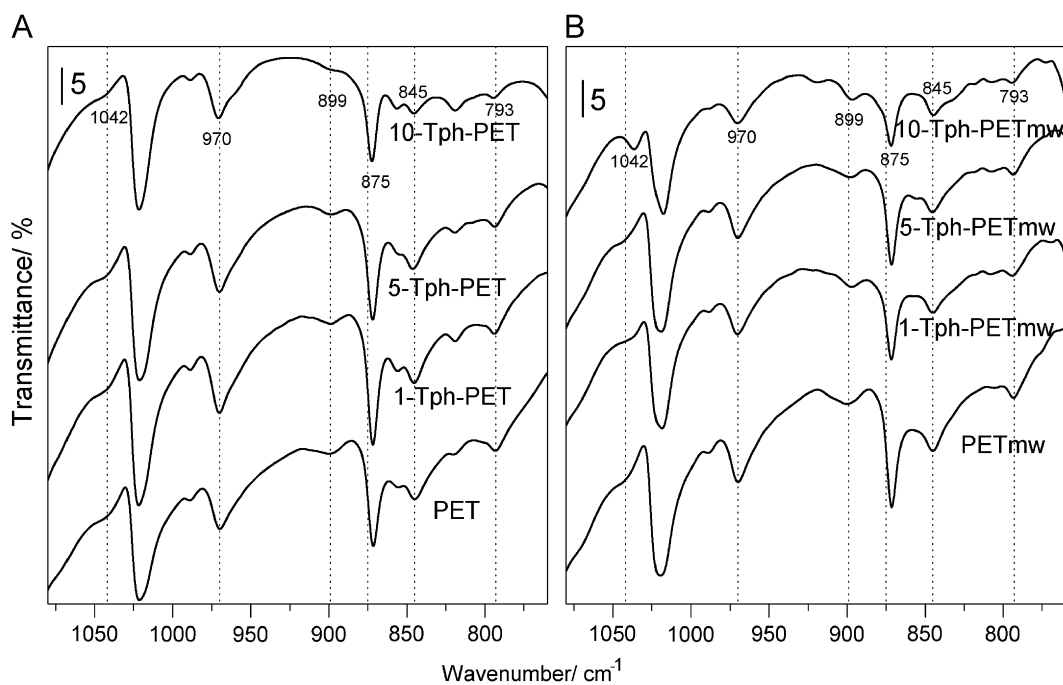
Fig. 3. FT-IR spectra of PET and nanocomposites with Tph-LDH prepared by conventional (left) and microwave heating (right) (1080–760 cm^{-1} range).
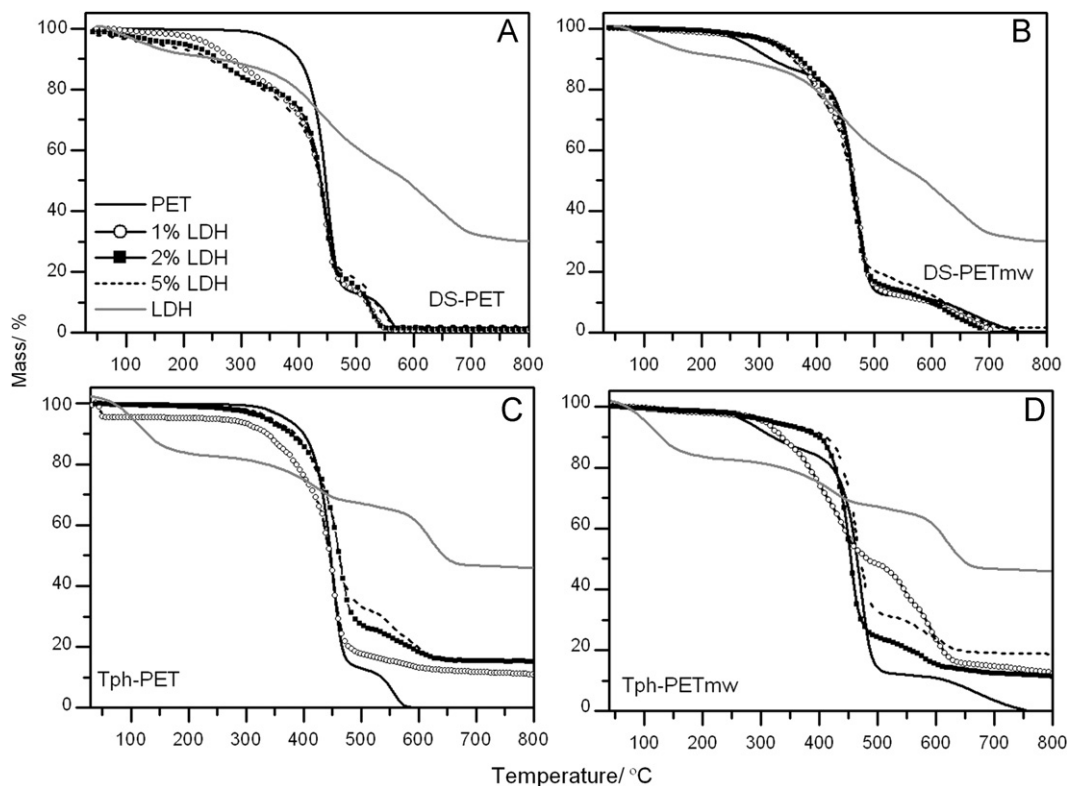

Fig. 4. Thermogravimetrical curves for PET, precursor LDHs and nanocomposites prepared.

under conventional heating, pointing out to a poor influence of the LDH on the short-range order of the polymer matrix.

The thermal stability of polymers can be modified upon formation of composite materials. The TGA curves (recorded in air) for PET and PET-LDH composites containing 0%, 1% and 5% (w/w) of LDH are shown in Fig. 4.

Degradation of PET obtained by conventional heating (panels A and C) takes place in two steps, the first one at 430 °C and the second one around 450 °C; PETmw (panels B and D) shows three degradation steps, the onset temperatures being 270, 440 and 620 °C. The first one is attributed to removal of water, although the mass loss observed is too large for corresponding exclusively to water release from the interlayer (as suggested by the FTIR data, the interlayer water content should be rather low, due to the hydrophobicity of the polymer), and should include the first stages of PET decomposition. The second and main mass loss is

due to the partial decomposition of the polymer, as for PET prepared by conventional heating; the last process corresponds to oxidative removal of the carbonaceous residue derived from the initial polymer degradation [46]. The polymer is completely burnt off in both cases.

The behavior of the composite samples depends both on the heating method and on the nature of the interlayer anion. Decomposition of polymer-nanocomposites obtained by conventional heating (panels A and C) starts at a lower temperature than that of the pure polymer; this process is due to the water release existing in pristine LDH; therefore the incorporation of hydrotalcite does not improve its thermal stability. The decrease in the decomposition temperature is even more evident as the loading of the inorganic component is increased, as the amount of water in the composite increases producing a hydrolytic degradation of PET [47], or probably because the basic LDH catalyzes the degradation of PET [48]. However, the nanocomposites obtained with Tph-LDH (panel C) are stable up to a higher temperature than pure PET. Formation of char at 650 °C, probably due to the presence of the aromatic rings which can assist the stabilization of the nanocomposites [1], is also observed.

The behavior observed for the polymer-nanocomposites prepared under microwave irradiation (panels B and D) was similar to that of the corresponding system obtained by conventional heating. However, regardless the anion intercalated in the lamellar material, the thermal stability improves at low temperatures. This behavior can be due to the differences between conventional or microwave heating: conventional heating is transmitted inside the material by conduction, a very inefficient process for materials with low thermal conductivities, as PET, whilst microwaves heat the material at a molecular level, avoiding temperature gradients and therefore internal stresses due to the absence of thermal gradient are minimized [49]. Also, this microwave radiation improves the thermal stability in the LDH precursor; this could be explained considering a better ordered material, both within the layers and the interlayer region, in which larger electrostatic interactions between the hydroxyl layers and the interlayer anions are established [18].

It is also interesting to highlight the difference of temperature reached by both the procedures; the conventional heating can reach 220 °C, whilst microwave heating can reach 270 °C; the loss of water molecules or other compounds with low decomposition temperature is rather probable at this temperature, accounting for the first mass loss observed for PET–LDH composites prepared under conventional heating.

Terephthalate favours formation of char in both cases, and if compared to conventional heating, microwave heating delays the beginning of the decomposition.

The DTA results are summarized in Table 1; they are typical for polymer/inorganic nanocomposites. Three processes are recorded: from room temperature to 150 °C (glass-transition, T_g, of the polymer); at ca. 220 °C (melting-transition temperature, T_m); and between 370 and 405 °C, due to the partial decomposition of the polymer.

The glass transition temperature of PET nanocomposites increased when the LDH loading was increased from 0 to 2 wt%. This can be due to two reasons: (i) the effect of small amounts of dispersed LDH layers in the PET matrix, or (ii) the interaction of the intercalated polymer chains with the inorganic matrix within the LDH galleries [10], 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 [50]. However, when the LDH loading is further increased to 5%, an opposite effect of the LDH on T_g is observed: the decrease in T_g seems to be a result of incipient

Table 1
Temperatures corresponding to glass transition (T_g), melting temperature (T_m) and combustion process for some samples prepared in this study.

Sample	T_g (°C)		T_m (°C)		Combustion (°C)	
	conventional	mw	conventional	mw	conventional	mw
PET	104	102	220	216	350	372
1DS-PET	129	123	210	234	394	396
2DS-PET	136	132	203	246	404	417
5-DS-PET	130	129	221	237	403	372
						393
PET	104	102	220	216	350	372
1Tph-PET	139	136	217	235	355	391
2Tph-PET	140	145	222	230	367	307
						382
5Tph-PET	148	115	220	229	345	310
						373
						398

LDH agglomeration, LDH particles blocking end groups needed for the polymerization chains during reaction and thus the crosslink density might decrease at high LDH contents, resulting in lower T_g values.

The value of T_m is directly related to the LDH loading. The results suggest that small amounts of LDH increased the crystallization degree of the polymer; in agreement with previous reports by Cho, fillers may act as nucleating agents thus improving the crystallization [51]. Desharun et al. [52] also mentioned such a T_m increase and the crystallinity of the polymer matrix was 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.

TEM studies were carried out to examine the qualitative dispersion of the LDH layers in the polymeric matrix. Microphotographs for nanocomposites are shown in Fig. 5. Samples 5-DS-PET and 5-DS-PETmw show typical nanocomposite morphologies, the second one showing better defined and narrower dark lines than the sample without microwave treatment.

This behavior suggests that microwave heating improves the dispersion and probably the delamination of the inorganic filler in the polymer matrix. On comparing samples PETmw, 5-DS-PETmw and 10-DS-PETmw, it can be observed that the dark zones corresponding to the layered particles are stronger and broader when the LDH content is increased, confirming, as concluded from the PXRD studies, that dispersion is not as efficient as for the lower loaded samples.

4. Conclusions

Conventional and microwave heating routes were used to prepare PET–LDH (polyethylene terephthalate–layered double hydroxide) composites by *in situ* polymerization with 1–10 wt% LDH content. To enhance the compatibility between the PET polymer and the LDH, terephthalate (Tph) or dodecyl sulphate (DS) was previously intercalated in the lamellar structure.

The powder X-ray diffraction patterns show that incorporation of DS improves the delamination of the layers and the compatibility between the LDH material and the organic polymer. However, the LDH crystal structure is not destroyed completely in the Tph conventional samples, the dispersion and probably
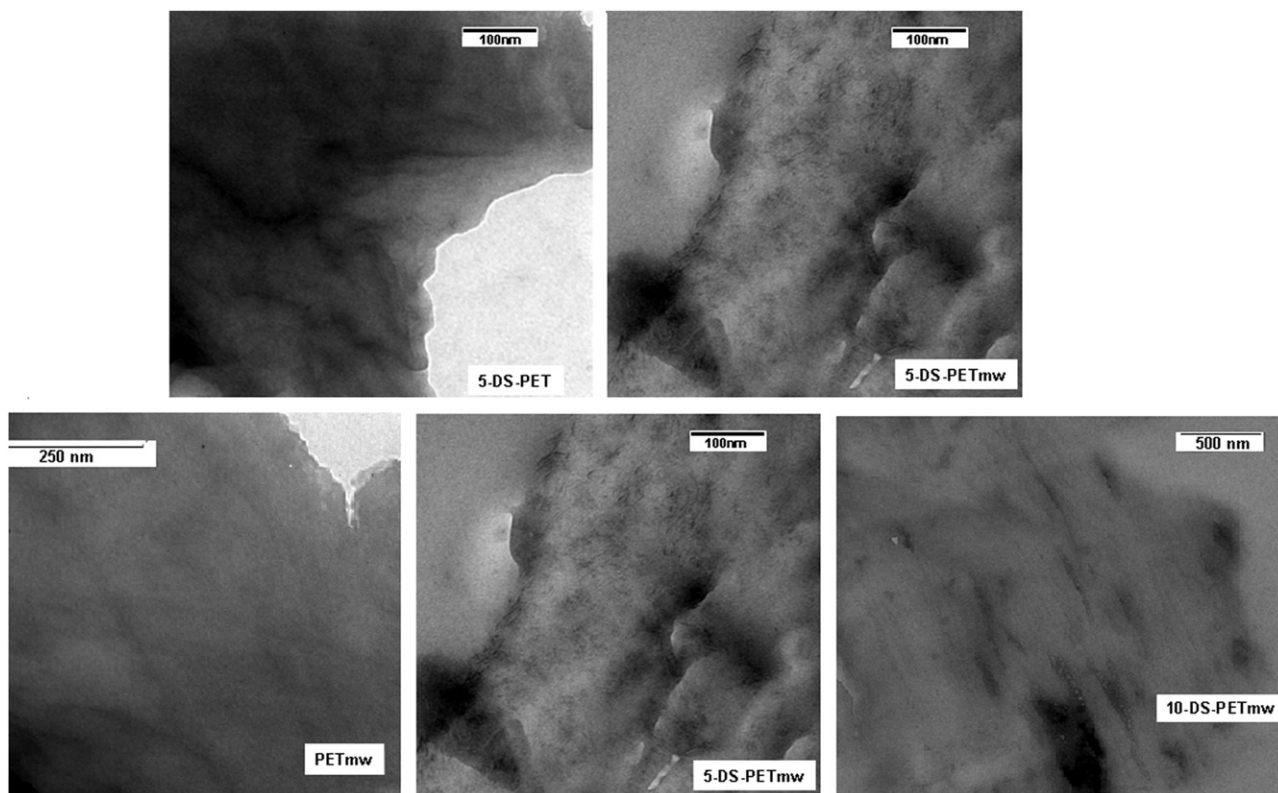
Fig. 5. TEM images of representative nanocomposites.

delamination only improved when they were submitted to microwave heating.

The thermal behavior is dependent both on the heating method used to prepare the polymer and on the nature of the interlayer anion. Incorporation of hydrotalcite within the PET matrix does not increase the thermal stability of pure PET, but the thermal stability of samples prepared under microwave irradiation improves at low temperatures, as microwave 'volumetric' heating favors the absence of internal stress.

The microwave process improves the dispersion and the thermal stability of polymer-nanocomposites due to the interaction of the microwave radiation and the dipolar properties of EG and the homogeneous heating.

Acknowledgments

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