

Influence of clay modification process in PA6-layered silicate nanocomposite properties

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Abstract

The melt intercalation method was employed to prepare layered silicate polyamide 6 nanocomposites. Low cost bentonite clay was purified and modified with octadecylamine using different experimental conditions in order to improve efficiency in the modification step. Nanocomposites properties as a function of clay nature, solid content during the modification process and the excess of surfactant in the organophilic clay were analysed. Small Angle X-Ray Diffraction (SAXD) and Transmission Electron Microscopy (TEM) gave a qualitative picture of the microstructure and a correlation to mechanical properties has been established. Thermogravimetric Analysis was used to investigate the surfactant location in the organophilic layer silicates by the identification of the observed thermal degradation transitions. Surfactant excess was found to be one of the crucial parameters to be taken into account.

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1. Introduction

Polymer clay nanocomposites are a new class of materials that show improved properties at very low loading levels compared with conventional filler composites. Among these improved properties are mechanical, dimensional, permeability, thermal stability and flame retardant enhancements with respect to the bulk polymer [1]. In order to obtain good interfacial adhesion and mechanical properties the hydrophilic clay needs to be modified prior to introduction in most polymer matrices that are organophilic. Clay modification is generally achieved by ion exchange reactions of organophilic cations by sodium ions [2,3], and the polymer-clay nanocomposites may be obtained mainly by three methods: intercalation of a suitable monomer followed by polymerization [4,5], polymer intercalation from solution [6] and direct polymer melt intercalation [7].

Nanocomposite materials have attracted great interest

because nanoclays can reinforce almost all types of polymer matrices with similar properties than traditional composites but less weight and better processability. Most of the previous works on the preparation and characterization of polymer-layered nanocomposites used commercial modified layered silicates (LS) [8,9]. However, some works dealing with the modification process in order to improve the quality of the nanoclays to produce nanocomposites with enhanced properties have been published [10,11]. In general, LS are treated with several organic onium bases, and in most of the modification processes around 2–5% weight of solids is used, in order to diminish the viscosity and get a more homogenous solid solution. Isomorphic substitution within the layers generates a negative charge, defined through the cation-exchange capacities (CEC). This excess of negative charge is balanced by cations (Na^+ , Ca^{2+} , Li^+) that exist hydrated in the interlayer [12]. To render nanoclays miscible with polymers one must exchange the alkali counterions with cationic surfactants, such as alkylammonium. Although an excess of surfactant is normally used to complete the interchange reaction, the

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properties of the final nanocomposite can diminish and, therefore, several drying processes in hot water or water/alcohol mixing must be realized. Morgan et al. [13] found that the removal of excess organic treatment by Soxhlet extraction resulted in improvements in bending modulus, clay dispersion, time to ignition and heat release rate during burning.

The aim of this study is to investigate the effect of the modification process of the LS on the morphology and mechanical properties of a Polyamide-6 nanocomposite. A series of different parameters have been controlled during the process of clay modification in an attempt to reduce cost and to obtain nanocomposites with optimal properties, increasing the output of the process. Bentonite is a high quality clay mineral that contains about 60–95% of the mineral montmorillonite. Thus the bentonite directly obtained from the deposit is a low cost raw material. Two aspects are taken into account in the present work, first the substitution of montmorillonite clay for bentonite clay in order to evaluate the presence of impurities and, second the excess of surfactant in bentonite clays in order to understand their effect. PA 6 nanocomposites were studied and their mechanical properties were correlated to the characteristics of the organophilic clays and the nanocomposite morphology.

2. Experimental procedure

2.1. Materials

A commercial PA6 (Bergamid B 90, PolyOne) having a high viscosity was employed. Two different clays were used: a commercial montmorillonite (MMT) from Nanacor, modified with octadecylammonium (MMT-I30.TC) was used as reference, and a sodium bentonite (BT-Na) from Tolsa (Spain) which was purified and modified with octadecylammonium ions (ODA) following the method described later. The characteristics of the LS are detailed in Table 1. The purified bentonite clay used for the modification process shown only 63% of montmorillonite type clay. It may interest to remark that the rest of the components shown low or none exchange capacity so they will act mainly as microfillers. The particle size estimated as diameter from SEM and TEM observations of the layered silicate clays are smaller in bentonite than in MMT.

2.2. Clay modification

Prior to the clay modification, a purification process was necessary to eliminate impurities that might act as microfillers in the polymer and disturb the final properties. The purification process consisted in the following steps: (a) water dispersion of the as received clay and 24 h aging to ensure swelling of clay, (b) elimination of supernatant organic phases, (c) wet sieving through 100 μm nylon

mesh, (d) 2 h milling with steatite balls to reduce agglomeration and (e) high shear dispersion treatment in an IKA Labor Pilot 2000/4 machine to exfoliate the LS. The resulted slips were solid content adjusted to 8 and 16% wt. A 0.4% wt referred to the solid content of lignin sulfonate surfactant was used to maintain the viscosity of the suspension in an adequate level for processability. The cation exchange capacity, CEC, of the resulted clay was 80 meq/100 g.

The organic modified bentonite was synthesized by ion exchange reaction between Na-bentonite and octadecylammonium salt, ODA. This material was obtained after protonation of octadecylamine by adding hydrochloric acid to the reaction medium during the process, before the ion exchange reaction can occur. Thus, octadecylamine was previously mixed with HCl in water and heated at 80 °C for a few minutes. The CEC ODA/clay ratio was 1.5 and the molar ODA/HCl ratio was 1:1. The as-protonated surfactant was drop wise added to the clay suspension and maintained at 80 °C for 1 h under vigorous stirring. Then the suspension was cooled to room temperature. This suspension was dispersed and washed with water twice. A third dispersion and washing was accomplished using a 50/50 ethanol/water mixture.

The final washed modified clay was dispersed in water and spray drying in a Rotatory Spray Drier NIRO 2267. Two set of spray drying conditions were chosen: (a) Low temperature, the inlet temperature was set at 180 °C and an outlet temperature of 70–80 °C; and (b) High temperature, the inlet temperature was set at 300 °C and an outlet temperature of 110–120 °C was selected.

This method is similar to the method described on the literature [14,15]. However, in this work the solid percent of the clays that is modified during the process has been varied (8% and 16%) and a different clay drying procedure has been used.

2.3. Preparation of PA 6-clay nanocomposites

Nanocomposites were obtained in a Leistritz 27 GL intermeshing twin-screw extruder operating at 240–250 °C and 450 rpm in corrotating mode. The polymer matrix was added through the first side and the organophilic clay through a side feeder. PA 6 granulates were dried at 80 °C for 8 h, and the modified clay was dried at 60 °C for 24 h prior to blending in the extruder.

Nanocomposites were injection moulded into test pieces by using an injection molder Margarite JSW110 after being dried at 80 °C for 8 h. The temperature of the cylinders was 240–250 °C and mould temperature was 80 °C.

2.4. Characterization

Morphology studies of the unmodified and modified clays were achieved using a Zeiss DSM 950 Scanning Electron Microscope (SEM) after gold coating. X-ray

Table 1
Characteristics of the layer silicate clays

Clay name	Clay composition (dry wt%)	Humidity (%)	Agglomerate size (μm)	Particle size ^a (μm)	C.E.C (meq/100 g)
MMT	100 montmorillonite-	8–12	16–22	1.5–2	120
BT-Na	63 montmorillonite 18 dolomite 10 illite 4 quartz 3 calcite 2 plagioclase	8–12	10	1–2	80
MMT-I30.TC	67.7 MMT 31.3 Octadecylammonium	0.3	18–23	1–1.5	–
BT-1	63.9 BT-Na 36.1 Octadecylammonium	0.3	40–60	0.7–1.5	–
BT-2	58.1 BT-Na 41.9 Octadecylammonium	0.3	40–60	0.7–1.5	–
BT-3	67.7 BT-Na 31.3 Octadecylammonium	0.3	40–60	0.7–1.5	–

^a Equivalent diameter of montmorillonite layered silicate.

diffraction of the clays and nanocomposites was performed in a Philips X'Pert MPD using Cu K α radiation in order to evaluate the evolution of the clay d_{001} reflection. Transmission Electron Micrographs (TEM) were taken using a Jeol JEM 2000FX Electron Microscope with 200 kV accelerating voltage from 100 nm microtomed sections of the nanocomposites obtained with a Reichert-Jung Ultracut E microtome.

Thermogravimetric Analysis was used to study surfactant decomposition and to determine the clay content in the obtained nanocomposites. Thermograms were obtained in nitrogen atmosphere with a heating rate of 10 °C/min using a Mettler Toledo TGA851. The LS content was measured by thermogravimetric analysis, being around 5% wt for all the nanocomposites.

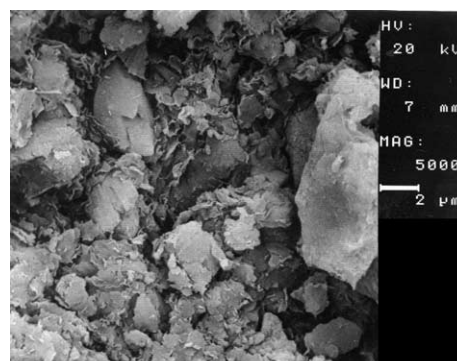
Young Modulus and Tensile Strength were measured according to UNE-EN ISO 527-1 and 527-2 with a Instron Model 5500R60025. Heat deflection temperature (HDT) was determined in an HDT-VICAT tester microprocessor, ATS-FAAR, A/3M model according to UNE-EN ISO 75-1 and using a load of 1.8 MPa.

3. Results and discussion

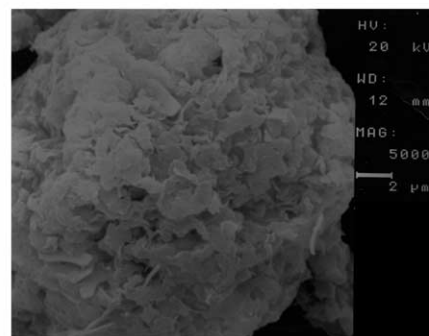
3.1. Characterization of modified LS

In Figs. 1 and 2 SEM micrographs of un-modified and modified bentonite and montmorillonite are shown. Both clays were granulated in the spray dryer following the low temperature procedure. The average granulates ranges from 40–60 μm , due to both the rotating speed of the spray drier rotor and the viscosity of the suspension. Granulates show

an irregular shape derived from the spherical drops that shrunk during the drying process because of water evaporation. By comparison of unmodified and modified bentonite and montmorillonite granules, a more open



(a)



(b)

Fig. 1. SEM photomicrographs of (a) un-modified and (b) ODA modified bentonite.

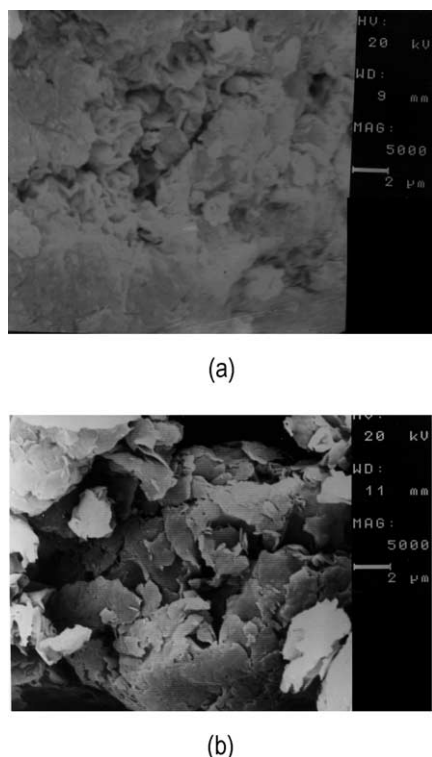


Fig. 2. SEM photomicrographs of (a) un-modified and (b) modified montmorillonite.

structure is detected in both modified clays, and SEM distinguishes individual layer blocks. During drying of un-modified clays, physical bonding of face to face and face to edge takes place and thus a rigid structure is conformed. In contrast, the presence of ODA surfactant on the LS surface and inside the galleries produces a more open structure that will favour further exfoliation during nanocomposites fabrication.

Clay structure was investigated by X-Ray Diffraction (XRD) analysis (Fig. 3). The basal spacing data d_{001} for modified clays increased due to ion exchange with the

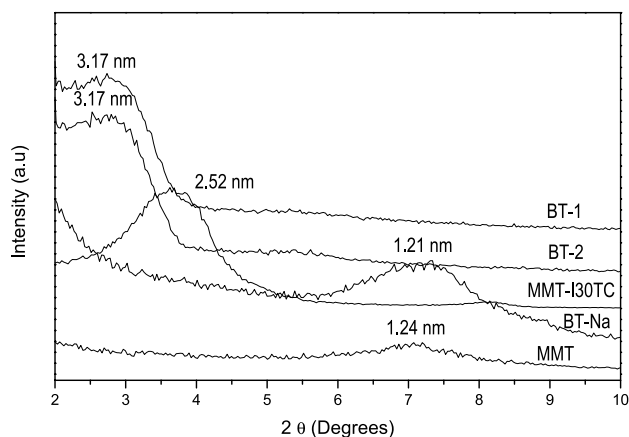


Fig. 3. X-ray diffraction patterns of un-modified (MMT) and modified (MMT-I30.TC) montmorillonite and un-modified (BT-Na) and modified (BT-1 and BT-2) bentonite.

alkylammonium surfactant. A more efficient intercalation was observed in the modified bentonites in comparison to montmorillonite. No differences in the XRD results for the modified bentonites obtained under different modification conditions (BT-1 and BT-2) were observed, and therefore a similar intercalation of the surfactant in the modified bentonites is produced, when different slip solid contents during the modification process are employed. The use of a high shear dispersion treatment in combination with a surfactant improves the efficiency of the modification process with high solid content (BT-2).

Thermogravimetric analysis of the un-modified clays showed two thermal degradation transitions (Fig. 4): (a) the adsorbed water that volatilize at low temperatures; and (b) the crystallization water at higher temperature. The ODA salt adsorbed on the secondary phase of bentonite and free surfactant thermally decomposes between 200–300 °C (peaks 1 and 2 in Fig. 5), but this transition moves to higher temperatures when the modified agent is adsorbed on the silicate layers and intercalated into the clay galleries (peak 3 and 4 in Fig. 5). It was also observed that the absorbed water was removed after the modification process, although the crystallization water still remains.

Modified bentonite and montmorillonite showed a slightly different behaviour. Four thermal transitions were observed for the modified bentonite. The first one was detected in the 200–250 °C range and it is associated with the surfactant adsorbed on other mineral components present in the clay. In the range 250–350 °C two thermal transition overlapped were observed one of them; between 250–325 °C associated to the decomposition of free surfactant and the other one in the range of 325–350 °C related with the elimination of surfactant adsorbed on montmorillonite clay surface was observed. Finally thermal degradation of the surfactant intercalated between the clay galleries was detected at 350–450 °C.

However, for the modified montmorillonite only two thermal transitions were observed, which are assigned respectively to the surfactant adsorbed on the clay surface and the surfactant intercalated in the clay galleries.

Weight loss at 200–350 °C was 22% and only 8% for modified bentonite and modified montmorillonite respectively, indicating that there exists a significant amount of surfactant which is weakly linked to the clay surfaces. The weight loss associated to the decomposition peak of the intercalated surfactant was 19% wt in modified bentonite and 24% wt in modified montmorillonite. The higher CEC of the montmorillonite clay is probably the reason of such a large incorporation.

From these analyses, it can be concluded that a high amount of ODA is situated on the surface of the LS and also an important amount is adsorbed on the impurities that are present in the bentonite clay. This excess of surfactant can affect the nanocomposite processing and properties. In order to eliminate the free surfactant, the modified bentonite was thermally treated at 300 °C under nitrogen atmosphere in the

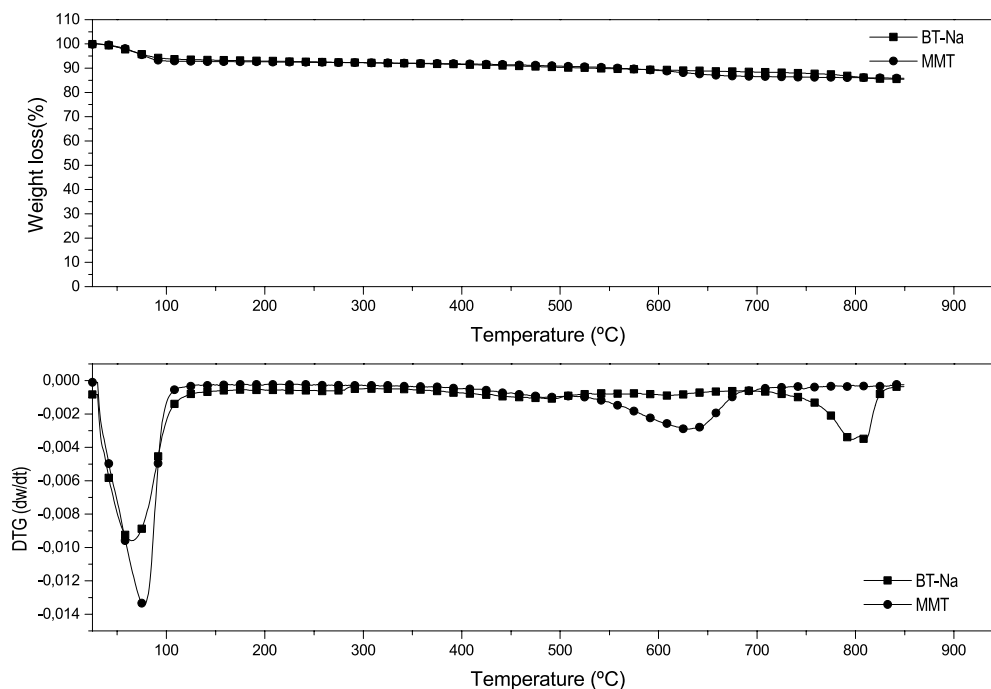


Fig. 4. TGA thermograms of montmorillonite (MMT) and bentonite (BT-Na).

heating chamber of the TGA instrument. The thermogram of this calcined clay is shown in Fig. 6. The weight loss of both the first and the second peak (non-intercalated ODA) was then reduced to the 5% wt. A small amount of surfactant is observed located on the surface of LS.

In order to translate this result to the modification process, a high temperature process in the spray drier was introduced. The thermogravimetric curve for this modified

bentonite is shown in Fig. 7. Although the adsorbed ODA was not completely eliminated, their presence is deeply reduced and only 12% wt of adsorbed ODA was detected. In the thermogram of BT-3 the thermal peak 2 is partially eliminated. The excess of surfactant that do not interact with the solids kept in solution in the water; thus, the high inlet temperature (higher than the temperature of decomposition of the free surfactant) of the spray dried forced a faster

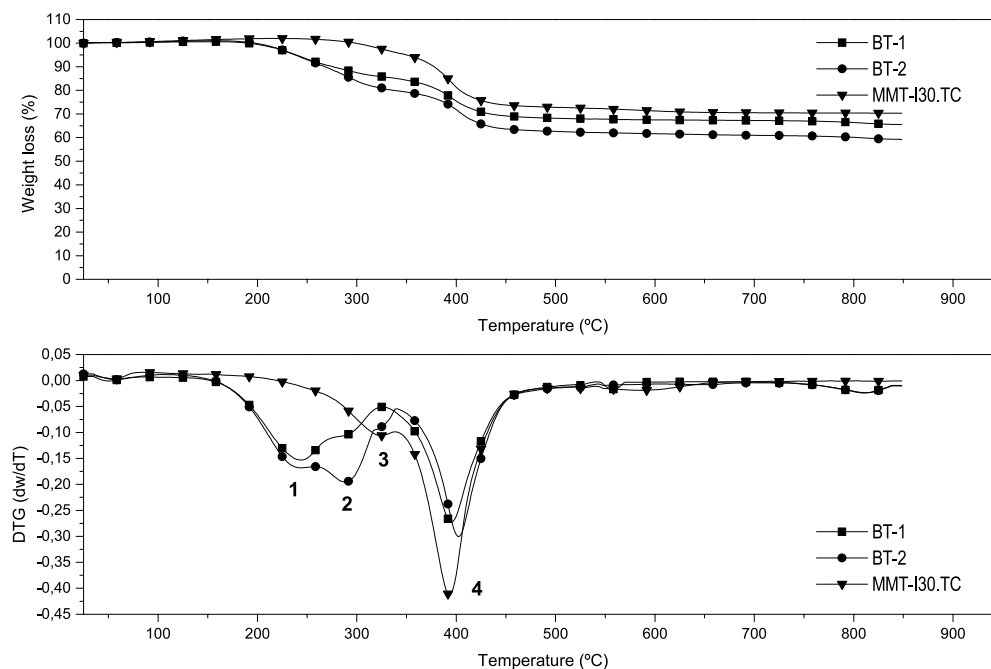


Fig. 5. TGA thermograms of organophilic clays: MMT-I30.TC, BT-1 and BT-2.

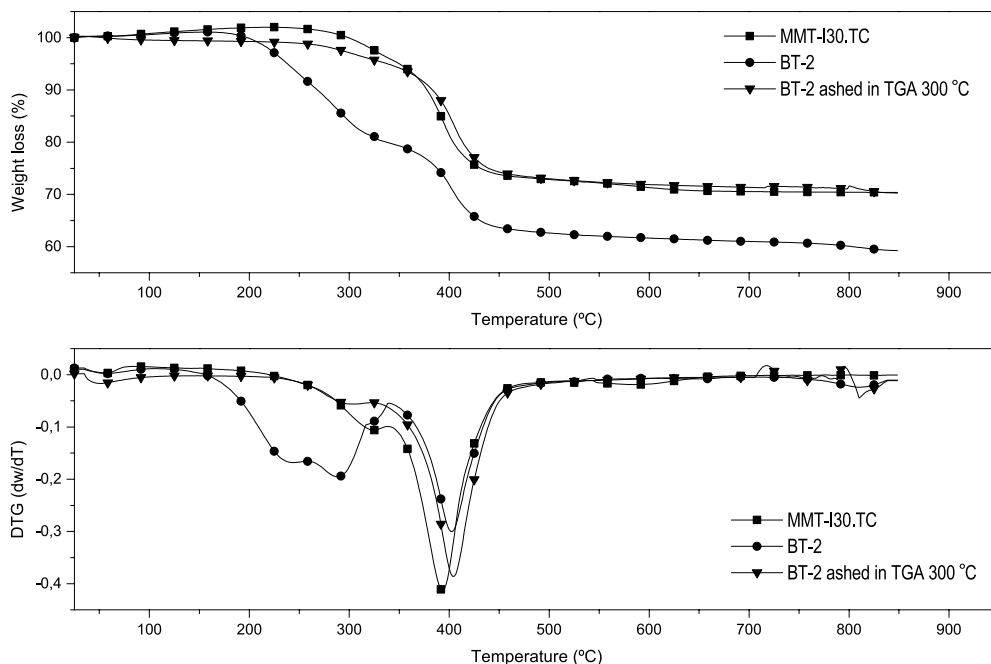


Fig. 6. TGA thermograms of calcined BT-2 bentonite (for comparison purposed TG curves of BT-2 and MMT-I30.TC are included).

drying that evaporates the free surfactant. On the contrary, when the inlet temperature is lower than the decomposition temperature of the surfactant, BT-2, the process allows the free surfactant to concentrate when the water was evaporated. The surfactant adsorbed on the surface of both the impurities (peak 1) or the montmorillonite clay (peak 3) was not removed in both processes. The drops that enter in the spray dried camera first experimented the air inlet temperature and travelled in the camera faster enough to approach the air outlet temperature ($< 120\text{ }^{\circ}\text{C}$) without

reach their decomposition temperature. It is concluded that this process has successfully eliminated free ODA but fails to eliminate completely the adsorbed ODA. The spray drying process possibilities the selective elimination of free surfactant and if elimination of surfactant is needed, outlet temperatures higher than the decomposition of the surfactant will be required. The use of bentonite in this modification process evidence the presence of surfactant adsorbed that in the case of pure montmorillonite has been considered as a non-relevant issue.

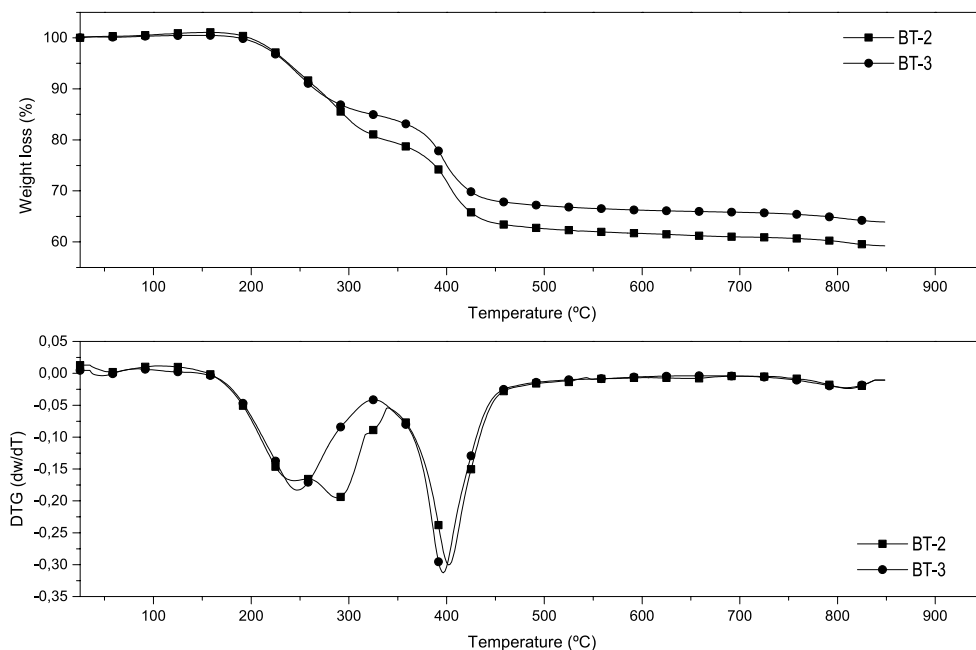


Fig. 7. TGA thermograms of low temperature (BT-2) and high temperature (BT-3) spray dried organophilic clays.

On the other side, the higher solid content in BT2 favours retain of the surfactant in the nanoclay because suspension viscosity increased. Meanwhile BT1 suspension prior to drying is a liquid and BT2 is a gel. The typical pseudoplastic behaviour of bentonite suspensions favour the droplet formation but the viscosity increased rapidly when the droplet enter into de spray drying camera and the elimination of surfactant is not favoured.

3.2. Characterization of PA6/LS nanocomposites

Table 2 summarizes the Young's modulus and HDT values of the PA 6-LS nanocomposites. The addition of the modified organophilic clays leads to substantial improvement in stiffness and heat deflection temperature (HDT). In this sense, the Young's modulus increased $\sim 50\%$ for all the nanocomposites, and in the case of PA 6-MMT, a remarkable increase of $\sim 100\%$ in HDT was registered. A smaller increase in HDT for the modified PA6 nanocomposite was detected. Moreover, in the latter case, there was a slight dependence of the HDT on the modification process conditions: HDT values decrease when the solid content increases, and this indicates a negative effect of the adsorbed surfactant on LS. Higher clay solid content hinders the removal of free surfactant, being adsorbed on LS surfaces

In Fig. 8 the XRD pattern of the nanocomposites prepared using a twin-screw extruder are shown. Due to polymer chains intercalation, an increase in the interlayer distance in the nanocomposites in comparison to the organophilic LS is observed. A more efficient introduction of the polymer chains in the LS galleries that resulted in a stronger organic-inorganic interaction is achieved for PA 6-MMT nanocomposite than for PA 6-BT-1 nanocomposite. On the other hand, when modified bentonite is spray dried at high temperature, a higher increase of the interlayer distance owing to the removal of surfactant excess is observed (PA-BT-3).

TEM images of montmorillonite nanocomposite (Fig. 9) revealed that the organophilic clays were uniformly dispersed into the PA 6 matrix, given an intercalated/exfoliated structure with high degree of exfoliation and individual layers aligned along the injection flow direction.

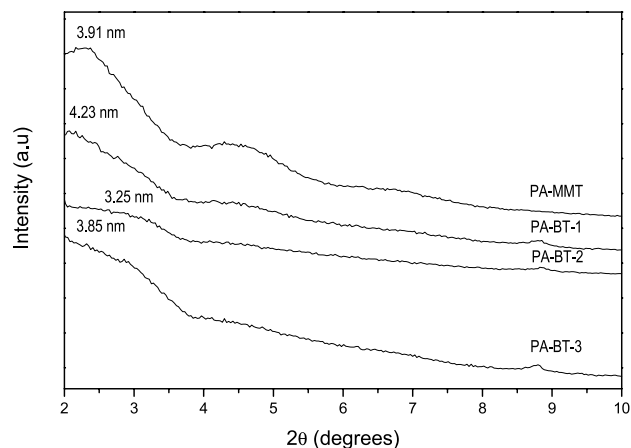


Fig. 8. X-ray diffraction patterns of PA 6-LS nanocomposites.

A similar but apparently less exfoliated structure was observed for PA 6-BT1, PA6-BT2 and PA6-BT3 nanocomposites. Only slight differences in the exfoliation degree were observed by TEM for PA 6-BT1, PA6-BT2 and PA6-BT3 nanocomposites, which are in agreement with the different interlayer distances detected by XRD. Consequently, a more efficient exfoliation seems to be achieved when the excess of surfactant (PA6-BT3 nanocomposite) is removed.

In conclusion, mechanical properties of all bentonite based nanocomposites shown similar tensile modulus, slightly lower in comparison to the montmorillonite based nanocomposite, and significantly lower HDT (Table 2). This may be related to a minor proportion of exfoliation and the presence of the impurities in the bentonite clay. Partial removal of surfactant excess had a significant effect on Young's Module and HDT (PA-BT-3 nanocomposite), indicating that the excess of surfactant plays a crucial role on the degree of polymer chain introduction in organophilic clays.

4. Conclusion

All the nanocomposites obtained in this work using modified montmorillonite and bentonite showed an

Table 2
Nanocomposites composition and mechanical properties

Sample	Clay	Clay treatment	Surfactant	Clay (wt %)	TGA Clay content (wt %)	Tensile modulus (MPa)	HDT (°C)
PA	–	–	–	–	–	2637	48
PA-MMT	MMT-I30.TC	–	ODA	5	4.5	4100	96
PA-BT-1	BT-1	8% solid Spray dried	ODA	5	4.7	3940	74
PA-BT-2	BT-2	16% solid Spray dried		5	4.6	3909	66
PA-BT-3	BT-3	16% solid Spray dried high temperature		5	4.2	4010	73

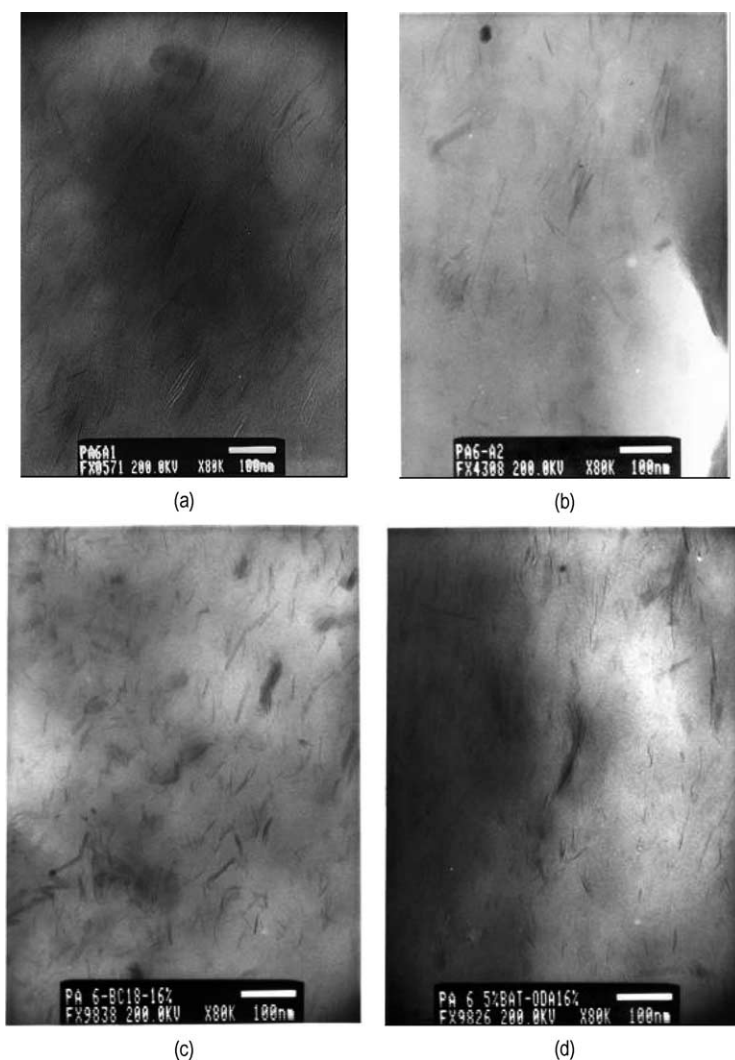


Fig. 9. TEM micrographs of PA 6-LS nanocomposites with different organophilic clays (a) PA-MMT, (b) PA-BT-1, (c) PA-BT-2, (d) PA-BT-3.

intercalated/exfoliated structure, with slight differences in the exfoliation degree according to XRD and TEM results.

No significant dependence of the solid content during the modification process of bentonites on microscopic and macroscopic properties of PA6 nanocomposites was observed. Consequently it is cost saving to process high percentage of solid in the industrial scale.

The excess of the surfactant adsorbed on bentonite clays may be reduced when high temperature is used to dry the LS after the modification process is accomplished. Improved mechanical properties, mainly HDT values, for this nanocomposite when a spray drier process at high temperature (300 °C) is used for bentonite modification, were observed.

Acknowledgements

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