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ORIGINAL PAPER

Influence of the compatibilizer/nanoclay ratio on final properties of polypropylene matrix modified with montmorillonite-based organoclay

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Abstract The use of nanoclays as additives for polymer matrices requires, in some cases (with non-polar matrices) the use of a compatibilizer agent which will act as a bridge or permanent buffer for nanoclay-matrix interaction. In this research, we have worked on the improvement of mechanical and thermal properties of polypropylene matrices by adding montmorillonite based nanoclays (MMT) which have been previously modified with an organic component (a quaternary ammonium salt modifier). In this particular case, we have worked on the optimization of the compatibilizer:nanoclay ratio. As a compatibilizer agent it has been used a propylene graft maleic anhydride copolymer (PP-*g*-MA) and the PP-*g*-MA:MMT ratio has varied from 0.25:1 to 4:1. Nanoclay dispersion and intercalation–exfoliation degree has been investigated by X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM). Also, mechanical and thermal properties for different PP-*g*-MA:MMT ratios have been determined. The results show optimum dispersion and intercalation–exfoliation levels for PP-*g*-MA:MMT ratios close to 3:1 and 4:1 and also we can observe a slight increase in mechanical and especially in thermal properties for similar ratios.

Keywords TEM · XRD · Montmorillonite · Polypropylene · Compatibilizer

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Introduction

In the last years, the addition of materials at a nanometric scale into polymer matrices has increased in a remarkable way [1–4]. In some cases, particles are supplied in an aggregate form (micrometric scale range) and this requires optimum mixing process to provide the appropriate particle dispersion [5, 6].

Many researches on nanoparticles have been focused on modified nanoclays [7–9]. These are composed of organic modified laminar silicate structures which allow obtaining a hybrid organic–inorganic structure. Montmorillonite based clays (MMT) offer high interest from an industrial point of view since the use of small amounts of them is enough to improve the overall properties of a polymer matrix at a relatively low cost [10–12].

Maximum interaction between nanoparticles and polymer matrix is needed in order to obtain the high specific surface that nanoparticles offer. In the case of modified nanoclays, it is important to break the crystal structure to increase interactions [13, 14]. So, the mixing process acquires a relevant role in the improvement of overall properties [15], since it must accomplish two main objectives: firstly it must be able to break the micrometric clay particles to obtain a homogeneous dispersion of silicate platelets; on other hand the mixing process must be capable to open the clay structure by increasing the basal plane distance thus allowing the interaction between the organic (modifier) component of clay and some polymer chains [16, 17].

The use of two screw co-rotating extruder systems offer optimum results since particles are subjected to high shear stress and this promotes breakage of microparticles and homogeneous dispersion [18]; furthermore, the laminar structure (silicate crystal) of the clay can be opened by shear stress, thus leading to intercalation (platelet separation) and exfoliation (platelet dispersion). Intercalation and/or exfoliation are not enough to ensure optimum interaction; also high affinity between organic modifier of clay and polymer chains is needed. This affinity is very low when polymer matrix is a non-polar polymer such as polyolefin, so in this case it is difficult to achieve the expected properties [12, 19]. With this purpose it must be added a compatibilizer agent which will act as a bridge or permanent buffer for interaction between non-polar polymer chains and the organic (modifier) component of the clay.

The aim of this work is to determine the optimum compatibilizer:nanoclay ratio to achieve an improvement on overall properties of polypropylene matrices using as a compatibilizer agent a propylene graft maleic anhydride copolymer (PP-*g*-MA). We have also studied the dispersion and intercalation–exfoliation level by using X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM) and furthermore, a study on the influence of the abovementioned ratio on mechanical and thermal properties of composites has been carried out.

Experimental

Materials

As a polymer matrix it was used a commercial polypropylene grade MOPLEN HP561S supplied by Basell Polyolefins (Basell Poliolefinas Iberica S.L., Tarragona, Spain). Moplen HP561S is a very narrow molecular weight distribution homopolymer, suitable for extrusion applications with a melt flow rate (MFR) of 33 g $(10\ \text{min})^{-1}$ and a Vicat softening temperature (A50) of 152 °C. This is suitable for filament and fibre extrusion.

The nanoclay used to improve thermal and mechanical properties was a montmorillonite (MMT) based nanoclay Cloisite 20A supplied by Southern Clay (Southern Clay Products Inc., Texas, USA) which has been modified with a quaternary ammonium salt. The organic modifier is a dimethyl, dihydrogenated tallow, 2M2HT (65%—18 C atoms in length, 30%—16 C atoms in length and 5%—14 C atoms in length) which provides high specific surface for interaction. It is supplied in a particulate form with sizes in the micro scale range (10% less than 2 μm, 50% less than 6 μm and 90% less than 13 μm).

As a compatibilizer agent, it was used a propylene-maleic anhydride graft copolymer (PP-*g*-MA) supplied by Sigma Aldrich (Sigma-Aldrich Química, S.A., Madrid, Spain) which is characterized by a maleic anhydride content of less than 10 wt% so high miscibility with polypropylene matrix is expected. As process stabilizer it was used a commercial grade 92098 supplied by Alcolor (Alcolor, Alicante, Spain). This stabilizer is based on a phosphite–phenolic mixture and it is heavy metal free; it is widely used in toy industry, packages, and technological applications due to its high light stability and appropriate processing temperature (in the 260–280 °C range).

Composite processing

The amount of clay was fixed to 2 wt%; this amount was selected because it is typical of many industrial formulations and represents excellent balance between performances and cost. The high specific surface [95 meq $(100\ \text{g})^{-1}$] of the clay, once the crystal structure is broken, is enough to provide good interaction with polymer chains. Higher clay amounts could lead to a slight increase in overall properties but the material cost also increases. The amount of phosphite–phenolic stabilizer was fixed to 0.4 wt% for all composites. Various PP-*g*-MA amounts in the 0.5–8 wt% range were used to obtain different PP-*g*-MA:MMT ratios which cover the 0.25:1–4:1 range. The appropriate virgin polypropylene was calculated to complete 100 wt%. Due to the low maleic anhydride content in the PP-*g*-MA, good interaction with polypropylene matrix is expected even with higher compatibilizer amounts [7]; on other hand, the polarity introduced by the maleic anhydride groups will play a decisive role for interaction with the organic component of the modified clay (2M2HT).

The composites' processing is a critical stage to obtain the expected properties since it has to be capable to break microparticles and promote homogeneous dispersion. PP-organoclay composites were prepared by melt mixing using a two screw co-rotating extruder model ZSK 18 Mc (Coperion Werner & Pfleiderer, Stuttgart, Germany). The main features of this extruder are: outer diameter of screws = 18 mm; channel depth = 3.2 mm; motor power = 10 kW; operating window in the 1–40 kg h^{-1} range; small batch sizes starting from 200 g. The extruder is divided in seven barrels able to be heated until 450 °C and is provided with a gravimetric side feeder to dose any additional component. The temperature profile for the seven barrels was set to: 170, 170, 175, 180, 180, 185, 185 °C and the polymer melt temperature at the output was measured ranging from 192 to 193 °C. The screw rotating speed was set to 200 rpm to avoid overheating and good intercalation–exfoliation together with homogeneous dispersion.

The mixing process was carried out in two steps; in a first step, the appropriate PP-*g*-MA as described previously, was dosed in the side feeder and was premixed with the appropriate virgin polypropylene and phosphite–phenolic stabilizer amounts to obtain PP:PP-*g*-MA blends. After this, in a second step PP:PP-*g*-MA was extruded again together with the clay appropriate amounts which were dosed in the side feeder. After this, PP:clay composites compatibilized with PP-*g*-MA were obtained in pellet form.

Normalized samples for different tests were prepared by injection moulding on a hydraulic Babyplast 6/6 (Cronoplast SL, Barcelona, Spain) with an injection volume of 6 cm^3. This is equipped with three barrels, a plasticization chamber and an injection chamber; the temperature profile was set to 180, 185, and 190 °C.

Characterization of clay dispersion and intercalation-exfoliation

Characterization of intercalation–exfoliation levels achieved by the mixing process in the presence of the compatibilizer agent was carried out using small angle X-ray spectroscopy (SAXS) and transmission electron microscopy (TEM). The XRD equipment was a Seifert model JSO-DEBYFLEX 2002 (Rich. Seifert GmbH & Co. KG, Freiberg, Germany) provided with a copper cathode and a nickel filter. The radiation wavelength was λCu = 1.54 Å. The following test conditions were used: voltage = 40 kV; current intensity = 40 mA. By considering the Bragg's law we have estimated the distance between silicate platelets and compared with the basal plane distance of Cloisite 20A to determine whether intercalation or exfoliation occurs. Considering the main diffraction peak of Cloisite 20A which is located at $2\theta = 3.72°$, (which corresponds to an interplanar distance of about 23.20 Å) the 2θ angle scanned range has varied from 1.5° to 7.0° at a step of 0.02°. As the peak is displaced to low 2θ angles, the interplanar distance is increased (intercalation) up to values of 70 Å which involves 2θ angles close to 0 and this could be considered as exfoliation.

XRD provides information about intercalation and/or exfoliation, but it does not give any information about particle or platelet dispersion. For this purpose it is necessary to use a microscopic technique to see platelet distribution. For the TEM analysis it was used a JEOL model JEM-2010 (Jeol USA Inc., Peabody, USA). As polypropylene is a soft polymer, the use of an ultramicrotome (RMC model MTXL) in cryogenic conditions was needed to cut samples for TEM analysis.

Thermal and mechanical characterization

Thermal characterization of the polypropylene-nanoclay system was carried out using differential scanning calorimetry (DSC) with a Mettler-Toledo 821e (Mettler-Toledo Inc., Schwerzenbach, Switzerland). Mass weight for DSC analysis varied in the 3–5 mg range; DSC scans were carried out on samples taken from pellets from the mixing process and the thermal program was set from 30 to 350 °C in air atmosphere (50 mL min^{-1}) at a heating rate of 5 °C min^{-1}. As polypropylene is very sensitive to thermal degradation (thermo-oxidation) in air, the thermal stability was measured in terms of the degradation onset which represents the beginning of the irreversible oxidation process which leads to plastic degradation.

Mechanical characterization was carried out using an electromechanical universal test machine Ibertest Elib 30 (S.A.E. Ibertest, Madrid, Spain). The tensile tests were performed at a crosshead speed of 20 mm min^{-1} with a 5 KN load cell following the guidelines of the ISO 527 standard; at least five samples were tested an average values were calculated to obtain significant results.

Results and discussion

Characterization of intercalation–exfoliation

Firstly, the clay dispersion and intercalation and/or exfoliation processes have been studied. As we have described before, the mixing process must be able to break the microclay particles and lead them to a homogeneous dispersion of silicate platelets. This situation can be seen in Fig. 1 which shows different TEM microphotographs of non-campatibilized PP-nanoclay composites.

For low magnification (Fig. 1a) we can observe some aggregates (in the microscale range) with sizes in the 0.2–0.4 μm range which are representative of nanoclay particles. At higher magnification (Fig. 1b) we can observe the structure of the aggregate which is composed of many parallel silicate platelets; as we have described previously the organic modifier of the clay (2M2HT) has been intercalated between these platelets to form a hybrid inorganic–organic structure.

The mixing process must be capable to open the basal plane of the clay in order to intercalate some polymer chains in the matrix (intercalation) and even to break the crystal structure of the clay to ensure maximum specific surface and contact (exfoliation) between the organic modifier (2M2HT) of the clay and some intercalated polymer chains [20, 21]. For this purpose, the X-ray diffraction technique has been used since it allows to identify intercalation and/or exfoliation levels by identifying the main diffraction peaks in the crystalline clay structure [22]. Figure 2 shows XRD diffraction patterns of non-mixed materials (polypropylene Moplen HP561-S and Cloisite 20A) as well as XRD diffraction patterns of some composites containing 2 wt % of nanoclay with different compatibilizer:nanoclay (PP-*g*-MA:MMT) ratios.

The XRD pattern of the clay shows a diffraction peak at about 3.72° corresponding to 2θ; this peak corresponds to the (001) plane and the angle

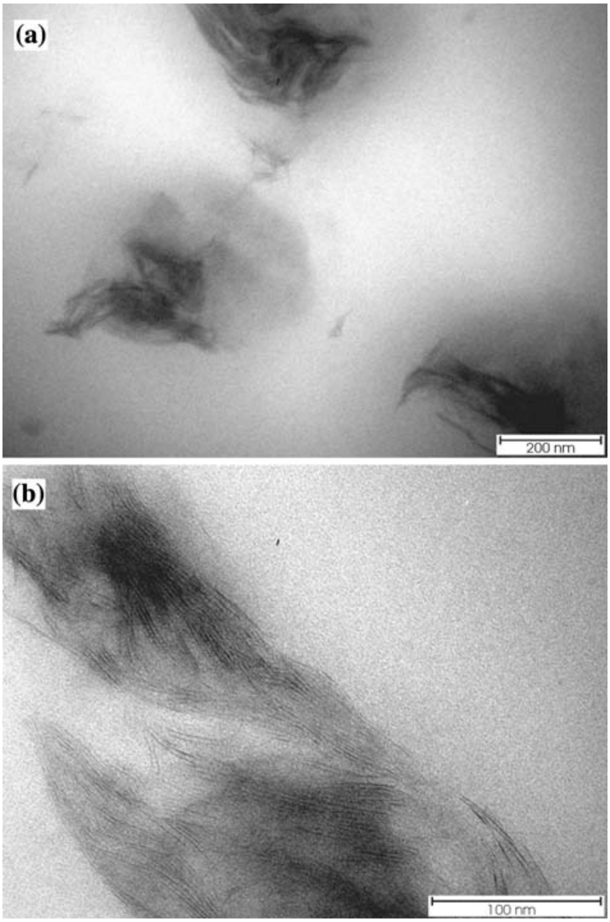

Fig. 1 TEM microphotographs of non-compatibilized polypropylene-MMT composites

position (2θ) is representative of an interplanar distance of about 23.20 Å; on other hand, the diffraction pattern of polypropylene does not show any significant peak in the scanned range (1.5–7.0°), so the peak corresponding to clay in this range will act as a reference peak to study intercalation and/or exfoliation. Interplanar distances over 70 Å are representative for total exfoliation (2θ values close to 0°). The XRD patterns for composites with different PP-*g*-MA:MMT ratios show a decrease in the peak intensity (dilution effect) as a consequence of the small amount of clay in the composites (2 wt %) together with high exfoliation levels; despite this, we can observe a peak displacement towards lower 2θ values in the 3.1–3.2° range for PP-*g*-MA:MMT ratios of 1:1 and 3:1 (similar results are obtained with other ratios).

This is indicative of some crystalline zones attributable to the clay, but the lower 2θ values indicate an increase in interplanar distance up to values of about 30 Å and this is indicative of some intercalation together with high exfoliation as a consequence of the decrease in the peak intensity. A local zoom of the range

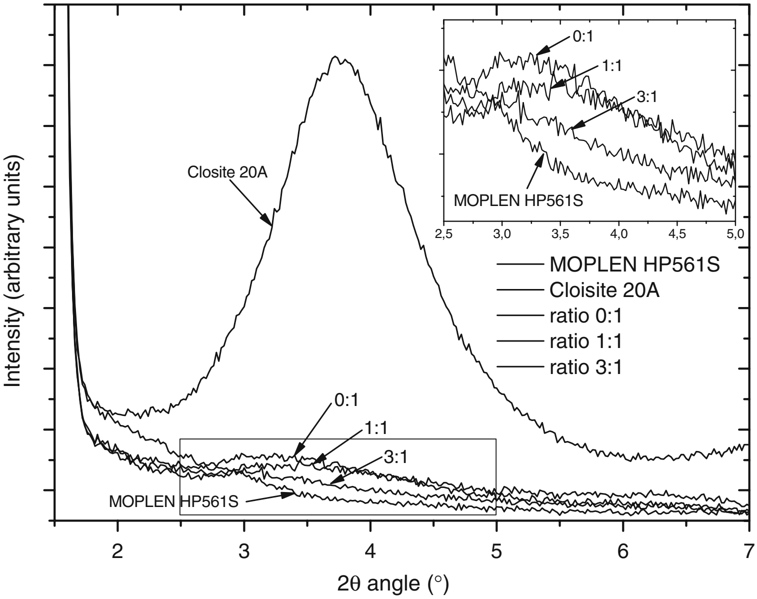

Fig. 2 XRD patterns of polypropylene-MMT composites with different PP-*g*-MA:MMT compatibilizer ratios

corresponding to the clay peak as presented in Fig. 2 shows in a clear way the diffraction peaks. Nevertheless, for a PP-*g*-MA:MMT ratio of 3:1 (and higher) this peak practically disappears and this is indicative of high exfoliation levels since the crystal structure of the clay has been broken thus enabling maximum interaction between the organic modifier (2M2HT) component and polymer chains.

As we have seen before, XRD shows important evidences of some intercalation and high exfoliation; nevertheless it is difficult to observe breakage of microparticles to form highly dispersed separated platelets in the polymer matrix. For this purpose, we need transmission electron microscopy (TEM). Figure 3 shows some PP:clay (2 wt %) TEM microphotographs with different PP-*g*-MA:MMT ratios.

As we can see, for low PP-*g*-MA:MMT ratios (Fig. 3a, b) we observe the presence of aggregates of 0.2–0.4 μm in size. The presence of these aggregates indicate that the mixing (extrusion) process has not allowed good particle breakage and subsequent particle dispersion and this is evidenced by the particle size that remains in the microscale range [23]. Despite this, for intermediate PP-*g*-MA:MMT ratios (in the 1:1–2:1 range, Fig. 3c, d) we can observe a remarkable decrease in the aggregate size thus indicating good particle breakage and even we can observe presence of some laminar silicates (platelets) with sizes in the nanoscale range. This better dispersion is attributed to the presence of the compatibilizer agent which acts as a bridge or permanent buffer to establish interactions between polymer chains and the organic modifier of the clay (2M2HT). For higher PP-*g*-MA:MMT ratios (3:1 or even 4:1) we can observe better particle dispersion leading to a homogeneous structure.

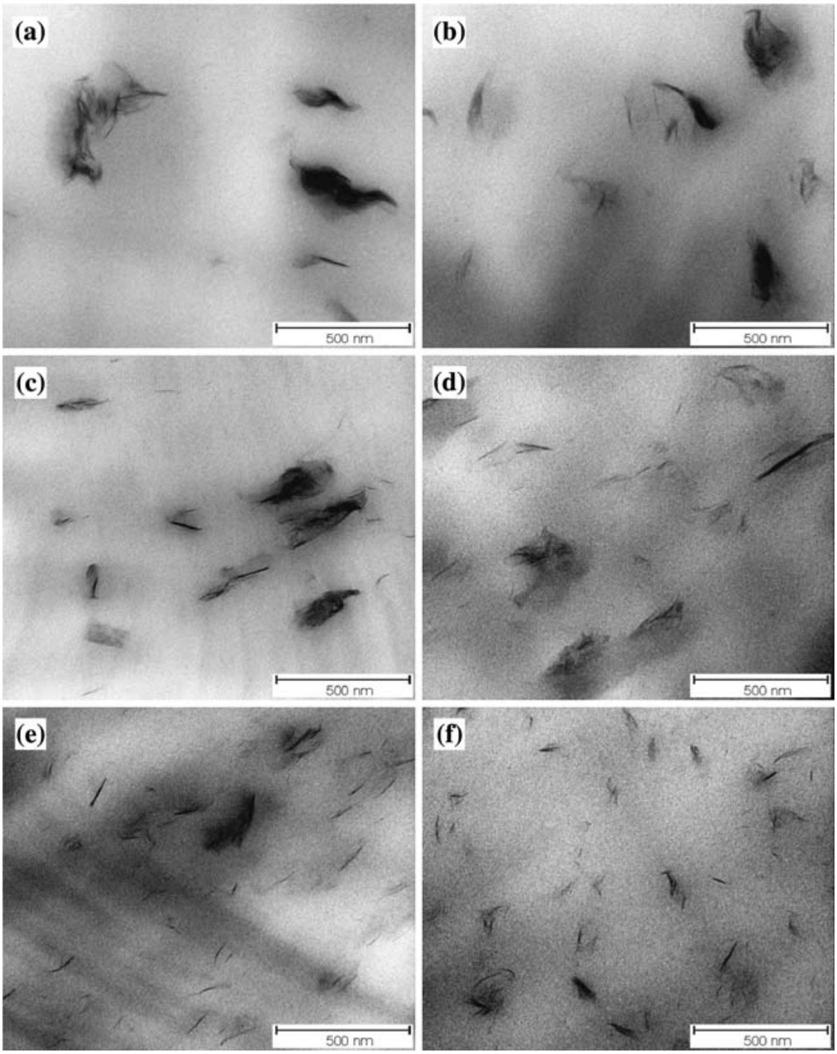

Fig. 3 TEM microphotographs of polypropylene-MMT composites with different PP-*g*-MA:MMT compatibilizer ratio **a** 0.25:1 **b** 0.5:1 **c** 1:1 **d** 2:1 **e** 3:1 **f** 4:1

Mechanical performance of polypropylene-nanoclay composites

Figure 4 shows the evolution of the elastic modulus in terms of the PP-*g*-MA:MMT ratio. As we can see, the initial modulus is considerably increased as the PP-*g*-MA:MMT ratio increases. The overall effect of the clay addition is a remarkable increase in elastic (in the 700–890 MPa) modulus regarding the unfilled material with an elastic modulus of about 220 MPa. Despite changes in elastic modulus in terms of the PP-*g*-MA:MMT ratio are located in a narrow range, we can see that optimum results are obtained for PP-*g*-MA:MMT ratios of 2:1 and higher, but it is

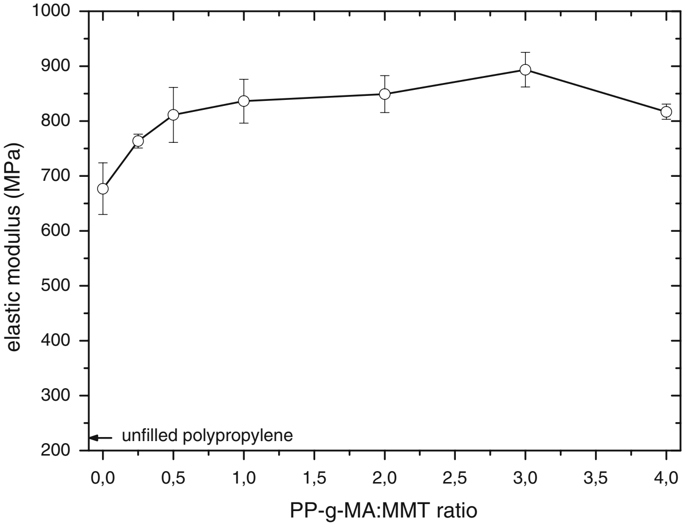

Fig. 4 Plot of the evolution of the elastic modulus of polypropylene-MMT composites in terms of the PP-*g*-MA:MMT ratio

important to remark that higher ratio do not lead to significant increase in elastic modulus values.

For lower ratios, we can also observe an important increase in elastic modulus values (higher that 700 MPa) but the optimum results regarding stiffness are obtained for high ratios (3:1). These results are in agreement with those obtained with XRD and microscopic study; the bigger exfoliation level in the clay structure is responsible for the improvement of mechanical resistance properties, since exfoliation allows high contact between polymer chains and the organic modifier (2M2HT) of the clay. In these conditions, the presence of a compatibilizer agent enables interaction between non-polar polypropylene chains and the organic component of the clay, thus acting as a bridge or buffer for the formation of interlock points between them, and this has a positive effect on material stiffness.

Figure 5 shows the evolution of the elongation at break as a function of the PP-*g*-MA:MMT ratio. Obviously, an increase in elastic modulus leads to a decrease in mechanical ductile properties; as a consequence of this, the elongation at break changes from 440% for polypropylene without clay addition up to values around 12% for filled polypropylene with different PP-g-MA:MMT ratios. Nevertheless, many applications need the use of high stiffness and low deformation materials to ensure high dimensional stability.

Regarding tensile strength (Fig. 6), it is important to remark the role of nanoclay in the fracture of composites with polypropylene matrix. Usually, the addition of an inert filler into a polymer matrix (without filler-matrix interaction) promotes an important decrease in tensile strength since the filler particles are incoherent with the polymer matrix (this means that no interaction particle-polymer is achieved); this leads to a stress concentration effect in some points that promote an early

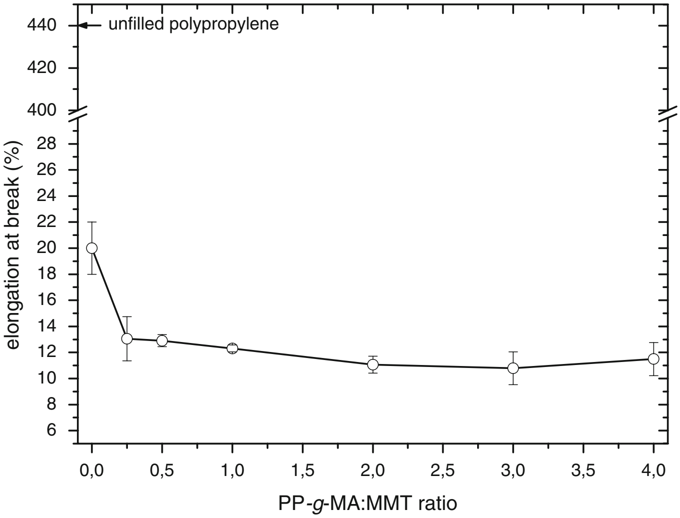

Fig. 5 Plot of the evolution of the elongation at break of polypropylene-MMT composites in terms of the PP-*g*-MA:MMT ratio

fracture [24]. The modified organoclay acts in a different way; the aperture (intercalation) of the basal plane together with the breakage of the crystalline structure (exfoliation) enables the contact between some polymer chains and the organic modifier (2M2HT). Nevertheless, as a consequence of the low polarity of the polymer matrix, it is necessary to add a compatibilizer agent to act as a bridge joint or permanent buffer to establish some interactions, so good exfoliation levels are critical to obtain the best results. In these conditions, the interaction among the matrix and the organic component of the clay is very high and this leads to the formation of interaction areas which are responsible for the improvement of mechanical resistance properties such as elastic modulus and tensile strength. So that, the tensile strength of polypropylene is increased from 27 MPa for virgin polypropylene to higher values in the 31–32 MPa range as the PP-*g*-MA:MMT ratio increases.

Thermal behaviour of organoclay-polypropylene composites

As we have described previously, the presence of a compatibilizer agent high PP-*g*-MA:MMT ratios (2:1 and higher) leads to strong interactions between polymer matrix and the organic modifier (2M2HT) of the clay; this fact promotes a restriction on polymer chains displacements and movements; for this reason, mechanical resistance properties increase while mechanical ductile (plastic) properties are decreased. This partially immobilized structure does not only affect to mechanical properties but also it favors high dimensional stability since plastic materials are very sensitive to temperature. This phenomenon can be clearly observed in Fig. 7 which shows the variation of Vicat softening temperature (VST) values in terms of the PP-*g*-MA:MMT ratio.

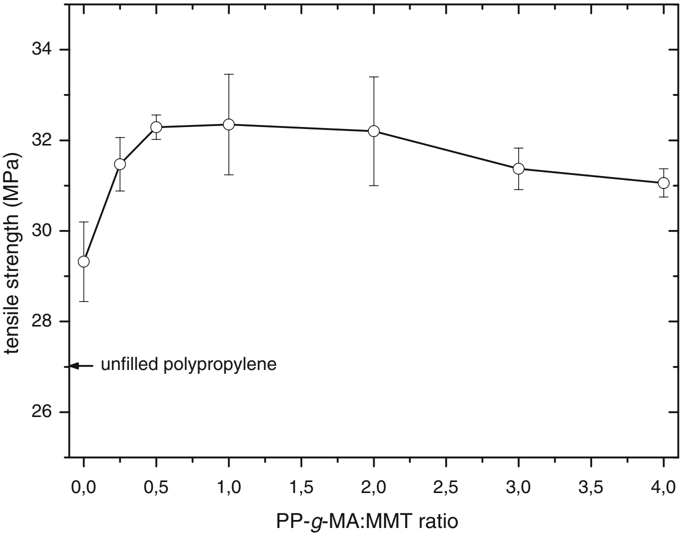

Fig. 6 Plot of the evolution of the tensile strength of polypropylene-MMT composites in terms of the PP-*g*-MA:MMT ratio

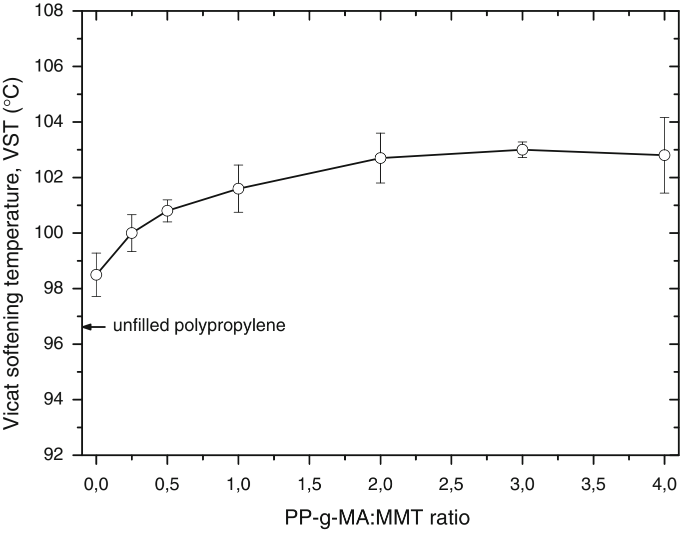

Fig. 7 Plot of the evolution of the Vicat softening temperature (VST) values of polypropylene-MMT composites in terms of the PP-*g*-MA:MMT ratio

The VST value for the unfilled polypropylene is around 96.6 °C. The only addition of 2 wt % of nanoclay (without any compatibilizer agent) increases this value up to 98.5 °C. The presence of small compatibilizer amounts (PP-*g*-MA:MMT ratios of 1:0.5 and 1:1) promotes a slight increase in VST values up to 100 °C. Nevertheless, as this ratio increases, the thermal stability is also increased up to values close to 102 °C for 3:1 PP-*g*-MA:MMT ratios. Similar ratios are observed for 2:1 and 4:1 ratios thus indicating that optimum thermal stability is achieved for PP-*g*-MA:MMT of 2:1 and higher. This phenomenon can be explained if we take into account the role of the compatibilizer agent which acts as a permanent buffer for interactions between polymer chains and modified nanoclay. As we have described, the interaction points restrict chain displacements and movements and this has a positive internal reinforcement effect, so that the material needs higher temperature values to perform chain displacements (and, consequently, a material softening). This phenomenon increases in a significant way the technological possibilities of polypropylene since the addition of modified nanoclays promotes an overall properties improvement from properties ranged in the commodities group to properties of some engineering plastics, and this is not only for mechanical properties but also for thermal stability [25–27].

Many authors have studied the thermal stability of polymer:clay composites at high temperatures using TGA techniques; nevertheless, the thermal stability improvement can also be observed by a DSC study by determining the degradation onset temperature (onset of oxidation processes that leads to thermal degradation). As we can see in Fig. 8, as the PP-*g*-MA:MMT ratio increases, the oxidation onset temperature is shifted to higher values. The oxidation onset point of a non-filled polypropylene is about 225 °C and this is increased up to values in the 245–250 °C range for PP-*g*-MA:MMT ratios of 3:1 and 4:1 thus indicating an increase in thermal resistance. These results are in accordance with the previous results regarding intercalation and/or exfoliation as well as mechanical results in terms of the PP-*g*-MA:MMT ratio. Regarding polypropylene fusion, it is important to remark that very small changes in fusion temperature and degree of crystallinity have been observed. The fusion peak has varied in the 168–169 °C range for all samples and the degree of crystallinity has remained almost constant with values close to 41%.

As we have observed previously, changes in mechanical properties, mainly elastic modulus and tensile strength, in terms of the PP-*g*-MA:MMT ratio are small and, consequently, they are not significative in a great extent. Despite this, the optimum properties are obtained for high PP-*g*-MA:MMT ratios and this is in agreement with the thermal behaviour described so we can conclude that the effects of the clay addition are more evident on thermal properties of composites.

Conclusions

The use of nanoclays as additives for polymer matrices is an efficient method to obtain an overall improvement on mechanical and thermal properties of polymer matrices. The mixing process is a critical step in order to obtain the expected performance in composites since it must be able to obtain a homogeneous dispersion as well as to be capable to open and break the clay crystal structure to provide the maximum specific surface for the establishment of interactions between the organic modifier of the clay and polymer matrix. The establishment of interactions between the components is highly dependent on the affinity between them so it is necessary to use a compatibilizer agent as a consequence of

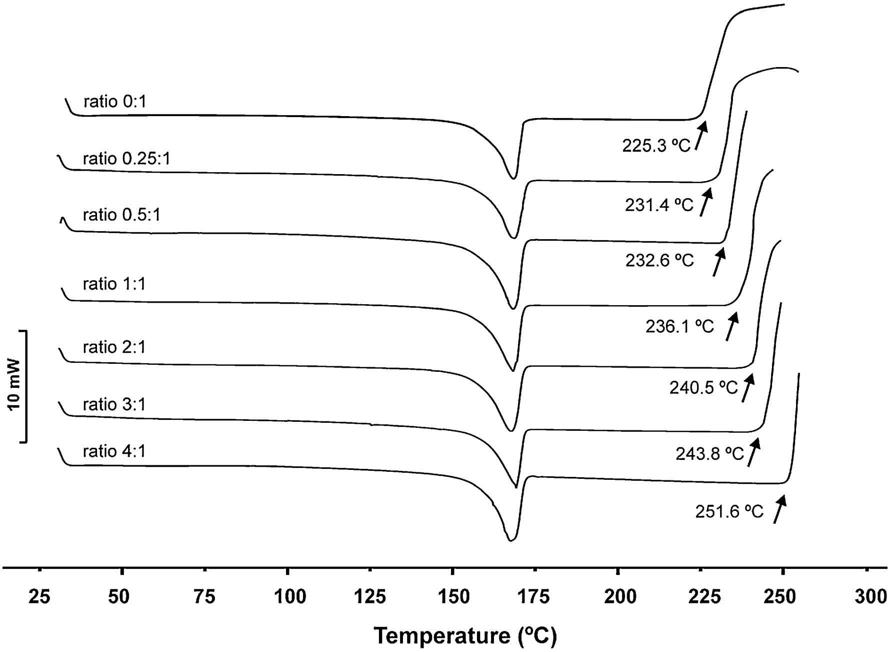

Fig. 8 DSC thermograms of polypropylene-MMT composites for different PP-*g*-MA:MMT ratios

the non-polar nature of the polypropylene matrix. This compatibilizer acts as a bridge between non-polar polypropylene polymer chains and the organic component of the clay to form interlock points at structural level which are responsible for the thermal and mechanical stability improvement. The compatibilizer:nanoclay ratio is one of the most important factors influencing on final properties of composites. The optimum ratio for these composites is in the 2:1–3:1 (weight ratio) as mechanical and thermal characterization has showed. Also XRD and TEM study have revealed a good dispersion of clay and good balance between intercalation and exfoliation level.

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