POLYPROPYLENE/CLAY NANOCOMPOSITES. SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Polypropylene nanocomposites were synthesized by using the method of mixing in the molten state. Nanocomposites were obtained in twin-screw co-rotating extruders and the nanocomposites were prepared with percentage of nanoclay (C₂) from 5 wt-%, with and without compatibilizer agent (PP-g-MA).

The thermal (DSC, TGA), morphology (XRD, TEM), and dynamical mechanical (DMA) properties of the nanocomposites were characterized.

All nanocomposites prepared are in intercalated state as corroborated by XRD and TEM. The T_m and X_c were not affected by the presence of clay, PP-g-MA, or processing support. The incorporation of clay and compatibilizer agent increases the thermal stability and heat deflection temperature (HDT).

Keywords: Nanocomposites, polypropylene, clays, compatibilizer agent

1. INTRODUCTION

Polypropylene is a polymer widely used in many applications, and their thermal (1-2), rheological (3), mechanical (4-5), and gas permeation properties (6-7) need to be improved. A large number of studies have focused to improve a range of capabilities for these materials used in the automotive industries, and which show a great potential for use in the aeronautical field (7).

The study of polymer nanocomposites has focused on enhancing the conventional properties of this polymeric material (8), *i.e.*, the properties change drastically using a small fraction of nanofiller (9-12). Since the development of the reinforced nanocomposite of nylon 6, no successful examples of reinforcement using clay nanocomposites has been reported for polyolefins since 1997, when the polyolefins were first intercalated into the clay gallery using a polyolefin oligomer, incorporating hydroxyl groups (5). The inclusion of functional groups has shown to be responsible for the affinity, as in the case on anhydride and amides, improving the affinity for the silicate surface (13). Differing from other functionalized polymers, polyamide has shown that organically modified clays can be efficiently exfoliated in polar polymers, using appropriate melt processing techniques and conditions (14-15). Polypropylene (PP) is one of the most widely used polyolefins and does not include any polar group in its backbone. The PP nanocomposite was not formed even when using an organophilically modified Montmorillonite (MMT). Kawasumi et al.(16) have reported a novel approach to prepare PP nanocomposite using a functional polyolefin oligomer (*e.g.* maleic anhydride grafted PP oligomer) as a compatibilizer between the matrix and filler (17). This approach has been well developed for polypropylene-based systems; the focus of most industrial research and development has been on formation of nanocomposites by melt-mixing or compounding processes because this is generally more attractive than *in situ* polymerization due to better commercial feasibility and lower cost (13). The Toyota group reported formation of PP/clay hybrid composites by direct melt-mixing of organoclays based on montmorillonite (MMT) with PP grafted with maleic anhydride (PP-g-MA) or hydroxyl groups as an additive to facilitate exfoliation and enhanced properties (5,16,17). Since this time, a great number of studies have addressed different aspects of the PP/nanoclay composites including: the effect of clay orientation on the tensile modulus (18) and attempts to quantify the effect of flow-induced clay orientation of syndiotactic polypropylene nanoclay composites. PP-PP-g-MA-MMT nanocomposites were successfully synthesized using melt interaction method in two steps; the nanocomposites with about 4 wt-% of MMT were obtained with different percentages of grafted PP. The PP-g-MA/clay relation has been optimized, resulting in good mechanical properties (19).

Melt intercalation is the main method to obtain nanocomposites, and normally a twin-screw extrusion is used (20). The success of the exfoliation by melt blending is associated with the presence of strong interactions between the clay and the polymer chain as well as the diffusion of the polymeric chains into the clay layers. (21) The process efficiency also depends on the temperature, residence time, and screw shear profile (22). The use of intermediary residence time, low process temperature, and medium shear rates were the best conditions to obtain the dispersion of the clay in exfoliated and intercalated structures (23).

2. EXPERIMENTAL PART

2.1 Materials

Polypropylene samples: PPH₁ (MFR 2.16 kg/230 °C): 2 g/10 min, PPH₂ (MFR 2.16 kg/230 °C): 6 g/10 min, PPH₃ (MFR 2.16 kg/230 °C): 13 g/10 min, and PPH₄ MFR 2.16 kg/230 °C): 17 g/10 min from PETROQUIM S.A.; IrganoxVVR B215 (antioxidant) from Ciba. Maleated polypropylene (PP-g-MA) with reactive MA modifier content 0.2 wt-% (MFR 2.16 kg/230 °C): 7 g/10 min from Crompton. The organophilic MMTs (montmorillonites) used were Nanofil SE 3000 (C₂) from Süd-Chemie.

2.2 Melt Processing

Nanocomposites were obtained in a twin-screw co-rotating extruder (Haake H-25, model Rheomex PTW 16/25, L/D ¼ 25) operating at 80 rpm. The temperature conditions, 170–190 °C for preparation and processing of nanocomposites were chosen to minimize possible degradation of the organic modifier and the matrix. The nanoclay was dried at 80 °C for 24 h prior to compounding to remove moisture. The nanocomposites were prepared with percentage of nanoclay from 5 wt-%, with and without compatibilizer agent. From the prepared PP nanocomposites, the films were obtained by compression heating the polymer above 190 °C, maintaining for 2 min to obtain the complete melting of the pellets, and a pressure of 6 lbs was applied for 3 min. The nanocomposites were prepared as described in Table 1.

Table 1: PP and nanocomposites preparation.

Polypropylene	Clay	Compatibilizer agent	Nanocomposites
PPH ₁	C ₂ (5 wt-%)	without	PPH ₁ /C ₂
PPH ₁	C ₂ (5 wt-%)	PP-g-MA (5 wt-%)	PPH ₁ /PP-g-MA/C ₂
PPH ₂	C ₂ (5 wt-%)	without	PPH ₂ /C ₂
PPH ₂	C ₂ (5 wt-%)	PP-g-MA (5 wt-%)	PPH ₂ /PP-g-MA/C ₂
PPH ₃	C ₂ (5 wt-%)	Without	PPH ₃ /C ₂
PPH ₃	C ₂ (5 wt-%)	PP-g-MA (5 wt-%)	PPH ₃ /PP-g-MA/C ₂
PPH ₄	C ₂ (5 wt-%)	Without	PPH ₄ /C ₂
PPH ₄	C ₂ (5 wt-%)	PP-g-MA (5 wt-%)	PPH ₄ /PP-g-MA/C ₂

2.3 Nanocomposites Characterization

The basal spacing of the clays and the structure of the nanocomposites were examined by X-ray diffraction (XRD) using Siemens D500 equipment with Cu $\lambda = 1.54$ Å. The basal spacing of the clays was estimated from the (001) peak in the XRD using the Bragg equation $\lambda = 2d \sin\theta$, where λ is the wavelength.

Differential scanning calorimetry (DSC) measurements were made on DSC Q200 TA Instrument. All measurements were carried out in nitrogen atmosphere. The samples were heated from 50 to 200 °C at a heating and cooling rate of 5 °C/min. The measurements were accomplished in the second heating and cooling cycle.

Thermogravimetric analyses were carried out on a T. A. model QA-50 to

obtain the inorganic and organic residue, and the clays' decomposition profile, and PP nanocomposites. The samples (films of 10.0 mg) were heated from 25 to 600° C at heating rate of 10° C/min under nitrogen flow.

A T.A. model QA 800 instrument was used for dynamic mechanical analyses (DMA) and heat deflection temperature (HDT) behavior of the materials at a fixed frequency of 1 Hz. DMA analyses were performed in single cantilever mode. The compression-molded samples were heated from -50° C to 120° C at heating rate of 3° C/min. The conditions for the HDT analyses were adapted from the ASTM D648, and carried out on three point bending mode, using specimens with approached dimensions of 50.0 x 3.2 X 12.7 mm³.

The morphologies of the nanocomposites were examined by Transmission electron microscopy (TEM), JEOL/JEM 1200 EX II model operating at an accelerating voltage of 80 kV.

3. RESULTS AND DISCUSSION

3.1. Nanocomposites characterization for XRD.

XRD in Figure 1 shows the characteristic diffraction peak corresponding to the 001 plane, and interlayer distances of the platelets. The peak of nanoclay SE3000 (C₂) appears at 6.9°, which corresponds to 3.6 nm interlayer distance. The nanocomposite PPH₁/C₂ appears at 2.2° (3.9 nm), moreover, the nanocomposite PPH₁/PP-g-MA/C₂ also appears at 2.2° (3.9 nm). Therefore, in the two previous cases the interlayer distance increases with respect to the clay alone, indicating that the PP is intercalated between the clay layers.

Figure 1: XRD Patterns of the organophilic clay (C₂), nanocomposite PPH₁/C₂ and nanocomposite PPH₁/PP-g-MA/C₂.

The mechanisms of intercalation and exfoliation in the melt state are not completely understood, but some authors suggest that the intercalation and exfoliation are obtained by the combination of shear forces produced during the extrusion process and the diffusion of molecules in the clay layers was promoted by the interaction of polar groups of the same and the surface of the clay (15, 24-25).

Figure 2: XRD Patterns of the organophilic clay (C₂), nanocomposite PPH₂/C₂ and nanocomposite PPH₂/PP-g-MA/C₂.

Figures 2, 3, and 4 show that intercalation process has occurred, which is supported by the increase in the intercalation that occurs independently of MFR PP used. Additionally, interlayer distance is compared for the clay alone and with the respective nanocomposites. Furthermore, the systems with or without the compatibilizer agent (PP-g-MA) experienced an increase in the interlayer distance with respect to the clay (C₂). This effect was observed due to the low concentration of the compatibilizer agent used in the preparation of nanocomposites.

Figure 3: XRD Patterns of the organophilic clay (C₂), nanocomposite PPH₃/C₂ and nanocomposite PPH₃/PP-g-MA/C₂.

Figure 4: XRD Patterns of the organophilic clay (C_2), nanocomposite PPH_1/C_2 and nanocomposite $PPH_1/PP-g-MA/C_2$.

3.2. Thermal Analysis for nanocomposites.

The thermogravimetric analyses were carried out to investigate the behavior of nanocomposites during heating in an inert atmosphere. PP degradation under these conditions involves cleavage chain reactions leading to the formation of smaller chains with free radicals at their ends; intramolecular transfer of the radical, forming a radical internal row of the b-elimination to form volatile products and residues of unsaturated polymers with endings (26).

Figure 5 presents the TGA curves of PPH_1 and the nanocomposites PPH_1/C_2 and $PPH_1/PP-g-MA/C_2$. For the nanocomposites PPH_1/C_2 and $PPH_1/PP-g-MA/C_2$, there are not changes in thermal stability with respect to PPH_1 alone. This effect is probably due to the low MFR polypropylene (MFR $PPH_1 = 2$ g/10 min), which hinders the incorporation of the polymer into the clay layers.

Figure 5: TGA curves of PPH_1 , nanocomposite PPH_1/C_2 and nanocomposite $PPH_1/PP-g-MA/C_2$.

On the other hand, the nanocomposites PPH_2/C_2 and $PPH_2/PP-g-MA/C_2$ show an increase in thermal stability with respect to PPH_2 alone (see Figure 6).

Figure 6: TGA curves of PPH_2 , nanocomposite PPH_2/C_2 and nanocomposite $PPH_2/PP-g-MA/C_2$.

In both cases, the nanocomposites increased the initial decomposition temperature ($T_{10\%}$) compared to PPH_2 (see Table 2) because the nanoclay migrates to the surface forming a protecting barrier that hinders the release of gases coming from the nanocomposite decomposition. Zanetti et al. (27) observed that the displacement of the initiation temperature for the degradation of nanocomposites PPH_2/C_2 and $PPH_2/PP-g-MA/C_2$ is probably due to the physical and chemical adsorption of the degradation products at the silicate surface. This effect shows product volatilization generated by thermal degradation of PP. Table 2 also shows the decomposition temperature ($T_{50\%}$), which increases about 40 °C in nanocomposites with respect to PPH_2 . In addition, the compatibilizer agent increases the polymer-clay adhesion causing partial intercalation of platelets in the matrix.

Table 2. Thermal properties of different kind PP and nanocomposites

Sample	$T_{10\%}$ (°C) ^a	$T_{50\%}$ (°C) ^b	T_m (°C) ^c	T_c (°C) ^d	X_c (%) ^e
PPH_1	443	454	160	122	43
PPH_1/C_2	444	454	161	121	42
$PPH_1/PP-g-MA/C_2$	445	454	161	121	42
PPH_2	354	406	161	128	43
PPH_2/C_2	435	445	161	124	41
$PPH_2/PP-g-MA/C_2$	443	451	162	125	42
PPH_3	391	443	162	127	47
PPH_3/C_2	433	444	162	127	47
$PPH_3/PP-g-MA/C_2$	440	450	161	126	47
PPH_4	417	442	162	122	42
PPH_4/C_2	439	447	163	122	43
$PPH_4/PP-g-MA/C_2$	440	448	162	123	43

a. $T_{10\%}$, Temperature at which 10% of weight loss occurs.

b. $T_{50\%}$, Temperature at which 50% of weight loss occurs.

c. T_m , Melting Temperature

d. T_c , Crystallization Temperature

e. X_c (%) = $\Delta H_m / f_p \Delta H_m^*$

ΔH_m = Melting enthalpy of sample, ΔH_m^* = Melting enthalpy of pure crystalline PP (207,1 J/g) (27), f_p = mass fraction of PP in the sample

Figures 7 and 8 show the thermogravimetric analysis for PPH_3 and PPH_4 respectively and their corresponding nanocomposites. The nanocomposites show an increase in thermal stability with respect to PPH_3 and PPH_4 alone.

Figure 7: TGA curves of PPH₃, nanocomposite PPH₃/C₂ and nanocomposite PPH₃/PP-g-MA/C₂.

The addition of clay and clay / compatibilizer agent causes an increase in $T_{10\%}$ in PPH₃ and PPH₄ (see Table 2), where this increase is greater when using PPH₄.

PPH₃ and PPH₄ and their corresponding nanocomposites have almost the same final decomposition temperature ($T_{50\%}$).

Figure 8: TGA curves of PPH₄, nanocomposite PPH₄/C₂ and nanocomposite PPH₄/PP-g-MA/C₂.

The degree of crystallinity (X_c), melting (T_m) and crystallization temperature (T_c) do not show major changes in the nanocomposites when compared with the PP (PPH₁, PPH₂, PPH₃ and PPH₄) since the concentrations of clay (5 wt-%) and compatibilizer agent (5 wt-%) are sufficiently low to not affect the thermal properties described above.

3.3 Dynamic mechanical properties.

The dynamic mechanical analysis relates macroscopic properties of the material with molecular relaxations associated with molecular conformational changes and microscopic deformations generated from molecular rearrangements.

In Table 3, it can be observed that the glass transition temperature (T_g) in all the samples remains constant between 7-9 °C.

Table 3: Dynamic mechanical properties of the polypropylene nanocomposites.

Sample	b Transition, T_g (°C)	Storage Modulus, E' 23° C (J/m)	Heat Deflection Temperature, HDT (°C)
PPH ₁	9	3941	80
PPH ₁ /C ₂	9	4496	88
PPH ₁ /PP-g-MA/C ₂	8	4986	89
PPH ₂	8	3890	74
PPH ₂ /C ₂	9	4010	75
PPH ₂ /PP-g-MA/C ₂	9	4120	79
PPH ₃	8	3190	73
PPH ₃ /C ₂	7	3666	74
PPH ₃ /PP-g-MA/C ₂	8	3752	77
PPH ₄	7	3936	69
PPH ₄ /C ₂	7	4113	70
PPH ₄ /PP-g-MA/C ₂	8	4455	76

HDT determined through the methodology proposed by Scoboo (28).
T_g, glass transition temperature

The storage modulus (E') is the measurement of stiffness, describing the range where the elastic property is higher. It is also possible to observe that the addition of clay material to non-modified (PPH₁, PPH₂, PPH₃ and PPH₄) causes a increase in the storage modulus for the entire tested temperature range. On addition of nanoclay, the modulus increased from 3941 to 4496 MPa due to the partial reinforcement, restricting the mobility of the chain segment in the case of PPH₁ and PPH₁/C₂. When the compatibilizer agent is added to the system, the module increases from 3941 to 4986 MPa (PPH₁/PP-g-MA/C₂). When the polymer diffused in the favorable bonding between the PP-g-MA, the clay surfactant was formed and the clay particles were placed in between the clay and the other layer.

In the case of systems PPH₂ and PPH₃, their nanocomposites also increase the storage module when the reinforcements C₂ and compatibilizer agent are added.

Figure 9 shows the dynamic mechanical analysis curves of PPH₄ and their nanocomposites. PPH₄/C₂ and PPH₄/PP-g-MA/C₂ systems show a sharp increase in the storage modulus for the entire temperature range analyzed with respect to PPH₄. This result is due to the partial reinforcement, which restricts the chain segment mobility.

Figure 9: Dynamic mechanical analysis curves of PPH₄ and their nanocomposites

The heat deflection temperature (HDT) can be obtained directly from the curve of the storage module in accordance with the methodology proposed by Scoboo (28). When one moves from the PP to the PP/C₂ or PP/compatibilizer agent/C₂, there is an increase in the HDT (see Table 3). The use of 5 wt-% clay and the compatibilizer agent increases the matrix's resistance.

3.4. Morphological Analysis

Figures 10 a), b), c), and d), which display the TEM microphotography

for the different nanocomposites PPH₁/C₂, PPH₂/C₂, PPH₃/C₂ and PPH₄/C₂ corroborate the DRX analysis in which all nanocomposites are in the intercalated state. C₂ penetrates into the spaces of the polymer chain, decreasing the intermolecular force, and thus favoring the interaction with C₂ and promoting the sheets to slip.

Figure 10: TEM images of PP nanocomposites

4. CONCLUSIONS

All nanocomposites prepared are in intercalated state as corroborated by the XRD and TEM. The T_m and X_c were not affected by the presence of clay, PP-g-MA, or processing aid. The incorporation of clay and compatibilizer agent increases the thermal stability and HDT. The clays with small d(001) presented a larger modulus, because their surface is free to interact with the PP matrix due to the low amount of ammonium salt. The modulus values were larger when the intercalated orientation was obtained, and it was favored when the proportion of C₂ and PP-g-MA was 1:1.

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