The Effect of Clay Type and of Clay–Masterbatch Product in the Preparation of Polypropylene/Clay Nanocomposites

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ABSTRACT: Clay containing polypropylene (PP) nanocomposites were prepared by direct melt mixing in a twin screw extruder using different types of organo-modified montmorillonite (Cloisite 15 and Cloisite 20) and two masterbatch products, one based on pre-exfoliated clays (Nanofil SE 3000) and another one based on clay–polyolefin resin (Nanomax-PP). Maleic anhydride-grafted polypropylene (PP-g-MA) was used as a coupling agent to improve the dispersability of organo-modified clays. The effect of clay type and clay–masterbatch product on the clay exfoliation and nanocomposite properties was investigated. The effect of PP-g-MA concentration was also considered. Composite morphologies were characterized by X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEG-SEM), and transmission electron microscopy (TEM). The degree of dispersion of organo-modified clay increased with the PP-g-MA content. The thermal and mechanical properties were not affected by organo-modified clay type, although the masterbatch products did have a significant influence on thermal and mechanical properties of nanocomposites. Intercalation/exfoliation was not achieved in the Nanofil SE 3000 composite. This masterbatch product has intercalants, whose initial decomposition temperature is lower than the processing temperature ($T \sim 180°C$), indicating that their stability decreased during the process. The Nanomax-PP composite showed higher thermal and flexural properties than pure PP. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2013–2025, 2011

Key words: Polypropylene/clay nanocomposite; organoclay; clay-masterbatch; extrusion

INTRODUCTION

Clays containing polymer nanocomposites are an alternative to conventional microcomposites due to improved mechanical, thermal, and processing properties as well as enhanced flammability resistance and barrier properties at very low filler loadings (<5 wt %). To make high performances nanocomposites, the silicate must be finely and uniformly dispersed i.e., intercalated and/or exfoliated in the matrix. Intercalated nanocomposites are formed when polymer chains are between the host silicate layers with more-or-less fixed interlayer distances. Exfoliated nanocomposites are formed when silicate layers are delaminated and dispersed in the polymer matrix, where this state is more effective in improving reinforcement and other performance properties. There are several techniques used for dispersing organoclay at a nanoscopic scale, including the addition of organoclay during polymerization ("*in situ*" method), or by addition to a solvent swollen polymer (solution blending) or to a melt polymer (melt intercalation method). From an industrial perspective, the preparation of thermoplastic polymer nanocomposites by melt blending using conventional plastic compounding tools remains the solution of choice, especially with commodity resins like polypropylene (PP), which is of great interest for the packaging and automotive industries.[1]

Extensive efforts have focused on the performance of PP nanocomposites prepared by melt compounding. Temperature processing, shear rate, screw speed, residence time, mixing strategies, and screw configuration have been the main challenges in the melt processing of polymer nanocomposites.[2,3] The type and content of the coupling agent in the formulation have been studied. It has been reported that a low content of coupling agent, i.e., maleic anhydride-modified polypropylene (PP-g-MA), does not

sufficiently enhance the degree of dispersion, although this improvement is obtained for 3:1 PP-g-MA : clay wt % ratio in one-step mixing.[4,5] Several studies have reported the effect of molecular weight and MA content of compatibilizer on the extent of delamination and on the performance of polypropylene/clay nanocomposites. Thus, Perrin-Sarazin et al.[6] studied the influence that two PP-g-MA, with different molecular weights and grafting contents, have on clay intercalation and matrix morphology. Clay intercalation was influenced by the characteristics of PP-g-MA: those composites prepared with low molecular weight PP-g-MA had good, uniform intercalation without signs of exfoliation. On the other hand, those composites prepared with high molecular weight PP-g-MA and low MA content had a heterogeneous intercalation with signs of exfoliation. Wang et al.[7,8] also studied the influence of MA content or the grafting degree of PP-g-MA in the preparation of PP/clay composite by melt compounding. Compatibilizers of low-melt flow index (corresponding to medium to high molecular weight) and a moderate degree of grafting presented a high degree of exfoliation and organoclay dispersion. They pointed out that the best mechanical properties are found in the composites modified by Polybond 3150 with the lowest melt flow index; however, those composites prepared with low-molecular weight PP-g-MA and high degree of grafting had the highest tensile modulus and yield strength. Some authors[2,9] have found that a coupling agent with high MA content improved the young modulus without remarkable changes in the impact strength. Subsequently, Reichert et al.[9] reported the use of distinct PP-g-MA with high MA content (at 2.3 and at 4.2 wt %) in the preparation of synthetic PP/clay nanocomposites. Those composites prepared with PP-g-MA of 4.2 wt % of MA showed an increase in the interlayer distances as well as in the mechanical properties; consequently, the Young's modulus and yield strength increased from 1490 to 3460 Mpa and from 33 to 44 Mpa, respectively, with respect to virgin PP. Marchant et al.[10] suggested that the molar ratio of functional group to compatibilizers chains is a better parameter for ranking compatibilizer effectiveness than the acid number, which is a weight ratio. They pointed out that with higher molar ratio values (acid number = 15 mg KOH/g and M_w = 47,000), lower compatibilizer concentrations are required for significant exfoliation.

The type and amount of organo-salt used in the modification also influence the performance of thermoplastic nanocomposites based in PP and organo-modified clays. Comparative studies have been performed using different types of commercial organo-modified clays in the preparation of these nanocomposites.[11–15] Santos et al.[12] studied the

effects of organic modifiers of three clays on the intercalation and exfoliation processes as well as mechanical properties. Those composites prepared with clays of larger d_{001} (Cloisite 15 and Nanofil 5) showed a considerable gain in impact strength, while the composites prepared with clays of smaller d_{001} (Cloisite 20) presented a larger modulus compared with those of virgin PP. However, Dong et al.[14] found that the clay type did not significantly influence the mechanical properties of nanocomposites. In the preparation of nanocomposites, they employed three types of organoclay with different hydrophilic properties and d_{001} values.

The aims of this study were to prepare PP/organoclay nanocomposites by a melt intercalation method in a twin screw extruder with two different types of clays and clay–polymer masterbatch products and then to comparatively study them. In addition, the influence of PP-g-MA content was studied in two types of polymer/clay nanocomposites. The organoclay content is kept constant at 5 wt % for all composites. The clay–polymer masterbatch products are Nanofil® SE 3000, a clay powdery masterbatch and Nanomax®-PP, clay PP resin masterbatch, both of them commercially available. These masterbatches are identified as Nanofil and Nanomax, respectively.

EXPERIMENTAL

Materials

An injection grade PP homopolymer, PH-1310, provided by Petroquim S.A. was used as matrix. The PH-1310 polymer is characterized by a melt flow rate of 13 g/10 min (2.16 kg/230°C), weight-average molecular weight, M_w, of ∼ 213 kg/mol and number average molecular weight, M_n, of 91 kg/mol. MA modified PP (PP-g-MA), "Licocene PP MA 6452." GR TP from Clariant was used as compatibilizer. The viscosity, acid number, and M_w were 1100 mPas at 170°C, 43 mg KOH/g and 10 Kg/mol, respectively.

Two commercial types of organoclays based on natural montmorillonite modified with alkyl ammonium, Cloisite®15 and Cloisite®20 were used as received from Southern Clay Products. These two clays have been modified by different levels of cation exchange reaction to broaden their gallery distances in different extents. Furthermore, two polymer–clay masterbatch products, Nanofil® SE 3000 and NanoMax®-PP, were also used as nanofiller. Nanofil® SE 3000 is a powdery masterbatch, where the clay has been modified with a pre-exfoliating additive or additive mixture of diverse chemical nature.[16] NanoMax®-PP is Nanomer resin masterbatch products, with 50 wt % of Nanomer® nanoclay and the remaining 50% contains the resin and

compatibilizers needed to promote clay dispersion. This resin masterbatch product is produced through melt compounding.[17]

The other relevant specifications of these materials are summarized in Table I.

Preparation of polymer/clay composites

Before extrusion, all materials were dried overnight at 80°C. A corotating twin-screw "TSA Industrial" extruder (screw diameter $D = 45$mm, $L/D = 40$) was used for compounding the PP/clay composites. The temperature profile was controlled at 190, 190, 175, 175, 175, 170, 170, and 175°C from hopper to the die. The designed screw configuration with sequential arrangement of conveying elements (SE) and kneading blocks (KB) are shown in Table II.

For nanocomposites prepared with Cloisite® 15 (Clo15) and Cloisite® 20 (Clo20); PP and PP-*g*-MA pellets were tumble mixed and introduced simultaneously in the hopper and organoclay powders were introduced in gravimetric feeder, located at the third zone of the extruder, so that the clay powders were fed downstream into the melted polymeric mixture.

For composites prepared with Nanofil® SE 3000 (Nanofil) and Nanomax®-PP (Nanomax), a coupling agent was not used.[16,17] The Nanomax composite was prepared by dry-blending PP and 10 wt % Nanomax and feeding the blend from the hopper. The Nanofil composite was prepared adding 5 wt % of Nanofil through the frontal feeder, located in the third zone of the extruder.

Single strands of PP/clay composite were cooled in a water batch and pelletized before further use.

In the first set, we investigated the effect of coupling agent in composites prepared with Clo15, and Clo20 by varying the PP-*g*-MA content (from 5 to 15 wt %) with the following conditions: screw speed of 180 rpm and feed rate of 20 kg/h. In the second set, we studied the effect of organoclay and masterbatch type applying the same melt compounding conditions: feed rate of 20 kg/h and the screw speeds of 180 rpm. All prepared composites had 5 wt % of clay. Table III summarizes all formulations prepared, expressed in mass fraction.

The extruded materials were injection molded into standard flexural test samples using an Arburg, model 420C, injection-molding machine. The processing temperature was kept constant at 180°C in the cylinder.

The compounded materials were prepared in thin films (10 × 10 × 1 mm) by compression-molding at 180°C for 3 min by X-ray diffraction (XRD) analysis, field emission gun scanning electron microscopy (FEG-SEM), and transmission electron microscopy (TEM) observations.

TABLE I
Specifications of Materials Used in this Work

Materials	Trade name	Description	Interlayer spacing[a] (Å)	Particle size range (μm)	Bulk density (g/cm³)	Supplier
Polypropylene Homopolymer	PH-1310	VICAT Softening Point (1 kg) = 154°C; MFI (2.16 kg/230 °C) = 13 g/10 min; IZOD Impact Test (23 °C) = 34 J/m; Tensile Strength (at Yield Point) = 34 MPa; Flexural Modulus = 1.500 MPa				Petroquim S.A.
Compatibilizer	Licocene PP MA 6452	Density at 23°C ~ 0.90 g/cm³; Acid value ~ 43 mg KOH/g; Softening point ~ 140°C; Viscosity at 140°C ~ 1200 mPa.s.				Clariant
Organoclay	Cloisite®15A		31.5	$D_{50} < 6$	0.30	Southern Clay Products
	Cloisite®20A		24.2	$D_{50} < 6$	0.22	Southern Clay Products
Clay-masterbach product	Nanofil® SE 3000 (Powder)		–	$D_{50} < 10$	0.45	Rockwood Clay additives GmbH
	NanoMax®-PP		–		–	Nanocor

[a] The interlayer spacing corresponds to the Bragg reflection peak (d_{001}) reported in technical data sheet of organoclays.

TABLE II
Screw Profile Used in the Experiments from Die to Hopper

540	45	180	540	45	45	90	315	Length (mm)
SE 45/45	KB 9/90	KB 9/45	SE 45/45	KB9/-45	KB 9/90	KB 9/45	SE 45/45	Pitch (mm)

KB (5/90) means a kneading disc of thickness 5 mm and staggering angle 90°

Neat PP processed under similar conditions was studied as reference polymer material.

Characterization

XRD was used to characterize the clays and to investigate the nature and extent of their intercalation in the filled samples. XRD patterns were recorded on a Rigaku Geigerflex diffractometer, model Dmax B, operating at 35 kV, 15 mA, and using Fe-Kα x-ray beam ($\lambda = 1.9373$ Å) at room temperature. The diffraction spectra were scanned in the reflection mode over a 2θ range 1.5–12°, in steps of 0.02°, rate 1°/min. The organoclay samples and Nanofil were studied as powders. Based on Bragg's Law ($n\lambda = 2 d_{001}\sin\theta$), the d-spacing (d_{001}) of the layered organoclay platelets was determined from the 2θ position of (001) diffraction peak of the clay. Peak fitting analysis was also made for all the XRD patterns using a Gaussian distribution function.

The dispersion of the clays inside the polymeric materials was assessed by a FEG-SEM Hitachi S-4700 to observe the microestructure of the materials. The polished samples were etched with a mixture of potassium permanganate, phosphoric acid, and sulfuric acid, which remove the amorphous domains and improve the contrast between the clay and the matrix.[18]

PP/clay composite morphologies were examined by TEM Philips CM200 operated at an acceleration voltage of 200 kV. Ultrathin sections (80nm) were prepared on a Leica Ultracut FC microtome at cryogenic temperature using a diamond knife. The observation was made on different sections retrieved onto coated Cu grids. The observation was made at different locations of the specimen.

TABLE III
Identification of the Sample

Sample identification	Clay Type	Clay content (wt %)	PP-g-MA content (wt %)
PH-Clo15-I	Cloisite®15	5	5
PH-Clo15-II	Cloisite®15	5	10
PH-Clo15-III	Cloisite®15	5	15
PH-Clo20-I	Cloisite®20	5	5
PH-Clo20-II	Cloisite®20	5	10
PH-Clo20-III	Cloisite®20	5	15
PH-Nanomax	NanoMax®-PP	5	–
PH-Nanofil	Nanofil® SE 3000	5	–

Melt rheology for the nanocomposite samples were studied using Rheocap S20 capillary rheometer at 180°C. The L/D ratios of the capillary die were 20/1, 30/1, and 40/1. For each specimen, the viscosity was measured for five different shear rates, which varied from 100 to 6000 s^{-1}.

Flexural mechanical testing was carried out on a universal Instron® 4465 machine according to the ASTM D-790/97 standard. Before measurement, all test samples were Conditioned for 40 h at 23°C and 50% moisture. The flexural measurements were performed using a three-point bending configuration at 1.27 mm/min deformation rate and up to 2% of deformation. The reported values correspond to the average from five individual measurements. The statistical analysis of variance (ANOVA) of flexural results was performed using the commercial software, Statgraphics plus 5.0. A one-way ANOVA and F-Test were used to check for statistical difference between groups (for $P > 0.05$).

Thermal stability, thermal degradation, and degree of crystallinity were investigated using a TA instrument, Q-50 and Q-200 for thermogravimetric (TGA) and differential scanning calorimetric (DSC), respectively. TGA scans were recorded at a rate of 10°C/min from room temperature to 590°C under nitrogen atmosphere (51 cm^3/min). DSC scans were performed at a heating rate of 10°C/min from 25 to 220°C, which were further subjected to isothermal condition for 5 min to eliminate thermal history. Then, it was cooled to 25°C at the same rate. The onset melt temperature ($T_{\text{m-onset}}$) and the peak melting temperature ($T_{\text{m-peak}}$) were obtained from DSC endotherms, whereas onset crystallization temperature ($T_{\text{c-onset}}$) and peak crystallization temperature ($T_{\text{c-peak}}$) were obtained from the DSC exotherms. The degree of crystallinity was calculated as the ratio of the melting enthalpy to the weight fraction of PP (w_{pp}) in the blend, i.e., $X_c = \Delta H_f^{\text{obs}}/w_{\text{pp}}\Delta H_f^\circ \times 100$, where ΔH_f^{obs} is the measured melting enthalpy and ΔH_f° is the ideal melting enthalpy of a perfect crystal of PP. A value of $\Delta H_f^\circ = 209$ J/g for a 100% crystalline PP homopolymer was used to calculate X_c.[19]

RESULTS AND DISCUSSION

Clay characterization

Clays and masterbatches were characterized by XRD and TGA. Table IV shows values of 2θ

Results of TGA and XDR Analysis for the Organo-Modified Clays and the Masterbatches

Sample	Modifier concentration (meq/100 g)[c]	2θ (°)	d_{001} (nm)	Organic residue (wt %)[d]	Inorganic residue (wt %)[e]	$T_{onset-decomp}$ (°C)	$T_{-5\%}$[f] (°C)
Clo15[a]	125	3.43	3.24	39.3	58.7	185	261
Clo20[a]	95	4.30	2.58	35.3	62.9	195	275
Nanomax	–	3.81	2.91	–	30.4	290	356
Nanofil[b]	–	2.90	3.83	–	44.3	145	268

[a] Organic modifier is dimethyl di(hydrogenated tallow) quaternary ammonium. The tallow is made of approximately 65% C18, 30% C16, and 5% C14.
[b] Organic modifier is mixture additive of diverse chemical nature.
[c] From technical data sheet of Southern Clay Products Inc.
[d] wt % calculated using the thermal decomposition range of ammonium salts (200–500°C).
[e] wt % inorganic residue was calculated at 590°C.
[f] The temperature at which the 5% of weight loss occurs.

corresponding to the 001 plane, d_{001} of the platelets as well as the onset decomposition temperature, the temperature at which the weight loss reaches 5%, and the amount of inorganic residues and of organic residue. The last one considered that the thermal decomposition of organic substances between silicate layers occurs mainly in the range 200–500°C.[12,20]

The clays Clo15 and Clo20, which were modified with the same type of ammonium salts but with different amount of intercalants (higher Clo15 than that Clo20), presented a difference in their interlayer space of around 0.7 nm. The d_{001} values was 3.24 nm for Clo15 and 2.58 nm for Clo20. These calculated values are in d_{001} range reported in a previous study based in these commercial clays.[6,12,13] The value of interlayer spacing of Nanomax is representative of a broad distribution of intercalated structure, which is related to the different intercalation level of the coupling agent or/and resin polymer inside the clay layers. In contrast, Nanofil presents a narrow distribution of intercalated structure and the largest values of interlayer distance (d_{001} = 3.83 nm). This difference could indicate that macromolecule polymer

diffusion into the clay layers during the preparation of nanocomposites by melt-mixed is easier when Nanofill is used as filler. However, other characteristics, such as decomposition temperature, which will be discussed later, also need to be taken into account.

The evolution of weight loss of organo-modified clays and masterbatches with temperature under nitrogen flow is shown in Figure 1(a). The organo-modified clays, Clo15 and Clo20, display a decomposition process in two stages: one between 185–400°C for Clo15 and 195–400°C for Clo20, and another between 400 and 500°C for both. In comparison with Clo20, Clo15 exhibited a higher weight loss in the first step, indicating that Clo15 has more organic matter, which accounted for its larger interlayer distance. Leszczynska et al.[20] have reported a two-steps decomposition process of the surfactant: mainly long carbon chains with chloro or amine groups were detected in the first step, whereas the evolved gases during the second stage were composed mainly of both short and long chains without the chloro groups. Below 200°C, the
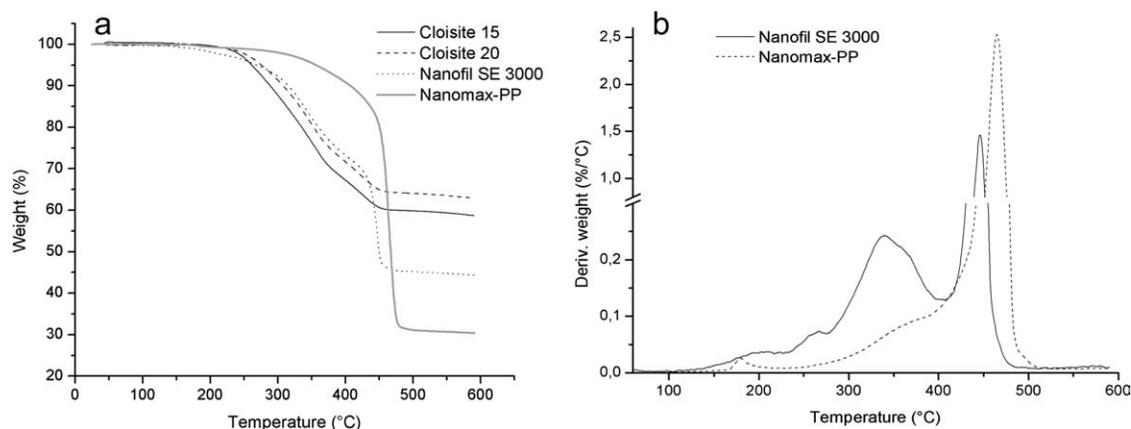

Figure 1 TGA (a) and DTG (b) curves of masterbatch and organo-modified clays under nitrogen flow and heating rate: 10°C min^{-1}.
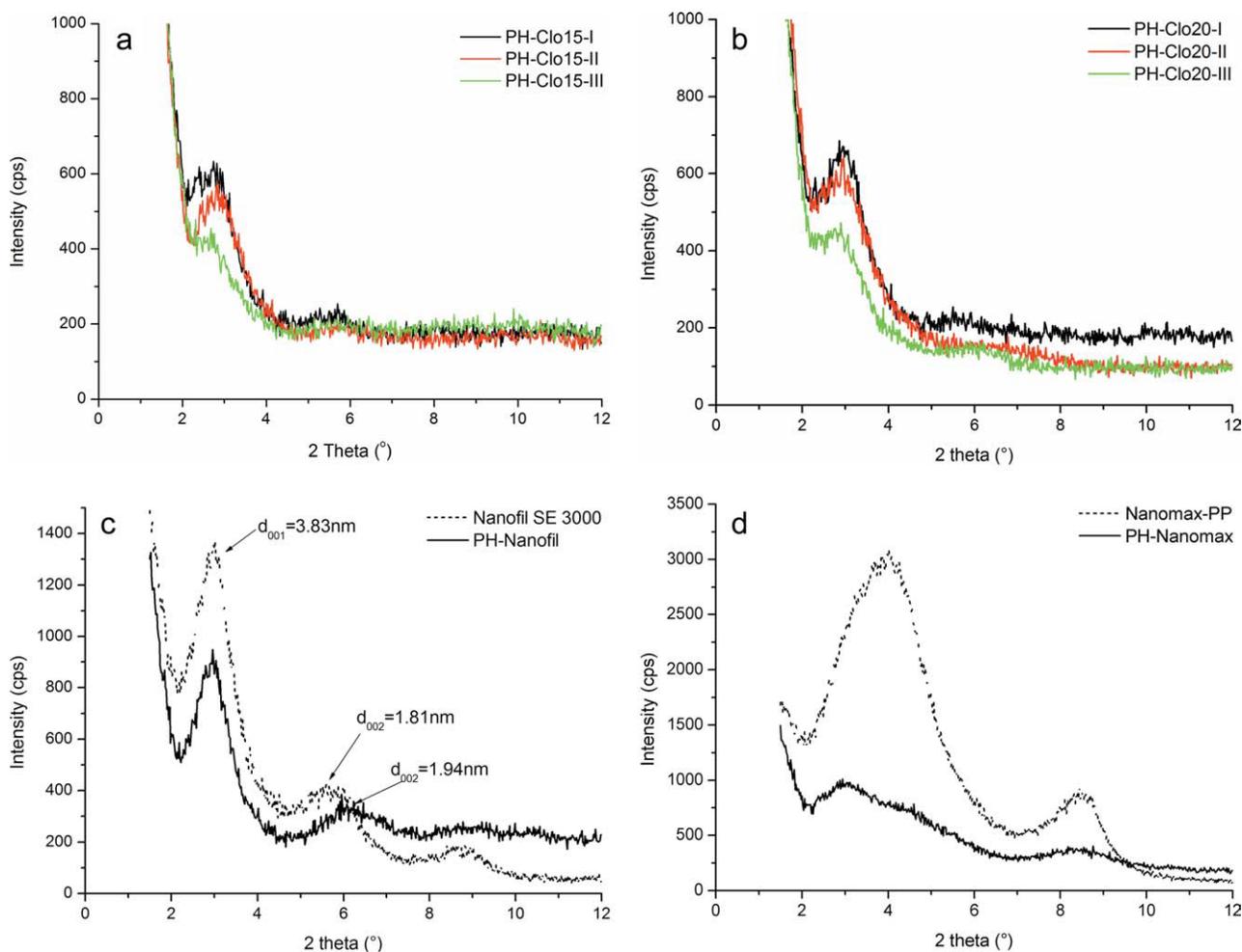
Figure 2 XRD patterns of clays and their composites; Clo15 composites (a), Clo20 composites (b), Nanofil and Nanofil composite (c), and Nanomax and Nanomax composite (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight loss has been associated to the elimination of free and physically adsorbed water in the internal layer of clay.[12]

Figure 1(b) represents Derivative Thermogravimetry (DTG) scans of two masterbatch products. Nanofil presents four regions: the first starting between 145°C–235°C; the second region between 235–283°C and the two last ones between 283–410°C and 410–500°C with 22 and 27% of weight loss, respectively. In the case of Nanofil, weight loss in the first and second regions is about 6% and could also be associated to nonexchanged surfactants, which in turn could also be responsible for product degradation at low temperatures. According to Nanofil patents, this characteristic has been modified with a pre-exfoliating additive or additive mixture of diverse chemical nature, such as fatty acid derivatives, polymer fatty acids, ethylene propylene copolymers, ethylene propylene terpolymers, and thermoplastic elastomers.[18] The total weight loss of Nanofil was higher than found for Clo15 and Clo20. On the other hand, in the DTG scan of Nanomax, three regions are shown: the elimination of free additive or water occurs between 170 and 200°C, resulting in limited weight loss of 0.5%; the second region between 200 and 390°C is observed as a shoulder and corresponds to part of the additives and clay modifier decomposition; the largest weight loss (61%) occurs in the third region between 390 and 510°C and should be associated to the resin decomposition.

Table IV presents the onset decomposition temperature, which was considered an index of thermal stability of organo-modified clay and clay masterbatch. The Nanofil exhibits the lowest onset decomposition temperature, and thus their organic modifier helps to increase the interlayer distance although it results in poor thermal stability. The value of the onset decomposition temperature of Nanofil is lower than the processing temperature used to prepare and characterize the PP nanocomposites and might cause reaggregation of clay platelet and performance loss. The onset decomposition temperatures of organo-

TABLE V
Interlayer Spacing for Composite Materials, Calculated from XRD Patterns

Sample	2θ (°)	d_{001}(nm)
Clo15	3.43	3.24
PH-Clo15-I	2.57	4.32
PH-Clo15-II	2.58	4.30
PH-Clo15-III	2.45	4.53
Clo20	4.30	2.58
PH-Clo20-I	2.88	3.85
PH-Clo20-II	2.78	3.99
PH-Clo20-III	2.69	4.13
Nanomax	3.81	2.91
PH-Nanomax	3.04	3.65
Nanofil	2.90	3.83
PH-Nanofil	2.88	3.85

The interlayer spacing corresponds to the Bragg reflection peak (d_{001}) from raw organoclays and clay masterbatch using X-ray diffraction (XRD) scan.

modified clays and Nanomax were higher than the processing temperature used to prepare PP/clay nanocomposites.

The inorganic residue was also calculated at 590°C from TGA (see Table IV). These remaining residues were attributed to the high thermal stability of clay. As expected, Clo20 presented the largest inorganic residue (around 63 wt %), followed by Clo15 (59 wt %), Nanofil (44 wt %) and Nanomax (30 wt %). The lower amount of inorganic residues in Namomax compared with Nanofil could be because Nanomax only has 50% of organoclay and their modifier also decomposes.

Structural and morphological characterization

Figure 2 presents the XRD patterns of the samples and Table V summarizes the calculated d_{001} values. The diffraction peak corresponding to (001) plane of clays, Clo15 and Clo20, shifts towards lower values after mixing with the polymers, suggesting that intercalation of PP and partial exfoliation are achieved. The d_{001} increased from 3.2 up to 4.5 nm and from 2.6 up to 4.1 nm for composites prepared at Clo15 and Clo20, respectively. In contrast, the XRD patterns of Nanofil and PH-Nanofil were similar, suggesting that the intercalation of polymer macromolecules was not possible. In addition, the d_{002} peak assigned as a second order peak shifts toward lower values, from 1.94 to 1.81 nm, in the Nanofil composite, suggesting a slight collapse of the platelets (see Fig. 2). This composite presented a yellowish appearance and clay particles can be observed in the final product. In the literature, the yellowish appearance has been attributed to amine degradation caused by the high temperatures of the melt processing, which causes reaggregations of clay layers.[21] The no-intercalation of polymer in Nanofil

masterbatch is probably due to the combined effect of relative lower compatibility between the PP and Nanofil modifiers and the modifiers' lower degradation temperature (T onset $\sim$ 150°C), which is lower than the processing temperature ($T \sim$ 180°C).

In the XRD patterns of composites prepared with Clo15 and Clo20 and different amount of PP-g-MA, the peak position (001 plane) is observed to not significantly change with the increase in PP-g-MA content. The interlayer spacing varies between 4.3–4.5 nm for Clo15 composites and between 3.9–4.1 nm for Clo20 composites; in some cases, such as the Clo15 composite prepared with 5 and 10 wt % of PP-g-MA, it does not change, indicating that the intercalation does not depend on the PP-g-MA content. Coupling agent with a high MA content (3.8 wt %) and low molecular weight in the preparation of PP/clay composites results in excellent, uniform intercalation.[6] The chain size of the coupling agent should regulate the interlayer spacing of the platelets. However, a gradual reduction in the (001) peak intensity with the increase of PP-g-MA content was also observed (see Fig. 2), suggesting a decrease in the coherent layer stacking (i.e., a more disordered system).[22]

In the case of the Nanomax composite, the broad peak corresponding to 001 plane of clay shifts to lower angle, so the d_{001} changed from 2.9 to 3.6 nm, indicating that the PP macromolecules are intercalated between the platelets with a wider distribution of the interlayer spacing.

To visualize clay particle dispersion into the PP matrix, SEM micrographs were recorded. Figure 3 displays representative micrographs of some of the PP/clay nanocomposites prepared. In the all samples, the clays were dispersed into the polymer matrix in the form of small and large aggregates with a predominance of smaller sizes. Aggregate size is difficult to estimate because they are nonisometric and randomly dispersed in the matrix. The micrographs of the Clo20 and Clo15 composites prepared with different PP-g-MA content were similar and no differences were observed between the composites prepared with same type of organo-clay and with different PP-g-MA content. These results suggest that the clay could be well dispersed in the PP even when using a smaller amount of PP-g-MA (5 wt %). The SEM micrograph of PH-Nanomax was similar to that of the Clo15 and Clo20 composites.

Based on the XRD and SEM results, composites of Clo15 and Clo20 prepared with 5 and 15 wt % of PP-g-MA were further investigated by TEM. The dark areas in the TEM images represent the clay particles and the gray ones represent the continuous PP. As can be seen in Figure 4 for composites prepared with 15% of PP-g-MA, the exfoliation of silicate sheets within the polymer matrix can be
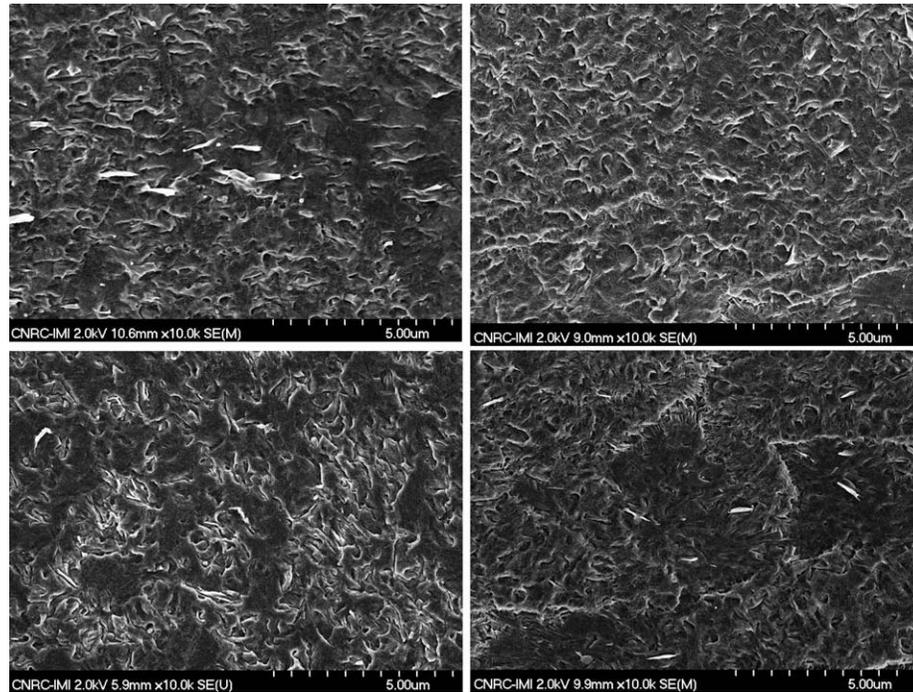
Figure 3 Typical SEM micrograph of PP/clay composites: PH-Clo20-I, PH-Clo20-III, PH-Clo15-II, and PH-Nanomax after surface etching.
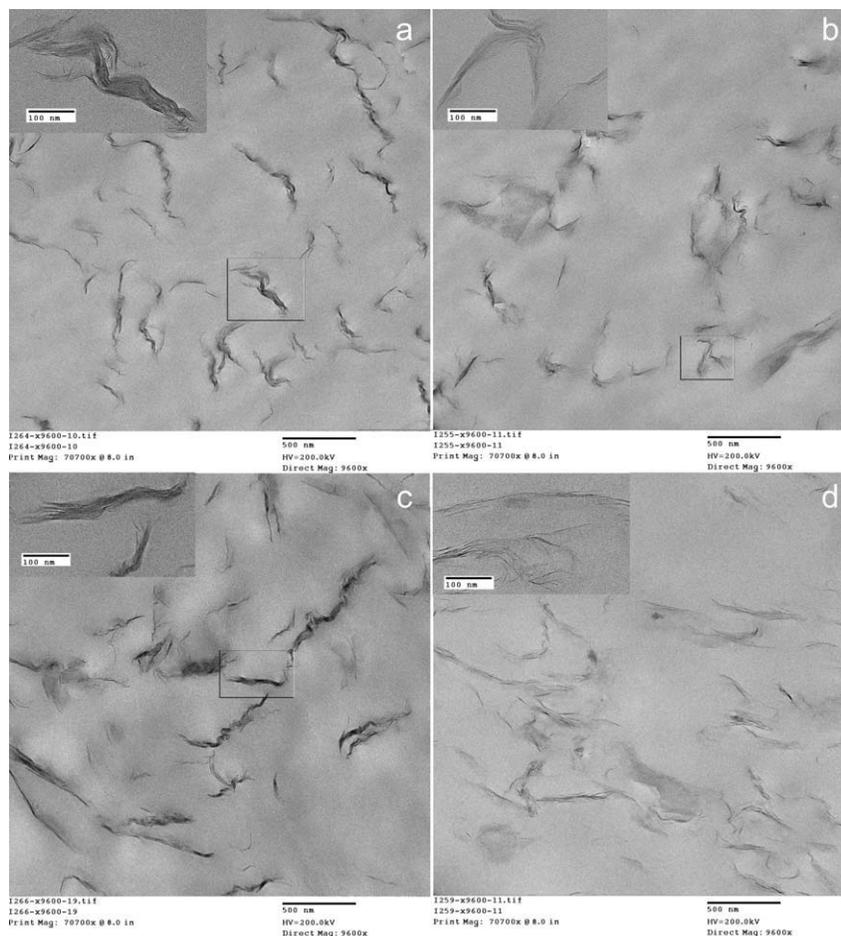

Figure 4 TEM images of the samples: PH-Clo15-I (a), PH-Clo15-III (b), PH-Clo20-I (c), and PH-Clo20-III (d) at 9.6 k magnification (scale bar = 500 nm). The insert in the top left of each figure shows the most typical structure (intercalate/exfoliate) of clay into PP matrix at 30 K magnification (scale bar = 100 nm).
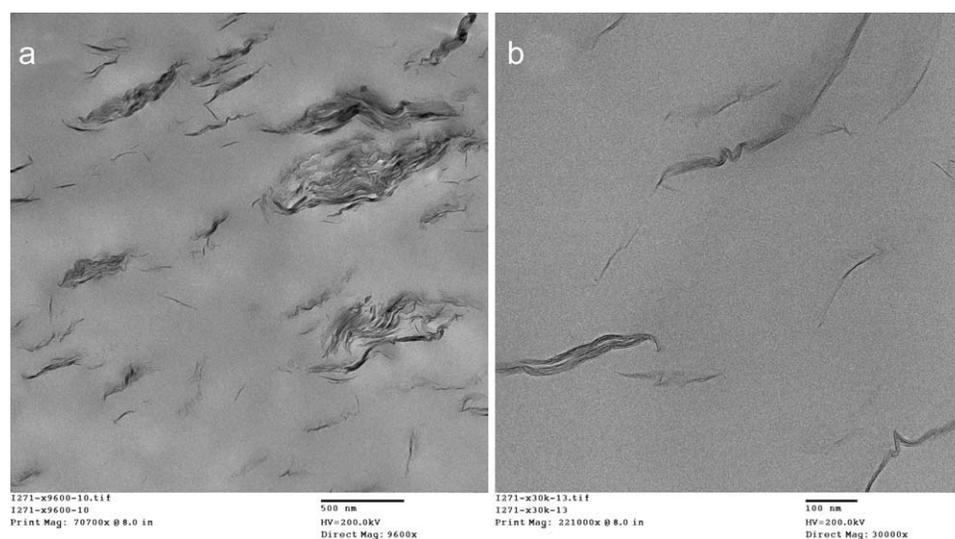
Figure 5 TEM images of the PH-Nanomax sample at 9.6 k (a) and 30 k (b) magnifications.

detected, the tactoid was not present and only some smaller stacks remained [see Figs. 4(b,d)]. In contrast in the composites prepared with 5 wt % of PP-*g*-MA [see Figs. 4(a,c)], tactoids and a larger number of layers per stack are observed in comparison with the composite prepared with 15 wt % of PP-*g*-MA. In the case of PH-Nanomax, different types of morphology, tactoids larger than 500 nm, dans smaller stack and individual silicate sheets were observed (see Fig. 5), corroborating the origin of a broadening peak of this composite obtained by XRD.

The influence of the PP-*g*-MA concentration became obvious in the TEM image; the blends prepared with 15 wt % of PP-*g*-MA presented a higher amount of exfoliate structures, in agreement with the XRD results discussed above. The ratio of the coupling agent to modified clay content 3:1 for direct melt mixing process has also been reported as proper to obtain PP/clay nanocomposites.[4,5]

Reological properties: rheometer capillary

The rheological properties of PP-based organoclay compounds were evaluated using capillary rheometry. The melt viscosity decreased rapidly with the increasing shear rate for neat PP and PP/clay composites, implying that these materials possess a shear thinning character. Figure 6 shows the effect of clay presence on the rheological properties of different blend polymeric formulations. In the range of the higher shear rates 10^2–10^4 s^{-1} used to simulate the extrusion and injection-molding processes, the molten blends prepared with organo-modified clays and Nanofil showed a shear viscosity below that of the pure PP as a result of preferential orientation of organoclay layers or even anisotropic tactoid to flow direction. Similar behavior has been reported by

Shu-Ying et al.[23] The effect on viscosity of organoclay addition in the PP matrix at a high shear rate is not obvious. When the shear rate is increased, the shear thinning effect is enhanced and the wall slip phenomenon occurred between organoclay/PP and the wall of capillary rheometer.[24] Nanomax composites showed higher viscosity in comparison with neat PP and the other composites. The increasing viscosity due to Nanomax masterbatch addition might be associated to the high viscosity of the PP resin with which was formulated. However, the difference in viscosity between neat PP and PH-Nanomax composites was lower at a higher shear rate, which is due to a preferential orientation of clay layers to the flow direction.
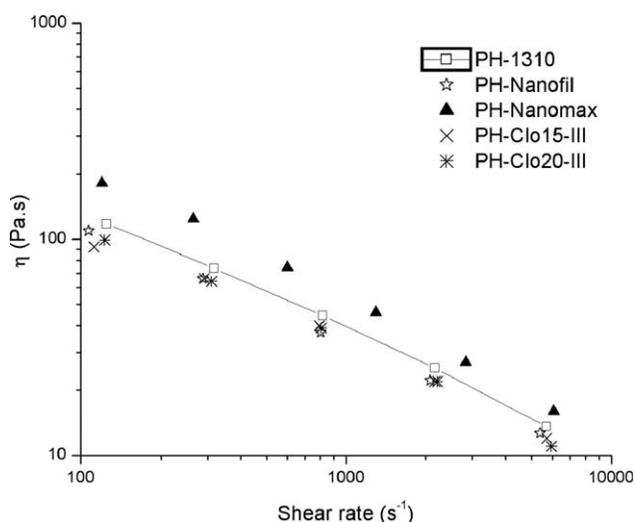

Figure 6 Effect of shear rate on the viscosities of neat PP and PP/clay composites at 180°C.
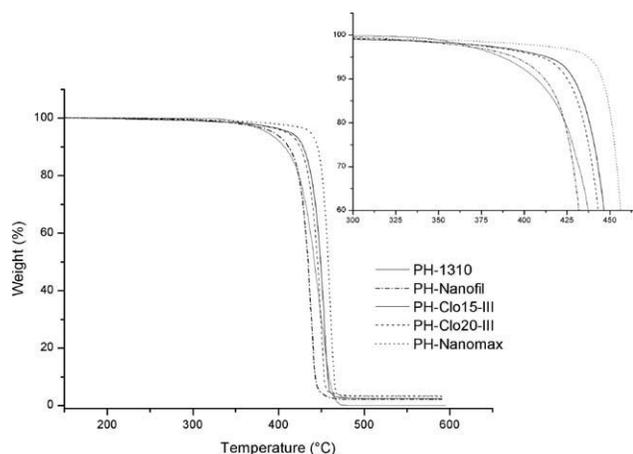
Figure 7 Thermogravimetric analysis of neat PP and PP/clay composites: PH-Clo15-III, PH-Clo20-III, PH-Nanomax and PH-Nanofil; under nitrogen flow and heating rate: $10°C\ min^{-1}$.

Thermogravimetric analysis

TGA curves for the PP/clay composites are shown in Figure 7. The initial thermal stabilities are characterized by the temperatures at which 5 and 10% weight loss occurred, referred to as $T_{-5\%}$ and $T_{-10\%}$, respectively, (data for the variation of these temperatures are summarized in Table VI). As shown in Figure 7, the TGA curves displayed single-step degradation processes for all samples. Once mass loss began, the sample weight percentages decreased continuously until reaching a residual level.

The incorporation of organoclays, which are in a platelet form, improved considerably the initial thermal stability of the PP, improvement also reported elsewhere.[25] The $T_{-5\%}$ increased strongly from about 386 to 437°C with the incorporation of 5 wt % organoclay. The $T_{-10\%}$ also showed a similar improvement to that of the $T_{-5\%}$. According to Ray and Okamoto,[26] the significant increase in the thermal stability of polymer/organoclay nanocomposites results from the exfoliated clay platelets retarding oxygen diffusion into the polymer matrix.

The fractions of nonvolatile material at 510°C referred to as "char residues" are shown in Table VI. It can be seen that the clay residue percentage by weight is between 30–45% lower in comparison with the actual weight added during processing. The total weight loss of 30–45% could be attributed to the decomposition of modifier intercalated into the clay layers. As expected, the weight loss of the Nanofil composites was largest ($\sim$ 55%) because their modifier and resin additives are more than half of their weight, as discussed in the clay characterization section. In this case, the weight loss results for Clo15 and Clo20 composites are in the range of the weight loss obtained for Clo15 and Clo20 with TGA.

Table VI also highlights the effect of PP-g-MA content on the initial thermal stability of composite prepared with Clo15 and Clo20. It can be seen that $T_{-5\%}$ decreased as PP-g-MA content increased from 5 to 15 wt %. This trend might be associated with the result that during PP-g-MA extrusion process under oxygen, moist and hot environment, some radical may be produced to favor chain scission reaction of PP, accelerating the decomposition process of clay nanocomposites. Park et al.[27] studied PP/Clay nanocomposites with different amounts of MA-grafted PP, showing that the thermal stability

TABLE VI
Results of TGA for Composite Materials

Samples	T_{decomp} (°C)	$T_{-5\%}$ (°C)	$T_{-10\%}$ (°C)	Char residues (wt %)
PH-1310	445.2	386.9	406.9	–
PH-Clo15-I	455.1	423.2	435.1	2.7
PH-Clo15-II	453.6	415.6	430.2	2.5
PH-Clo15-III	452.7	413.4	428.7	2.6
PH-Clo20-I	457.9	427.3	439.3	2.8
PH-Clo20-II	454.4	421.1	435.1	3.3
PH-Clo20-III	448.4	410.5	425.1	3.5
PH-Nanofil	448.2	432.2	437.6	2.2
PH-Nanomax	459.9	437.3	445.3	3.3

TABLE VII
Results of DSC for Composites Materials

Samples	T_m[a]	$T_{m\text{-onset}}$[a]	ΔH_m	T_c[a]	$T_{c\text{-onset}}$[a]	ΔH_c	X_c
PH-1310	163.8	156.6	85.3	122.8	126.3	70.8	40.8
PH-Clo15-I	162.7	156.2	70.6	119.8	123.2	76.6	37.5
PH-Clo15-II	161.4	155.6	61.0	119.0	122.5	69.5	34.3
PH-Clo15-III	162.4	154.0	76.9	116.9	121.2	74.4	46.0
PH-Clo20-I	161.9	156.4	77.7	120.1	123.3	73.4	41.3
PH-Clo20-II	163.8	154.5	75.1	118.6	122.5	74.4	42.3
PH-Clo20-III	162.9	153.6	75.7	116.1	120.6	71.9	45.2
PH-Nanomax[b]	163.9	158.2	81.6	126.5	130.1	78.4	43.4

[a] SD $\pm$ 1°C.
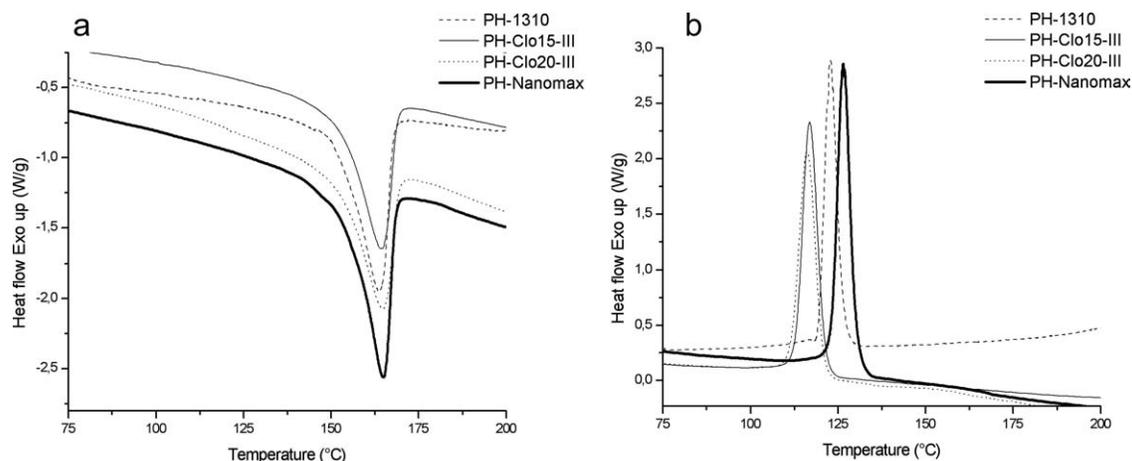[b] To calculate X_c was only considered % wt of PH-1310 used.

Figure 8 DSC heating (a) and cooling scan (b) curves of neat PP and PP/clay composites: PH-Clo15-III, PH-Clo20-III, PH-Nanomax.

drops with increasing MA contents because the MA results in clay dispersion but is also the heat source that accelerates the decomposition process.

DSC can be used to evaluate the thermal behavior of specimens and to estimate the percentage of crystalline phase in the samples. The effect of PP-g-MA on crystallization behavior of PP/Cloisite composites decreases. This idea is supported by the observed variation in $T_{c\text{-onset}}$ as shown in Table VII. In the composites prepared with PP-g-MA, the $T_{m\text{-onset}}$ are lower than found for the pure PP. The reason for delayed crystallization may be related to the presence of a coupling agent with a lower softening point (140°C) in the blends.[28] From Figure 8 and Table VII, it seems that the $T_{c\text{-onset}}$ of PH-Nanomax is higher than for pure PP, indicating an "easier" crystallization, namely a faster nucleation process.[19] The T_c values for composites with Clo15 and Clo20 and the same PP-g-MA content were similar, indicating

that the nucleating effect is likely dominated by coupling agent content.

Although the samples with a higher PP-g-MA/ Cloisite ratio have later crystallization, their degree of crystallinity was higher than pure PP. These nanocomposites presented the highest amount of exfoliated clay, as observed above in the TEM images [see Fig. 4b,d)], suggesting that the well-exfoliated clay layers can promote the surface-nucleated PP crystalline phase.[14]

Mechanical properties

Finally, we investigated the mechanical properties of the PP/clay composites. Because this study was primarily focused on the evaluation of how organo-modified clay and masterbatch type and PP-g-MA content affect the clay dispersion in PP matrix, only preliminary mechanical evaluations were made.
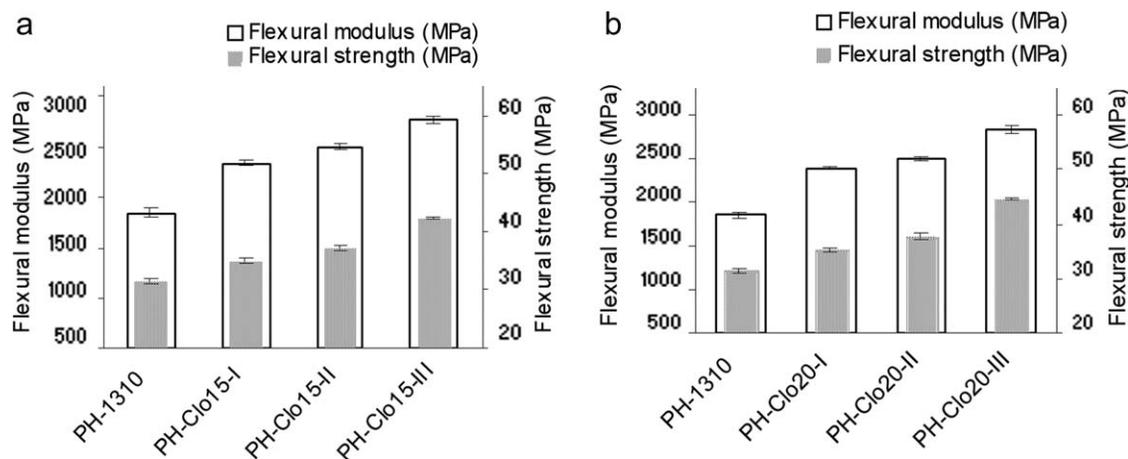

Figure 9 Flexural properties of the injection molding of composites prepared with Clo15 (a) and Clo20 (b), and different content of PP-g-MA.
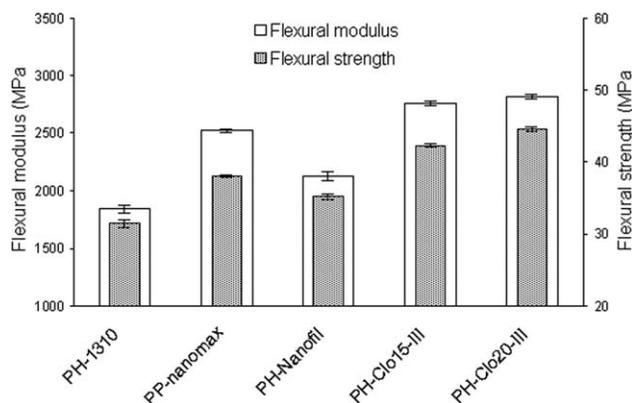
Figure 10 Flexural properties of the injection-molding samples: neat PP, PH-Clo15-III PH-Clo20-III, PH-Nanofil, and PH-Nanomax.

Figure 9 shows the effect of the coupling agent content on flexural properties of composites prepared with Clo15 and Clo20, and specifically on the flexural modulus and strength. Flexural properties of PP/Cloisite composites were improved by addition of PP-g-MA. Flexural modulus and strength of the samples with higher PP-g-MA/Cloisite ratio were enhanced $\sim$ 50% and $\sim$ 30%, respectively, when compared with neat PP.[28] The improvement on flexural properties should be attributed to a better degree of clay dispersion of composites prepared with 15 wt % of coupling agent.[4,5] The PH-Nanomax composites presented improvements in its flexural properties (see Fig. 10) when compared with pure PP, showing increases over 40% in flexural modulus and strength with respect to neat PP. As expected, the improvement of flexural modulus and strength was marginal for PH-Nanofil composites. The results indicate that clay type did not influence the flexural properties of the obtained nanocomposites (see Fig. 9). The high flexural modulus and strength obtained might also be related to the rigid nature of the nanocomposites with a 15 wt % of PP-g-MA. Further mechanical properties (tensile and impact testing) studies must be conducted to have a better understanding the influence of PP-g-MA (3.8 wt % MA) on mechanical properties of nanocomposites.

CONCLUSIONS

PP nanocomposites were prepared via direct melt mixing with two different types of organo-modified clays and two masterbatch products: one of them based on pre-exfoliated clays and another based on clay–polyolefin resin. TEM and XRD results revealed that the amount of coupling agent loading plays an important role in producing PP/

organo-modified nanocomposites with a better degree of dispersion. The thermal stability of all nanocomposites improved compared with pure PP. However, the thermal stability decreased as PP-g-MA content increased from 5 to 15 wt %. This trend might be related to the fact that during the PP-g-MA extrusion process under oxygen (a moist and hot environment), some radical may be produced to favor chain scission reaction of PP-g-MA, accelerating the decomposition process of clay nanocomposites. In general, the composites prepared with masterbatch products presented a lower degree of dispersion than the organo-modified nanocomposites prepared with 15 wt % coupling agent. The composites prepared with Nanofil presented lower flexural properties than other nanocomposites obtained. The poor Nanofil intercalation/exfoliation in PP matrix is related to the fact that the initial decomposition temperature of their intercalater is lower than the processing temperature ($T \sim 180°C$), and thus their stability decreases during process. The PH-Nanomax composite showed higher thermal and flexural properties than pure PP.

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