

# Use of PP Grafted with Itaconic Acid as a New Compatibilizer for PP/Clay Nanocomposites

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## Introduction

Polymeric nanocomposites are polymers filled with a small amount of particles, typically 1–5 wt.-%, for which one dimension of the dispersed particles is in the nanometer range. Natural clays of smectic type, the so-called 2:1 phyllosilicates with layered structures such as montmorillonite, hectorite, saponite, etc., where the individual clay layers have a thickness of the order of 1 nm, have been used to prepare polymeric nanocomposites. These nanocomposites can be prepared by techniques such as solution mixing, in situ intercalative polymerization and melt mixing. Polymer/clay nanocomposites have generated much interest during recent years mainly due to their superior mechanical, thermal, gas-barrier, inflammability and other properties compared to the conventional microcomposites. Surface modification of hydrophilic clays through ion exchange reaction, normally with long-chain alkylammonium ions increases the hydrophobic character as well as the interlayer spacing of these materials.<sup>[1–14]</sup> Therefore, the organically modified clays (O-clays) would be more compatible with non-polar polymers such as poly(propylene) (PP). However, in the case of PP, the main difficulty encountered in preparing nanocomposites with O-clays is the lack of sufficient interaction between the hydrophobic polyolefin matrix and still relatively hydrophilic O-clays.<sup>[1,7,9,15–17]</sup> However, depending on the hydrophilic/hydrophobic balance of a polymer, the polymer chains could enter into the interlayer space of the clay and form either tactoid, intercalated or an exfoliated nanocomposites.<sup>[1–17]</sup> In the tactoid hybrid structure, the polymer chains mainly surround the stacks of the clay resulting in a material with properties similar to those of microcomposites. In the intercalated hybrid structure, extended polymer chains are introduced between the silicate sheets, resulting in a

multilayered structure consisting of alternating polymer and inorganic clay layers. In the exfoliated hybrid structure, the clay nanolayers are dispersed as single layers in the polymer matrix. However, the challenge is to obtain exfoliated nanocomposites since these materials show superior properties than those of intercalated or tactoid hybrid materials. Owing to the strong hydrophilic nature of the clays, low adhesion between clays and non-polar polymers causes a considerable decrease in the mechanical properties of the nanocomposite, as the interface becomes a weak point in the hybrid material. To overcome this limitation and in order to adequately disperse the O-clays in PP matrix, functionalized PP materials such as PP grafted with maleic anhydride has been used as a compatibilizing agent.<sup>[1,15–17]</sup> A recent study by Lertwimolnun and Vargas<sup>[15]</sup> on the degree of dispersion of montmorillonite in PP nanocomposites, prepared by melt intercalation, showed that the dispersion of the clay in PP matrix was improved by the addition of a modified PP with maleic anhydride as compatibilizer. However, this improvement was obtained for concentrations of the compatibilizer higher than 10 wt.-% and up to 25 wt.-%. In a more detailed study on this subject, the effect of the molecular weight and content of the maleic anhydride of PP grafted with this monomer have been studied by Wang et al.<sup>[16]</sup> The results showed that not only the extent of grafting and the molecular weight of the compatibilizer but also the mixing temperature and processing conditions affected the structure of PP nanocomposites obtained with octadecylamine (ODA)-modified montmorillonite. It was found that the exfoliation depended mainly on the intercalation capability of the compatibilizer as well as its composition in the nanocomposite. On the other hand, the possible mechanism of interaction among the maleic anhydride-grafted PP, organically modified montmorillonite with two different surfactants and PP have been studied by Százdí et al.<sup>[17]</sup> They found that maleinated PP can react chemically with the surfactant applied for the organophilization of the filler if the latter contains active hydrogen groups. When hexadecylamine was used as a clay modifier, amide groups were detected as reaction product by Fourier transform infrared (FTIR) and matrix-assisted laser desorption-ionization/time-of-flight (MALDI-TOF) spectroscopy, while *N*-cetylpyridinium chloride did not react due to the absence of active hydrogen groups.

Table 1. Properties of commercial PP samples (*E*, Elastic modulus;  $\sigma_y$ , tensile strength;  $\epsilon$ , elongation at break).

PP	MFI	$\bar{M}_w$	$\bar{M}_w$	<i>E</i>	$\sigma_y$	$\epsilon$
		$\text{kg} \cdot \text{mol}^{-1}$	$\bar{M}_n$			
ZN 340	3	340	3.9	1 090 ( $\pm 30$ )	30 ( $\pm 1$ )	250
ZN 150	26	150	4.4	1 092 ( $\pm 45$ )	30 ( $\pm 2$ )	20

Table 2. Properties of different clays.

Clay	Sample code	Structure	CEC <sup>a)</sup>	SL <sup>b)</sup>	$d_{001}$ clays	$d_{001}$ O-clays
			$\text{eq} \cdot (100 \text{ g})^{-1}$	nm	Å	Å
Montmorillonite	M	$\text{Na} 0.3(\text{Al}, \text{Mg})_2 \text{Si}_4\text{O}_{10} \cdot n\text{H}_2\text{O}$	83	$500 \times 1$	12.1	22.8
Natural hectorite	Hn	$(\text{Mg}, \text{Li})_3 \text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot n\text{H}_2\text{O}$	100	$400 \times 1$	11.3	21.0
Synthetic hectorite	Hs	$(\text{Mg}, \text{Li})_3 \text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot n\text{H}_2\text{O}$	95	$50-100 \times 1$	14.2	18.0

<sup>a)</sup> Cationic interchange capacity.

<sup>b)</sup> Size of the clay laminates.

Table 3. Properties of IA-grafted PP samples (PP-g-IA) and PP grafted with maleic anhydride (PP-g-MA).

Sample code	PP-g-IA or PP-g-MA	$\bar{M}_w$	$\bar{M}_w$	$T_m$
	wt.-% of grafting onto PP	$\text{kg} \cdot \text{mol}^{-1}$	$\bar{M}_n$	$^{\circ}\text{C}$
PP-g-IA <sub>0.7</sub>	0.7	85	2.1	153
PP-g-IA <sub>1.0</sub>	1.0	90	2.0	151
PP-g-IA <sub>1.8</sub>	1.8	110	2.3	153
PP-g-MA <sub>0.6</sub>	0.6	85	2.1	153

Although acrylic acid has been used to modify PP,<sup>[18]</sup> other polar monomers such as itaconic acid (IA) and its derivatives have been recently studied by our group as potential monomers for modifying the PP.<sup>[19,20]</sup> IA is non-oil-based dicarboxylic acid monomer. It is obtained through large-scale fermentation of agricultural wastes such as molasses, a sub-product of sugar industry. Due to its double functionality, IA and its derivatives offer interesting possibilities as polar functional monomers for the modification of polyolefins. In this work, PP/clay nanocomposites were prepared by melt mixing method, where the organically modified clays were mixed with PP in a Brabender-Plasticorder at 190 °C. Functionalized PP samples with different degrees of grafted IA but with similar molecular weights were synthesized and were used as compatibilizers. The aim of this study is to determine the effect of the percentage of grafting in the compatibilizer as well as the molecular weight of the PP used as matrix on the formation of nanocomposite and their mechanical and morphological properties.

## Experimental Part

### Materials

IA of 98% purity was purchased from Aldrich and Lupersol 101 was from Akzo. Commercial PP homopolymer samples with different molecular weights, ZN 150 [melt flow index (MFI) = 26] and ZN 340 (MFI = 3), were kindly donated by Petroquim S. A., Chile, and were used as polymer matrix for the preparation of nanocomposites with different clays. PP samples were characterized and the results are shown in Table 1. A commercial PP sample with medium molecular weight ( $\bar{M}_w = 250 \text{ kg} \cdot \text{mol}^{-1}$ ) with MFI = 13  $\text{g} \cdot (10 \text{ min})^{-1}$  from Petroquim S. A. was used in the functionalization reactions. Montmorillonite (M), mineral hectorite (Hn) and synthetic hectorite (Hs) were from Netherland Organization for Applied Scientific Research – TNO and their characteristics are shown in Table 2. ODA of 90% purity was from Aldrich and was used for the modification of different clays.

### Methods

#### Functionalization of PP

PP with medium molecular weight ( $\bar{M}_w = 250 \text{ kg} \cdot \text{mol}^{-1}$ , MFI = 13) was functionalized through grafting with IA (PP-g-

IA) by using Lupersol 101 as initiator in a reactive melt polymer processing at 190 °C by using a Brabender-Plasticorder internal mixer. This particular PP was selected to be modified by grafting reactions since a systematic study carried out recently in our laboratory showed that by using this grade it is possible to obtain PP grafted with different percentages of IA but without significant variation in the molecular weights of grafted products.<sup>[21]</sup> Grafting reactions were carried out by mixing predetermined amounts of monomer, between 0.1 and 3% by weight of PP and a fixed concentration of initiator (1 wt.-%) before melt mixing at 190 °C under a nitrogen atmosphere, at 75 rpm for 6 min. At the end of the reaction, the product was dissolved in hot xylene and was precipitated into acetone. The unreacted monomer, initiator and possible homopolymer that would eventually form during the grafting reaction were separated from the grafted polymer by exhaustive extraction of the sample with methanol in a Soxhlet for 24 h as previously described.<sup>[20]</sup> The extracted samples were dried under reduced pressure before their analysis. The weight percentages of grafting obtained, under different grafting conditions, are presented in Table 3.

#### Preparation of O-Clays

ODA was dissolved at 70 °C in a 50:50 v/v water:ethanol mixture acidified to pH 3 with HCl. The clays (M, Hn and Hs) were first dispersed in distilled water at room temperature. The resulting suspension was then added to the amine solution and stirred vigorously for 2 h at 25 °C. The organically modified clays were recovered by filtration, washed with a large amount

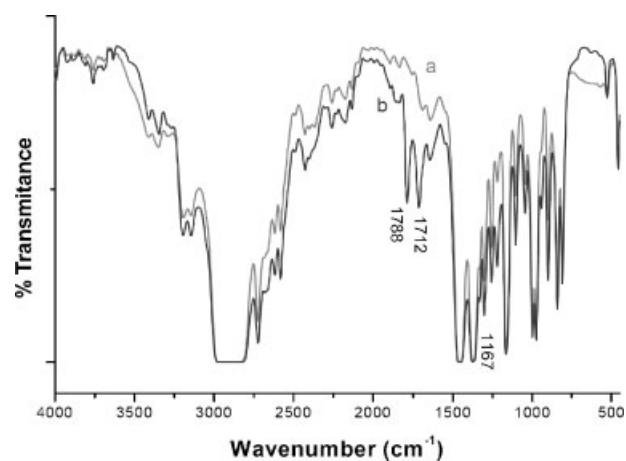
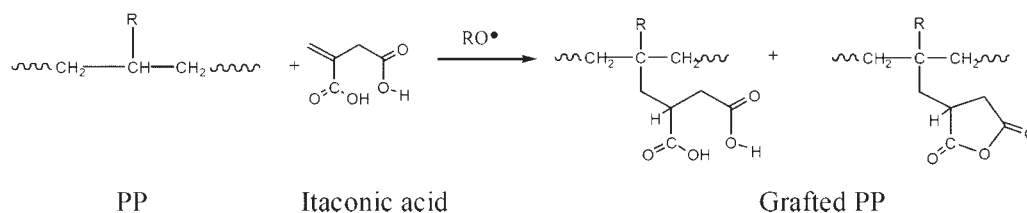


Figure 1. FTIR spectra of PP (a) and PP-g-IA (b).



Scheme 1. Functionalization reaction of PP by grafting with IA.

of water, filtered and then dried for one day. The organophilic clays obtained were designated as O-M, O-Hn and O-Hs and characterized by X-ray diffraction (XRD).

#### Preparation of Nanocomposites

Nanocomposites were prepared as follows: first a master batch was prepared by melt mixing of PP-*g*-IA, O-clays and antioxidants in a Brabender-Plasticorder at 190 °C and 110 rpm for 10 min and in nitrogen atmosphere. The ratio of PP-*g*-IA/O-clay was 3:1 by weight. Nanocomposites were prepared by melt mixing of different PP (Table 2) with antioxidant and a predetermined amount of the master batch in a Brabender-Plasticorder at 190 °C and 110 rpm for 10 min under nitrogen atmosphere in order to obtain nanocomposites containing 1 wt.-% of the clay.

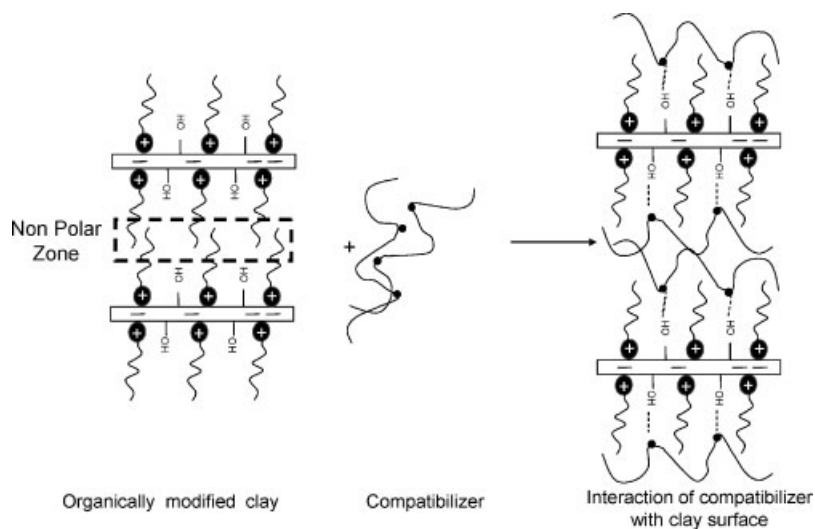
#### Characterization

The evidence of grafting as well as an estimation of its extent, expressed as weight percent of grafting, was determined by FTIR spectroscopy of the grafted PP samples after removing the unreacted monomer, initiator and homopolymer. FTIR spectra were recorded on a Bruker IFS-28 spectrometer from 4000 to 400  $\text{cm}^{-1}$  with an average of 16 scans at 4  $\text{cm}^{-1}$  resolution and 1  $\text{cm}^{-1}$  sensitivity. Films of 100  $\mu\text{m}$  thickness

from unmodified polymers and grafted samples were obtained by compression molding between steel plates covered with thin aluminium sheets at 190 °C for 1 min. The percentage of grafting was estimated from a calibration curve established by using PP samples containing a known amount of IA. Details of the procedure used can be found elsewhere.<sup>[19–21]</sup>

The intercalation of ODA in the silicate layers of the clays and the dispersion of its layers in the nanocomposites were evaluated by XRD using a Siemens D 5000 with  $\text{Cu } \lambda = 1.54 \text{ \AA}$  in the range  $2\theta = 1.6\text{--}12$ . The basal spacing of the clays was estimated from the (001) peak in the XRD by using the Bragg equation  $\lambda = 2d \sin\theta$ , where  $\lambda$  is the wavelength. Transmission electron microscopy (TEM) images of the nanocomposites were taken using a Zeiss model EM 902 microscope. Ultrathin samples of about 60 nm thickness were cut with a glass and/or diamond blade by using a cryogenic-ultramicrotome Leica model EMFCS at  $-80^\circ\text{C}$ . Molecular weights of PP samples were determined by high temperature gel permeation chromatography (GPC) using a Waters Alliance 2000 system equipped with a differential refractometer detector. Three GPC columns, HT6E, HT5 and HT3, previously calibrated with polystyrene standards of narrow molecular weight distributions were used. 1,2,4-Trichlorobenzene was used as the solvent and the flow rate for analysis was 1  $\text{mL} \cdot \text{min}^{-1}$  at 135 °C.

Tensile mechanical properties were determined by using a dynamometer HP model D-500. The materials were placed in a



Scheme 2. Model showing interaction of the organically modified clay with grafted PP used as compatibilizer.

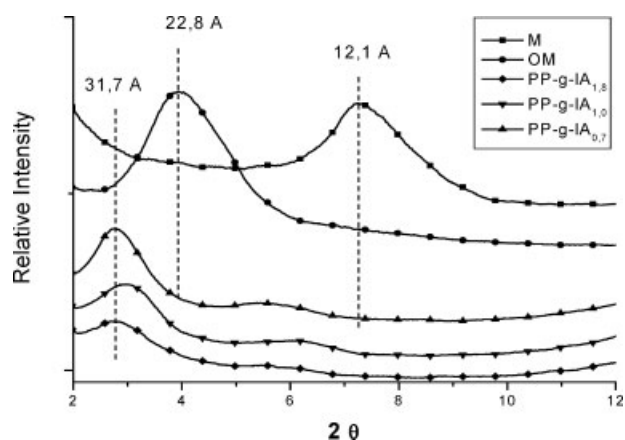


Figure 2. XRD patterns of nanocomposites obtained by using organically modified montmorillonite/PP ZN 340/PP-g-IA with different percentages of grafting.

stainless steel mould and molded for 5 min in an HP press under a pressure of 40 bars at 190 °C. The samples were cut as indicated in the ASTM standard test method D638-95 for tensile properties of plastics. The samples were tested at a rate of 50 mm · min<sup>-1</sup> at 23 °C and relative humidity of 50%. Each set of measurements was repeated at least four times.

## Results and Discussion

### Evidence of Grafting of IA onto PP

The existence of grafted IA in PP was confirmed by FTIR spectroscopy. FTIR spectrum of the grafted PP with IA (PP-g-IA) showed two absorption bands in the carbonyl region that are absent in the spectrum of unmodified PP (Figure 1). The absorption band at 1712 cm<sup>-1</sup> is due to stretching vibrations of the carbonyl groups of the carboxylic acid of the monomer. The second absorption band at 1788 cm<sup>-1</sup> could be due to a carbonyl absorption band coming from the monomer grafted as anhydride which could form during the grafting reaction. The formation of anhydride through dehydration of IA has been reported by our group in pre-

vious studies.<sup>[20]</sup> The general reaction scheme for grafting of IA is shown in Scheme 1.

The weight percentage of grafting was estimated from FTIR analysis of grafted PP by using the method we have described for melt functionalization of PP with methyl esters of IA.<sup>[20]</sup> The ratio of the sum of the intensities of the absorption bands at 1712 cm<sup>-1</sup> (A<sub>1712</sub>) and 1788 cm<sup>-1</sup> (A<sub>1788</sub>) to the intensity of the absorption band at 1667 cm<sup>-1</sup> (A<sub>1667</sub>), corresponding to the vibration of CH<sub>3</sub> groups of the PP, allows to determine the carbonyl index (I<sub>C</sub>). This can be considered as a measure of the extent of grafting of the monomer in PP in its both acid and anhydride forms. The extent of grafting was converted into the incorporated weight percent (wt.-% of grafting) of the monomer by using a calibration curve obtained from FTIR analysis of the physical mixtures of PP with different amounts of IA. These mixtures were prepared by melt mixing of PP and IA in a Brabender-Plasticorder at 190 °C under nitrogen stream for 6 min.<sup>[21]</sup> The percentage of IA grafted onto PP can then be estimated by using the existing linear relation between the I<sub>C</sub> values and the monomer concentration in the above-mentioned physical mixtures of IA and PP.

### Interaction of PP-g-IA with Clays

We propose that the grafted PP used as compatibilizer interact with clays, possibly through hydrogen bonding with OH groups on the surface of the clays as shown in Scheme 2. As can be seen from this scheme, the polar groups of grafted PP interact with clay surface and therefore the interlayer space of the clay increases as the result of this interaction, generating a less polar region. This facilitates the entry of non-polar PP chains into the clay gallery.

### Effect of the Percentage of Grafting of Functionalized PP on the Mechanical and Morphological Properties of PP/Clay Nanocomposites

#### PP/O-M Nanocomposites

With the aim of evaluating the effect of the percentage of grafting of functionalized PP, used as compatibilizer, on the

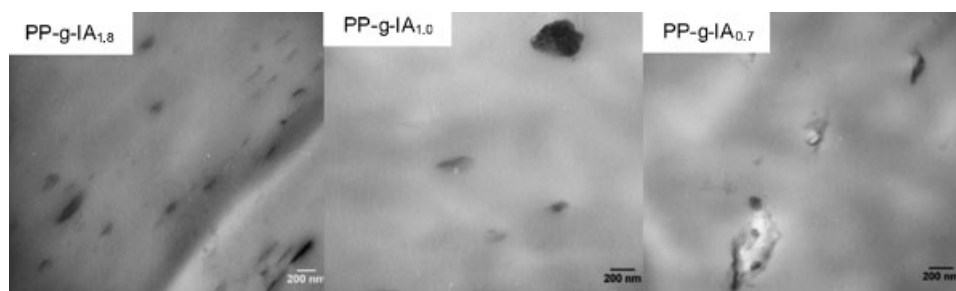


Figure 3. TEM images of nanocomposites obtained by using organically modified montmorillonite/PP ZN 340/PP-g-IA with different percentages of grafting.

Table 4. Mechanical properties of nanocomposites prepared by using PP of different molecular weights, 1 wt.-% of different clays and 3 wt.-% of functionalized PP grafted with different percentages of IA as compatibilizers ( $E$ , Modulus;  $\sigma_y$ , tensile strength;  $\epsilon$ , elongation at break).

PP	IA/PP wt.-%	O-M			O-Hn			O-Hs		
		$E$	$\sigma_y$	$\epsilon$	$E$	$\sigma_y$	$\epsilon$	$E$	$\sigma_y$	$\epsilon$
		MPa	MPa	%	MPa	MPa	%	MPa	MPa	%
ZN 340	1.8	1 573 ( $\pm 25$ )	42 ( $\pm 2$ )	20	1 723 ( $\pm 31$ )	48 ( $\pm 2$ )	13	1 653 ( $\pm 23$ )	41 ( $\pm 2$ )	15
	1.0	1 523 ( $\pm 30$ )	41 ( $\pm 2$ )	14	1 750 ( $\pm 22$ )	48 ( $\pm 1$ )	13	1 748 ( $\pm 19$ )	41 ( $\pm 1$ )	10
	0.7	1 470 ( $\pm 18$ )	40 ( $\pm 3$ )	8	1 850 ( $\pm 43$ )	50 ( $\pm 2$ )	15	1 880 ( $\pm 15$ )	46 ( $\pm 1$ )	15
ZN 150	1.8	2 117 ( $\pm 35$ )	40 ( $\pm 1$ )	17	1 791 ( $\pm 40$ )	49 ( $\pm 2$ )	9	1 717 ( $\pm 25$ )	40 ( $\pm 2$ )	9
	1.0	1 941 ( $\pm 33$ )	38 ( $\pm 2$ )	8	2 075 ( $\pm 35$ )	48 ( $\pm 1$ )	8	1 855 ( $\pm 29$ )	40 ( $\pm 1$ )	7
	0.7	1 900 ( $\pm 42$ )	38 ( $\pm 2$ )	8	2 137 ( $\pm 28$ )	51 ( $\pm 2$ )	9	1 966 ( $\pm 19$ )	45 ( $\pm 2$ )	8

mechanical and morphological properties of nanocomposites, functionalized PP samples with different percentage of grafted IA were used. These were characterized and the results are shown in Table 3.

The XRD patterns of PP (ZN 340) nanocomposites using organically modified montmorillonite (O-M) and functionalized PP with different percentage of grafted IA are shown in Figure 2. It can be seen from this figure that the interlaminar spacing of crystal planes of the original unmodified clay ( $d_{001}$ ) increases from 12.1 to 22.8 Å when treated with ODA to obtain O-M. This distance reaches 31.7 Å in different nanocomposites. This could be due to the partial intercalation/exfoliation of PP chains in the clay layers. The compatibilizing effect of PP-g-IA is clearly seen from this figure, where the intensity of the diffraction peak due to the interlayer spacing ( $d_{001}$ ) of the clay decreases as the percentage of grafting of the functionalized PP used as compatibilizer increases. This could indicate less crystalline order of the clay layers and therefore a better degree of exfoliation of the clay in PP matrix. TEM analyses of the nanocomposites, shown in Figure 3 verify this observation. The nanocomposite obtained by using functionalized PP with highest percentage of grafting (PP-g-IA<sub>1.8</sub>) shows a better dispersion and smaller particle size of O-M in the PP matrix as compared with those nanocomposites where modified PP samples with lower percentage of grafting, (PP-g-IA<sub>0.7</sub>) or (PP-g-IA<sub>1.0</sub>), were used. As the percentage of grafting of the modified PP decreases, the O-M particle size and tactoid state of the nanocomposite increases.

Mechanical properties of these nanocomposites are summarized in Table 4. Higher values for tensile modulus ( $E = 1\,573$  MPa) and tensile strength ( $\sigma_y = 42$  MPa) were obtained for the nanocomposite when modified PP with higher percentage of grafting (PP-g-IA<sub>1.8</sub>) was used as compatibilizer, compared with values obtained for initial PP presented in Table 4 (1 090 MPa and 30 MPa, respectively). The differences observed in mechanical properties of these nanocomposites are in agreement with the results of XRD and TEM analysis shown in Figure 2 and 3, respectively, where the tendency to nanocomposite for-

mation is observed when compatibilizer with highest percentage of grafting was used.

Similar results were obtained from XRD analysis when PP with lower molecular weight (ZN 150), 1 wt.-% of O-M as nanofiller and modified PP with different percentage of grafting as compatibilizers were used to prepare different nanocomposites (Figure 4). The diffraction peak corresponding to  $d_{001}$  appears at 32.5 Å and its intensity decreases as the percentage of grafting of the compatibilizer in the nanocomposite increases. TEM images of nanocomposites shown in Figure 5 reveal that a better dispersion as well as smaller size of O-M particles in the nanocomposite is obtained when compatibilizer with higher percentage of grafting was used.

The mechanical properties of these nanocomposites are in accordance with TEM and XRD analysis where higher values of modulus and tensile strength (2 117 and 40 MPa, respectively) were obtained for nanocomposites containing compatibilizer with highest percentage of grafting. This finding could be explained by considering the fact that this clay has a more polar character than other clays used in this study, as can be seen from Scheme 2. This is further supported by the lower value found for cation exchange

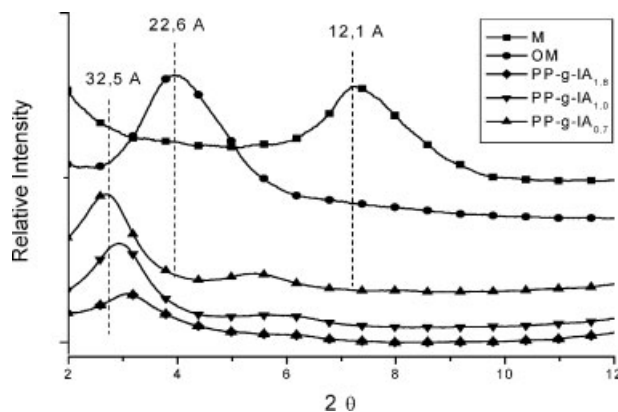


Figure 4. XRD patterns of nanocomposites obtained by using organically modified montmorillonite/PP ZN 150/PP-g-IA with different percentages of grafting.

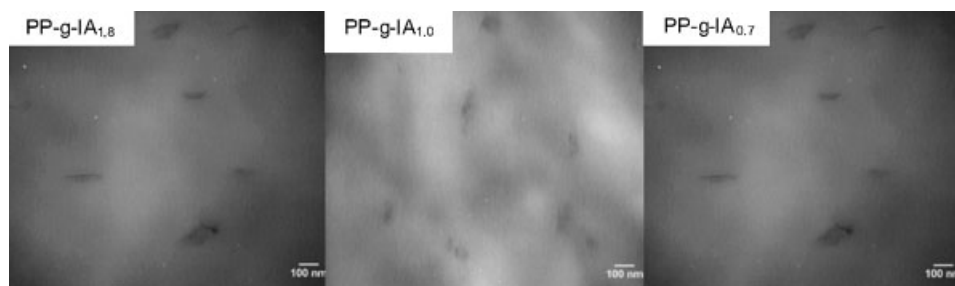


Figure 5. TEM images of nanocomposites obtained by using organically modified montmorillonite/PP ZN 150/PP-g-IA with different percentages of grafting.

capacity for this clay compared with values for natural or synthetic hectorites used in this study. Therefore, the compatibilizer with more polar character, i.e., with higher percentage of grafting, could enter more easily into the clay layers.

Analysis of the effect of molecular weight of initial PP used as polymer matrix on the formation of nanocomposites with O-M can be made by comparing the results obtained when PP of higher molecular weight (ZN 340) and PP of lower molecular weight (ZN 150) were used for the preparation of nanocomposites under the same conditions. The interlayer distance of O-M in the nanocomposites, prepared by using PP of lower molecular weight was 32.5 Å, as determined by XRD. This value is slightly higher than that obtained for PP of higher molecular weight, 31.7 Å. Higher degree of dispersion of the O-M is observed in TEM images of nanocomposites prepared by using PP of lower molecular weight than those prepared by using PP of higher molecular weight. Moreover, nanocomposites prepared by using low molecular weight PP showed better mechanical properties than those prepared by using PP of higher molecular weight. This behavior could be explained in terms of lower viscosity of low molecular weight PP where the diffusion of polymer chains in interlayer of O-M is facilitated.

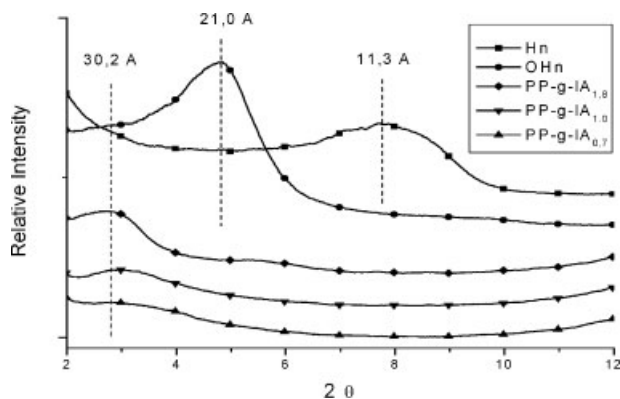


Figure 6. XRD patterns of nanocomposites obtained by using organically modified natural hectorite/PP ZN 340/PP-g-IA with different percentages of grafting.

### PP/O-Hn Nanocomposites

Figure 6 shows the series of XRD spectra of original Hn, O-Hn and those of PP nanocomposites prepared by using high molecular weight PP (ZN 340), 1 wt.-% of O-Hn and 3.0 wt.-% of functionalized PP with different percentage of grafted IA. The interlayer spacing of Hn (11.3 Å) increases to 21.0 Å as the result of its treatment with ODA and increases further to 33.1 Å in the nanocomposites. Contrary to the case where O-M was used as nanofiller, a better dispersion of O-Hn in the PP matrix was obtained when functionalized PP with lowest percentage of grafting, PP-g-IA<sub>0.7</sub>, was used as compatibilizer. The intensity of the XRD peak corresponding to the  $d_{001}$  spacing of the clay silicate layers is decreased as the percentage of grafting of IA in the compatibilizer is decreased. This peak almost disappears when compatibilizer with lowest percentage of grafted IA (0.7 wt.-%) was used. The decrease in intensity of the peak corresponding to the interlayer spacing of O-Hn could indicate that the stacks of layered silicate become more disordered as the result of partial exfoliation of the clay.

Although TEM images of nanocomposites obtained by using compatibilizers with different percentage of grafted IA show similar features (Figure 7), a better dispersion of O-Hn in the PP matrix can be observed for the nanocomposite prepared by using the compatibilizer with lowest percentage of grafted IA.

These results are further supported by comparing the mechanical properties of these nanocomposites, where higher values for modulus (1 850 MPa) and tensile strength (50 MPa) were observed for the composite containing compatibilizer having lowest percentage of grafted IA. As was already discussed, in the case of natural and synthetic hectorites, the higher cation exchange capacity of these clays, compared with that of montmorillonite, is the main driving force for the less polar compatibilizer to be more effective in the degree of clay dispersion in the polymer matrix.

The effect of molecular weight of PP was also studied in this case, where nanocomposites were prepared under the same conditions and by using PP of lower molecular weight

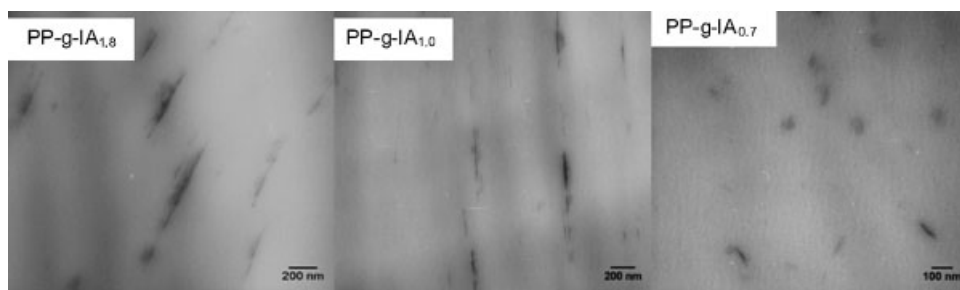


Figure 7. TEM images of nanocomposites obtained by using organically modified natural hectorite/PP ZN 340/PP-g-IA with different percentages of grafting.

(ZN 150). The result of X-ray analysis of these composites revealed that a better dispersion of the nanofiller was obtained ( $d_{001} = 33.1 \text{ \AA}$ ) when compatibilizer with lower percentage of grafted IA was used (Figure 8). Again, the intensity of the peak corresponding to the interlayer spacing of the O-Hn in the nanocomposite decreases as the percentage of grafting of the compatibilizer decreases. TEM images show similar dispersion of the nanofiller in all cases but with smaller particle size as compared with those prepared by using PP of higher molecular weight (Figure 9).

These nanocomposites showed slightly better mechanical properties than those prepared by using PP of higher molecular weight, where values of 2137 MPa for the modulus and 51 MPa for the tensile strength were found.

#### PP/O-Hs Nanocomposites

Organically modified synthetic hectorite (O-Hs) was also used as nanofiller for the preparation of PP nanocomposites. Both, high and low molecular weight PP samples together with functionalized PP with different percentage of grafted IA were used. The concentrations of O-Hs and compatibilizers in the nanocomposites were the same as those prepared by using O-M and/or O-Hn. Figure 10 shows the

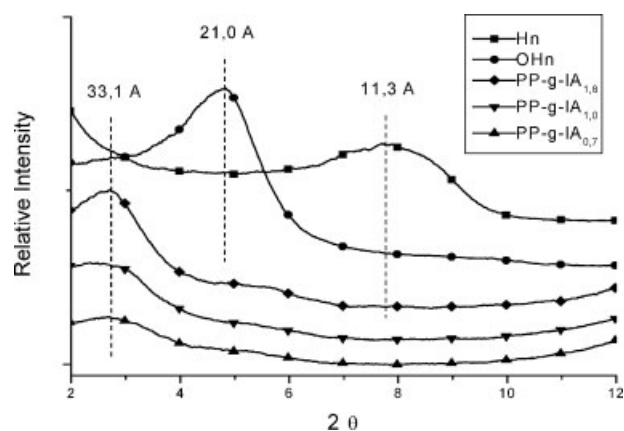


Figure 8. XRD patterns of nanocomposites obtained by using organically modified natural hectorite/PP ZN 150/PP-g-IA with different percentages of grafting.

series of XRD spectra of original synthetic hectorite (Hs), Hs modified by ODA (O-Hs) and those of nanocomposites prepared by using high molecular weight PP (ZN 340) and compatibilizers with different percentage of grafted IA. The interlayer spacing of original Hs ( $14.2 \text{ \AA}$ ) increased to  $18.0 \text{ \AA}$  by modification with ODA. This peak practically disappears in the XRD spectra of the nanocomposites indicating a possible disordered structure of the clay and/or certain degree of its exfoliation. TEM images of the nanocomposites are shown in Figure 11. Good dispersion of O-Hs in the PP matrix is observed for all nanocomposites, although nanocomposite prepared by using the compatibilizer with lowest percentage of grafted IA (PP-g-IA<sub>0.7</sub>) showed higher dispersion and smaller particle size of the nanofiller.

The diffraction peak corresponding to the interlayer spacing of O-Hs in the nanocomposite disappeared when PP with low molecular weight (ZN 150) was used as the polymer matrix (Figure 12). This indicates a more disordered structure of the clay and/or its complete exfoliation. Corresponding TEM images of these materials are shown in Figure 13, where good dispersion of nanoparticles is observed. As can be seen in Table 4, the nanocomposites prepared by using the compatibilizer with lowest percentage of grafting (PP-g-IA<sub>0.7</sub>) presented better mechanical properties when either low or high molecular weight PP was used as polymer matrix than those prepared by using compatibilizers with higher percentages of grafting.

The properties of two series of nanocomposites, prepared previously in our laboratories<sup>[22]</sup> by using a commercially available modified PP grafted with maleic anhydride, were compared with those reported here in order to evaluate the performance of IA-grafted PP as compatibilizer. These nanocomposites were prepared under the same conditions as those prepared in the present work by using PP grafted with IA and different clays. The percentage of grafted maleic anhydride (0.6 wt.-%) is very similar to that of PP grafted with 0.7 wt.-% of IA. Moreover, as can be seen in Table 3, these compatibilizers have similar molecular weights and molecular weight distributions. As can be seen in Table 5, the mechanical properties of these nanocomposites are lower than those obtained when PP grafted



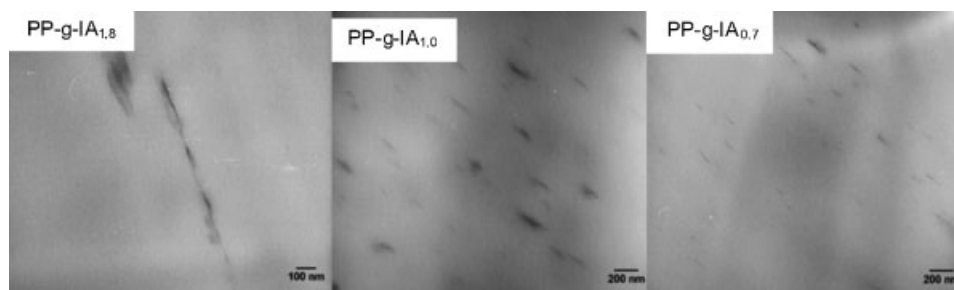


Figure 9. TEM images of nanocomposites obtained by using organically modified natural hectorite/PP ZN 150/PP-g-IA with different percentages of grafting.

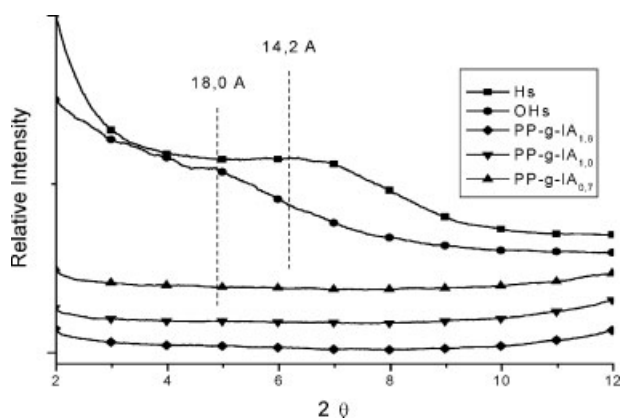


Figure 10. XRD patterns of nanocomposites obtained by using organically modified synthetic hectorite/PP ZN 340/PP-g-IA with different percentages of grafting.

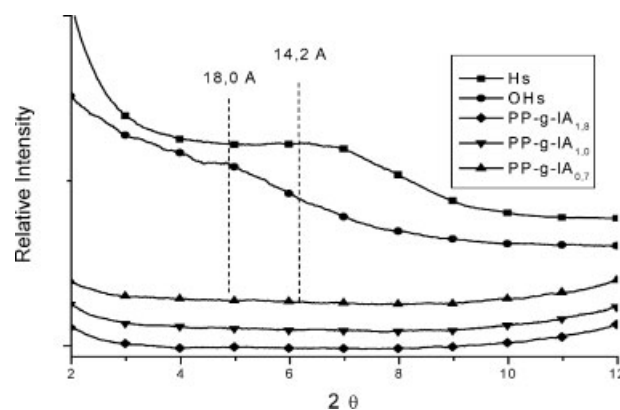


Figure 12. XRD patterns of nanocomposites obtained by using organically modified synthetic hectorite/PP ZN 150/PP-g-IA with different percentages of grafting.

with IA with similar percentage of grafting was used as compatibilizer.

Comparatively, the values obtained for the tensile modulus and tensile strength were always higher for IA-compatibilized nanocomposites (Table 4) than for maleic anhydride-compatibilized materials (Table 5). For instance, values of 2137 MPa for tensile modulus and 51 MPa for tensile strength were obtained compared to 1607 and 43 MPa, respectively, for maleic anhydride-modified composite when O-Hn was used as nanofiller. Similar results were reported by Ellis et al. when PP grafted with

maleic anhydride was used as compatibilizer in PP/montmorillonite nanocomposites.<sup>[23]</sup> The better compatibilizing effect of PP-g-IA in comparison with PP-g-MA with similar degree of grafting could be due to the structural differences between IA and MA monomers. PP-g-IA contains two acid carbonyl groups as well as anhydride carbonyl groups capable of forming a greater number of hydrogen bonds with hydroxyl groups of the clay surface in comparison with PP-g-MA. Therefore, PP-g-IA produces a better adhesion between clay and polymer which are dissimilar in polarity.

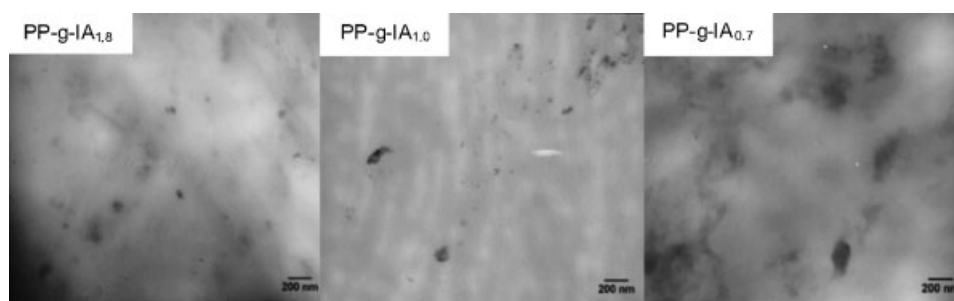


Figure 11. TEM images of nanocomposites obtained by using organically modified synthetic hectorite/PP ZN 340/PP-g-IA with different percentages of grafting.

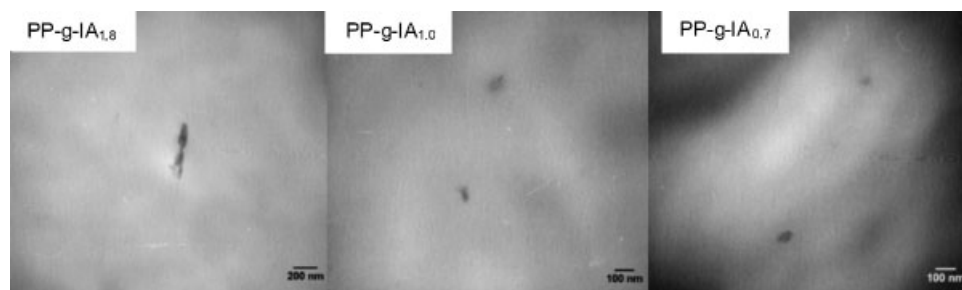


Figure 13. TEM images of nanocomposites obtained by using organically modified synthetic hectorite/PP ZN 150/PP-g-IA with different percentages of grafting.

Table 5. Mechanical properties of nanocomposites prepared by using 3 wt.-% of grafted PP with maleic anhydride as compatibilizer and 1 wt.-% of different clays ( $E$ , Modulus;  $\sigma_y$ , tensile strength;  $\epsilon$ , elongation at break).

PP	IA/PP wt.-%	MMT			Hn			Hs		
		$E$	$\sigma_y$	$\epsilon$	$E$	$\sigma_y$	$\epsilon$	$E$	$\sigma_y$	$\epsilon$
		MPa	MPa	%	MPa	MPa	%	MPa	MPa	%
ZN 340	0.6 <sup>a)</sup>	1 310 ( $\pm 32$ )	34 ( $\pm 1$ )	11	1 550 $\pm$ 42	42 ( $\pm 1$ )	13	1 410 ( $\pm 43$ )	39 ( $\pm 1$ )	10
ZN 150	0.6 <sup>a)</sup>	1 415 ( $\pm 37$ )	38 ( $\pm 3$ )	10	1 607 $\pm$ 32	43 ( $\pm 2$ )	10	1 405 ( $\pm 35$ )	41 ( $\pm 2$ )	9

<sup>a)</sup> From technical data sheet.

The results obtained in this work indicate that PP grafted with IA could replace the commercially available maleic anhydride-grafted PP as compatibilizer for preparation of PP/clay nanocomposites.

## Conclusion

Poly(propylene)/clay nanocomposites were prepared by melt mixing of PP of different molecular weights with different clays as nanoparticles and by using modified PP grafted with different percentages of IA as compatibilizers. The aim of this study was to investigate the effect of both, molecular weight of PP, used as polymer matrix, as well as the degree of grafting of the modified PP on the mechanical and morphological properties of nanocomposites. Depending on the molecular weight of PP and the extent of the grafting of IA in the compatibilizer, intercalation and/or exfoliation of organically modified clays such as montmorillonite, natural hectorite and synthetic hectorite in PP matrix was achieved. The degree of clay dispersion in the PP matrix and the mechanical properties of the resulting nanocomposite improved considerably by incorporation of PP-g-IA as a compatibilizer. However, this improvement depended on the grafting extent of the compatibilizer, type of the clay and molecular weight of the PP used as matrix.

Values of 2 137 MPa for the modulus and 51 MPa for the tensile strength were obtained when natural hectorite was used and 2 117 and 40 MPa were obtained

when montmorillonite was used. A comparative study was carried out, where PP grafted with maleic anhydride was used as compatibilizer. Inferior mechanical properties were obtained for nanocomposites prepared by using this compatibilizer, where values of 1 607 MPa for the tensile modulus and 43 MPa for tensile strength were obtained. This result indicated that IA-grafted PP was far more efficient as compatibilizer for the formation of nanocomposites than commercially available maleic anhydride-grafted PP.

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