## Comparative Effect of Metallocene and Ziegler-Natta Polypropylene on the Exfoliation of Montmorillonite and Hectorite Clays to Obtain Nanocomposites

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**ABSTRACT:** The present study was carried out on the effect of molecular weight and polydispersity of polypropylene (PP) obtained via Ziegler-Natta or metallocene catalysis on the formation of nanocomposites with montmorillonite and mineral and synthetic hectorite. The formation of the nanocomposites was achieved by the melt-mix method. X-ray diffraction, transmission electron microscopy, and analysis of mechanical properties showed that, using PP obtained via metallocene catalysis (polydispersity ~ 2), it is possible to achieve improved formation of nanocomposites compared with PP obtained via Ziegler-Natta catalysis (polydispersity

#### INTRODUCTION

Polymer/inorganic nanocomposites are a type of hybrid material composed of an organic matrix and an inorganic reinforcement in which the inorganic particles are of nanoscale size. The physical and mechanical properties of the polymer are changed dramatically by using a small amount of nanofiller.<sup>1–5</sup> Polymer nanocomposites have unexpected properties, such as higher heat distortion temperature, improved flame resistance, increased Young's modulus and yield stress, better gas barrier properties, and greater dimensional stability,<sup>1–10</sup> derived synergistically from the two components.

Nanoscale-size particles are obtained by treating clays that show a preferential direction of exfoliation, but they are not compatible with most polymers, particularly polyolefins. Because of this, the clay is chemically modified by surface treatment through an ionexchange reaction using organic ammonium cations

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~ 4). It was also found that the molecular weight of the PP affects the tendency toward clay exfoliation and consequently the properties of the nanocomposites. Montmorillonite type clay was evaluated at 1%, 3%, and 5% by weight in the nanocomposite. The nanocomposite with 1 wt % clay was found to have better mechanical properties compared with the nanocomposite containing 3 wt % and 5 wt %. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 698–706, 2007

**Key words:** polypropylene; clays; nanocomposites; Ziegler-Natta PP; metallocene PP; mechanical properties

with long nonpolar alkyl groups. These compounds serve to compatibilize the surface of the clays with the polymer matrix, turning the hydrophilic clay into a more organophilic material and expanding the spaces between the silicate layers.<sup>1,11,12</sup>

The field of polymer/clay nanocomposites has received much attention recently. Two major findings led to the revival of these materials: first, the report of nylon-6/montmorillonite materials from Toyota research,<sup>13,14</sup> and second, the report of Giannelis and colleagues,<sup>15</sup> who showed that it is possible to meltmix polymers with clays without the use of organic solvents. Several types of clays, such as montmorillonite, hectorite, vermiculite, and saponite, have been studied in order to obtain nanocomposites,<sup>3,5</sup> but montmorillonite is the one most widely used. Also, many types of polymers are used for nanocomposite preparation with layered silicate: vinyl polymers,<sup>16–19</sup> condensation polymers,<sup>20,22</sup> polyolefins,<sup>23–29</sup> and others.

There are three methods for the preparation of nanocomposites: mixing in solution,<sup>3,5</sup> melt-mixing,<sup>3–8,16–29</sup> and in situ polymerization.<sup>9,10</sup> The more common method is melt-mixing, due to its industrial use. Figure 1 presents a scheme of the melt-mixing process from which three different states of the composites can be obtained: tactoid, intercalated, and exfoliated. Tactoid correspond to microcomposites, while the other two are present as nanocomposites.<sup>1</sup> The best properties are

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Figure 1 Scheme of the melt-mixing process and the different states of the nanocomposites.

obtained if the clays are exfoliated, but substantial modifications are also generated by the intercalated state. The different states can be studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD).<sup>1–10,15–29</sup> Figure 2 shows the X-ray pattern of the different stages in the preparation of the nanocomposite: the pristine clay, the organically modified clay, the tactoid state (microcomposite), the intercalated state (nanocomposite), and the exfoliated state (nanocomposite). The main indication of the expansion of the space between the sheets is the displacement of the characteristic peak of the 001 plane of the clays toward smaller angles.

The polyolefin nanocomposites are highly attractive because polyolefins are the most widely used polymers for many applications due to their low cost, low density, high thermal stability, and corrosion resistance.<sup>16–19</sup>

Polypropylene (PP) does not have polar groups in its backbone and is not compatible with clays. Homogeneous dispersions of the silicate layer in the PP matrix cannot be generated using only modified hydrophobic clays.<sup>34</sup> As an aid to achieve compatibility between modified clays and PP, use is made of a compatibilizing agent, the most common of which is maleic anhydride (MA), which produces polypropylene grafted with MA (PP-g-MA).<sup>1,16–20</sup>

Metallocene catalysts have generated a great revolution in the polyolefin field,<sup>1,2</sup> especially PP, which

can be obtained with different stereoregularity (isotactic, syndiotactic, hemi-isotactic, atactic)<sup>30–33,36</sup> or narrow polydispersity (Mw/Mn) of the polymer chains, compared with Ziegler-Natta catalysts, which produces only highly polydisperse isotactic polymers.

A large amount of work on PP nanocomposites is being done using PP obtained via Ziegler-Natta catalysis,<sup>16–19</sup> but work using PP obtained with metallocene catalysts by the melt-mixing method are rare.<sup>30</sup>



**Figure 2** Typical X-ray pattern of the different nanocomposites obtained using the melt-mixing process.

Clay Characteristics						
Name	Structure	CEC (eq/100 g)	SL (nm)			
Mineral montmorillonite Mineral hectorite Synthetic hectorite	$\begin{array}{l} Na0.3(Al,Mg)_{2}Si_{4}O_{10}\cdot nH_{2}O\\ (Mg,Li)_{3}Si_{4}O_{10}(OH)_{2}\cdot nH_{2}O\\ (Mg,Li)_{3}Si_{4}O_{10}(OH)_{2}\cdot nH_{2}O \end{array}$	83 100 95	$500 \times 1$ $400 \times 1$ $50-100 \times 1$			

TABLE I

CEC, cationic exchange capacity; SL, size of layer.

In contrast, the effect of the molecular weight of a Ziegler-Natta PP on the exfoliation of montmorillonite<sup>35</sup> has been reported only recently. However, as far as we can tell, no studies have been published in relation to the effect of PP type on the intercalation or exfoliation of clays for the preparation of nanocomposites.

In this work we have studied the preparation of nanocomposites by the melt-mixing technique using Ziegler-Natta and metallocene PP of different molecular weight. In addition, different types of clays were tested: montmorillonite (M), mineral hectorite (Hm) and synthetic hectorite (Hs). The resulting materials were studied by XRD and TEM, and their mechanical properties were determined.

#### **EXPERIMENTAL**

#### Materials

The clays were supplied by the Netherlands Organization for Applied Scientific Research (NTO), and their properties are listed in Table I. Commercial isotactic polypropylenes of different molecular weight obtained by Ziegler-Natta catalysis (ZN PP) were supplied by PETROQUIM Chile S.A. (Table II). Metallocene isotactic polypropylenes (Met PP) (Petroquim, Chile) of different molecular weight were synthesized by our group (Santiago, Chile). Their preparation can be found elsewhere.<sup>32,36</sup> Polypropylene grafted with maleic anhydride (PP-g-MA with MFI 115) from Aldrich was used as the compatibilizing agent. Its molecular weight (85 kg/mol) was determined by GPC. Octadecylamine (ODA) of 90% purity (Aldrich) was used as organic modifier of the layered silicates.  $\beta$ - Hydroxytoluene (BHT) and Irganox 1020 were used as antioxidants.

#### Preparation of organophilic clays

The ODA (1.60 g) was dissolved in a 50:50 v/v water/ ethanol mixture (acidified to pH 3 with HCl) at 70°C. The organic clays (O-Clays), i.e., M, Hm, and Hs (5.00 g), were dispersed in the amine solution and stirred vigorously for 2 h at 25°C, then washed with an excess of 50: 50 v/v water/ethanol mixture at  $50^{\circ}\text{C}$ , filtered, and dried at 70°C for 1 day. The final products were organophilic clays (O-M, O-Hm, O-Hs).

#### **Preparation of nanocomposites**

Nanocomposites were prepared as follows: PP-g-MA with O-clays and antioxidants were melt-mixed in a Brabender Plasticorder at 190°C and 110 rpm for 10 min in a nitrogen atmosphere; the PP-g-AM : O-Clay ratio was 3 : 1 w/w. Thereafter, different PPs (see Table II), antioxidants and the product obtained previously (first step) were mixed in the Brabender with 1% and/or 3% and/or 5% w/w O-Clay.

#### Analytical techniques

X-ray diffraction analysis

XRD patterns were evaluated by powder X-ray diffraction (Siemens D 5000 with Cu  $\lambda = 1.54$  Å). The intercalation of ODA in the silicate layers and the dispersion of the layers in the nanocomposites, as well as the basal spacing of the clays, were estimated from the (001) peak in the XRD.

TABLE II **Polypropylene Characteristics** 

			<b>JI IJ</b>			
PP code	MFI	$\overline{M}w$ (kg/mol)	$\overline{M}w/\overline{M}n$	Young modulus (MPa)	Yield stress (MPa)	Fracture strain (%)
ZN 340	3	340	3.9	1090 (±30)	30 (±1)	250
ZN 250	13	250	3.4	1080 (±40)	30 (±2)	100
ZN 150	26	150	4.4	1092 (±45)	32 (±2)	20
Met 315	_	315	1.8	1116 (±32)	30 (±1)	400
Met 190	—	190	1.8	1102 (±42)	30 (±2)	100

MFI, gram polymer/10 min; Met, metallocene PP; ZN, Ziegler-Natta PP.



**Figure 3** Effect of montmorillonite content for obtaining nanocomposites using ZN PP of  $\overline{M}w = 250 \text{ kg/mol.}$ 

#### Morphological observations

The morphologies of the specimens were examined by TEM (Zeiss EM 902). Ultrathin specimens with a thickness of  $\sim 60$  nm were cut with a glass and diamond blade in a cryogenic-ultramicrotome (Leica EMFCS).

#### Molecular weight of PP

The molecular weight of PP was determined by GPC in a Waters Alliance 2000 system equipped with a differential optical refractometer. Three separation columns, HT6E, HT5 and HT3, previously calibrated with narrow molecular weight distribution polystyrene standards, were used, and the solvent was 1,2,4-trichlorobenzene. The flow rate for the analysis was 1 mL/min at 135°C.

#### Mechanical properties

The polymer obtained was placed in a stainless steel mold and molded for 5 min in an HP press under a pressure of 40 bar at 190°C. The samples were cut as prescribed in the standard test method (ASTM) for tensile properties of plastics (D638-95), and they were tested in an HP model D-500 dynamometer at a rate of 50 cm/min at room temperature. Each set of measurements was repeated at least four times.

#### **RESULTS AND DISCUSSION**

#### Effect of clay content on the nanocomposite

The XRD in Figure 3 shows the influence of the percentage of M, 1 wt %, 3 wt %, and 5 wt %, on nanocomposite formation with PP ZN 250 (Table II). It is seen that nanocomposites obtained with 1% clay show the largest interlayer distance (2.79 nm). This implies a better nanocomposite formation.<sup>1-10</sup> However, the interlayer distance decreases as the percentage of M increases, with values of 2.37nm and 2.31 nm for 3% and 5% clay, respectively. Table III shows that the improvement in mechanical properties is very slight for products containing 3% or 5% clay compared with those of the nanocomposite with 1% clay; so the latter can be considered as the most convenient composition for practical purposes. This is a typical behavior of polyolefin/layered-inorganic nanocomposites, where there is a sharp increase of Young's modulus for very small inorganic loads (< 3%), followed by an insignificant increase at higher loads. Moreover, it has been reported<sup>7</sup> that increased loads do not lead to noticeable changes compared with the pristine polymer values, in agreement with our results.

# Effect of molecular weight and polydispersity on the nanocomposites

The molecular weights, MFI, polydispersity, and mechanical properties of the ZN PP and Met PP used in

TABLE IIIMechanical Properties of Nanocomposites Using ZN 250 and 1 wt %, 3 wt %, and 5 wt % of Clays

	1 wt %		3 wt %		5 wt %	
Clays	Young	Yield	Young	Yield	Young	Yield
	modulus (MPa)	stress (MPa)	modulus (MPa)	stress (MPa)	modulus ( MPa)	stress (MPa)
M	1375 (±23)	36 (±1)	$1350 (\pm 35)$	33 (±1)	$1370 (\pm 25)$	$30 (\pm 2)$
Hm	1550 (±33)	42 (+2)	$1600 (\pm 28)$	42 (+2)	$1650 (\pm 45)$	$40 (\pm 1)$
Hs	1411 (±30)	40 (±2)	$1500(\pm 38)$	$37 (\pm 1)$	$1550 (\pm 36)$	35 (±2)

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**Figure 4** Effect of the molecular weight of Ziegler-Natta PP on the formation of nanocomposites with 1% montmorillonite. 1, Ziegler-Natta PP; 2, metallocene PP; 3, Ziegler-Natta and metallocene PP.



Figure 5 TEM of nanocomposites obtained with 1 wt % of M and Ziegler-Natta PP of different molecular weight. ZN 340; (b) ZN 250; (c) ZN 150.

this study are given in Table II. Figures 4, 7, and 10 display the XRD. The change in the characteristic peak of the 001 plane of the clays is seen as an effect of the inclusion of ODA and PP of different molecular weight between the clay layers. This change toward small angles indicates increased interlayer distance.

The XRD pattern in Figure 4 shows the effect on nanocomposite formation when M was used. Figure 4 (1) shows that as molecular weight decreases in Ziegler-Natta PP, the peak is deformed and displaced toward lower angles (greater interlayer distances), showing intercalated and exfoliated states. Therefore, lower molecular weight leads to better nanocomposite formation. When Met PP was used, as shown in Figure 4 (2), a similar trend was found. This effect is probably due to the low viscosity of the low-molecular-weight polymers at the temperature of the Brabender mixer (190°C), which allows better diffusion toward the interlayer spaces of the clay.

When ZN PP and Met PP of similar Mw are compared [Fig. 4 (3)], the product obtained with Met PP the 001 peak of the clay shows a displacement toward lower angles. Therefore, an improved tendency to exfoliation and consequently better nanocomposite formation is achieved than in the case of Ziegler-Natta PP. This can be due to the difference in polydispersity shown by these two types of PP, since the higher-

Figures 5, 6, 8, 9, and 11 display the TEM micrographs of the different nanocomposites. It is seen that

graphs of the different hanocomposites. It is seen that there is agreement between particle size and distribution and the effect of PP molecular weight as determined by DRX on the extent of exfoliation of the clays (Fig. 4). In materials prepared with high-molecularweight ZN PP [Fig. 5(a)], the particles are mainly in the intercalated state, with some exfoliated particles, and when molecular weight decreases [Fig. 5(b) and (c)], larger quantities of exfoliated particles are seen. Furthermore, when Met PP (Fig. 6) of similar molecu-

molecular-weight fraction present in ZN PP can be

less efficient toward exfoliation, as explained above.



**Figure 6** TEM of nanocomposites obtained with 1 wt % of M and metallocene PP of different molecular weight. (a) Met 315; (b) Met 190.



Figure 7 Effect of PP type and its molecular weight on the formation of nanocomposites with 1 wt% of Hm. 1, Ziegler-Natta PP; 2, metallocene PP; 3, Ziegler-Natta and metallocene PP.



Figure 8 TEM of nanocomposites obtained with 1 wt % of Hm and Ziegler-Natta PP of different molecular weight. (a) ZN 340; (b) ZN 250; (c) ZN 150.

lar weight as that of ZN PP is used, a smaller relative number of particles in the intercalated state and a larger number in the exfoliated state are seen. This is also directly related to the mechanical properties of the corresponding materials, as will be shown below.

In contrast, the effect of the molecular weight of ZN PP on the tendency of Hm toward exfoliation increases noticeably (Fig. 7) when compared with that of M (Fig. 4). In general, when Met PP or ZN PP of lower molecular weight was used, improved formation of nanocomposites was achieved. However, when the clay was replaced by Hs, no dependence on molecular weight or on polydispersity could be found, since total disappearance of the 001 plane peak occurred. However, the mechanical properties of the composites discussed below suggest exfoliation in all cases.

Figures 8 and 9 show micrographs corresponding to nanocomposites of Met PP and ZN PP with Hm. It is seen that a better exfoliated state of this clay is achieved in all cases compared with M. The same as with the nanocomposites with M, it was found that better exfoliation is achieved with lower Mw polymers, and also that Met PP has a greater tendency for exfoliation than ZN PP. Correspondingly, Hm causes a great improvement in the mechanical properties of the materials when compared with M.

When Hs were used, the signal of the 001 plane was not visible in the XRD diffractogram of the composites. The disappearance of the low angle peak can be due either to good exfoliation or to the fact that the peak in the pure organically modified material (Fig. 11) is broader and weaker than in the corresponding MMT and Hm cases. No conclusions on the exfoliation can therefore be deduced from XRD. However, TEM micrographs of the nanocomposites prepared with Hs showed good exfoliation (Fig. 11), confirmed by the improvement in mechanical properties (Table IV).

#### Effect of the clays on the nanocomposites

The XRD peaks of Hm and M are deformed, indicating intercalated and exfoliated states. The relative amount of exfoliated state is larger with Hm, indicating better formation of nanocomposites as reflected in the XRD, the micrographs and the mechanical properties.



**Figure 9** TEM of nanocomposites obtained with Hm and metallocene PP of different molecular weight. (a) Met 315; (b) Met 190.

	Montmorillonite		Mineral hectorite		Synthetic hectorite	
Code	Young modulus (MPa)	Yield stress (MPa)	Young modulus (MPa)	Yield stress (MPa)	Young modulus (MPa)	Yield stress (MPa)
ZN 340	1310 (±32)	34 (±1)	1550 (±42)	42 (±1)	1410 (±43)	39 (±1)
ZN 250	1375 (±25)	$36(\pm 2)$	1550 (±39)	42 (±1)	1411 (±45)	$40(\pm 2)$
ZN 150	1415 (±37)	$38(\pm 3)$	$1607(\pm 32)$	43 (±2)	$1405(\pm 35)$	41 (±2)
Met 315	1452 (±39)	43 (±2)	$1550(\pm 34)$	$53(\pm 1)$	$1380(\pm 39)$	$40(\pm 2)$
Met 190	1505 (±42)	44 (±2)	1604 (±44)	53 (±3)	1402 (±49)	40 (±2)

 TABLE IV

 Mechanical Properties of Nanocomposites Obtained with 1 wt % of Different Clays and ZN PP or Met PP

To explain these results, we have attributed the increased effect of nanoparticles on the properties of the nanocomposites to morphological aspects. Specifically, Hs has layers with the smallest lengths among the clays that were studied (Table I), which decrease in the order M > Hm > Hs, and this sequence corresponds to an increasing tendency toward exfoliation and nanocomposite formation. We suggest that the effects shown by the different clays in the synthesized materials are influenced by differences in the length of the clay's platelets. As far as we can tell, studies on the effect of the length of the clay nanoparticle layers have not been reported yet in the literature.

#### Mechanical properties

Table IV shows the mechanical properties of the various nanocomposites obtained from ZN PP and Met PP with 1 wt % of different clays. In general, the nanocomposites obtained from low-molecular-weight ZN PP and Met PP with M and Hm show a greater increase of Young's modulus (ZN150/M = 30%, ZN150/Hm = 48% and Met190/M = 37%, Met190/Hm = 47%, respectively) and yield stress (ZN150/M = 20%, ZN150/Hm = 34% and Met190/M = 47%, Met190/Hm = 77%, respectively) compared with materials prepared with the corresponding higher-molecular-weight PP, where the increases were ZN340/M = 20%, ZN340/Hm = 42% and Met315/M = 30%, Met315/Hm = 42%, respectively, for Young's

modulus and (ZN340/M = 13%, ZN340/Hm = 40% and Met315/M = 43%, Met315/Hm = 77%, respectively, for yield stress. The reason why in Met-PP-based nanocomposites the increase in yield stress is considerably higher than that of Young's modulus remains unclear, but this is an interesting characteristic of these kinds of nanocomposites.

The results are found to be in good agreement with those shown in the XRD pattern and TEM micrographs, since the nanocomposites that have smaller shifts of the 001 plane signal (i.e. intercalation) are those that show a smaller improvement of the mechanical properties relative to those of PP without load. In the case of Hs, considering that the improvement in mechanical properties is the same for all the nanocomposites prepared in this work (Table IV), this clay is apparently better exfoliated with all the PP samples used.

By combining Met PP with M, the increase of Young's modulus (1450 MPa) was greater than that of ZN PP with the same clay (1300 MPa). As noted previously, this can be due to the difference in polydispersity of both PP types. The values of Young's modulus determined for ZN PP/M materials in this work are comparable to those described in the literature.<sup>24,29</sup>

Nanocomposites obtained with Hm have similar Young's modulus and yield stress values with the two types of PP, and they are higher that those obtained when M was used (Table IV). This finding is in agreement with a larger shift in the sign of the 001 plane of



Figure 10 Effect of the molecular weight of Ziegler-Natta PP on the formation of nanocomposites with 1% of Hs. 1, Ziegler-Natta PP; 2, metallocene PP; 3, Ziegler-Natta and metallocene PP.

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Figure 11 TEM of nanocomposites obtained with Hs and Ziegler-Natta PP of different molecular weight. (a) ZN340; (b) ZN250; (c) ZN150.

Hm compared with M (Figs. 4 and 7), and it implies a greater presence of exfoliated state than of intercalated state for Hm compared with M in the nancomposite.<sup>1</sup>

When Hs was used (Figs. 10–12), even though this clay shows exfoliation and an apparent dispersion as good as that of Hm [Figs. 8(c) and 9], Young's modulus is lower than that of Hm, reaching values comparable to those of M (Table IV). Moreover, the size of the Hs-layer is approximately five times smaller than that of the other clays (Table I). Therefore, by considering the results of Table IV, it can be suggested that in the case of almost two-dimensional particles, like clay platelets, there may be a minimum size that hinders the efficient movement of polymer chains or chain segments, thereby increasing Young's modulus and yield stress. In relation to this assumption, S. Ray and Okamoto<sup>3</sup> mention that in the case of this kind of nanocomposites the extent of improvement of the modulus depends directly on the average length of the dispersed particles, and hence on the aspect ratio.

The largest changes in the mechanical properties were those of the nanocomposites obtained with metallocenic PP of two molecular weights (Met 190 and Met 315) and Hm; values of 53 MPa for yield stress with both Met PPs, and 1604 MPa and 1550 MPa, respectively, for Young's modulus were obtained.



**Figure 12** TEM of nanocomposites obtained with Hs and Metallocene PP of different molecular weight. (a) Met 315; (b) Met 190.

#### CONCLUSIONS

The dramatic effect of the type and molecular weight of PP as well as its polydispersity on the exfoliation and mechanical properties of nanocomposites prepared with different clays has been shown. With ZN PP as well as with Met PP the samples with lower molecular weight help to achieve better nanocomposite formation. This effect is attributed to better diffusion toward the interlayer spaces of the clay due to the lower viscosity of the low-molecular-weight polymers. Met PP shows better tendency toward exfoliation and consequently better nanocomposite formation than Ziegler-Natta PP of similar Mw, probably due to the difference in polydispersity between both types of PP.

The effects on the tendency toward exfoliation of different clays are related to layer length. Hs has the smallest layer size of the clays studied (Table I), changing in the order Hs < Hm < M, and the same sequence corresponds to a decreasing order of the tendency toward exfoliation and nanocomposite formation. The nanocomposites with the highest elastic modulus and highest elastic limit values were obtained using mineral hectorite and metallocene PP.

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