Catalytic Activity During the Preparation of PE/Clay Nanocomposites by *In Situ* Polymerization with Metallocene Catalysts

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ABSTRACT: Catalytic activity during the formation of polyethylene (PE)/clay nanocomposites by *in situ* polymerization with metallocenes was studied. Ethylene polymerization was carried out with the homogeneous metallocene in the presence of the clay particles and using the clay-supported metallocene catalyst. It was found that the catalytic activity of the homogeneous metallocene does not decrease in the presence of the clay particles and only a slight decrease of activity occurs using the clay-supported catalyst. The modification of the clay with MAO cocatalyst as well as its intercalation with ODA surfactant were found to play an important role during the *in situ* formation of the PE/clay nanocomposite. ODA-intercalated clay apparently facilitates the activation and monomer insertion processes on zirconocene centers located in internal sites of the clay structure. Although metallocene supported on MAO-treated clay exhibited somewhat lower catalytic activity than that supported directly on the ODA-intercalated clay, both systems favored the production of PE nanocomposites containing highly exfoliated clay particles. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2368–2377, 2009

Key words: ethylene polymerization; metallocene catalyst; polyolefin nanocomposites; clays

INTRODUCTION

Polymer nanocomposites are hybrid materials consisting of an organic polymer matrix with a dispersed inorganic filler material that has at least one dimension in the nanometer range.[1,2] These nanofillers may significantly modify the macroscopic properties of the polymer even when a very small amount of them is used.[3] Layered clay silicates such as 2 : 1 phyllosilicates appear as the most widely used nanofillers in the preparation of polymer nanocomposites. These clays possess diverse intercalation properties, making them attractive materials for the preparation of novel polymer nanocomposites and supported catalysts.[4,5] Polymer nanocomposites can be prepared by three main routes, namely solution blending, melt blending, and *in situ* polymerization.[6] The latter consists in placing the monomer and the catalyst between the clay layers where the polymerization occurs. As polymerization progresses, the spacing between the clay layers increases gradually and the dispersion state of the clays changes from intercalated to exfoliated.[7,8] Some advantages of this method are (1) a one-step synthesis of the polymer nanocomposite, (2) improved compatibility between the clay and the polymer, and (3) enhanced clay dispersity in the polymer matrix.[9] For those reasons *in situ* polymerization has been shown to be a promising method for preparing fully exfoliated clay nanocomposites of polyolefins.[1,10]

Metallocenes have become an important class of catalysts for olefin polymerization, due to the possibility of modeling the molecular structure of the polymers. In comparison with conventional Ziegler-Natta catalysts, metallocene-based systems offer great versatility and flexibility in the control of the polyolefin structure. Remarkably, the use of immobilized metallocene catalysts results in the formation of uniform polymer particles with a narrower size distribution and higher bulk density than with the homogeneous metallocene catalyst.[11,12] In recent years, there has been special interest in the development of an effective method for the immobilization of metallocene catalysts on inorganic or organic materials. Many studies concerning supported metallocenes[11,13] indicate that the nature of the support as well as the technique used to support the metallocene play an important role in the catalytic activity of the heterogeneous catalyst as well as in the final

properties of the polymers, such as their morphology and molecular weight. Methods for immobilizing metallocenes fall into two broad categories: (1) direct adsorption of the catalyst on the support's surface, and (2) modification of the support's surface with the methylaluminoxane (MAO) cocatalyst prior to the fixation of the catalyst.[11,14–16] In the case of clay supports, the layered material is commonly modified with some long-chain organic cation to increase the interlayer spacing and thereby improve the fixation of the catalyst in the interlayer zone. The clay organomodifier agent also plays an important role in improving the compatibility of the clay with the polymer matrix during the preparation of nanocomposites. Octadecylamine (ODA) has been widely used as a clay-organomodifier agent in the preparation of polyolefin nanocomposites. In this field, some of us have made some contributions related to the preparation of metallocene and Ziegler-Natta polypropylene (PP) nanocomposites by the melt-mixing process using montmorillonite (MMT) and hectorite clays modified with ODA.[17,18] PP/MMT nanocomposites prepared with 1 wt % clay were found to have better mechanical properties compared to nanocomposites containing 3 wt % and 5 wt %. Other authors prepared an isotatic i-PP/MMT composite through *in situ* polymerization on rac-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$[19] supported on MMT modified with the functional surfactant (2-hydroxylethyl)hexadecyl diethylammonium iodide and treated with excess MAO. The metallocene catalyst confined in the interlayer galleries of MMT has high activity, and MMT showed good dispersion into the i-PP matrix. Kuoa et al.[9] attempted to improve the catalyst activity in mPE/cetyl pyridinium–modified clay nanocomposite polymerization by sequential addition of clay, MAO, metallocene, and ethylene monomer. It was found that the polymerization activity decreased with increasing clay content. Analysis of the Kim–Bae equilibrium melting depression equation indicated that intermolecular interactions between PE and clay are indeed present in the nanocomposite.[9] Lee et al.[20] prepared PE nanocomposites by *in situ* polymerization using the Cp$_2$ZrCl$_2$ metallocene supported on both clay montmorillonite and on its organo-modified form. The system supported on the organo-clay allowed achieving a better degree of exfoliation of the clay particles in the final PE/clay nanocomposite. Huang et al.[21] improved the stability of the PE/MMT nanocomposite by preparing a hydroxy-functionalized (PEOH)-MMT nanocomposite by intercalative copolymerization of ethylene and 10-undecen-1-ol on MMT-supported Et[Ind]$_2$ZrCl$_2$ metallocene. In another work, these authors[22] conducted the polymerization in the presence of p-methylstyrene (p-MS), resulting in a p-MS-containing PE/OMMT nanocomposite. This p-MS-PE/MMT composite subsequently functionalized with maleic anhydride and poly(methyl methacrylate) groups showed improved miscibility between the PE matrix and MMT layers.

Although different aspects of the preparation of polyolefin nanocomposites by the *in situ* polymerization method have been studied, less emphasis has been placed on the catalytic activity of these systems. Finding optimum polymerization conditions in the preparation of polyolefin nanocomposites using metallocene catalysts is also a relevant aspect to retain the catalytic activity of the metallocene in the presence of the inorganic particles.

In this work, we studied the preparation of clay/PE nanocomposites by the *in situ* polymerization method through two routes: (1) ethylene polymerization with the homogeneous metallocene catalyst in the presence of the clay particles, and (2) ethylene polymerization using the clay-supported metallocene. The metallocene catalyst was directly supported on the clay, ODA-intercalated clay, and on thise clay forms previously treated with MAO. The effect of these different preparation procedures on the catalytic activity of polymerization and on the degree of exfoliation of the clay into the final PE nanocomposites was studied.

EXPERIMENTAL

Materials

Sodium montmorillonite (Na-Clo, Southern Clay) with a cation exchange capacity (CEC) of 92.6 meq/100 g was used as starting clay material. For clay modification, octadecylamine (ODA) of 90% purity (Aldrich) and MAO (Witco) were used.

The metallocene bis(n-butylcyclopentadienyl) zirconium dichloride ((nBuCp)$_2$ZrCl$_2$) (Aldrich) was used as ethylene polymerization catalyst and MAO as cocatalyst. Ethylene monomer was deoxygenated and dried by passing through columns of Cu catalyst (BASF) and activated molecular sieve (13X), respectively. Toluene solvent was purified by refluxing, and it was freshly distilled under nitrogen from a Na/benzophenone system. All manipulations during catalyst supporting and polymerization were carried out in an inert nitrogen atmosphere using the Schlenk technique.

Modification of Na-Clo with ODA

Octadecylamine (ODA), 1.6 g, was dissolved in a 50 : 50 v/v water : ethanol mixture acidified with HCl at 70°C (pH 3.5). First, 5 g of Na-Clo was dispersed in 500 mL of 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 clay (O-Clo) was recovered by filtration, copiously washed with ethanol and water, filtered, and dried at 70°C for 24 hours.[18]

Preparation of clay-supported metallocene catalyst

The metallocene catalyst was supported on MAO-treated clay support and directly on the clay. Clay samples (Na-Clo and O-Clo) were used after drying in vacuum at 120°C for 24 h. For MAO pretreatmet of the clays, 1.g of clay was placed in contact with a 4 wt % MAO (0.88 ml) solution in toluene for 8 h at 60°C. The mixture was filtered through fritted glass and the solid was washed several times with toluene at 60°C to remove excess MAO. The solid was then dried for 8 h in vacuum at room temperature. Metallocene impregnation was carried out by contacting 1 g of clay with a $(nBuCp)_2ZrCl_2$ toluene solution and stirred for 8 h at 60°C. To remove the unreacted metallocene, the clays were washed several times with toluene at 60°C and then dried for 8 h in vacuum at room temperature. The effect of the concentration of metallocene solution on the amount of zirconium fixed on the support was studied in the 0.73 to 2.92 mmol/L range.

Homogenous polymerization

Polymerization reactions took place in a 600 mL glass reactor (Parr) provided with mechanical stirring and temperature control. The homogeneous polymerization reactions were carried out by adding the MAO and metallocene solutions and allowing the ethylene monomer to enter the reactor. For each experiment 3×10^{-6} mol of metallocene catalyst were added to the reactor, using an amount of soluble MAO in an Al/Zr mole ratio of 1400. The final volume of the solution in the reactor was 240 mL. The reaction was carried out at 60°C and 2 bar during 30 min, stirring at 1000 rpm. The polymerization was then stopped by quenching with an acidified (HCl) methanol solution (20 mL). The polyethylene product was recovered by filtration, washed with ethanol, distilled water, and acetone, and dried overnight at room temperature. Catalytic activity was expressed as the mass of polyethylene produced per unit time per mol of Zr and per unit pressure (kg mol^{-1} bar^{-1}h^{-1}). All the polymerization reactions were repeated twice to verify reproducibility.

Homogeneous polymerization in the presence of clay particles

The reaction conditions were the same as those of the homogenous polymerization. Ethylene polymerization in the presence of the clay particles was performed by first adding 180 mL of toluene and 10 mL of MAO solution to the reactor, and mixing with the catalyst solution for 2 min. The clay suspension in toluene was then added, mixed for 2 min, and finally saturated with ethylene. 1 and 5 wt % of clay with respect to the weight of the standard polymerization product was used.

Polymerization on clay-supported metallocene catalyst

The heterogeneous polymerization was carried out by first adding the MAO, followed by the clay-supported catalyst, mixing during 5 min, and finally saturating with ethylene during 30 min. The amount of metallocene, MAO, solvent, and operating conditions were the same as those used in the homogeneous polymerization. The clay content added during the reactions was estimated considering the weight of the PE product obtained with the homogenous catalyst.

Characterization

The interlayer spacing of clay, organo clay, and supported catalysts were analyzed by X-ray diffraction (XRD) on a Siemens D5000 apparatus with Cu $\lambda = 1.54$ Å. The basal spacing was estimated from the (001) peak in the XRD pattern using Bragg's equation.[22]

The characteristic functional groups of starting clay, ODA-modified clay, and supported catalysts were identified by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) on a Bruker Vector 22 model instrument in the 4000 to 400 cm^{-1} range with a resolution of 4 cm^{-1} at 100°C. The Zr content of the supported catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin Elmer P-400 instrument.

The viscosimeter molecular weight (M_v) was calculated from intrinsic viscosities determined in decahydronaphtalene (decaline) at 135°C using a Viscosimatic-Sofica viscometer. The M_v values were obtained from the Mark-Kuhn-Houwink equations, and the values of the constants were $K = 6.2 \times 10^{-4}$ dL/g and $\alpha = 0.7$.[21]

The melting temperature and enthalpy of fusion of the standard and nanocomposite polyethylene were measured by differential scanning calorimetry (DSC) on a TA Instruments DSC 2920. The samples were heated from 25°C to 180°C and cooled to 25°C at a rate of 10 °C/min; the values were taken from the second heating curve to eliminate any thermal history.

Percent cristallinity was calculated using the enthalpy of fusion of an ideal polyethylene having 100% criystallinity (289 Jg^{-1})[8] as reference.
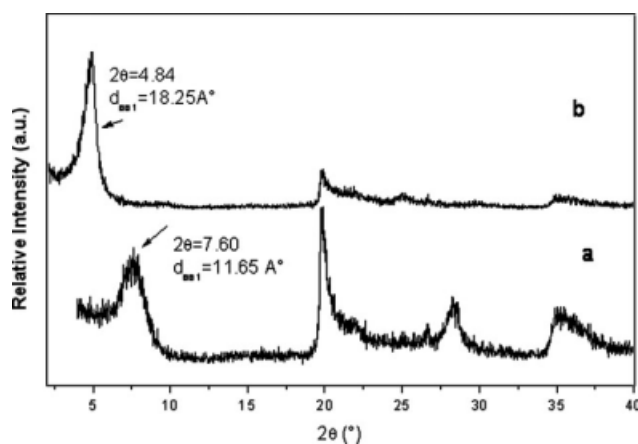
Figure 1 XRD patterns of (a) Na-Clo and (b) O-Clo clay samples.

Percentage cristallinity was measured using the following equation[23]:

$$\chi(\%) = \frac{\Delta H_c}{(1 - \varphi)\Delta H_0} \times 100$$

where ΔH_c is the melting enthalpy (Jg^{-1}) of the polymer nanocomposite, ΔH_0 is the value of the enthalpy corresponding to the melting of a 100% crystalline sample (289 Jg^{-1}), and φ is the weight fraction of the filler in the nanocomposite.

The dispersion of clay particles in the composites was observed by transmission electron microscopy (TEM) on a JOEL JEM-1200EXII microscope operated at 200 kV. Ultra-thin specimens of PE nanocomposites with a thickness of about 80 nm were cut with glass and diamond blades in an ultramicrotome (MT 5000, Sorvall) at -40 °C.

RESULTS AND DISCUSION

Clay characterization

Figure 1 shows the XRD patterns of an Na-Clo clay sample and its ODA-modified form. The first peak of Na-Clo corresponds to the interlayer spacing of the clay's (001) plane. It is seen that the interlayer spacing increases from 11.65 Å (2θ = 7.60) to 18.25 Å (2θ = 4.84) after the ODA treatment due to the presence of ODA in the clay intergallery. This ODA treatment is an important step for improving the properties of the clay as a catalyst support, because the metallocene catalyst can be fixed more easily into the clay interlayer space than when the sodium form is used. Furthermore, ODA gives a more hydrophobic character to the clay's surface, which is an important aspect to improve clay-polymer compatibility in the nanocomposite. DRIFT spectra of Na-Clo, pure ODA, and O-Clo are shown in Figure 2. The spectrum of Na-Clo shows a band

at 3620 cm^{-1} in the OH— stretching region, typical of hydroxyl groups coordinated to Al cations in the octahedral interlayer of the montmorillonite-type clay. The intense bands at 1256 cm^{-1} and 653 cm^{-1} are attributed to the characteristic Si—O stretching and bending vibrations of montmorillonite.[24-26] The 1620 cm^{-1} band is due to the bending vibration of the hydroxyl groups of water molecules remaining in the clay interlayer spacing. When Cloisite is modified with ODA [Fig. 2(c)], new bands appear in its spectrum at 2920 cm^{-1} and 2850 cm^{-1} corresponding to the asymmetric and symmetric CH_2-stretching vibrations of the ODA molecule intercalated into the clay, whereas the quaternary amine group of ODA is identified by a band around 1715 cm^{-1}. These DRIFT observations confirm the XRD results regarding the presence of ODA in the interlayer spacing of the clay structure.

Characterization of the clay-supported metallocene catalyst

The metallocene catalyst was directly supported on Na-Clo, O-Clo, and the corresponding MAO-treated clay samples. DRIFT analysis of the supported catalysts (Fig. 3) shows that when the metallocene is fixed on Na-Clo, new bands appear in the 3100-2800 cm^{-1} region of the Na-Clo spectrum [Fig. 3(a,b)] corresponding to aromatic and alkyl signals (C—H stretching) of the $(nBuCp)_2ZrCl_2$ metallocene fixed on the Na-Clo clay.[27] In the case of O-Clo-supported catalyst [Fig. 3(e,f)], alkyl DRIFT bands of the metallocene overlap with those of the ODA molecules existing in the clay, so they are not clearly distinguished in the spectrum. Grafting of the metallocene complex is also accompanied by the appearance of two new bands at 3660 and 3606 cm^{-1} in the OH—stretching region of the Na-Clo and O-Clo spectra
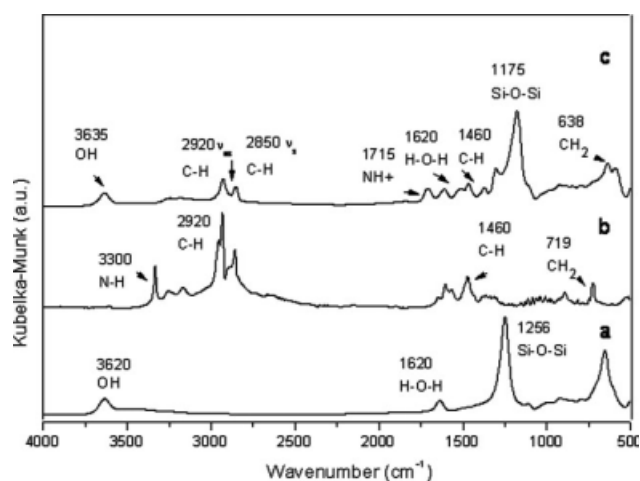

Figure 2 DRIFT spectra of (a) Na-Clo, (b) ODA, and (c) O-Clo samples.
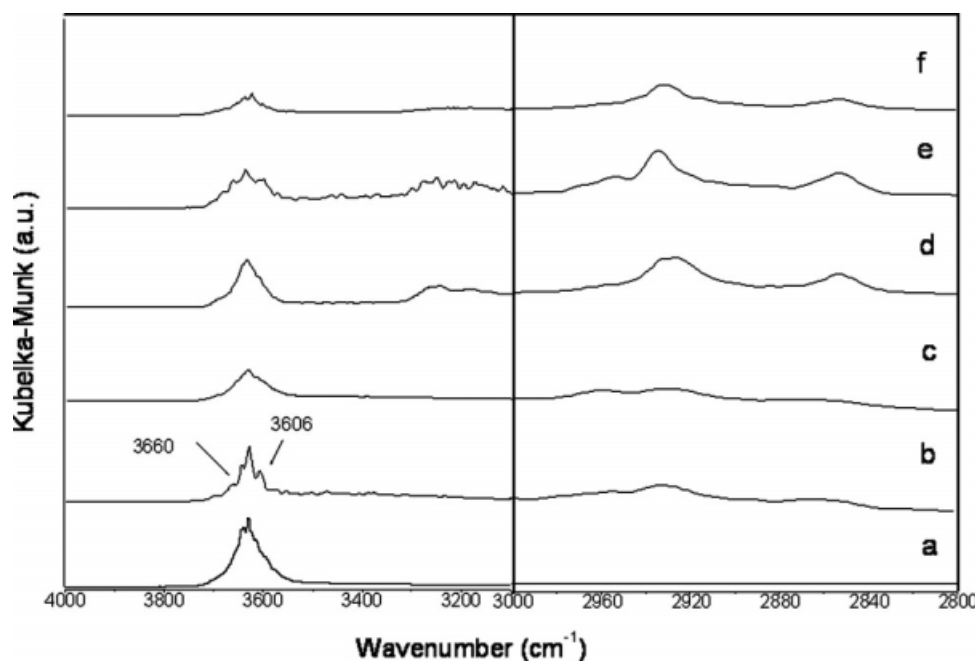
Figure 3 DRIFT spectra of (a) Na-Clo, (b) Cat/Na-Clo, (c) Cat/MAO/Na-Clo, (d) O-Clo, (e) Cat/O-Clo, and (f) Cat/MAO/O-Clo samples.

[Fig. 3(b,e)] which indicate that the surface silanol groups of the clays are strongly affected by the presence of the grafted metallocene. It has been found that those bands may result from the interaction between surface silanols and the aromatic groups of the metallocene.[27,28] In addition, the intensity of the silanol groups decreases with the presence of the metallocene, indicating that the metallocene reacts with the silanol groups and is immobilized through the $\equiv$Si-O-ZrCl(nBuCp)$_2$ form. This type of silanol–metallocene interaction has already been established for metallocene supported on other hydroxylated supports, such as silica and zeolites.[15,28] However, treatment of O-Clo and Na-Clo with MAO also tends to decrease the intensity of the silanol bands [Fig. 3(c,f)] due to reaction of silanol groups with the MAO molecule.

To detect some variation in the interlayer spacing of the clay as a result of the fixation of the metallocene and MAO cocatalyst, the clay-supported catalysts were analyzed by XRD (Fig. 4). In the case of the Na-Clo supported catalyst no changes were detected in its interlayer spacing caused either by fixation of the metallocene or by the MAO treatment. If the average sizes of the metallocene ($\sim$ 7.9 Å)[29] and MAO (10–18 Å)[30,31] molecules are considered, the metallocene catalyst should be able to penetrate into the interlayer spacing of the Na-Clo ($\sim$ 11 Å) without producing a significant variation in the d-spacing of the Na-Clo. On the other hand, the MAO molecule is more stererically impeded for its fixation into the 11 Å spacing of Na-Clo. Thus, for the case of the Cat/MAO/Na–Clo catalyst, MAO could only

occupy the outer surface of the Na–clay particle. In the same way, O-Clo supported catalysts retain the d-spacing value of the initial O-Clo clay ($\sim$ 18 Å), which is an expected result because both metallocene and MAO have molecular sizes smallerer than the O-Clo interlayer spacing.

Homogeneous polymerization in the presence of clay particles

Table I shows the catalytic activity results and the main properties of the polyethylene products
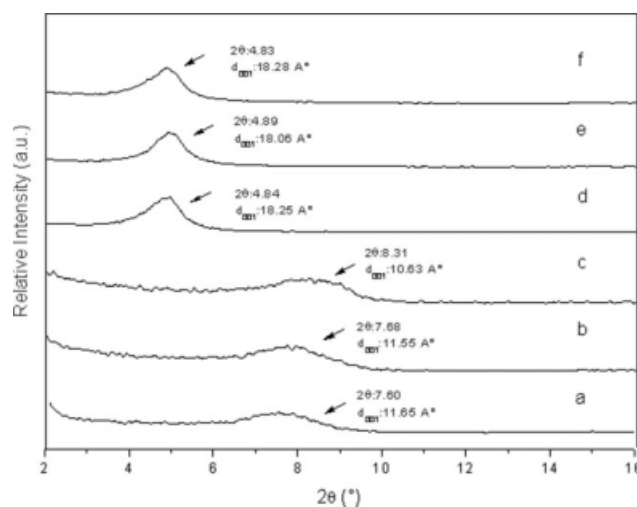

Figure 4 XRD patterns of (a) Na-Clo, (b) Cat/Na-Clo, (c) Cat/MAO/Na-Clo, (d) O-Clo, (e) Cat/O-Clo, and (f) Cat/MAO/O-Clo samples.

TABLE I
Results of Ethylene Polymerization in the Presence of Clay as Filler

Catalyst	Clay type	Catalytic activity ($kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$)	M_v ($kg \cdot mol^{-1}$)	T_m (°C)	χ (%)	Clay content (%)
Homogeneous	–	3900	280	139	67	–
Homogeneous	Na-Clo	4800	280	138	70	1
Homogeneous	Na-Clo	4500	370	136	73	5
Homogeneous	O-Clo	4200	270	139	75	1
Homogeneous	O-Clo	3900	350	136	75	5

Polymerization conditions: [Zr]: 3×10^{-6} mol, Al(MAO)/Zr = 1400; ethylene pressure = 2 bar, temperature = 60°C, time = 0.5 h, solvent: 200 mL of toluene; M_v: Viscosimeter molecular weight, χ: percent crystallinity.

obtained using clay particles as filler. It is seen that the catalytic activity of the metallocene in the presence of 1 wt % of clay is in some cases higher than that of the pure system. This result may be due to the fact that clay particles can to act as spacer centers hindering the bimolecular deactivation between neighbor zirconocenes in the solution, thereby having a positive effect on the catalytic activity. This effect has also been observed in other studies using soluble functionalized silica particles as filler.[32] When O-Clo was added to the reaction, the catalytic activity decreased slightly with respect to that obtained with Na-Clo, perhaps due to a deactivating effect of the ODA amino group of O-Clo on the metallocene catalyst. This decrease in the catalytic activity is more pronounced with increasing O-Clo load in the reacting system (5 wt %). On the other hand, the molecular weight of the PE products tends to increased with the clay content (5 wt %). This result may be associated with a decrease of chain transfer and termination reactions produced by the polymer growth from active metallocene centers located in the layered structure of the clay particles.[1] On the other hand, crystallinity values of the PE and composites did not present significant differences, which indicates that the incorporation of the clay particles into PE matrix within the content range evaluated in this work do not seem to alter the crystalline properties of the neat PE. Melting temperature values (T_m)

of the PE/Clay products were also similar to that of the neat PE product.

Polymerization using clay-supported metallocene catalyst

In situ ethylene polymerization was also carried out using the clay as support for the metallocene catalyst. The results of ethylene polymerization using the metallocene directly supported on the clay samples are shown in Table II. When Na-Clo was used as support the catalytic activity decreased with respect to the homogeneous system, and it was apparently independent of the metallocene content in the support. The loss of activity caused by the catalyst's heterogenization process is a commonly observed phenomenon in metallocene catalysts. The activity of the metallocene may decrease due to deactivation reactions with neighboring hydroxyl groups on the clay surface or as a consequence of the fixation of the metallocene on less accessible sites in the clay structure. When ODA-modified clay was used as metallocene support, the polymerization activity tended to increase with the zirconium content of the heterogeneous catalyst. This result can be attributed to the greater interlayer spacing of the ODA-modified clay (6.6 Å), which facilitates the activation and monomer insertion processes on zirconocene centers located in the internal sites of the clay

TABLE II
Results of Ethylene Polymerization on Metallocene Catalyst Supported Directly on the Clay Samples

Catalyst	Zr (%) (fixed)	Catalytic activity ($kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$)	M_v ($kg \cdot mol^{-1}$)	T_m (°C)	χ (%)	Clay content (%)
Homogeneous	–	3900	280	139	67	–
Cat/Na-Clo	0.37	2970	350	138	66	0.7
Cat/Na-Clo	0.29	2900	380	137	68	0.8
Cat/Na-Clo	0.13	2950	380	136	71	1.8
Cat/O-Clo	0.57	4500	410	137	66	0.4
Cat/O-Clo	0.47	4300	300	136	66	0.5
Cat/O-Clo	0.21	3650	305	137	66	1.3
Cat/O-Clo	0.05	2200	350	137	66	5.0

structure. Moreover, the ODA-alkylamine groups present in the interlayer may act as spacer groups of the metallocene in the clay, thus reducing the deactivating bimolecular reactions. Clay-supported catalysts with different zirconium content were used to control the clay load in the PE product. Obviously, catalysts with lower Zr content allow increasing the clay load in the final polymer; but at the expense of lower polymerization activity. On the other hand, melting temperature and crystalline properties were maintained and molecular weight of the PE products increased significantly when the metallocene was supported on the clays. It has been found that when the polymerization is carried out on metallocenes immobilized in a nanoscopic space, the active species can be protected from other chemicals that cause termination of the polymer chain propagation.[10] Thus, the production of higher molecular weight PE is favored by using the clay-supported metallocene.

Polymerization using metallocene supported on MAO-treated clays

Metallocene was also supported on Na-Clo and O-Clo previously treated with MAO. Polymerization activities using the MAO-treated clays (Table III) were lower than those obtained on the untreated clays. Although MAO-treatment increases the efficiency of pure silica supports,[33] metallocenes supported on MAO-modified aluminosilicate supports such as zeolites have been found to exhibit lower activity than those supported directly on the unmodified support.[28] This effect is attributed to the fact that the metalloceniun active cation seems to be better stabilized on a support with a negatively charged structure (zeolites, clays) than on an MAO-modified surface. Moreover, sizable MAO molecules may also block entry toward the interlayer spacing of the clay, thereby reducing the free space available in the support for metallocene fixation. It can also be seen that the MAO treatment of ODA-intercalated clay (Cat/MAO/O-Clo) yields better activity values than when using the clay in its sodium form (Cat/MAO/Na-

Clo), which was also observed with the catalysts directly supported on the clay samples. When the Zr content in the O-Clo support was increased up to 0.87 wt %, the catalytic activity decreased slightly. This may be due to the fact that a high metallocene content favors bimolecular deactivation between neighboring Zr centers on the support's surface. On the other hand, the molecular weight values of the PE/clay products were of the same order as those obtained with the untreated Na-Clo and O-Clo supports.

Although, the catalysts supported on the MAO-treated clays showed somewhat lower polymerization activity, the presence of MAO in the clay interlayer spacing could generate a different exfoliation behavior of the clay during the *in situ* formation of the composite.

Characterization of PE/clay nanocomposites

PE/clay composite products were analyzed by XRD in order to evaluate the degree of exfoliation of the clay particles in the polymer matrix. Figure 5 shows the XRD patterns of the homogeneous PE product and the PE/clay composites obtained in the presence of Na-Clo particles as filler. In all cases, the characteristic peaks corresponding to the orthorhombic crystalline form of PE are seen.[9] The $d_{(001)}$ peak due to the presence of clay in the polymer matrix was not detected when 1 wt % of clay was used. This may be because the clay sheets are mostly exfoliated. On the other hand, when 5 wt % of clay was used, the $d_{(001)}$ peak (11.65 Å) appears more diffuse and the clay's interlayer spacing is increased to 16.65 Å. This result suggests an important degree of intercalation caused by the *in situ* polymer growth. The XRD patterns of PE/clay composites obtained on Na-Clo-supported catalysts are shown in Figure 6, where the presence of the $d_{(001)}$ clay peak is seen. The $d_{(001)}$ spacing is shifted from 11.65 Å to 17.66 Å during the formation of the composite, and it became significantly diffused, indicating that intercalation and to a lower degree the exfoliation of the clay sheets occurred during the polymerization.[34]

TABLE III
Results of Ethylene Polymerization on Metallocene Catalyst Supported on MAO-Treated Clay

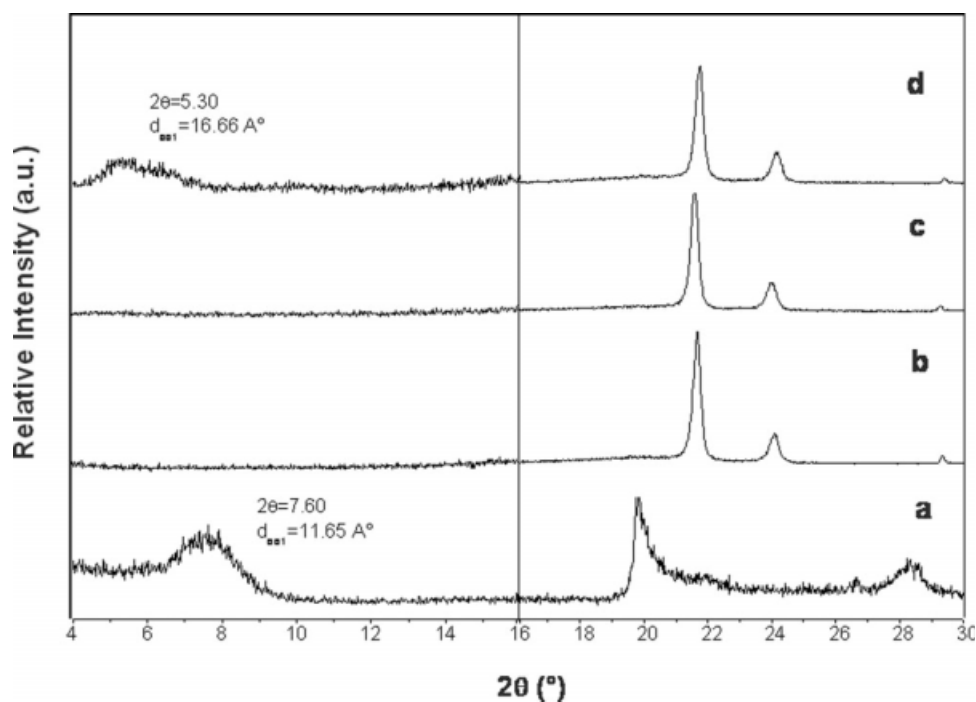| Catalyst	Zr (%) (fixed)	Catalytic activity (kg·mol^{-1}·h^{-1}·bar^{-1})	M_v (kg·mol^{-1})	T_m (°C)	χ (%)	Clay content (%)
Homogeneous	—	3900	280	139	67	—
Cat/MAO/Na-Clo	0.67	1200	340	138	66	0.4
Cat/MAO/Na-Clo	0.52	1500	320	140	66	0.4
Cat/MAO/ Na-Clo	0.22	1060	350	139	66	1.2
Cat/MAO/O-Clo	0.87	2300	340	139	65	0.3
Cat/MAO/O-Clo	0.46	3000	370	140	65	0.5
Cat/MAO/O-Clo	0.38	1400	330	139	65	0.6
Cat/MAO/O-Clo	0.21	1000	360	139	66	1.1

Figure 5 XRD patterns of (a) Na-Clo, (b) homogeneous PE, (c) PE/Na-Clo (1 wt %), and (d) PE/Na-Clo (5 wt %) composite products obtained in the presence of Na-Clo as filler.

When the clay/PE composite was obtained with the catalyst supported on the MAO–treated Na-Clo, the $d_{(001)}$ peak was not detected on the XRD pattern of the composite, indicating that the clay was totally exfoliated in this method of preparation. MAO treat-

ment of the clay favors metallocene activation and polymer chain growth at sites located within the clay's interlayer spacing, thereby facilitating the complete exfoliation of the clay sheets. In the case of the composites obtained using the catalyst supported
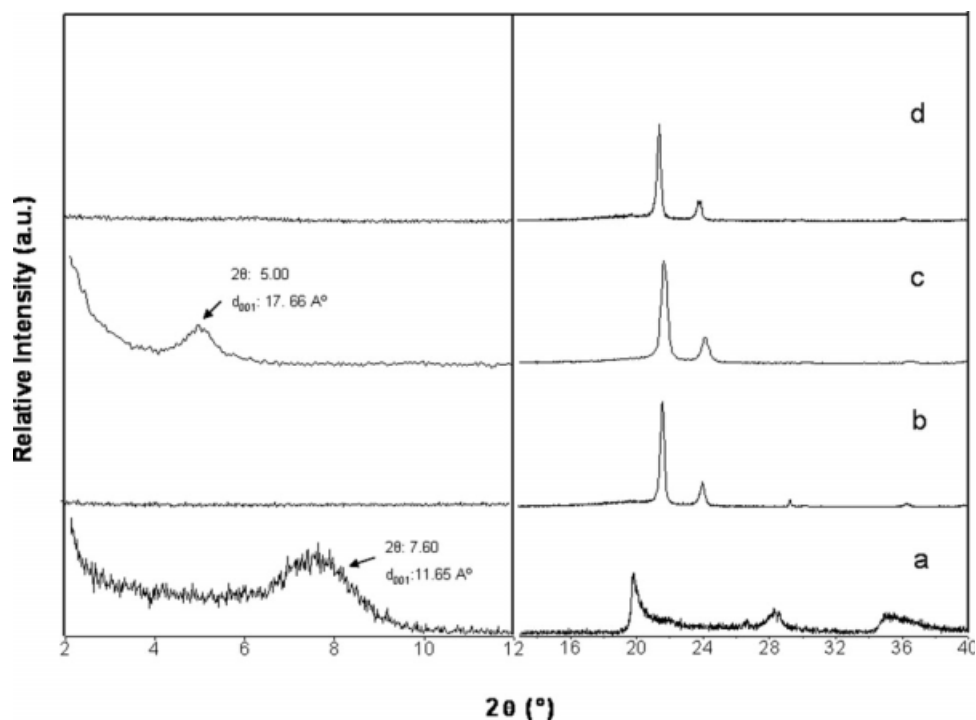

Figure 6 (a) Na-Clo, (b) Homogeneous PE, (c) PE/Cat/Na-Clo (1.8 wt %), and (d) PE/Cat/MAO/Na-Clo (0.5 wt %) composite products obtained on Na-Clo-supported catalysts.
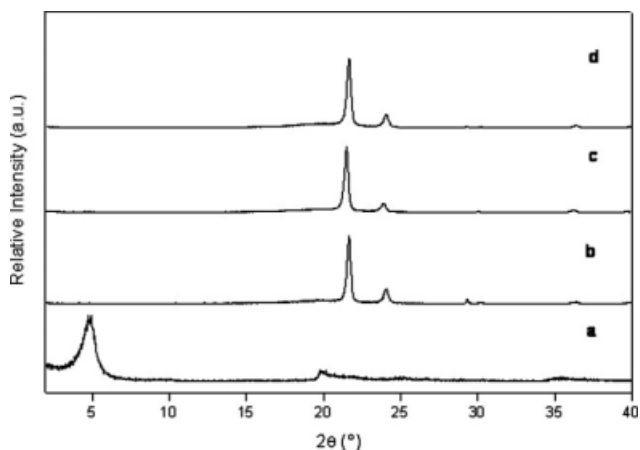
Figure 7 (a) O-Clo, (b) Homogeneous PE, (c) PE/Cat/O-Clo (0.5 wt %), and (d) PE/Cat/MAO/OClo (0.5 wt %) composite products obtained on O-Clo-supported catalysts.

on ODA-intercalated clays, no XRD reflections corresponding to the interlayer spacing of the clay were detected (Fig. 7). This result indicates that an essentially exfoliated PE/clay nanocomposite was obtained using the ODA-intercalated clay which, as already discussed, strongly favors the complete exfoliation of the clay sheets. From these results it can be deduced that MAO modification as well as ODA

intercalation of the clay supports play an essential role in improving the exfoliation characteristics of the PE/clay composites.

TEM analysis of some PE/clay composite samples was also performed. From TEM image of the composite obtained by using 1 %wt of Na-Clo as filler [Fig. 8(a)] can be observed nanometer-scale silicate layers into the polymer matrix. Although some regions of agglomerated silicate layers can be also seen, clay particles seem to be fully exfoliated in agreement with the XRD analysis of this composite [Fig. 5(c)]. In addition, no micron-sized clay particles were observed into the PE matrix. When the composite was prepared through *in situ* polymerization by using the metallocene catalyst directly supported on Na-Clo (1.8 wt %), thicker clay layers are observed in the composite [Fig. 8(b)]. This observation is indication that Na-Clo particles were not totally exfoliated during the polymerization and that the clay are predominantly in an intercalated state into polymer matrix, as already detected through XRD analysis [Fig. 6(b)]. Figure 8(c) shows a TEM image of the composite obtained through ethylene polymerization by using the catalyst supported on ODA-modified clay. In this case it was not possible to distinguish the clay layers into polymer matrix with clarity, probably due to the low clay content
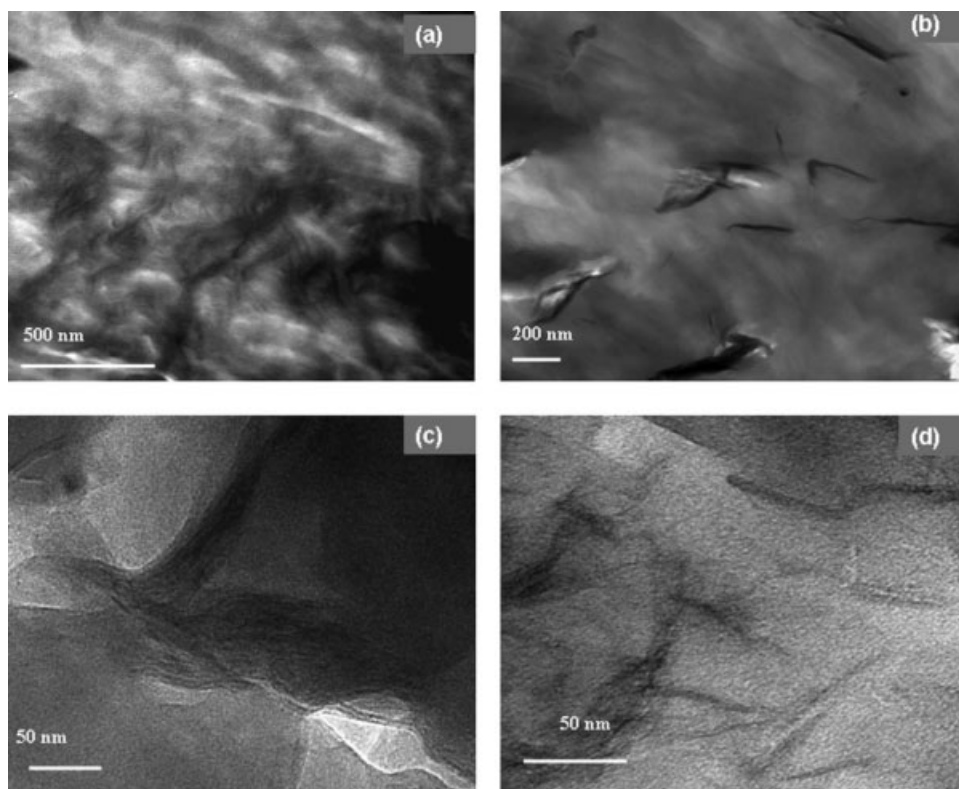

Figure 8 TEM images of (a) PE/Na-Clo (1 wt %) composite obtained by using Na-Clo as filler, (b) PE/Cat/Na-Clo (1.8 wt %) composite obtained on Na-Clo-supported catalyst, (c) PE/Cat/O-Clo (0.5 wt %) composite obtained on O-Clo-supported catalyst, and (d) PE/Cat/MAO/O-Clo (1.3 wt %) composite obtained on O-Clo-supported catalyst.

(0.5 wt %) of this composite. However, as already found by XRD analysis, the clay particles should to be fully exfoliated in this PE/O-Clo nanocomposite. TEM image of the composite obtained with 1.3 wt % in clay content by using the catalyst supported on MAO-treated O-Clo [Fig. 8(d)] shows the layer clay exfoliated into polymer matrix. This result confirms that predominatly exfoliated PE/clay nanocomposites can be obtained with metallocenes supported on ODA-intercalated clay, even when higher clay content are incorporated.

CONCLUSIONS

It was found that the catalytic activity of the homogeneous metallocene catalyst is not decreased by the presence of the clay particles during the preparation of PE nanocomposites by *in situ* polymerization. When the metallocene is supported on the clay particles, only a slight decrease of the activity occurs due to known heterogenization effects. Both, modification of the clay with MAO co-catalyst as well as the intercalation of it with ODA were found to play an important role during the *in situ* formation of the composites. ODA-intercalated clay apparently facilitates the activation and monomer insertion processes on zirconocene centers located in the internal sites of the clay structure. Although metallocene supported on MAO-treated clay exhibits somewhat lower catalytic activity than that supported directly on the ODA-intercalated clay, both systems favors the production of PE nanocomposites containing clay particles highly exfoliated.

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