PREPARATION OF NANOCOMPOSITES BY IN SITU POLIMERIZATION

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ABSTRACT

Polyethylene nanocomposites were obtained by *in situ* polymerization using both montmorillonite (natural clay) and montmorillonite organically modified with octadecylamine (O-Clo). In this proposed methodology the clays were added directly in the reactor together with the catalytic system (metallocene catalyst and methylaluminoxane) and ethylene. The nanocomposites were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and transmission electron microscopy (TEM), and by tensile stress-strain tests.

It was found that the catalytic activity increased around 20% when natural clay was used compared with the standard polymer. But when modified clay was used the catalytic activity did not show important changes.

On the other hand, XRD and TEM showed that the clays are in a disordered state and well dispersed in the polyethylene matrix. Finally, the nanocomposites showed an increase of about 30% in Young's modulus compared with the standard polymer

Keywords: Nanocomposites, Montmorillonite, Polyethylene, Metallocene.

INTRODUCTION

Polymer nanocomposites are hybrid materials composed of an organic polymer matrix with dispersed inorganic filler that has at least one dimension in the nanometer range[1].

These nanofillers, with a very high aspect ratio, strongly modify the macroscopic properties of the polymer even when a small amount of filler is used[2]. So nanocomposites usually have improved properties compared to neat polymers, such as better mechanical properties and higher thermal stability[3,4].

Among the most commonly used nanofillers for obtaining nanocomposites are layered silicates, especially 2:1 phyllosilicates that are present in the form of sheets about one nanometer thick and hundreds to thousands of nanometers long.. The layers are in turn linked together by Van der Walls forces and organized in stacks with a regular gap between them called "interlayer or gallery". As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy. In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium. When the clay is modified, its surface energy is lowered and it becomes more compatible with organic polymers[5]. Due to the lack of polar groups in polyolefins, many efforts have been made to improve the dispersion of inorganic fillers like clay and silica in a polyolefin matrix for the preparation of the effective polyolefin nanocomposites[2,6].

The preparation of nanocomposites can be done by three routes, which are solution blending , the molten state, and *in situ* polymerization. The latter consists in placing the monomer and the catalyst between the clay layers, and polymerization takes place in the gap, so as polymerization progresses the d-spacing between the clay's layers increases gradually and the dispersion state of the clays changes from intercalated (the ordered of layered silicate gallery is retained) to exfoliated (delamination with destruction of the clay sheet order) [3,4]. The advantages of this method are 1) the one step synthesis of the metallocene polymer nanocomposites; 2) improved compatibility of the clay and the polymer matrix; and 3) enhanced clay dispersity[7].

It has been found that in the case of polyolefins the metallocene catalysts supported on clays with different pretreatments and modification such as alkyl amine,[6] alkyl ammonium, methyl esters, L-amino acids [6], alkyl siloxane[8,9], results in different ethylene polymerization behavior and in polymers with different properties. In spite of the importance of *in situ* polymerization, few publications have studied in a systematic way the different variables involved in these systems.

In this study we describe the preparation of polyethylene nanocomposites by *in situ* polymerization using both natural and organic modified montmorillonite as filler, and different percentages of clay (1 and 5%wt respect to the weight of the standard). The effect of the percentage of clay on catalytic activity was studied, as well as the properties of the polymer obtained.

EXPERIMENTAL

Materials

Natural sodium montmorillonite (Cloisite Na$^+$) was supplied by Southern Clay. These clays were used after drying in vacuum at 110 °C during 15 hours. The amount of clay used in each reaction was 1% and 5 % with respect to the weight of the standard (homopolymer).

The cocatalyst used was methylaluminoxane (MAO) supplied by Witco, and the metallocene catalyst ((n-BuCp)$_2$ZrCl$_2$) was supplied by Aldrich. All manipulations were carried out in an inert nitrogen atmosphere.

Commercial solvent toluene was purified by refluxing over metallic sodium, with benzophenone as indicator.

Ethylene used as polymerization monomer was dried by passing trough a column of molecular sieves.

Octadecylamine (ODA) of 90% purity was supplied by Aldrich and was used to modify the clay.

Preparation of modified Cloisite Na$^+$ (O-Clo)

Octadecylamine (ODA) was dissolved at 70 ºC in a 50:50 v/v water: ethanol mixture acidified with HCl to pH 3. The clays (Cloisite Na$^+$) 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 ºC. The organically modified clays were recovered by filtration, washed with a large amount of ethanol and water, filtered and then dried for one day[10]. The organophilic clays obtained were designated as O-Clo and characterized by X-ray diffraction (XRD).

Ethylene polymerization

Standard *polymerization*

Ethylene was deoxygenated and dried before use by passing it through columns (BASF) and activated molecular sieves (13 Å). Polymerization was performed at 2 bar in a 400 ml glass reactor (Parr). The homogeneous polymerization standard reactions were carried out by addition of ethylene, and a solution of metallocene ((n-BuCp)$_2$ZrCl$_2$) in purified toluene was added. The amounts of metallocene and MAO were adjusted to 3X10^{-6} moles of Zr and an Al/Zr molar ratio of 1400. The final volume of the solution was 240 ml. The polymerization was carried out at 60 ºC during 30 min with a stirring speed of 1000 rpm.

The ethylene *in situ* polymerizations with clay were carried out under the same polymerization conditions, with the addition of clay directly to the reactor. One and five weight percent of natural and modified clay with respect to the standard were used

Acidified methanol solution (20 mL) was used to terminate the polymerization. The precipitated polymer was recovered by filtration and washed with ethanol, distilled water and acetone, and dried overnight at room temperature. The 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}).

The amount of metallocene and MAO, and total volume were the same as in the homogenous case.

All the procedures were repeated two times to have good reproducibility.

Characterization

The basal spacing of the clays and the structure of the nanocomposites were examined by X-ray diffraction (XRD) using Siemens D5000 equipment with Cu λ = 1.54 Å. The basal spacing of the clays was estimated from the *(001)* peak in the XRD using the Bragg equation $\lambda = 2d \sin\theta$, where λ is the wavelength.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was studied on a Bruker Vector 22 model, in the range of 4000 to 400 cm^{-1} with resolution of 4cm^{-1}.

The molecular weight of the polyethylene samples was 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 narrow molecular weight distribution polystyrene standards, were used. 1,2,4-Trichlorobenzene was used as the solvent, and the flow rate for analysis was 1 mL/min at 135 °C.

Differential scanning calorimetry (DSC) measurements were made on Modulate TA DSC 290 instruments. The samples were heated from 25 °C to 180 °C and cooled down to 25 °C at a heating rate of 10 °C/min to determine the melting temperature, and the values were taken from the second heating curve.

Tensile mechanical properties were determined with an HP model D-500 dynamometer. The materials were placed in a stainless steel mold and molded for 5 min in an HP press under a pressure of 50 bar at 170 ºC and cooled quickly with water. The samples were tested at a rate of 50 mm/min at 20 ºC. Each set of .measurements was repeated at least four times.

The dispersion of clay in the composites was observed on a Philips CM 100 transmission electron microscope (TEM) at 80 kV. The specimens were ultrathin-sectioned using an ultramicrotome with a diamond blade.

RESULTS AND DISCUSSION

The results corresponding to the characterization of the clays will be presented first, followed by the ethylene polymerization in which clays were used as filler

Characterization of natural clay and montmorillonite organically modified with octadecylamine(O-Clo)

Figure 1a shows the characterization of natural clay by DRIFTS. The band characteristic of montmorillonite at 3620 cm^{-1} is typical of smectites with a large amount of Al in the octahedral interlayer. The other characteristic band of montmorillonite is the Si-O stretching which absorbs at 1256 cm^{-1} [11,12]. At 1620 cm^{-1} there is a band characteristic of the hydroxyl groups of water .

Figures 1b and 1c show the spectra of ODA and O-Clo. The characteristic peaks of ODA at 2920 cm^{-1} and 2850 cm^{-1} correspond to the CH$_2$ asymmetric and symmetric stretching vibration, respectively. The other important band of ODA is at 3300 cm^{-1}, characteristic of the amine group. Figure 1c shows the absorption bands due to amine cations near 1715 cm^{-1}, and the bands characteristics of ODA and montmorillonite [13].
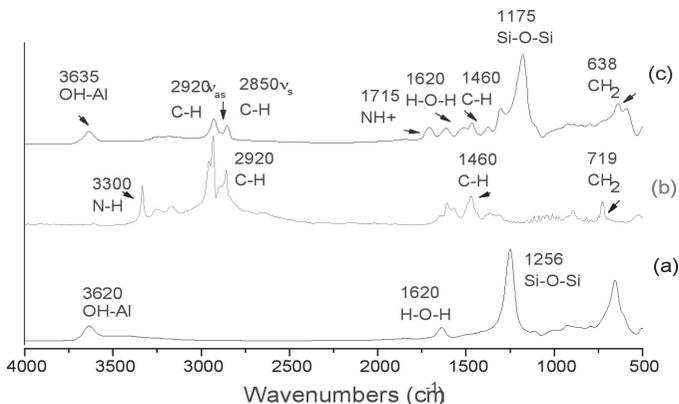

Figure 1. DRIFT spectra of a) Cloisite Na$^+$, b) ODA c) Modified Cloisite with ODA (O-Clo).

Figures 2a and 2b show the characterization by XRD of cloisite Na$^+$ and the cloisite intercalated with ODA, respectively. As seen in Figure 2a, the first peak of cloisite Na$^+$ corresponds to the interlaminar spacing of the 001 plane of clay, which increases from 11.65 Å (2θ = 7.6) to 18.25 Å (2θ = 4.8) when it is treated with ODA to obtain O-Clo. That means an 6.6 Å increase in the *(001)* plane, confirming that ODA is present in the interlaminar spacing of clays, and it is also possible to see it by DRIFT.
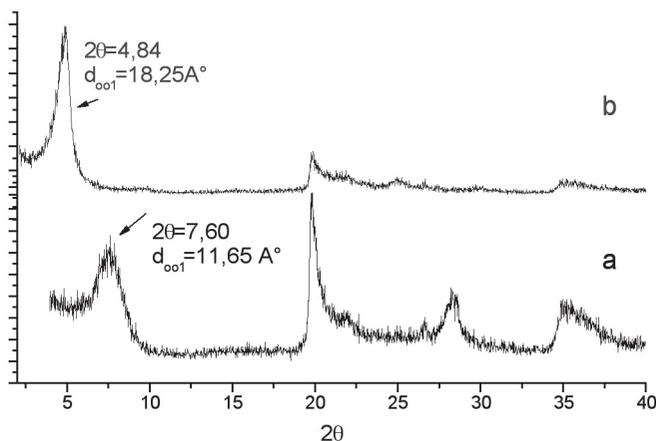

Figure 2. XRD standards of (a) Cloisite Na$^+$ and (b) .

Study of the catalytic activity and properties of the polymer

Table 1 shows the results of the catalytic activity, and the main properties of the synthesized polymers: molecular weight, polydispersity, melting temperature, and crystalline percentage for standards and polymers obtained when different percentage of unmodified and modified clay (1 and 5%) were used. For comparisons, results coming from the standard are also shown.

Table 1. The influence of the clay in the catalytic activity, molecular weight, polydispersity, and thermal properties of the polymer.

Process	Clay Type	Clay (%)	Activities (Kg/ mol Zr *h*bar)	Mw (Kg/ mol)	Mw/ Mn	Tm (°C)	X (%)
Standard	0	0	3900±332	161	2.14	139	67
Clay as filler	Cloisite Na$^+$	1	4800±450	165	2.04	138	66
	Cloisite Na$^+$	5	4500±65	232	1.81	139	60
	O-Clo	1	4200±50	168	2.04	139	65
	O-Clo	5	3900±20	261	2.00	137	63

Mw: Molecular weight, Mw/Mn:Polydispersity, Tm:Melting temperature, χ: Crystalline percentage

Higher values of catalytic activity were obtained (increased about 20 %) when cloisite Na$^+$ was used compared to the standard. This may be due to the fact that clay does not allow bimolecular deactivation of the catalyst, generating a positive effect in the catalytic activity.

When clay is modified with octadecylamine the catalytic activity presents a slight decrease compared with natural clay, and that may be due to amine cations blocking some actives centres of the catalyst, decreasing the overall activity.

It was found that the molecular weight increase when 5% of Cloisite Na$^+$ y O-Clo were used, and that may be associated with a decrease of chain transfer and termination reactions, due to the laminated structure of clay, which influences the molecular weight of the polymer.[1]

With respect to thermal properties the melting temperature and crystalline percentage do not show a significant change compared with the standard.

The polydispersity of about 2.0 of the polymer obtained is typical of metallocene catalysts.

Characterization of the nanocomposites: XRD and TEM.

Figures 3 show the XRD of the original cloisite, the standard and the composites when 1% and 5% of clay was used.
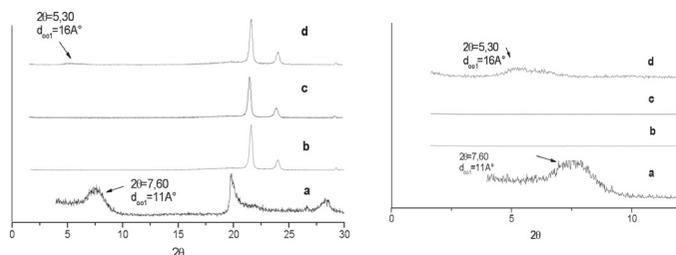

Figure 3. XRD of (a) cloisite Na⁺, (b) polyethylene (standard), (c) composite with 1% of clay and (d) composite with 5% of clay.

Figures 3b, c, d show that the nanocomposites retain the orthorhombic crystallite form of pure polyethylene (standard).[7] Figures 3c also show that the (001) peak of Cloisite Na⁺ in the composite disappears when 1% percent of clay was used, indicating possible exfoliation of the clay. On the other hand, when 5% of clay is used the (001) peak of the Cloisite Na⁺ shifted from the original 11 Å (2θ = 7.6) to 16 Å (2θ = 5.30) and became significantly diffused, as can be seen in Figure 4d, indicating that the gallery distance increased gradually during polymerization, and both intercalation and exfoliation may have occurred. The same behavior is presented for O-Clo.

Figure 4 shows the TEM micrograph of the nanocomposite when 5% of Closite Na⁺ was used. The dark lines in the figure denote discrete silicate layers. The silicate layers are in a disordered state, randomly and well dispersed into the polyethylene matrix. However, it can be seen that thick dark lines form stacks in different parts of the polymer matrix, due to possible agglomerations.
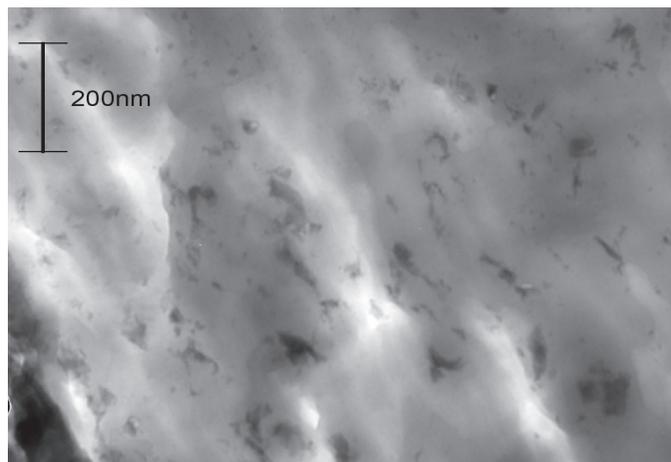

Figure 4. TEM photograph of Cloisite Na ⁺/polyethylene nancomposite

Tensile properties of nanocomposites.

Table 2 shows the mechanical properties of the nanocomposites obtained with different percentages of Cloisite and O-Clo. Young's modulus values indicate that clay improves the rigidity of the polymer. Although low amounts of filler were used, there was an improvement in Young's modulus, independent of the percentage and type of clay used,

Elastic limit do not present significant changes in the nanocomposites obtained. Important aspect is related to values for at elongation at rupture, which in contrast with other nanocomposites does not undergo decrease. This means that these nanocomposites present excellent plastic properties.

Table 2. Mechanicals Properties of nanocomposites with clays as filler

Process	Clay Content (%)	E (Mpa)	σ_y (Mpa)	$\varepsilon_{rupture}$ (%)
Standard	--	610±61	24±2	300±51
Cloisite	1	790±62	26±1	300±16
Cloisite	5	800±39	23±1	250±11
O-Clo	1	820±70	27±1	300±21
O-Clo	5	770±44	27±5	250±24

E: Young's modulus, σ_y: Elastic limit, $\varepsilon_{rupture}$: Elongation at rupture

CONCLUSION

PE/Clay nanocomposites were prepared by *in situ* polymerization. It was found that the clay increases the catalyst activities of polymer in special when unmodified and 1% of clay was used. The amount of clay is independent of Young's modulus values. An increase of rigidity of polymer was found due a good dispersion and strong interaction between the clays and the polyethylene matrix.

REFERENCES

1. Q .Wang, Z. Zhou, L. Song, H. Xu, L. Wang, J. polym. Sci. Part A. **42**, *38*, (2004)
2. M. Alexandre, P. Dubois, T. Sun, M. Garces, R. Jeronime, Polym. **43**, *2123,* (2002)
3. J. Xu, Q .Wang , Z. Fan, Eur. Polym. J. **41**, *3011*,(2005)
4. J.Xu, Q .Wang, Z. Fan, Polym. **46**, *11978*, (2005)
5. M. Alexandre, P. Dubois, Mater.Sci. Eng. **28**, *1*, (2000).
6. D. Lee, H. Kim, K. Yoon, K. Min, K. Seo, S. Noh, Sci. Techn. Adv. Mater. **6** , *457*, (2005)
7. S. Kuo, W. Huang, S. Huang, H .Kao, F .Chang, Polym. **44**, *7709*, (2003)
8. C.Liu, T .Tang, D .Wang, B.Huang, J.Cat. **221**, *162*, (2004)
9. L. Wei, T.Tang, B.Huang, J.Polym. Sci. Part A:Polym. Chem. **42**, *941*, (2004)
10. E. Moncada, R. Quijada, I. Lieberwirth, M Yazdani-Pedram., Macromol. Chem.Phys. **207**, *1376*, (2006)
11. J. Madejová, Vibrat. Spectr. **31**,*1*, (2003)
12. B.Tyagi, C.Chudasama, R.Jasra, Spectroch. Acta Part A, **64**, *273*, (2006)
13. A.Santano, R. Trujillano, C. Belver, A .Gil, M. Vicente, J.Colloid Interf. Sci. **284**, *239*, (2005)