

Polyethylene-Montmorillonite Nanocomposites Obtained by *In Situ* Polymerization of Ethylene with Nickel-Diimine Catalysts

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ABSTRACT: Nanocomposites of exfoliated montmorillonite in polyethylene were obtained using a combination of 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine-dichloronickel(II), montmorillonite, and methylalumoxane (MAO) or trimethylaluminum (TMA) to polymerize ethylene. The properties of the polymers were strongly influenced by the amount of clay they contained. The addition of 2.5% commercial montmorillonite (KSF or Cloisite 15A) enhanced the storage modulus from 5 to 878 MPa. Transmission electron microscopy (TEM) analyses provided

evidence of exfoliation of the montmorillonite with the formation of a polyethylene nanocomposite. The enhanced mechanical properties were explained as a consequence of the reinforcement due to the presence of nanoscale layers formed from exfoliation of the clay included in the polyethylene matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2159–2165, 2011

Key words: polymer synthesis and characterization; nanocomposites; thermal properties; mechanical properties

INTRODUCTION

Polymer/clay nanocomposites are a class of hybrid materials composed of an organic polymer matrix containing inorganic particles, generally alumino-silicates, with at least one dimension on the nanometer scale. Furthermore, to consider a hybrid material as a true nanocomposite, the inorganic compound must be uniformly dispersed throughout the polymer and should not be aggregated.¹ Silicates, kaolin, hectorite, and mica are the primary minerals used to prepare nanocomposites with polymers. Montmorillonite clay is frequently cited because its incorporation inside an organic matrix in small amounts can improve certain polymer properties such as the modulus, thermal resistance, gas barrier, and fire resistance.

The methods for the preparation of nanocomposites can be divided into three main groups according to the starting materials and the processing techniques: (i) solution processes, in which the intercalation is performed by adding the inorganic compound to the polymer solution; (ii) melt-intercalation

processes, in which the inorganic phase is added to the molten polymer; and (iii) *in situ* intercalative polymerization processes, in which the polymer is synthesized in the presence of the inorganic compound contained in the reaction medium.²

Polymer composites obtained through solution processes are prepared by blending the polymeric solution and the inorganic suspension. The layers are aggregated in thin stacks consisting of a few individual layers. The morphology of the modified silicate filler that is incorporated by such processes in high-density polyethylene (HDPE) and nitrile copolymer matrices has been investigated.³ The hydrophilic clay was previously modified through an ion exchange reaction, thus enabling the introduction of dodecylamine into its structure. These modified clays, which were finely dispersed throughout benzonitrile, were successfully intercalated in the polymeric matrix. Due to the high dispersion and the morphology of the inorganic compound, enhancement of the barrier and mechanical properties of these nanocomposite systems was observed.

The melt-intercalation processes consist of mixing the molten organic matrix with the inorganic phase. This operation can be performed in a masterbatch process or during an extrusion process. Improvements in the mechanical properties were observed for polyethylene containing exfoliated montmorillonite, obtained by melting the compound in a masterbatch process.⁴ Polypropylene (PP)-clay hybrids have been prepared

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by melt-mixing maleic-anhydride-modified PP (PP-MA) with silicates.^{5–9} These nanocomposites showed higher storage moduli compared with the original PP-MA. The fabrication of nanocomposites by melt-intercalation or extrusion results in functionalized PPs and common clays or unmodified polymers with functionalized clays. Such methods have been applied to produce PP/silicate hybrid compounds. The modified polymer could be ammonium chain-end-functionalized PP¹⁰ and the functionalized clay a semi-fluorinated silicate.¹¹

The *in situ* intercalative polymerization method is attractive because it allows for the intercalation of highly reactive and catalytically active organometallic species in several layers of aluminosilicates. These intercalated species can react with the monomer, leading to polymerization inside the lamellar porosity.^{13,14} Polyolefin-clay nanocomposites with enhanced properties such as reduced thermal expansion coefficients, improved melt-flow strengths, increased heat-distortion temperatures, lowered gas diffusion coefficients, and improved Young's moduli are obtained by *in situ* metallocene polymerization.^{13,14} Clay minerals like montmorillonite, kaolin, hectorite, and mica containing intercalated titanocene and zirconocene catalysts were also tested as inorganic carriers for the polymerization of ethylene and propylene.^{15,16} In the last case, the inorganic solid was modified by introducing an organic functional group to react as, or with, a ligand of the organometallic complexes to improve the immobilization of the active species inside the clay phase. Ethylene polymerization has been successfully carried out using a Ti-based Ziegler-Natta catalyst immobilized in the layers of montmorillonite previously modified by intercalated agents containing hydroxyl groups.¹⁷ Intercalation of a palladium-diimine complex in an organically modified fluorohectorite produces an active system that yields an exfoliated polyolefin-silicate nanocomposite material.¹⁸ In the case of polyethylene nanocomposites, some *in situ* intercalative catalytic polymerization processes have been described as being more effective than the melt method.¹⁹

Herein, a study of *in situ* polyethylene nanocomposites obtained using a nickel- α -diimine catalyst intercalated in two commercial montmorillonite clays (KSF and Cloisite 15A) and the thermal and mechanical properties of these materials are described.

EXPERIMENTAL

All experiments were performed under dry argon using standard Schlenk tube techniques. Cyclohexane was distilled under argon from sodium/benzophenone immediately before use. Solids were dried under reduced pressure. Methylalumoxane (MAO)

was purchased from Witco and trimethylaluminum (TMA) purchased from Akzo Chemicals. Both were used without further purification.

The KSF montmorillonite was purchased from Sigma-Aldrich and the Cloisite 15A was purchased from Southern Clay Products and treated under reduced pressure (10^{-2} mbar) for 24 h at 80°C. KSF is a natural montmorillonite treated with sulfuric acid at room temperature, resulting in an exchange of Na^+ , Ca^{2+} , and Mg^{2+} by protons. Cloisite 15A is a natural montmorillonite modified with a quaternary ammonium salt; the organic modifier is dimethyl dihydrogenated tallow ammonium (2M2HT): dimethyl, dehydrogenated tallow, quaternary ammonium, where HT is hydrogenated tallow (65% C18; 30% C16; 5% C14), presenting a cation exchange capacity (CEC) of 74 meq Na^+ /100 g) and an interlamellar distance (d_{100}) of 31.5 Å. 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine-dichloro-nickel (II)(1) was synthesized according to procedures in the literature.²⁰

Polymer melting points (T_m), crystallization temperatures (T_c), and crystallinities (χ_m) were determined using Thermal Analysis Instruments DSC-2010 equipment. Polymer samples were heated in open pans from 40 to 180°C, held at this temperature for 5 min, cooled to -20°C and then heated again to 180°C. The heating and cooling rate was 10°C/min. Analyses were performed under nitrogen. The melting point temperatures and degree of crystallinity were determined in the second scan. Crystallinity was calculated using the enthalpy of fusion of perfectly crystalline polyethylene (293 J/g).²¹

Dynamic-mechanical experiments (DMA) were performed on TA Instruments DMA Q800 equipment operating at 1 Hz. The temperature range used was -80 to 80°C, and the heating rate was 10°C/min. The samples were rectangular films, (10-mm wide, 12-mm long, and 0.2–0.3-mm thick) with homogeneous thickness, prepared in a Carver press Monarch series, model 3710 ASTM, with pressures of 5–10 tons at 80–130°C.

Transmission electron microscopy (TEM) analyses were carried out in a JEOL-JEM 1200ExII microscope with an acceleration voltage of 100 kV. Polymeric films were deposited onto grids by solvent evaporation.

The polymer microstructure was qualitatively and quantitatively analyzed by ¹³C Nuclear magnetic resonance spectroscopy. The branches were classified as methyl, ethyl, propyl, butyl, pentyl, and longer (hexyl and longer), as detailed in a previous work.²² The spectra were obtained with a Varian Inova 300 MHz spectrometer operating at 75 MHz and 80°C, with a 70° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. Sample polymer solutions were prepared in hot trichlorobenzene (TCB) and benzene-*d*₆ (20% v/v) in a 5-mm tube.

TABLE I
Effect of the Nature and Amount of Clay and Co-Catalyst on the Performance and Properties of Ethylene Polymerization with (1), Cloisite 15A or KSF and MAO or TMA^a

		Entry			GPC		DSC		DMA ^b		
Co-catalyst	Clay	Clay content (wt %)	Productivity (kg _{PE} mol _{Ni} ⁻¹ h ⁻¹)	TOF ^c (s ⁻¹)	$M_w \times 10^{-3}$ (g mol ⁻¹)	M_w/M_n	T_m (°C)	χ_m^d (%)	E' (MPa)	E^* (MPa)	
1		0	1620	16	n.d.	n.d.	78	<5	4	4	
2	TMA	KSF	1.0	780	8	n.d.	n.d.	121	29	52	52
3			2.5	740	7	n.d.	n.d.	123	30	125	126
4			5.0	560	6	n.d.	n.d.	124	35	408	410
5			0	2300	23	n.d.	n.d.	–	–	5	5
6	MAO	KSF	1.0	2600	26	n.d.	n.d.	–	–	6	6
7			2.5	2500	25	n.d.	n.d.	–	–	5	5
8			5.0	2700	27	n.d.	n.d.	–	–	5	5
5			0	2300	23	331	3.5	–	–	5	5
9			1.0	1600	16	288	2.8	106	90	11	13
10	MAO	15A	1.5	1300	13	366	6.3	111	95	29	40
11			2.0	1000	10	616	8.3	120	102	254	878
12 ^e			2.6	1550	15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

^a Reaction conditions: ethylene pressure: 6 atm, 10 μ mol of nickel, Al/Ni = 200, 100 mL of cyclohexane, 10°C, 1 h.

^b Mechanical properties at 25°C, E' (Storage modulus); E^* (Young's modulus).

^c TOF = turnover frequency = mol ethylene converted per mol of Ni per second.

^d Crystallinity calculated using the enthalpy of fusion of a perfectly crystalline polyethylene (293 J/g).

^e Al/Ni = 400.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC). Analyses were performed on a Waters GPCV 2000 liquid chromatograph equipped with refractive index (RI) and viscometer detectors. Analyses were carried out using four Toso-Hass columns (HT3, HT4, HT5, HT6) and a 500 Å precolumn. Polymer solutions were prepared in TCB with 0.1 g/L of butylhydroxytoluene (BHT), and the analyses were performed at 140°C.

Polymerization reactions

Ethylene polymerization reactions were performed in a 450 mL Parr stainless steel autoclave equipped with magnetically driven mechanical stirring, a thermocouple and a pressure gauge. The reaction temperature was controlled by a thermostatic circulation bath with a cooling loop inside the reaction vessel. A typical reaction run was performed by introducing 2 mmol of alkylaluminum (MAO or TMA) and 180–1200 mg of clay (Cloisite 15A or KSF) in 90 mL of cyclohexane. After 1 h under stirring, at 10°C and under ethylene, 10 μ mol of 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine-dichloro-nickel(II)(1) in 10 mL of cyclohexane was added. The ethylene pressure was raised to 6 atm and continuously fed for 1 h. Then, the pressure was released, the reactor was opened and the polymer was precipitated with acidified ethanol, filtered, washed with water and ethanol, and dried for 48 h at 40°C under reduced pressure.

RESULTS AND DISCUSSION

Polyethylene nanocomposites were obtained by performing ethylene polymerization in the presence of an cyclohexane suspension of 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine-dichloro-nickel(II)(1) in presence of clay (Cloisite 15A or KSF) and a convenient alkylaluminum cocatalyst (MAO or TMA). The typical reaction conditions were 6 atm of ethylene, and 10°C for 1 h.

Table I shows the performance of the system and some of the properties of the polymeric materials obtained with different amounts of montmorillonite clay (KSF and Cloisite 15A) added to the system to obtain from 1 to 5 wt % exfoliated clay in the polymer matrix.

The results of Table I show that the addition of clay decreased the productivity from 1620 kg PE mol Ni⁻¹ h⁻¹, obtained in the absence of clay, to 560 kg PE mol Ni⁻¹ h⁻¹ with 5 wt % of clay (entries 1–4) for TMA/KSF and from 2300 kg PE mol Ni⁻¹ h⁻¹ to 1000 kg PE mol Ni⁻¹ h⁻¹ with 2.5 wt % for Cloisite15A/MAO (entries 5, 9–11).

A plausible explanation for this effect is that the large amount of clay present in the system reacted with the alkylaluminum cocatalyst, with a corresponding decrease in productivity. This hypothesis was tested by including more cocatalysts, as described in entry 12, and gave rise to the expected increase in activity. It may also be due to the barrier effects of clay layers which retard the diffusion of ethylene into the gaps between clay layers, where significant amount of catalyst is.

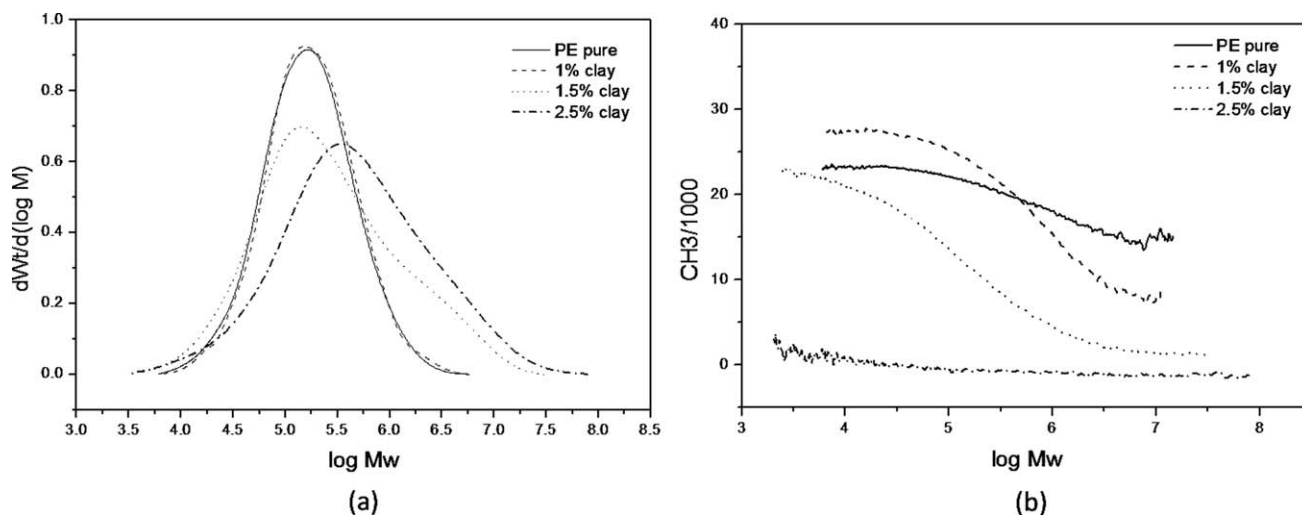


Figure 1 (a) Molecular weight distribution and (b) branching distribution in the different molecular weight fractions of the PE obtained using the 1/Cloisite 15A/MAO system. Effects of the amount of clay.

However, when MAO was used, the addition of KSF clay did not affect productivity (entries 5–8). A possible explanation is that MAO is too large a structure to access the small interlayer distance into KSF clay.

When Cloisite 15A/MAO was used, the molecular weight of the polyethylene obtained was almost constant until the addition of 1 wt % of Cloisite 15A. For higher amounts, the polydispersity increased significantly, suggesting the formation of different active centers. This effect may also be due to the barrier effects of clay layers resulting in different molecular weight of PEs between formed inside clay gaps and formed outside clay gaps. The GPC analysis performed with double detection, a RI and viscosimetry (DV) was informative because it contained both the molecular weight

distribution (MWD), as shown in Figure 1(a), and the branching distributions of the different molecular weight fractions, as shown in Figure 1(b).

It is worth-noting that the branching degree decreased with the increase in molecular weight, and that this tendency was more pronounced with increasing clay content. The decrease in branching with the increase in the molecular weight of the nanocomposite polymer can be explained by the decrease of β -elimination, which can be hindered in the presence of clay.

The decrease in the branching degree for the similar molecular weight PE provoked the corresponding enhancement of the T_m , as shown in Figure 2(a,b).

The effect of the addition of Cloisite 15A on the crystallinity (χ_m) was attractive. The polyethylene

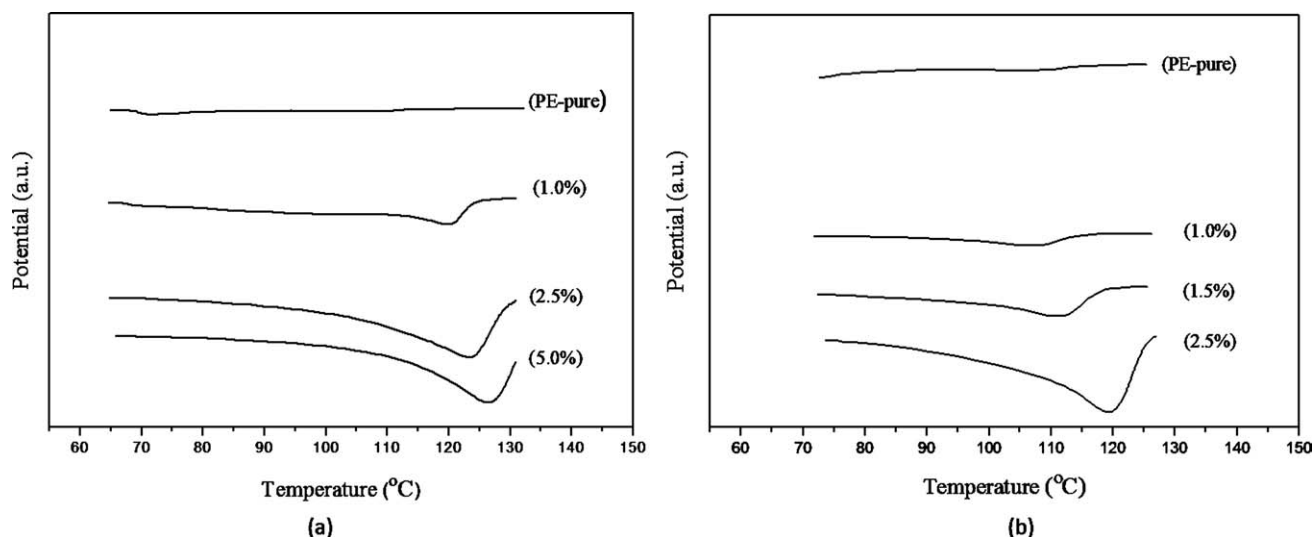


Figure 2 (a) DSC analysis of polyethylene nanocomposites obtained with 1/TMA and different amounts of KSF and (b) with 1/MAO and different amounts of Cloisite 15A.

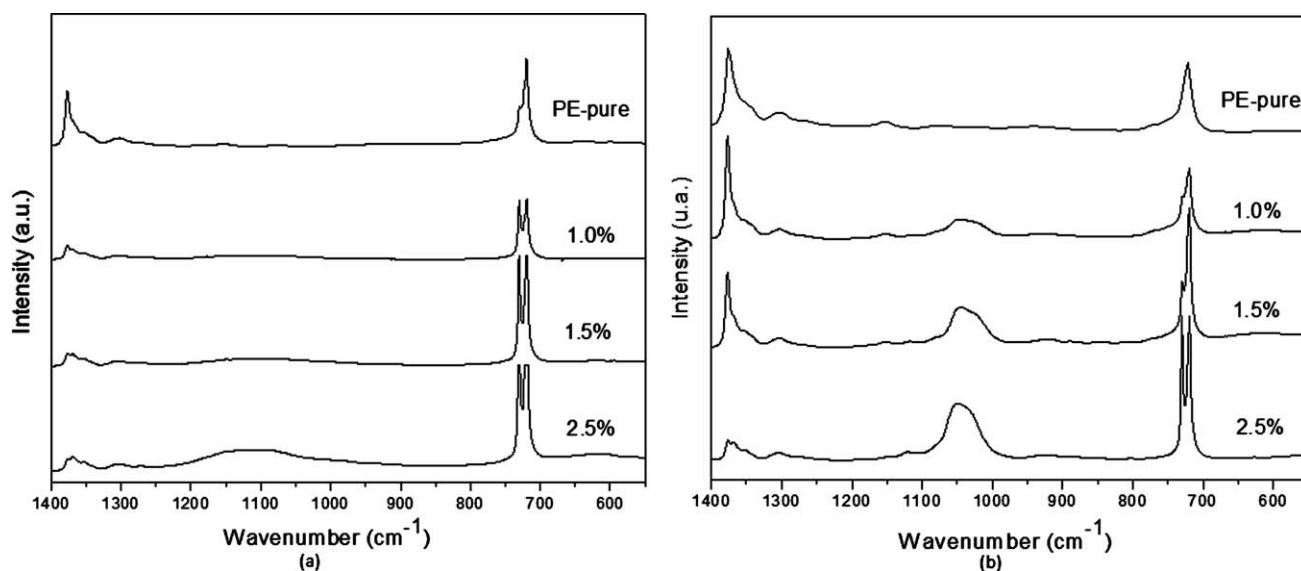


Figure 3 (a) IR analysis of polyethylene synthesized in polymerization reactions with the 1/KSF/TMA system and (b) with the 1/Cloisite 15A/MAO system.

obtained in the absence of clay, under the conditions of this study, was almost amorphous, but the crystallinity grew until 23% with increasing amounts of clay added to the system, as shown in Table I. The increase in crystallinity can be explained by the presence of clay, which induced the formation of polyethylene crystallites. The IR analysis of the synthesized polyethylenes is shown in Figure 3.

The FT-IR analyses of the PE and PE-clay polymers showed that the addition of KSF or Cloisite 15A was accompanied by the appearance of a new band at 730 cm^{-1} , characteristic of methylene rocking perpendicular to the polymer chain in crystalline regions.²³ This peak increased with increases in the clay content. It is interesting to note that the 1370

cm^{-1} band, characteristic of symmetrical deformation of methyl groups of a ramified chain, decreased with increasing clay content. This means that the IR analysis confirmed that the incorporation of clay into the polymeric matrix decreased the branching and increased its crystallinity.

Moreover, one can observe an increase in the intensity of the band at 1050 cm^{-1} when the Cloisite 15A content increased. This band was attributed to the silicon-oxygen stretching vibrational modes,²⁴ which are characteristic of the clay. It has been mentioned that the intensity of the 1050 cm^{-1} band increases when exfoliation of the clay occurs,²⁴ confirming that the Cloisite 15A has been exfoliated.

The ^{13}C NMR spectra of the polyethylene confirmed the formation of different amounts of branching when the catalytic system was 1/MAO or 1/

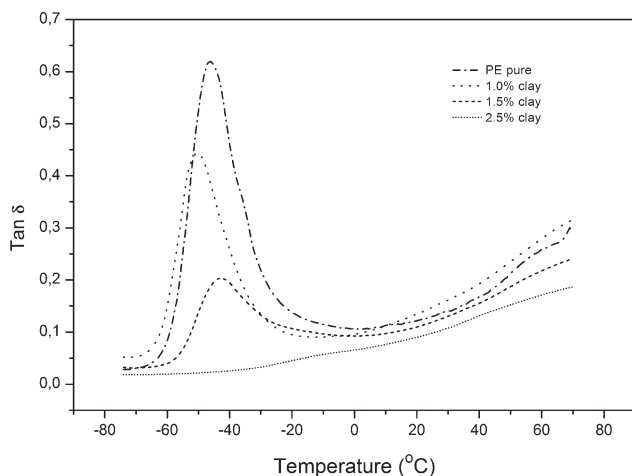


Figure 4 Mechanical damping ($\tan \delta$) of the polyethylene nanocomposites obtained using the 1/Cloisite 15A/MAO system.

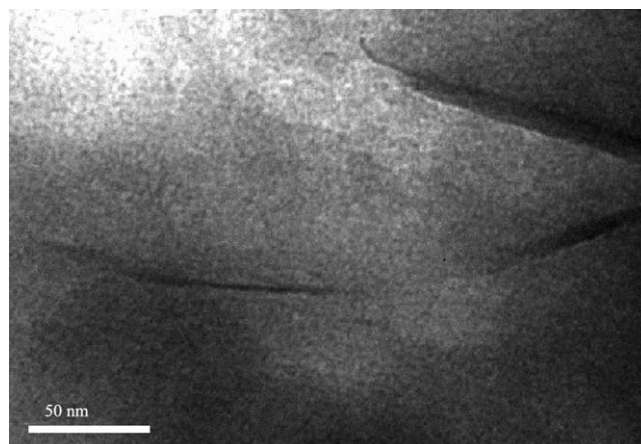


Figure 5 TEM of the polyethylene nanocomposite obtained using the 1/Cloisite 15A/MAO system.

Cloisite 15A/MAO. The parent PE had a total branch content of 132 branches/1000C (68 methyl branches, nine ethyl groups, five propyl groups, two butyl groups, 10 amyl groups, and 22 longer branches), whereas the nanocomposite with 2.5% clay only exhibited 42 branches/1000C (only methyl branches), in agreement with the infrared analyses.

The mechanical properties of the polyethylene nanocomposites obtained with both systems (1/TMA/KSF or 1/MAO/Cloisite 15A) were remarkably improved by the addition of clay.

Table I shows both the storage and Young's moduli, E' , and E^* , which were improved with increasing clay content. These variations improved the elasticity and plasticity of the polyethylene nanocomposites. These properties were expected as a natural consequence of the incorporation of exfoliated clay into the polyethylene matrix. As shown before, the nanolayers have a pronounced nucleation effect, increasing the crystallinity and leading to materials with enhanced mechanical strength.

The $\tan \delta$ curves of polyethylene and its nanocomposites, shown in Figure 4, are quite interesting. The β transition appears as a strong peak in $\tan \delta$ and is related to the presence of branching in the PE.²⁵ The presence of clay decreased the β peak intensity, and it even disappeared for samples with 2.5 wt % clay content. These mechanical damping results show that adding the clay decreased the branching formation.

The sample composite with the 2.5% clay content was analyzed by TEM.²⁶ As shown in Figure 5, nanolayers were formed between the dispersion state of the organic clay and the exfoliation of the layered silicate.

The presence of exfoliated clay dispersed throughout the polymeric matrix is in agreement with the explanation for the increase in the E' and E^* moduli (Table I). Therefore, it was concluded that the exfoliated nanocomposite can be formed by *in situ* polymerization using Ni-diimine combined with MAO when Cloisite 15A is present in the reaction medium.

All of the techniques described above showed that incorporation of the 1,4-bis(2,6-diisopropylphenyl)acenaphthenediimine-dichloro-nickel(II)(1) in Cloisite 15A and further activation with MAO created reactive sites that were active in ethylene polymerization, but that the product had lower degrees of branching than the homogeneous parent system. The explanation for this decrease in branching formation can be ascribed to the incorporation of the complexes inside the clay layers. Under such conditions, these active sites still polymerize ethylene, giving rise to exfoliation of the clay, but they decrease the chain walking process due to the steric hindrance during chain growth.

CONCLUSIONS

In summary, we have described an effective way of obtaining clay-polyethylene nanocomposites with enhanced thermal properties compared with pure polyethylene. We employed the method of *in situ* polymerization. This is an efficient strategy compared with those typical for nanocomposites in which the clays are added to a previously synthesized polymer. The catalyst system consisted of a nickel α -diimine complex combined with alkylaluminum (TMA or MAO), as the clay activator and cocatalyst, respectively. The polymerization activity and clay loading were adjusted by controlling the amount of clay added and the Al/Ni molar ratio. The TEM analysis provided direct evidence for exfoliation of the inorganic phase, promoted by polymer growth inside the clay platelets during the formation of polyethylene nanocomposites. Incorporation of montmorillonite as nanometric-scale elements inside the polymer matrix was correlated with the ramification rate, crystallinity and mechanical properties, suggesting the potential for enhanced reinforcement of these nanocomposites.

The incorporation of exfoliated clay in the polyethylene obtained by *in situ* catalytic polymerization provides materials with improved mechanical moduli, crystallinities and melting temperatures (T_c and T_m) in a technically attractive procedure for the fabrication of nanocomposites.

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