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POLYPROPYLENE/ORGANOPHILIC CLAY NANOCOMPOSITES USING METALLOCENE CATALYSTS THROUGH *IN SITU* POLYMERIZATION

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Abstract. The organophilic clays employed for the preparation of supported metallocene catalysts Viscogel B8, Claytone HY and Cloisite 15A were evaluated in propylene polymerization. These supports were chemically pre-treated with trimethylaluminium (TMA). The organoclays, as well as the prepared metallocene catalysts, were analyzed by X-ray diffractometry (XRD). The polymers were also characterized by XRD, infrared absorption spectrometry (FTIR) for the determination of the isotactic index, by thermogravimetric analysis (TGA) for the determination of degradation temperatures, by differential scanning calorimetry (DSC) to determine thermal characteristics of the produced polypropylene, and by transmission electron microscopy (TEM) to examine the morphology of the materials obtained. All materials produced with the catalysts supported on organoclays showed higher melting and crystallization temperatures than the polypropylene (PP) obtained from the homogeneous catalyst as well as high dispersion of nanolayers of clays in PP matrix, although the catalyst activities of the supported system were much lower than the homogeneous one.

Keywords: polypropylene, propylene polymerization, organophilic clays, supported metallocene catalysts, *in situ* polymerization.

1. Introduction

The use of metallocene catalysts in industrial processes of olefin polymerization is regarded as a revolutionary step in the history of polymers. The number of publications in the areas of synthesis and applications of metallocenes polyolefins has grown rapidly in recent decades. Compared to Ziegler-Natta catalysts, the metallocene systems exhibit high catalytic activities and stereospecificity. The polymers have obtained high structural uniformity and narrow molar mass distribution [1-3].

Polymerizations catalyzed by metallocene systems are conducted in the presence of large quantities of aluminoxane, compared to the transition metal compound, to achieve high activities. The major disadvantages of homogeneous catalysts are the need to use large quantities of solvents and the difficulty of controlling polymer morphology causing fouling in reactors. Therefore, the metallocene complex has to be heterogenized in appropriate supports, such as clays, and mesoporous materials, among others [4-8]. The supported metallocene catalysts can be used in modern production processes such as gas phase or bulk, which can use smaller quantities of aluminoxane as cocatalyst. Polymers obtained have in general high melting temperatures, high molar mass and greater stereoregularity compared with those synthesized with the homogeneous precursor system [1-3].

The improvement of the barrier properties, stiffness and module is expected by the addition of nanoparticles or nanoclays to polypropylene (PP) matrix. PP is a plastic of better performance/price relationship, for application in automotive and packaging sectors. The composite of polypropylene and clay is an effective way for the modification of PP to broaden its applications. The nanocomposites with exfoliated structures are desirable, but difficult to obtain due to the incompatibility of the hydrophobic polymer with clays, even the modified ones, to allow higher organophilicity. The use of surfactants like alkylammonium salts aims the improving compatibility between PP and clay; however, high processing temperatures needed to produce nanocomposites by melt intercalation not only accelerate the deterioration of PP due to the degradation of surfactant in such conditions, but also promote the re-stacking of silicate layers. The literature has shown the presence of clay layers cluster during the processing of these composites for the production of nanocomposites in the melting state [9].

The process of *in situ* polymerization has been suggested as the most efficient method for obtaining nanocomposites from a thermodynamic and experimental point of view compared to the method of mixing in solution or in the melting state [10].

The aim of the present work was to study the synthesis of polypropylene using an isospecific metallocene catalyst supported on different organoclays pre-treated with aluminum alkyl.

2. Experimental

2.1. Materials

All the reagents were manipulated under inert atmosphere of nitrogen using the Schlenk technique. Propylene and nitrogen were purified by sequential passage through columns containing 4 Å molecular sieves and copper catalyst to remove oxygen, carbon dioxide, and moisture. Toluene was refluxed over metallic sodium/benzophenone and was distilled under a nitrogen atmosphere prior to use. Methylaluminoxane (MAO) (10 wt % solution in toluene, obtained from Chemtura, Germany), Trimethylaluminium (TMA) (10 wt % solution in heptane, obtained from Crompton GmbH, Germany), $\text{SiMe}_2(2\text{-Me-Ind})_2\text{ZrCl}_2$ -dimethyl silyl *bis*-(2-methyl-indenyl) zirconium dichloride, from Crompton GmbH, Germany, were used without further purification. Commercial organoclays used as supports were: Claytone HY (dimethyl-benzyl-HT ammonium), purchased from Bentonit Uniao Nordeste, Brazil; Cloisite 15A (dimethyl-diHT ammonium), from Southern Clay, EUA (where HT = hydrogenated-tallow (~ 65 % C18; ~ 30 % C16; ~ 5 % C14)); and Viscogel B8 (trimethyl-octadecyl ammonium), from Bentec Rheol. Add., Italy. All organoclays were submitted to a thermal treatment at 333 K for 24 h.

2.2. Support Chemical Pretreatment

In a Schlenk bottle with about 2.5 g of dry clay, under atmosphere of nitrogen, a solution of TMA in toluene was slowly added (5 mmol Al/clay), remaining under magnetic stirring for 4 h at room temperature. Then, there were successive washes with toluene for the withdrawal of excess TMA.

2.3. Preparation of Supported Catalyst

Under atmosphere of nitrogen, a solution of catalyst $\text{SiMe}_2(2\text{-Me-Ind})_2\text{ZrCl}_2$ was prepared in toluene. This catalyst solution was put in contact with TMA pre-treated support. The concentration of metallocene was set at 0.05 mmol/g. In the case of homogeneous system the prepared solution of $\text{SiMe}_2(2\text{-Me-Ind})_2\text{ZrCl}_2$ in toluene was added directly in the reaction of polymerization as catalyses.

2.4. Polymerization

Heterogeneous propylene polymerization was carried out in a 1000 ml glass reactor. MAO was used as cocatalyst (Al/Zr = 1000). The reagents were added into the reactor in the following order: toluene, MAO solution, and propylene. After saturation of propylene (10^2 kPa) at 600 rpm, the suspension of the supported catalyst was injected into the reactor and the pressure of propylene was increased to $2 \cdot 10^2$ kPa, initiating polymerization. The reaction was interrupted after one hour and polymer was precipitated in solution of ethanol/HCl. After 24 h under magnetic stirring, polymer was filtrated, washed with NaHCO_3 solution and ethanol, and dried at 333 K to constant weight.

The homogeneous polymerization was also carried out in a similar way as the heterogeneous one. After charging the reactor with toluene, MAO solution and propylene, a solution of the catalyst in toluene was then injected into the reactor, starting the polymerization.

2.5. Support and Catalyst Characterization

The chemical characteristics of the organoclays and catalysts were evaluated through X-ray diffractometry (XRD). They were measured in the Rigaku - Miniflex model, working with a potential difference of the tube 30 kV and electrical current of 15 mA. The scan was made in the range of 2θ from 2 to 30° , with the goniometer speed of $0.05^\circ/\text{min}$. The radiation used was $\text{Cu}_{K\alpha}$ of $\lambda = 1.5418 \text{ \AA}$.

2.6. Polymer Characterization

Differential scanning calorimetric analyses (DSC) were used to determine the melting temperature and degree of crystallinity. The analyses were carried out in equipment TA series Q – model Q1000. The samples were heated in the temperature range from 313 to 473 K with heating rate of $10^\circ/\text{min}$. The material went through two heatings, the first one serves to erase the thermal history of the polymer synthesized. Then the sample was cooled to 233 K at the rate of $10^\circ/\text{min}$ with nitrogen flow and then again heated to $10^\circ/\text{min}$. The standard substance for calibration of DSC was the indium. The melting temperature and the melting enthalpy were calculated from the thermograms obtained at the second scan. The values of melting enthalpies were used to estimate the degree of crystallinity of each material using 209 J/g as the theoretical value of the ΔH_m of a completely crystalline polypropylene [11].

The infrared absorption spectroscopy (FTIR) technique was used for determining the stereospecificity of obtained polymers. Spectra were obtained with 50 scans, resolution of 4 cm^{-1} in the range between 4000 and 400 cm^{-1} .

The obtained polypropylenes were also characterized by X-ray diffractometry (XRD). The method and equipment were the same as for catalysts and organoclays analyses.

The degradation temperatures of polymers were analyzed by thermogravimetry (TGA). The analyses were carried out in equipment TA series Q – model Q500. The samples were heated in the temperature range from room to 973 K, in inert atmosphere, with heating rate of 10°/min.

Transmission electron microscopy (TEM) was carried out to examine the morphology of filler and its distribution in the polymer matrix. For the TEM analysis the sample was melted into a heating plate in a mold and then cooled to room temperature to form a body sample. This sample was cut with a ultramicrotome glass knife at the angle of 6° to room temperature. The cut thickness was about 70 nm. The cut was placed in a copper grade and was taken to the equipment.

3. Results and Discussion

3.1. X-ray Diffractometry Analysis (XRD)

The type of organophilic clays used in the preparation of the supported catalysts, the resulting propylene polymerization yields, and activities of the metallocene supported and homogeneous catalysts for the polymerization using MAO as cocatalyst are shown in Table 1. A very sharp drop in catalyst activities compared with the performance of the homogeneous catalyst was noticed for each of the supported systems evaluated in this study. Therefore, it should be noted that the clay contents in the end materials were high, above 18 wt %. These results eliminate the possibility of zirconocene sites lixiviation to the reaction

medium during the polymerization. In fact, TMA was used for modifying the organophilic clays before the impregnation with the zirconocene. This reaction would not affect the compatibility of the produced polymer with the clay.

In this case, it is expected that the reaction of excess of TMA with the hydroxyl groups on the clay layer surface would protect the metallocene against its deactivation with these groups. Therefore, our strategy for the fixation of the metallocene active sites takes the advantage of its cationic nature and we expect the direct exchanging of the zirconocene cations with those of the original clays. The very low activities observed in our systems could be explained in two ways. TMA has not achieved all the OH groups in the clay surface because of the high sterical hindrance due to the long chains of the ammonium cations in their galleries and the zirconocene has reacted with these groups and has deactivated. It is also possible that the metallocene complex was deactivated in the reaction with amine molecules coming from the clay ammonium salt.

Figs. 1-3 show diffractograms of clays, catalysts, and polypropylenes obtained in the heterogeneous reactions in toluene as reaction medium. The diffraction peaks for each organophilic clay in the range of angles lower than 10° are used as reference in research investigation of nanocomposites, by the displacement to lower angles or the decrease in their intensity. In the XR diffractograms of the clay and the catalyst prepared with this silicate, a peak can be found at 2 θ (approximately 21°). This peak represents the (110) reflection of the montmorillonite. The (hk0) plane characterizes the atomic arrangement in the plane that is parallel to the z-axis. This peak is therefore independent of the distance between silicate platelets, and its location can be used as a reference.

Through diffractograms of Fig. 1, it can be seen that the only peak characteristic of the interlayer spacing for Cloisite 15A which appeared in this analysis was the second order reflection d(002) at 2 θ = 7.5° and it has shifted to 2 θ = 6.1° in the produced polypropylene. This (002) reflection represents the half-length of the actual average distance between two silicate layers, whose interplanar distance was calculated to be around 2.9 nm. It can be also noticed the beginning of the d₀₀₁ peak with intensity below 2 θ =2.0°, indicating an intercalation of PP in the clay galleries or even a partial exfoliation of the clay in the PP matrix. The diffractogram of PP obtained with the homogeneous catalyst was also presented in Figure 1, which shows the diffractions at 2 θ = 13.9; 16.8; 18.4, and 21.8° corresponding respectively to the planes (110), (040), (130), and (111) of crystal ordering of α -phase isotactic polypropylene.

In Fig. 2, the diffractogram of Claytone HY also showed only the d(002) reflection which appeared at the same angle (2 θ = 7.6°) as Cloisite 15A. On the other hand, the catalyst prepared with this clay showed very broad reflections in the range of low angles with a displacement of

Table 1

Catalysts produced with different clays and the results of polymerization performed in toluene at 333 K and cocatalyzed by MAO

Clay	Catalyst	Yield, g	Catalyst activity, tonPP/molZr·h	*Clay content, wt %
Cloisite 15A	A	0.55	109	18
Claytone HY	B	0.22	44	46
Viscogel B8	C	0.45	91	22
-	Homo	71.48	14297	-

*theoretical clay content, considering the yield and the amount of catalyst added. Conditions of reaction: temperature = 333 K; $P_{propylene}$ = 2·10² kPa; stirring \cong 600 rpm; homogeneous polymerization = solution of catalyst metallocene/cocatalyst in 10 ml of toluene; heterogeneous polymerization = suspension of 100 mg of supported catalyst/cocatalyst in 10 ml of toluene; time of pre-contact = 15 min; reaction time = 60 min, [Al]/[Zr]_{MAO} = 1000; Homo = homogeneous

the $d(002)$ peak to lower angle ($2\theta = 6.4^\circ$), which means that the catalyst components were intercalated between the clay layers. As can also be seen in this figure, the polymer obtained with this catalyst practically does not present any characteristic peak of the clay, although the clay content was very high (46 wt %). The presence of the clay reference peak at around 21° in both the catalyst and the produced polymer is clearly seen. Therefore, it indicates that no microparticle was found in the sample. The polypropylene crystalline diffractions also appeared in PP/Clay nanocomposite, indicating that although the crystalline form of the matrix was still of α -crystal type, the diffraction peaks at 13.9° ; 16.8° ; 18.4° have decreased and that of 21.8° has broadened. This indicates that the presence of nanoclay made the crystal phase of the PP change, probably due to the interaction of clay layers with the macromolecular chains of PP, so that there was a compatibility of nanoclay particles with PP matrix, despite the organoclay modification with TMA. This material with very high amounts of clay is an especially interesting product since it could be used as a high-value masterbatch for further mixing with virgin polypropylene in a regular extruder to lower clay content for the production of PP nanocomposites.

In the diffractograms presented in Fig. 3, both (001) and (002) reflection peaks can be seen in the clay Viscogel B8 at $2\theta = 3.7^\circ$ and 7.2° , which corresponds to an interplanar distance of 2.3 nm between the clay platelets, although those peaks do not appear clearly in the diffractogram of the supported catalyst. In the synthesized polypropylene nanocomposite, the second order peak shifted towards lower angle, at around $2\theta = 6.0^\circ$ (2.5 nm), and also became very broad and with low intensity. This may occur particularly if the platelets show a significant distribution in layer distances, rather than a stronger, sharper peak due to repeated distances of the same length. This is an indication of intercalation of the clay in the PP matrix. It may also be noticed that the presence of the nanoclay has changed to some extent the crystal phase of the PP.

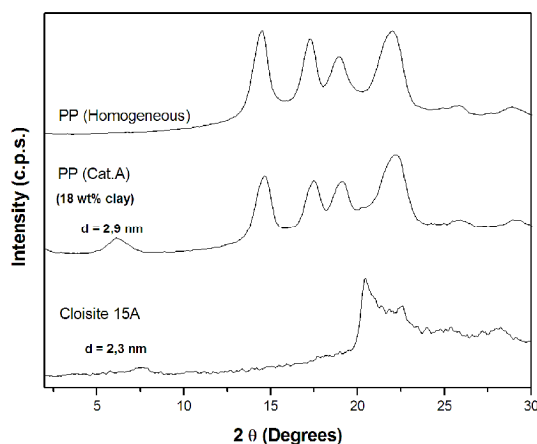


Fig. 1. Diffractograms of clay Cloisite 15A, catalyst A, and polypropylenes obtained with the catalyst supported on this clay and with the homogeneous catalyst

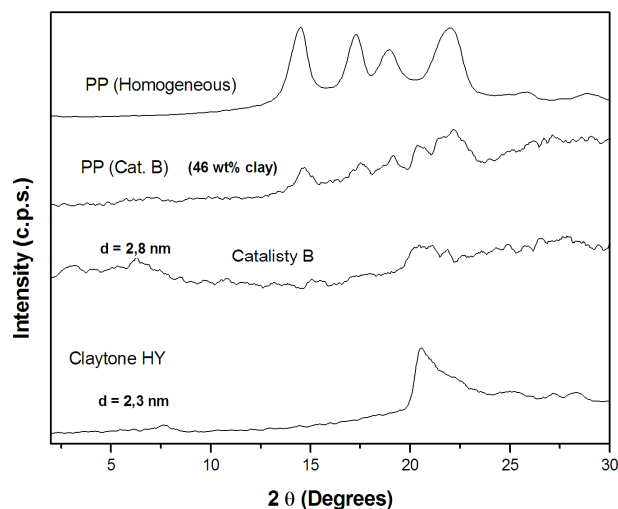


Fig. 2. Diffractograms of clay Claytone HY, catalyst B and the polypropylene obtained with clay supported catalyst and with the homogeneous system

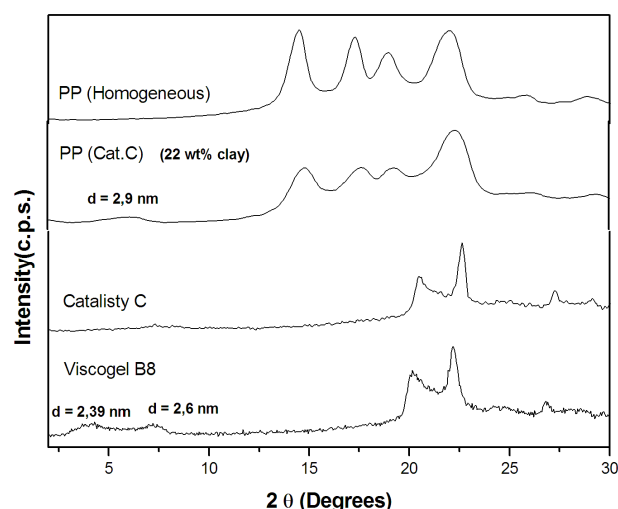


Fig. 3. Diffractograms of clay Viscogel B8, catalyst C, and polypropylene obtained with supported catalyst and homogeneous

3.2. Infrared Absorption Spectrometry (FTIR), Thermogravimetric (TGA) and Differential Scanning Calorimetry Analyses (DSC)

The results of thermogravimetric analyses of the employed clays as well as the absorption infrared spectrometry, differential scanning calorimetry, and TGA of the polypropylenes obtained in this work are shown in Table 2.

All polymers obtained by the supported metallocene systems showed higher crystalline melting temperatures (T_m) compared to that produced with the homogeneous catalyst, indicating the formation of thicker crystals

possibly due to lower density of stereo and region-errors. In fact, the polymers produced by the supported catalysts showed higher isotacticity index. The increase in the polymer stereoregularity can be explained by the

stabilization of the active sites fixed on the support and also by the hindrance caused by the support surface which allows higher control of stereo/region insertion of propylene in the polymer chain.

Table 2

Characteristics of the employed clays and polypropylenes obtained with the homogeneous catalyst $\text{SiMe}_2(2\text{-Me-Ind})_2\text{ZrCl}_2$ and supported on those clays

Clay				PP/Clay							
	T_{onset} , K	T_{max} , K	^b Residue, %	Cat	^a I.I., %	T_c , K	T_m , K	X_c %	T_{onset} , K	T_{max} , K	^b Residue, %
Cloisite 15A	497	539	60.9	A	100	382	412	34.2	571	653	10.5
Claytone HY	507	576	62.1	B	nd	385	414	30.9	622	642	47.7
Viscogel B8	524	604	65.9	C	100	391	418	34.3	633	672	9.5
-	-	-	-	Homo	77	379	411	32.0	606	657	0.2

Notes: nd – not defined; ^aisotactic index % of triads (mm %), obtained by FTIR; ^bafter heating up to 973 K; X_c = crystallinity degree; T_{onset} and T_{max} = degradation temperature; Homo = homogeneous

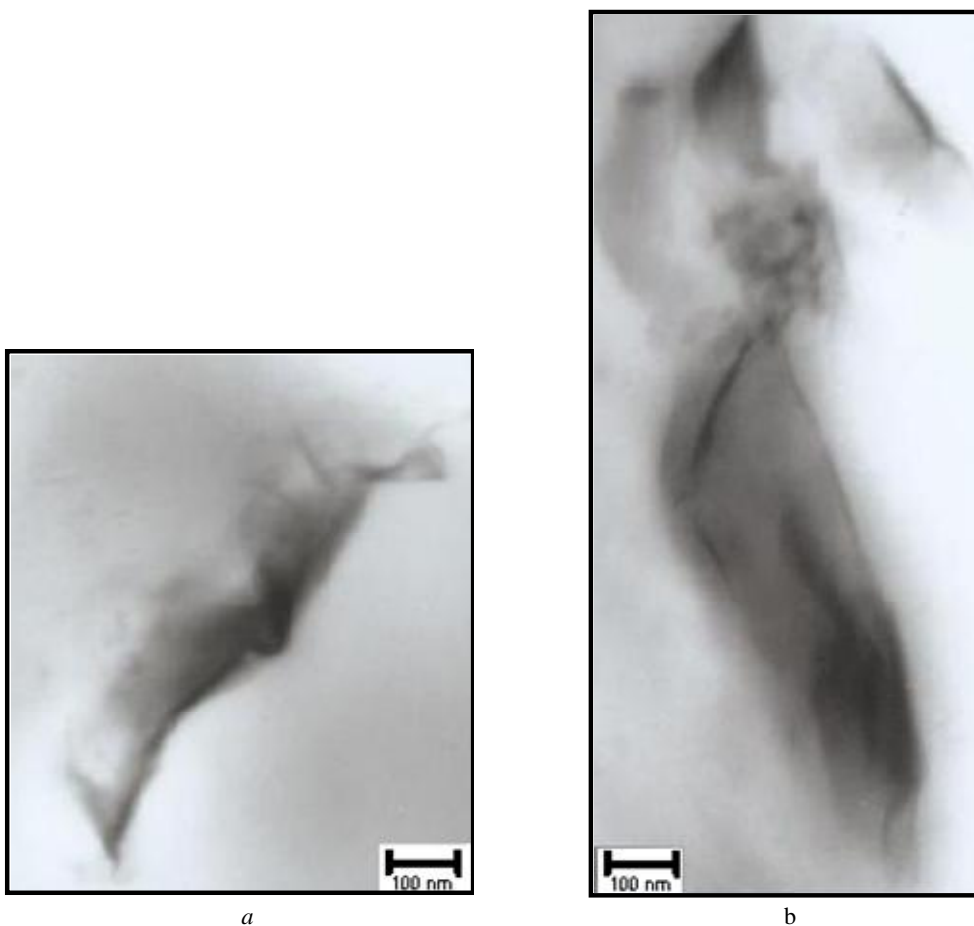


Fig. 4. TEM microographies of polypropylene nanocomposite synthesized with catalyst A in toluene. Magnification: x40000 (a) and x50000 (b)

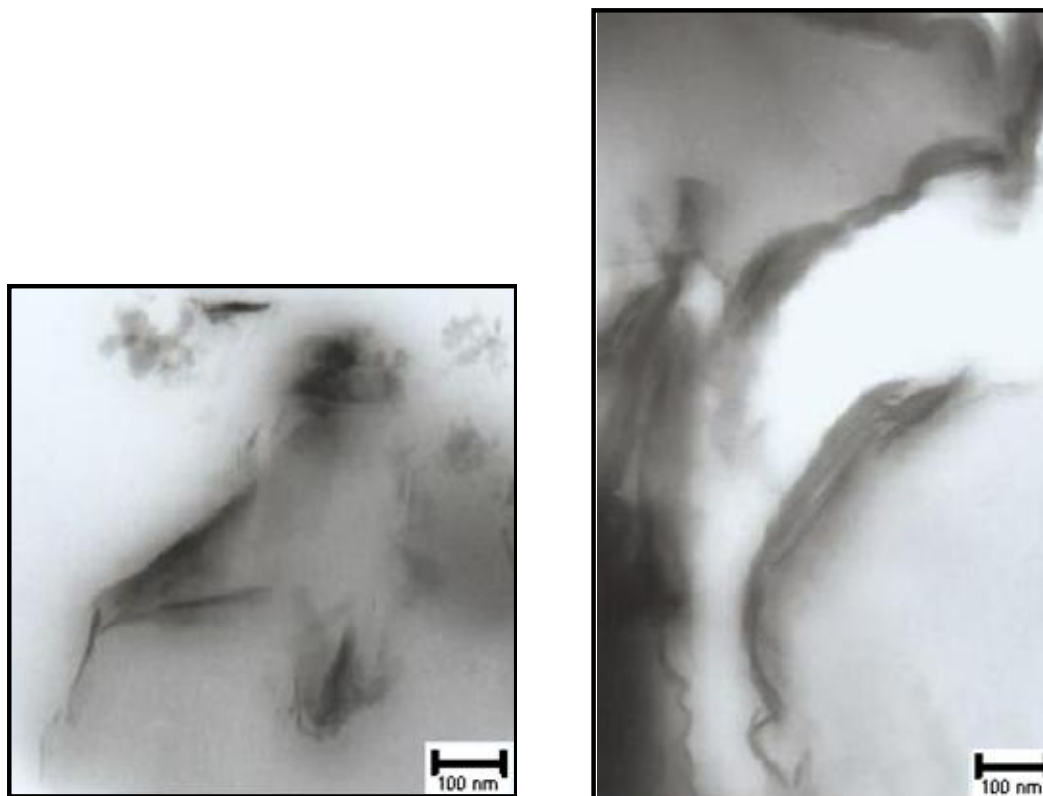


Fig. 5. TEM micrographies of polypropylene nanocomposite synthesized with catalyst supported on Claytone HY. Magnification: x50000

Similarly, the crystallization temperatures (T_c) have also increased in relation to the homogeneous PP, probably also due to a nucleation effect caused by the clay.

Regarding the TGA analysis, it can be seen that the lowest degradation temperature (T_{onset}) was observed for PP obtained with the catalyst supported on Cloisite 15A compared to the PP synthesized with the homogeneous system and this was probably due to the degradation of organic material contained in this clay. On the other hand, especially the nanocomposite PP/Viscogel B8 has increased T_{onset} and T_{max} , which may be due to both greater regularity of the PP material produced by supported catalysts and better dispersion of the clay in polypropylene matrix.

3.3. Transmission Electron Microscopy (TEM)

Figs. 4 and 5 show some micrographies of synthesized polypropylene nanocomposites obtained through transmission electron microscopy. In these micrographies the intercalated clay can be observed with possible exfoliated regions in polypropylene matrix synthesized with metallocene catalyst supported on clays Cloisite 15 A (Fig. 4) and Claytone HY (Fig. 5). No microparticle was found in the examined samples, although

the clay tactoids were not homogeneously distributed in the matrix.

In Fig. 5a it is interesting to observe how the clay opens into layers during the polymerization, when the polymer grows. The clay tactoids open building an angle and expelling some platelets with clay exfoliation.

4. Conclusions

The activities of the synthesis of polypropylene obtained with the metallocene catalysts supported on commercial organophilic clays were much lower than those of the homogeneous systems in polymerization of propylene to 333 K. Moreover, the X-ray diffractometry analyses of the supported catalysts apparently indicated an intercalation of the catalyst components in the clay galleries and the platelets show a significant distribution in interlayer distances. Through the XRD analyses of the synthesized polymers it was also observed that the obtained materials with the supported metallocene catalysts have intercalated nanocomposite morphology due to the displacement of the peaks corresponding to the interlayer distance typical of the clay to the values of 2θ below 2° . The crystallization (T_c)

and melting temperatures (T_m) of heterogeneous polymers were higher than those of the homogeneous ones. Analyses of transmission electron microscopy (TEM) of the polypropylene nanocomposites obtained by *in situ* polymerization with metallocene supported on clays showed the intercalation with possibly exfoliated regions of dispersed clay.

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ПОЛІПРОПІЛЕН/ОРГАНОФІЛЬНІ ГЛИНИСТІ НАНОКОМПОЗИТИ З ВИКОРИСТАННЯМ МЕТАЛЛОЦЕНОВИХ КАТАЛІЗАТОРІВ ПОЛІМЕРИЗАЦІЇ *IN SITU*

Анотація. Органофільні глини Viscogel B8, Claytone HY і Cloisite 15A використано для одержання металлоценових каталізаторів полімеризації пропілену. Попереднє оброблення носіїв проводилось триметилалюмінієм (ТМА). Аналіз органоглин, а також приготовлених металлоценових каталізаторів проводився методом рентгенівської дифракції (РД). За допомогою інфрачервоної абсорбційної спектроскопії визначено ізотактичний індекс полімерів; термогравіметричним аналізом – деградацію температур; диференціальною скануючою калориметрією – теплові характеристики виробництва поліпропілену; просвічуючою електронною мікроскопією – морфологію отриманих матеріалів. Всі продукти, одержані за участі каталізаторів на основі органоглин, характеризуються вищою температурою плавлення і кристалізації порівняно з поліпропіленом, отриманим на гомогенному каталізаторі, а також високою дисперсією наношарів глини в матриці поліпропілену, не зважаючи на нижчу активність каталізаторів на носіях у порівнянні з гомогенними.

Ключові слова: поліпропілен, полімеризація пропілену, органофільні глини, металлоценові каталізатори на носіях, полімеризація *in situ*.