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Synthesis of Poly(propylene)/Graphite Nanocomposites by *in Situ* Polymerization

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Summary: This work presents the synthesis of polypropylene/graphite nanocomposites by *in situ* polymerization using the catalytic system $C_{20}H_{16}Cl_2Zr$ (*rac*-ethylenebis (indenyl)zirconium(IV)) dichloride/Methyoluminoxane (MAO). 60 nm graphite nanosheets (GNS) were obtained by means of the chemical exfoliation, thermal and ultrasound treatment. GNS previously treated with MAO were added into the reactor at percentages of 0.3, 1.0 and 2.2% (w/w) in relation to nanocomposite yields. The morphology of graphite nanosheets and nanocomposites was studied by Scanning Electron Microscopy (SEM). Moreover, the structural properties of natural graphite flake (NGF), graphite nanosheets (GNS) and nanocomposites were observed through the X-Ray diffraction (XRD) analysis and by Transmission Electron Microscopy (TEM).

Keywords: graphite nanosheets; *in situ* polymerization; nanocomposites; poly(propylene)

Introduction

Nanocomposites are a new class of materials filled with dispersed particles in which one of the dimensions is in the nanometer range (1 - 100nm).[1] In recent years, inorganic fillers were dispersed in polymeric matrix to form nanocomposites with improved mechanical and barrier properties as well as electrical conductivity over the unmodified polymer.[2] Fillers such as clay, alumina, carbon nanotubes, silver, silica, and graphite nanosheets are used.[3]

Polypropylene (PP) is the most widely used thermoplastics due to their well-balanced physical and mechanical properties. In fact, PP has lower density in comparison to engineering thermoplastics, allowing potential weight reductions, very good heat resistance and, due to its high crystallinity, has excellent barrier properties.[4,5]

Graphite is found in the nature in the form of graphite flakes or powder of various particle sizes. Graphite flakes are composed by thin layers, normally smaller in thickness than 100 nm and each one is still subdivided in aggregates of graphene sheets.[3] The preparation of nanocomposites by direct intercalation can be very difficult due to the small distance of 3.35 Å between the graphene sheets. Therefore, the graphite is usually submitted to a chemical and physical modification.[6] The chemical treatment consists of intercalating different chemical species, called intercalating agents, followed by expansion by thermal shock which decomposes the intercalating agents and forces the graphite layers to separate randomly.[7,8] The use of an ultrasound bath transforms the expanded graphite into graphite nanosheets. The dispersion of these nanoparticles in commodity resins results in polymer/graphite nanocomposites.[9,10]

There are three different ways of introducing the graphite in the polymeric

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matrix to form composites or nanocomposites.[11] For instance, the filler can be treated with a polymer in blending solution, and then the solvent is evaporated to yield the filled polymer. They can also be prepared by melt mixing processes, in which molten polymer and the filler are mixed under the influence of shear forces, and by the *in situ* polymerization, in which the polymer is synthesized directly in the presence of the filler.[1,12,13] The first possibility is inappropriate for polypropylene because of the poor solubility in most organic solvents. In addition, a good dispersion of particles in polyolefin matrices can not be easily achieved by simple melt compounding, especially at high filler content.[10] The *in situ* polymerization approach results in a better dispersion of nanoparticles in the polymer matrix. The polymer grows between the nanoparticles avoiding a glomeration that it is usually the problem afforded by other methods.

There are several works in the literature related to the synthesis of polymer/graphite nanocomposites using *in situ* polymerization. However, only monomers such as aniline,[14] styrene[15] and methylmethacrylate[16] have been used so far. No reports on *in situ* polymerization with polypropylene/graphite have been published yet. Chen[17] developed a new process for the dispersion of graphite in the polymer matrix using *in situ* polymerization to produce polystyrene/graphite conducting nanocomposite. As a result, an electrically conducting polystyrene/graphite nanocomposite films with much lower percolation threshold and much higher conductivities than those of composites made by conventional methods was obtained.

The purpose of this paper is to present the synthesis of polypropylene/graphite nanocomposites by *in situ* polymerization, where the monomer is polymerized in the presence of different percentages (0.3 – 1.0 and 2.2 wt %) of graphite nanosheets, using catalytic system $C_{20}H_{16}Cl_2Zr$ (rac-ethylenebis (indenyll)zirconium(IV) dichloride/MAO.

Experimental Part

Materials

The graphite used for the preparation of graphite nanosheets in the present study was natural graphite flake (NGF) from Sigma Aldrich (332461). Concentrated sulfuric acid and concentrated nitric acid (Chemical Pure) from Chemical Company of Brazil (Vetec) were used as chemical intercalant and oxidizer to prepare expanded graphite. Toluene (Nuclear) was distilled with metallic sodium and benzophenone. Methylaluminoxane (MAO) (Witco, 5 wt.-% Al solution in toluene) and ($C_{20}H_{16}Cl_2Zr$) [*rac*-ethylenebis(indenyl)]-zirconium(IV) dichloride (Sigma – Aldrich) were used as received. All manipulations were performed under inert atmosphere (argon) using standard Schlenk techniques.

Intercalation of Graphite (IG)

A mixture of concentrated sulfuric acid and nitric acid (4:1, v/v) was mixed with NGF at room temperature. The reaction mixture was stirred continuously for 24 hours. After the reaction, intercalation within graphite sheets took place to form intercalated graphite compound. Then the acid-mixture was washed with enough distilled water until neutralization and was then dried in a furnace above 110 °C for 3 hours to remove any remaining water.

Expanded Graphite (EG)

The intercalated graphite compound was subject to a heat treatment temperature of 1000 °C for a period of 30 seconds. The rapid expansion gave expanded graphite particles.

Preparation the Graphite Nanosheets (GNS)

The expanded graphite was immersed in a 70% of ethanol solution and subjected to powdering in an ultrasound bath for 9 hours. The resulting dispersion was filtered and dried in a furnace at 110 °C for 3 hours, obtaining the graphite nanosheets (GNS).

Treatment of Graphite Nanosheets with MAO

The GNS were stirred with 15 wt.-% of MAO during 0.5 hours in toluene. The solvent was, then, eliminated under reduced pressure. A sample of GNS was treated with MAO during 24 hours and this was used to prepare PP/GNS 1%.

Polymerization in Situ

PP nanocomposites were prepared using a PARR reactor (100 mL PARR4843). Toluene was used as solvent, MAO as cocatalyst (Al/Zr = 1500) and $C_{20}H_{16}Cl_2Zr$ as catalyst (2.10^{-6} mol).[18] The reactions were done at 70 °C, using a propylene pressure of 2.8 bar during 30 minutes. The GNS previously treated with MAO, were added to the reactor as filler using variable amounts (0.3; 1.0 and 2.2% w/w in relation to nacomposites yields). The reaction was interrupted using acidified ethanol. The resultant polymer was filtered, washed abundantly with distilled water and dry until constant weight.

Characterization of the GNS and Nanocomposites

The morphologies of the graphite and the nanocomposites (PP/GNS) were investigated using Scanning Electron Microcopy (SEM). SEM was performed with a Phillips microscope, model XL30, operating at 20 kV. Samples of PP/graphite nanocomposite for SEM analysis were used as polymer particle surface. The samples were prepared by material deposition in an aluminum stub and gold metalized.

X-ray diffraction (XRD) measurements were taken on a diffractometer Shimadzu (XRD 7000) equipped with a Cu tube and a secondary monochromator, the goniometer used was Siemens D500 and the detector was the scintillator (NaI and Tl), was carried out in the continuous mode with a scan speed of 0.05°/16s, covering angles 2θ between 10 and 30°. The samples were analyzed in the powder form at room temperature.

The Transmission Electron Microscopy (TEM) images of graphite were obtained using a transmission electron microscope JEOL 2010 operated at 200 kV. The images of nanocomposites were obtained using a transmission electron microscope JEOL 1011 operated at 100 kV. All samples were prepared by deposition a solution drop in a grid of copper of 300 mesh covered with amorphous carbon.

Results and Discussion

Synthesis of the Nanocomposites

The nanocomposites were prepared by means of metallocene/MAO-catalyzed *in situ* polymerization of propylene in the presence of GNS. The GNS were impregnated with MAO before polymerization in order to deactivate polar groups on the graphite surface, resulting from the graphite oxidation with acid treatment, which might be detrimental to the catalyst. Table 1 shows the percentage of graphite in the nanocomposites calculated using the polymer yields and the graphite masses put in the reactor.

According to Table 1, when the GNS load increases, the nanocomposite catalytic activities have not changed significantly and

Table 1.
Amount of graphite in the nanocomposites and catalytic activity.

Graphite mass (g)	Theoretical Graphite percentage (%)	Polymer yield (g)	Graphite percentage calculated from the polymer yield (%)	Catalytic Activity (kgPol/molZr.h.bar)
0	–	8.7	–	3107
0.04	0.5	15.5	0.3	5536
0.08	1.0	8.7	1.0	3107
0.17	2.0	8.1	2.2	2893

even it increased with 0.04g of graphite content, showing that the GNS did not deactivate the metallocene.

Scanning Electron Microcopy (SEM)

The characterization of graphite nanosheets by SEM is shown in Figure 1. Figure 1-a shows an image of NGF with an extremely close flake layers with a smooth and uniform surface. The chemical treatment with acids (H_2SO_4/HNO_3) resulted in intercalated graphite. Indeed, Figure 1-b shows that, after the treatment, the flake is formed by multiple layers.

The expanded graphite (EG) is basically formed by the collapse of the parallel boards of the intercalated graphite, which deforms randomly, resulting in many pores of different sizes (Figure 1-c). Figure 1-d shows the SEM images obtained after exposing the expanded graphite to an ultrasound bath during 9 hours. This image reveals that thick flakes were decomposed in many thin lamellae with the thickness close to 60nm. It also confirms that individual graphite nanosheets are not single graphenes, but consist on several layers of graphite sheets, as it has already been observed.[19]

The properties of polymer nanocomposites strongly depend on the morphology.[20] Morphologic analysis of neat PP and nanocomposites (PP/GNS) were investigated by Scanning electron microscopy (SEM). Figure 2-a shows the morphology of homogenous polypropylene with uniform surface. Figure 2 (b-c-d), shows the morphology of the nanocomposites with 0.3, 1.0 and 2.2%(w/w) of GNS, respectively. The addition of the GNS in the polymeric matrix changed the morphology of the nanocomposites. Differently from

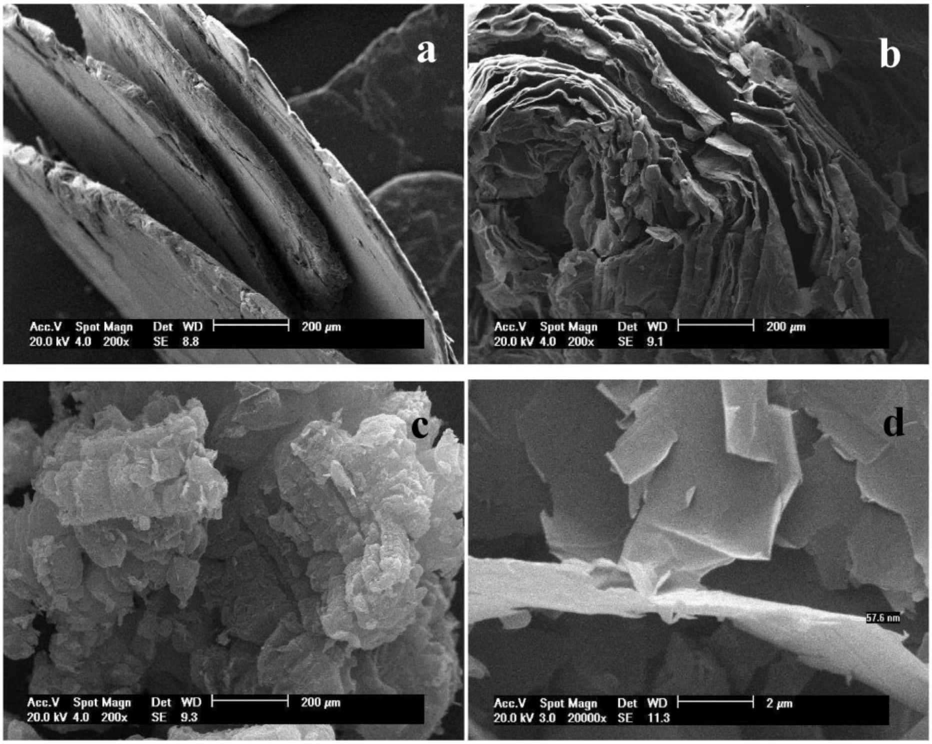

Figure 1.
SEM images: (a) natural graphite flake, (b) expanded graphite, (c) intercalated graphite, and (d) graphite nanosheets.

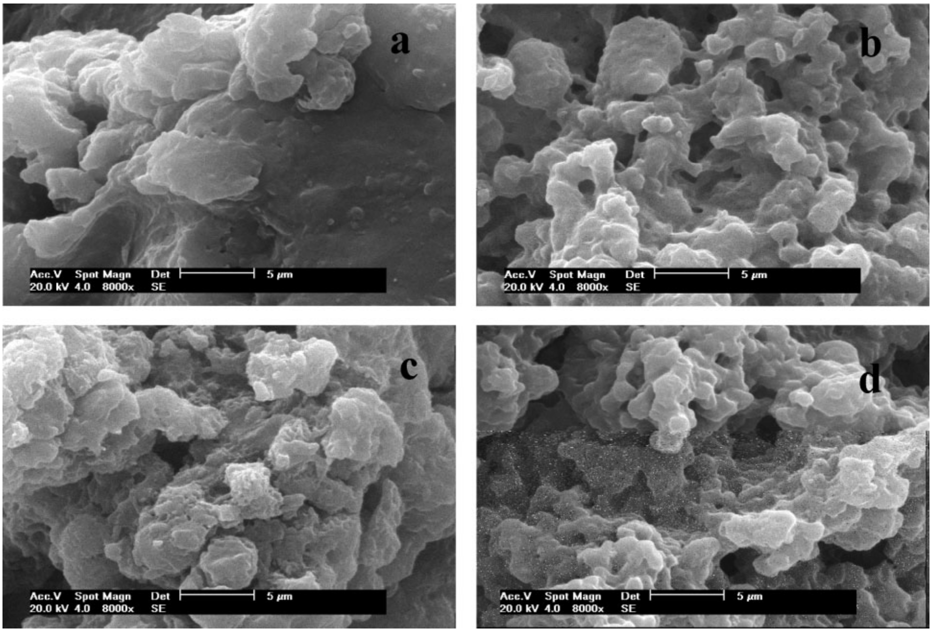

Figure 2.
SEM images with magnification of 8000 times. (a) Neat polypropylene, (b) PP/GNS 0.3%, (c) PP/GNS 1.0% and (d) PP/GNS 2.2%.

neat PP, the polypropylene grows around the GNS forming particles in the globule form.

The influence of time in the previous treatment of the nanosheetss with MAO was also investigated by SEM, and is shown in the micrographs of Figure 3. Two graphite nanosheets samples were treated for different periods, 0.5 and 24 hours with a MAO solution of 15wt% MAO/GNS. Figure 3-a shows that when the GNS were treated for a shorter period (0.5 hour) there is a better interaction of the nanoparticles with the polymeric matrix. Figure 3-b shows the formation of micro-cavitations probable due to the agglomeration of the nanofillers as consequence of a longer treatment (24 hours) with MAO that favored the sticking of the nanoparticles in the solution.

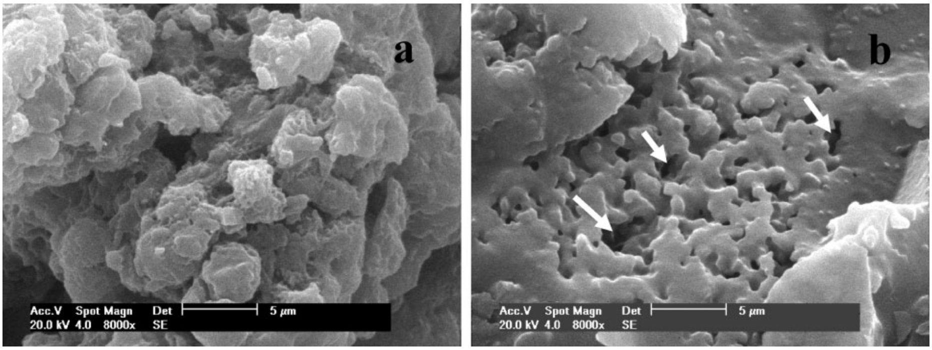

Figure 3.
SEM images of PP nanocomposites with magnification of 8000 times. (a) PP/1%GNS treated for 0.5 hour; (b) PP/1%GNS treated for 24 hours.

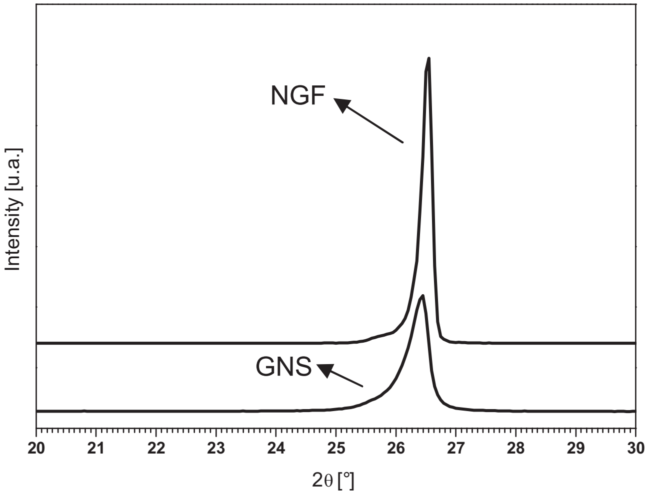

Figure 4.
XRD: NGF ($2\theta = 26.55^\circ$) and GNS ($2\theta = 26.45^\circ$).

X-ray Diffraction (XRD)
The structural properties of NGF and GNS were characterized using the XRD analysis, as shown in Figure 4. The strong peaks at $2\theta = 26.45^\circ$ and 26.55° are the results of the diffraction of the NGF and GNS (002) planes, respectively, and correspond to the typical d-spacing between the carbon layers in graphite. They indicate a highly organized crystal structure. Table 2 shows the interlayer distances (d_{002}) among graphenes and the crystal size (C) that were estimated by the Bragg's Law and by the Scherrer's Equation, respectively. The interlayer spacing was 0.335 nm for NGF and 0.337 for GNS, showing that the exfoliation increases the distance between graphenes as related by Kang. [21] Furthermore, the crystal size decrease and it can be explained considering that some graphite crystals were cracked during the exfoliation process decreasing the number of stacked graphene sheets.

Table 2.
Interlayer distances among graphenes and the crystal size of GNF and GNS.

Sample	2θ (°)	d $_{002}$(nm)	C (nm)
NGF	26.55	0.335	39.04
GNS	26.45	0.337	20.99

Figure 5 shows the high resolution Transmission Electron Microscopy (TEM) micrographs of the GNS. In Fig. 5-a, it can be observed parallel lines that are the cross-sections of the graphite layers. In Fig. 5-b the white arrows indicate a graphite nanosheets with 4.10 nm of thickness with more than 10 graphenes. The distance between the graphenes obtained using the TEM micrograph in Fig. 5-b, varies from 0.22 to 0.34 nm being the majority between 0.30 and 0.32, this data is in accordance to XRD results. Furthermore, the uniform distribution of the nanosheets confirms that the graphite layer structure is retained after high temperature expansion, as has also been showed by Zheng.[22]

Figure 6 shows the X-ray difractograms of neat polypropylene and of the nanocomposites with 0.3, 1.0 and 2.2% of GNS. Four peaks are observed in the XRD pattern of neat PP at $2\theta = 14$, 17, 18.5 and 22° that corresponds to the (110), (040), (130) and (041) planes, respectively.[23–25] This pattern is in accordance to the α-form crystals of isotactic polypropylene (iPP). The diffraction at 26.45° corresponds to plane (002) of GNS. In the nanocomposites with 0.3 and 1.0% of GNS this peak has a

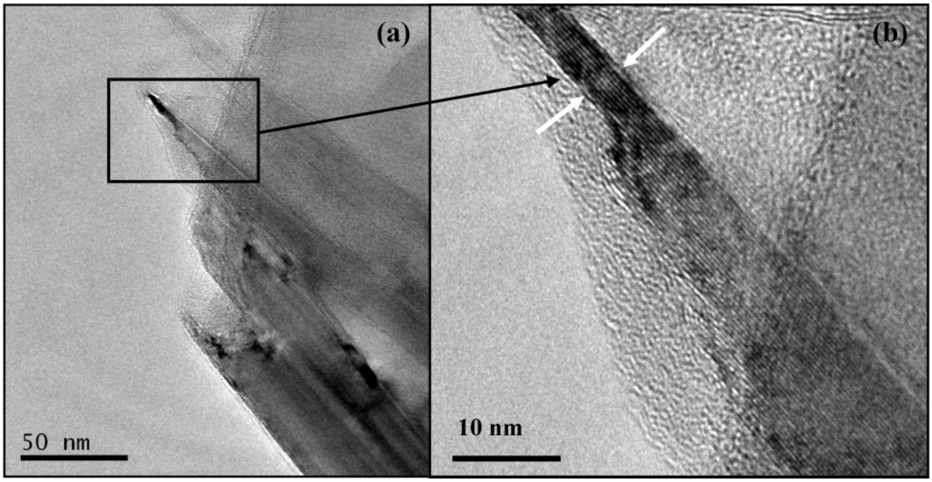

Figure 5.
TEM micrographics of the graphite nanosheets with uniform distribution of the nanosheets: (a) magnificationof 50 nm, (b) magnification of 10 nm.

very small intensity due to the small percentage of graphite compared to the amount of polymer, and also to the good exfoliation of graphite in the polypropylene matrix. Moreover, the intensity of the graphite peak increases when 2.2% of filler is added. This fact can related to the higher amount of nanoparticles added in polymeric matrix, making the homogenization and dispersion difficult.

The sample with 2.2% of GNS shows a peak at 26.45°, corresponding to the interlayer distance (d_{002}) of 0.336 nm and the crystal size (C) of 48.01 nm. The crystal size (C) of these nanocomposites with 2.2% GNS is higher in comparison to the graphite

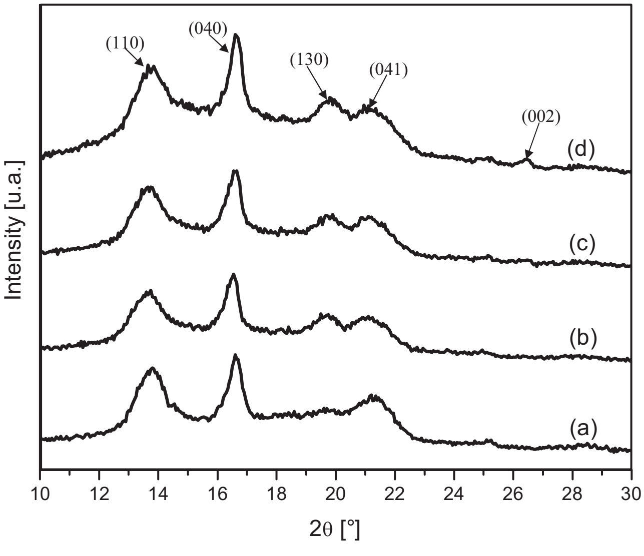

Figure 6.
XRD (a) Neat polypropylene, (b) PP/GNS 0.3%, (c) PP/GNS 1.0% and (d) PP/GNS 2.2%.

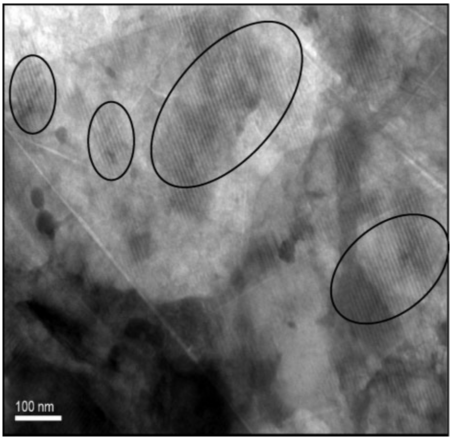

Figure 7.
TEM micrographics of nanocomposites PP/1.0% of GNS.

nanosheets. It is possible that the higher amount of graphite in these nanocomposites produces some GNS agglomeration increasing the number of graphene in each crystal. The nanocomposites with 0.3 and 1.0% of GNS have a better dispersion of the filler in the polymeric matrix compared to the sample with 2.2% of GNS. This indicates that smaller amount of graphite produces a better dispersion in the polymer matrix.

Figure 7 shows the TEM micrographics of polypropylene/graphite nanosheets nanocomposites. In this images it can be observed the graphite profile (black lines) dispersed in more than one direction, the graphite platelets seen from above (deformed black sheets) and the polypropylene between the GNS (white domains).[26] The distance between the graphene aggregates varied from 4.8 to 26.8 nm. We can conclude that the graphite that has been introduced in the form of graphite nanosheets has been further exfoliated by the polyethylene growing between them.

Conclusion

A process of *in situ* polymerization of propylene and GNS treated with methylaluminoxane was developed to form polymer nanocomposites. The SEM images of the graphite show that the graphite nanosheets are in nanometric dimension, and that the exfoliation methodology using ultrasound was satisfactory. The SEM images of the polymeric nanocomposites show a better interaction of the nanoparticles with the polymer matrix when the graphite was treated with MAO during 0.5 hour.

The interlayer distance among graphenes in the nanosheets is 0.337 nm and the crystal size is 20.99 nm (XDR). A good interaction of the graphite nanosheets with percentage of 0.3 and 1.0% in the polypropylene was observed in the difractograms of the nanocomposites. However, with 2.2% of GNS the homogenization and the dispersion in polymer matrix was found to be more difficult. XRD and TEM analysis of nanocomposites showed that the graphite was further exfoliated by the propylene polymerization giving graphite crystals with smaller number of graphene layers than the exfoliated graphite initially added.

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