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## POLYOLEFIN NANOCOMPOSITES BY *IN SITU* POLYMERIZATION

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**Abstract** - Polyethylene and polypropylene nanocomposites using graphene nanosheets and treated chrysotiles have been synthesized by *in situ* polymerization using metallocene catalysts. The fillers have been submitted to acid, thermal and/or ultrasound treatments before to introduce them into the polymerization reactor. A complete characterization of the fillers has been done. The nanocomposites have been characterized by SEM, TEM, DRX and AFM. The thermal, mechanic -dynamic, mechanical and electrical properties of the nanocomposites are discussed.

**Keywords:** *nanocomposites, polyolefins, in situ polymerization, graphene nanosheets, chrysotile.*

### Introduction

In recent years, great interest has emerged, both for research and industry in the area of nanotechnology. This area covers all sorts of technological development within the nanometer scale, usually less than 100 nm. The breakthrough in this field has been driven by the interdisciplinary fields of physics, chemistry, biology and computation.[1] The nanobiotechnology, the nano-systems and the nano-electronics are currently the biggest highlights in relation to nanotechnology, but the demand in nano-structured materials is growing, being the nanocomposites a significant share.[1,2] The polymeric nanocomposites are hybrid materials composed by an organic matrix and by inorganic nanoparticles.[3] Most of the nanocomposites exhibit better mechanical, thermal, optical and physicochemical properties than those of traditional composites. An example is the increase in modulus of elasticity, thermal stability, gas barrier and resistance to fire.[2,4] Recent studies in nanocomposites have involved fillers such as clays[5], carbon nanotubes[6], carbon nanofibers[7], silica[8], and graphite.[9-11] The main problem in obtaining nanocomposites is the homogeneous dispersion of the nanoparticles in the polymeric matrix. A good dispersion in the polymer is difficult to obtain by melt processing or mixture, that are the most used methods, due to the tendency of the nanoparticles to agglomerate. Other method of obtaining these nanocomposites is through *in situ* polymerization[12]. This method is very promising, because the nanoparticle is present during the polymerization, leading to a better dispersion of nanoparticles in the polymer matrix.[13]

Polyolefins are among the main polymers produced in the world due to their low cost, recyclability and versatility. On the other hand, polyolefins have properties that could be improved to broaden its applications, such as, barrier to gases, thermal stability and electrical conductivity. The improvement of these properties could be achieved with the addition of fillers into the polyolefin matrix.[14]

In this contribution we obtained polyolefin nanocomposites using graphene nanosheets and chrysotile as fillers. All the nanocomposites were obtained using *in situ* polymerization of the olefins with metallocenes as catalysts and methylaluminoxane (MAO) as cocatalyst.

Graphite is chemically similar to carbon nanotubes and structurally analogous to layered silicate and hence is a potential nanofiller to improve the properties of neat polymer.[15] Graphite combines the lower price and layered structure of clays with the superior thermal and electrical properties of carbon nanotubes and it can be an effective alternative to both. Graphite has been introduced into polyethylene or polypropylene to form composites or nanocomposites through fusion of the polymeric matrix[16,17] and intercalation in solution[18], however *in situ* polymerization has only been used to obtain composites[19]. In this work graphene nanosheets were obtained by ultrasonification of exfoliated graphite.

Chrysotile is a fibrous natural mineral belonging to the serpentine group. Its structure with formulation  $Mg_3Si_2O_5(OH)_4$  consists of two layers one tetrahedral of silica (tridymite) and another octahedral of magnesium hydroxide (brucite). These two layers are superimposed to form a fibril with a diameter of nanometric dimensions, comparable to the carbon nanotubes.[20,21] Chrysotile emerges here as a new proposal for use as nanoparticle due to its properties and characteristics such as flexibility, durability, incombustibility and mechanical resistance. In this work we treated chrysotile using two methods to reduce its toxicity and prepare it for use as nanofiller in olefin polymerization.[22] Chrysotile was first leached with hydrochloric acid (at either 0.1 or 3.0 M) then submitted to a thermal treatment. The surface treatment is important because a high concentration of hydroxyl groups on the chrysotile surface can deactivate the polymerization catalyst. Thus, the goal is to maintain the characteristics of nanoparticles of this valuable inorganic material and at the same time eliminate most of the vicinal hydroxyl groups on its surface.

The novelty and importance of this contribution is the use of commodity materials as fillers (graphite and chrysotile) in commodity polymers such as the polyolefins to increase the aggregate value of both materials by the method of adding the filler during the polymerization that has the potentiality to give better dispersions.

## Experimental

### *Preparation of the graphene nanosheets*

The intercalated graphite (GIC) was heated in air at 1000°C during 30s and it was obtained the expanded graphite (EG). The EG was suspended in ethanol 70% and the suspension was treated with an ultrasound bath during 8h, obtaining the graphene nanosheets (GNS). The GNS were stirred with 15 wt.-% of MAO during 30 min in toluene before the polymerization.

### *Preparation of the chrysotiles*

Raw chrysotile was treated by two methods: A) Chrysotile transformed in amorphous silica by treatment with HCl 3.0M [22] was weighed, suspended in toluene and added to an amount of MAO equivalent to 100-wt % of chrysotile. The suspension was stirred for 30 min, filtered through a sintered glass filter and washed with 5 aliquots of 10 mL of toluene. The chrysotile/MAO solid was dried under vacuum and stored in Schlenk under inert atmosphere. B) Chrysotile treated with HCl 0.1M [22] was weighed, suspended in toluene and added to an amount of MAO equivalent to 100-wt % of chrysotile. The suspension was stirred for 2h, then the catalyst in toluene was added and stirred for 1h. Chrysotile/MAO/catalyst were filtered on sintered glass filter, washed with twelve 2 mL aliquots of toluene, dried under vacuum and kept in Schlenk.

### *Preparation of the nanocomposites*

The polymerization reactions were carried in a 100 mL PARR reactor. Toluene was used as solvent, MAO as cocatalyst (Al/Zr=1000), Cp<sub>2</sub>ZrCl<sub>2</sub> as catalyst (2.10<sup>-6</sup> mol) for ethylene and Me<sub>2</sub>SiInd<sub>2</sub>ZrCl<sub>2</sub> as catalyst for propylene. The reactions were done at 40- 70°C, using an ethylene or propylene pressure of 1.6 or 2.8 bar during 30 min. The nanofiller was added after MAO treatment before the monomer and the catalyst.

### *Characterization of the fillers*

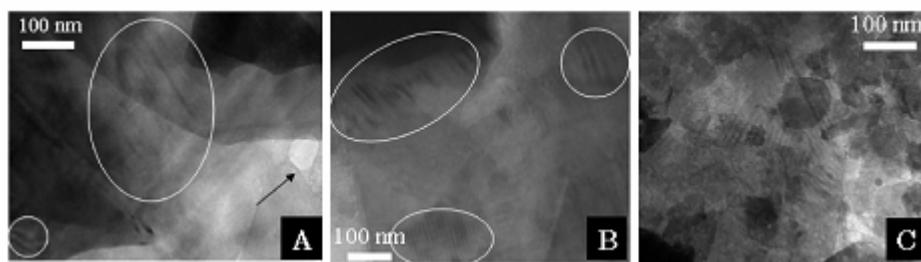
Graphene nanosheets and the treated chrysotiles were characterized by the following techniques: SEM-EDX, BET, DRX, TEM and DRIFTS;

### *Characterization of the nanocomposites*

The nanocomposites were characterized by TGA, DSC, SEM, TEM, DMTA and EIS.

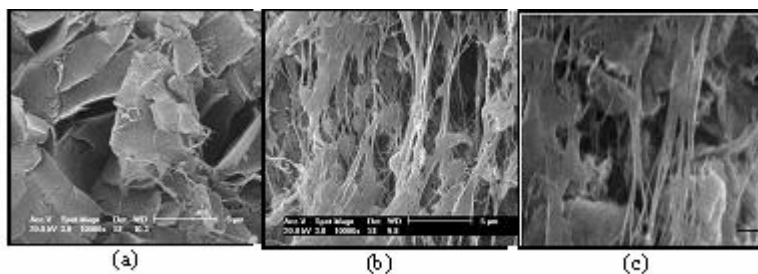
## **Results and Discussion**

Polyolefin/graphene nanosheets and polyolefin/chrysotile nanocomposites with nanofiller contents between 0.5 to 14 wt-% have been obtained with catalytic activities close to those obtained with the neat polymers. Graphene nanosheets introduced in the polymeric matrix were composed by about 10 graphenes and the graphene nanocomposites obtained showed the presence of regions where the graphite maintained an organized structure (intercalated graphite) and others where the graphene were more disorganized (exfoliated graphite), as it can be seen in Fig. 1.



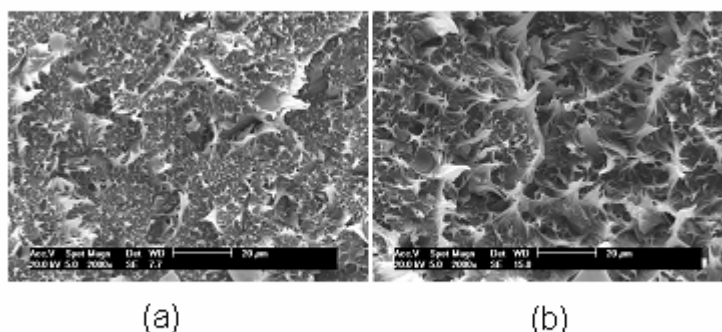
**Figure 1** – TEM micrographics of nanocomposites: PE/2.8%GNS (a and b), PE/5.6% Graphite (c)

The study of chrysotile/polyethylene nanocomposites by SEM showed that the nanocomposites have a fibrous morphology very different to neat polymer as it can be seen in Fig. 2.



**Figure 2** – SEM micrographics of: (a) Neat Polyethylene; (b) PE/3.6%chrysotile method A; PE/4.8% chrysotile method B.

On the other hand, polyethylene/GNS nanocomposites have a very different morphology due to the layered structure of graphite, as it is shown in the SEM images obtained from a tensile broken section (Fig. 3).

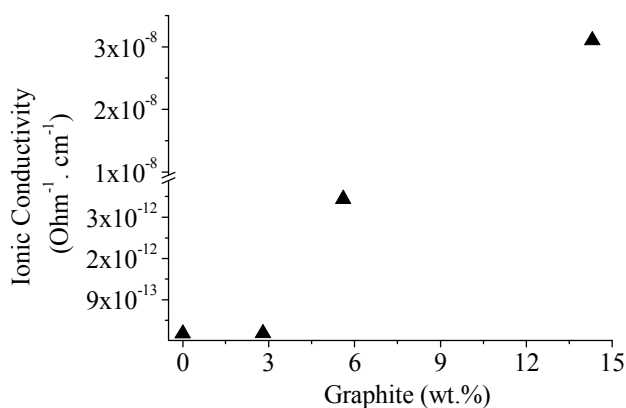


**Figure 3** – SEM micrographics of nanocomposites: (a) PE/2.8%Graphene nanosheets. (b) PE/5.6% Graphene nanosheets.

Thermal stability of all the nanocomposites was improved (30°C in the case of the nanocomposite with PE/GNS and 22°C with PE/chrysotile).

The storage modulus that is related with stiffness increased at -130°C about 240% for the PE/2.8%GNS nanocomposite, about 140% for the PP/5%GNS and 290 % for the PE/2.3% chrysotile (method A) compared with neat polyethylene.

Measurements of conductivity of PE/GNS nanocomposites made by electrochemical impedance spectroscopy showed an increase of over ten thousand times in the ionic conductivity of the nanocomposite with 14.3 wt.% of GNS, transforming the isolating polyethylene in a conductor material (Fig. 4)



**FIGURE 4** - Dependence of the Ionic Conductivity on variation of the GNS.

## Conclusion

Nanocomposites of polyethylene and polypropylene with different nanofillers were obtained. In general the nanocomposites were stiffer and thermal more stables than the original polymer. Depending on the filler they can have interesting properties such as conductivity when the original polymer was an insulator. The *in situ* polymerization is an interesting method of synthesis of this kind of material.

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