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Synthesis, characterization and properties of poly(propylene-1-octene)/graphite nanosheet nanocomposites obtained by *in situ* polymerization

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ABSTRACT

Poly(propylene-1-octene)/graphite nanosheet (PPC8/GNS) nanocomposites with different comonomer and graphite nanosheet (GNS) contents were synthesized by *in situ* polymerization using metallocene catalyst. There was a significant increase in the crystallization temperature of all the nanocomposites. Isothermal crystallization studies by optical microscopy confirmed that the GNSs act as nucleating agent increasing the crystallization rate in the nanocomposites. Transmission electron micrographs showed a good dispersion of the nanoparticles. Mechanical properties confirm the reinforcing effect that the nanoparticles confer to the polymer, especially increasing the modulus. Impedance measurements proved that the conductivity of the nanocomposites increase up to 11 orders of magnitude compared to neat polymers. The main novelty of this work is the control of the nanocomposite properties through the variation of the comonomer and the graphite nanosheets contents.

1. Introduction

The demand for materials containing graphite has been significantly increasing in recent years. Even more interesting is the use of graphene or graphite nanosheets (GNS or GNP), which have outstanding mechanical, electrical and barrier properties and are some of the most promising materials of the future [1,2]. The introduction of these particles into polymeric matrixes for the preparation of micro- or nanocomposites has shown great potential due to the improvements that these fillers are able to provide in the polymers [3–5].

An important feature that some studies with graphite or its derivatives and polyolefins have been reported is the increase in the crystallization temperature (T_c), which decreases the number of processing cycles [6]. In our recent work using *in situ* polymerization to obtain polyethylene/GNS nanocomposites, the crystallization temperature did not show a clear trend [7]; however, polypropylene/GNS nanocomposites had an increase in the T_c up to 10 °C depending on the amount of GNSs added to the reactor [8,9]. However, fillers normally produce polymers that exhibit low elongation and become more brittle in the presence of the nanoparticles. Depending on the matrix used, it may be interesting to prepare composites of copolymers, which are generally more flexible [10,11]. The preparation of nanocomposites with graphite or its derivatives and polyolefin copolymers by mixing the components in an extruder or in solution has been reported by some authors [12–16]. However, only a few works have used *in situ* polymerization to prepare nanocomposite copolymers with graphite or its derivatives, which can have an even better ability to disperse the nanofillers in the polymer matrix [17,18]. Most of these studies are related to polystyrene (PS) copolymers [19–21].

Recently, we were among the first groups to report the synthesis and full characterization of nanocomposites of polypropylene homopolymers with graphite nanosheets (GNS) by *in situ* polymerization using metallocene catalysts [8,9]. These studies showed a remarkable strengthening effect of the matrix with the incorporation of GNS through significant increase in Young's and storage modules, but the stiffness that the graphite nanosheets provided to the polypropylene matrix made those polymers too brittle. Thus, in this work we chose to synthesize PP copolymers, which should be

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more flexible than the homopolymer, even in the presence of a nanofiller, being the first study to synthesize nanocomposites of polyolefin copolymers with GNS by *in situ* polymerization. The purpose was also to study how the filler influences the catalytic activity of the system and the resulting polymer properties such as crystallization, degradation temperature, mechanical reinforcement and conductivity.

2. Experimental

2.1. Materials

Expanded graphite (Micrograf HC11) with platelet diameter of around 50 μm was provided by Nacional de Grafite Ltda. (Brazil) [22]. X-Ray diffraction, the transmission and scanning electron microcopies and the atomic force microscopy of the filler has been published in reference 7. GNS has a crystal size of 28 nm [7]. CHN showed an amount of C: 97.5% and O: 2.4%. Raman spectra is provided in the supplementary data.

Toluene and 1-octene were distilled with metallic sodium and benzophenone. Methylaluminoxane -MAO- (Chemtura, 5 wt.% Al solution in toluene) and the metallocene catalyst *rac*-$Me_2Si(Ind)_2ZrCl_2$ (Chemtura) were used as received.

2.2. Preparation of the graphite nanosheets (GNS)

The expanded graphite was suspended in 70% ethanol, and the suspension was treated with an ultrasound bath for 8 h. Then, the suspension was filtered, and the graphite nanosheets were dried at 120 °C for a period of 48 h [7].

2.3. Polymerization reactions

The polymerization reactions were performed at a controlled temperature (40 °C) using a 1000 mL Büchi glass reactor equipped with mechanical stirring. First, toluene as the solvent, MAO (Al/Zr = 1000) as the cocatalyst and 1-octene as the comonomer were added to the reactor. Afterwards, the reactor was fed with propylene, and the catalyst *rac*-$Me_2Si(Ind)_2ZrCl_2$ (5×10^{-6} mol) was added. The reactor was continuously fed with propylene to maintain a constant pressure of 2.8 bar during 0.5 h. In the polymerizations to obtain nanocomposites, graphite nanosheets were added to the reactor using variable amounts. The polymerizations were terminated by the addition of a 10 vol.% HCl in ethanol solution. The polymers were washed with water and dried until they maintained a constant weight.

2.4. Characterizations of polymers

The molecular weights were estimated using a Waters Alliance GPC 2000 instrument equipped with three Styragel HT-type columns (HT3, HT5, and HT6E). 1,2,4-Trichlorobenzene was used as the solvent with a flow rate of 1 mL min^{-1} and temperature of 135 °C. The polymeric microstructure was determined by ^{13}C NMR. The spectra were attained at 130 °C in a Varian Inova 300 operating at 75 MHz. Sample solutions of the polymers were prepared in *o*-dichlorobenzene and benzene-d_6 (20% v/v) in 5 mm sample tubes. The tacticity and percentage of incorporation of the comonomers were determined from the spectra [23,24]. Transmission electronic microscopy (TEM) images were achieved using a JEOL 1200 ExII transmission electron microscope operated at 100 kV. Samples were prepared from ultrathin films (~70 nm) cut under cryogenic conditions with a Leica Ultracut UCT microtome at −80 °C and placed on a copper grid of 300 meshes covered with amorphous carbon. For monitoring the crystallization, an optical microscope (Leica DMLM) was used with a coupled temperature-controlled stage (Linkam LTS350). The samples were placed between glass slides, melted above the melting point, quenched to the desired isothermal crystallization temperature, and examined under crossed polarizers to view the structure evolution. Film samples of polymers (around 350 μm) were obtained from the reactor powder by compression molding in a Collin press between hot plates (about 30 °C above T_m) at a pressure of 20 bar for 5 min. A fast quench (rate around 80 °C/min) between plates refrigerated with cold water was applied after melting in the press. Calorimetric analyses were carried out in a TA Instruments Q100 calorimeter calibrated with different standards, operating at a heating rate of 20 °C min^{-1} and in a temperature range from 25 to 160 °C. The melting temperature, T_m, was determined in the second scan, and the degree of crystallinity was calculated from the enthalpy of fusion data obtained from the DSC curves (162 J g^{-1} was used for a 100% crystalline material [25]). For nanocomposites analysis the mass content of graphite was discounted. Thermogravimetric analysis (TGA) was performed on an SDT Q600 thermal analyzer Q20 (TA Instruments) at a scanning rate of 20 °C min^{-1} within a temperature range from 25 to 1000 °C. The tensile properties were evaluated in an Instron model 3366 dynamometer with a 100 N load cell. Dumbbell-shaped samples with an effective thickness of 0.3 mm, a gauge length of 15 mm and a width of 2 mm were cut from those compression-molded sheets. The samples were tested at a rate of 10 mm min^{-1} at room temperature. Each set of measurements was repeated five times. Viscoelastic properties were measured in a Polymer Laboratories MK II dynamic mechanical thermal analyzer working in a tensile mode. The complex modulus and the loss tangent for each sample were determined at 1, 3, 10 and 30 Hz over a temperature range from −140 to 150 °C, at a heating rate of 1.5 °C/min. A Vickers indentor attached to a Leitz microhardness (MH) tester was used to carry out microindentation measurements. Experiments were undertaken at 25 °C. A contact load of 0.98 N and a contact time of 25 s were employed. MH values (in MPa) were calculated according to the relationship: $MH = 2 \sin 68° \, P/d^2$, where P (in N) is the contact load and d (in mm) is the diagonal length of the projected indentation area. Electrical conductivity of the nanocomposites was obtained by impedance measurements. The experiments were performed Novocontrol broadband dielectric spectrometer (Hundsagen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface in the frequency range $10^{-2} - 10^7$ Hz The electrodes used were gold disks of 10 mm of diameter. The temperature was controlled by a nitrogen jet (QUATRO from Novocontrol) with a temperature error of 0.1 K during every single sweep in frequency. Thus, the electrical conductivity of the polymeric film could be calculated by the following equation: $\sigma = 1/Rb \, (d/S)$. Where σ is the electrical conductivity, d is the film thickness, S is the area of electrodes contacting the polymeric film and Rb the bulk resistance.

3. Results and discussion

3.1. Synthesis of the PPC8 matrix

1-Octene comonomer was chosen to be inserted in the polypropylene chain with the aim of obtaining a polymer with long branches that would decrease the crystalline organization of the chains. As the final objective of the copolymerization was to obtain a more flexible polypropylene than the PP homopolymer, but with good mechanical properties, we used small amounts of 1-octene because the comonomer normally decreases the molecular weights and the Young's modulus of the polymers.

Three copolymers with different amounts of comonomers were synthesized and characterized by GPC, ^{13}C NMR and DSC (Table 1).