Research Article

Polypropylene Nanocomposites Obtained by *In Situ* Polymerization Using Metallocene Catalyst: Influence of the Nanoparticles on the Final Polymer Morphology

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Polypropylene nanocomposites containing silica nanospheres based on the sol-gel methods were produced via *in situ* polymerization using a rac-Et(Ind)$_2$ZrCl$_2$/methylaluminoxane (MAO) system. Two different routes were used depending on the interaction between the silica nanoparticles with the catalytic system. In route 1 the nanoparticles were added together with the catalytic system (rac-Et(Ind)$_2$ZrCl$_2$)/(MAO) directly into the reactor, and in route 2 the metallocene rac-Et(Ind)$_2$ZrCl$_2$ was supported on silica nanospheres pretreated with (MAO). SEM images show that when the nanospheres were added by both routes, they were replicated in the final polymer particle morphology; this phenomenon was more pronounced for PP obtained by route 2. The polypropylene (PP) nanocomposites obtained by both routes had a slightly higher percent crystallinities and crystallinity temperatures than pure PP. Transmission electron microscopy (TEM) images show that the nanospheres were well dispersed into the polypropylene matrix, particularly in the nanocomposites obtained by the support system (route 2).

1. Introduction

Metallocene-based catalysts offer versatility and flexibility for the synthesis of polyolefins with control of their structure [1, 2]. These catalysts activated by methylaluminoxane (MAO) have become an important class of catalytic systems for olefin polymerization, obtaining high activities and narrow molecular mass distributions [3–8]. However the homogeneous metallocenic systems present some disadvantages such as difficult control of polymer particle morphology that results in reactor fouling. One way to overcome these problems has been the effective immobilization of metallocene catalysts on inorganic or organic materials [9]. Fink [10] reported that the objective of supporting a catalyst is to immobilize and template it in order to get good polymer morphology in a low-temperature heterogeneous process.

The nature of the support and the method used for supporting the metallocene influence the catalytic activity, the final properties of the polymer, and especially the polymer particle morphology and molecular weight distribution [11–16]. The morphology of polypropylene particles of systems supported on microsilica has been widely studied, and it depends strongly on the form of the SiO$_2$ support used [10, 17, 18]. But there are few reports in the literature in which the final polypropylene particle morphology is studied with the incorporations of nanoparticles [19–21].

The incorporation on nanoparticles in the polymerization reactions has the advantage that the nanoparticles can be distributed in the polymer generating a polymer nanocomposite by *in situ* polymerization [22]. Two methods can be used to obtain the *in situ* nanocomposite. The first route consists in the direct synthesis of the PP in the presence

of the nanoparticles, with the nanoparticles placed in contact with the catalytic system (metallocene catalyst/MAO) [23]. The second route is the previous fixation of the catalytic system on the surface of the nanoparticle acting as support [24, 25]. Some advantages of both routes in comparison with other methodologies for nanocomposites preparations are (1) one-step synthesis of the polymer nanocomposite; (2) improved compatibility between the inorganic particles and the polymer; (3) enhanced dispersity of the particles in the polymer matrix [13].

It is well known that nanotechnology is widely considered as a major area that will undergo great technological progress in the future. In materials category as polymer nanocomposites, it is regarded as a radical alternative to conventional filled polymers or polymer blends, and new classes of materials will be available with improved properties.

Our group have prepared PE/silica nanocomposites by *in situ* polymerization by routes 1 and 2 using ((nBuCp)$_2$ ZrCl$_2$)/MAO) as catalytic system [23–25]. Incorporation of the nanoparticles in the PE by routes 1 and 2 improved the final polymer particle morphology of the PE, particularly when the polymer was obtained by a support system (route 2), where the polymer particles are platelet-like with a size of ~200 nm.

Although different aspects of the preparation of PP nanocomposites by *in situ* polymerization method have been studied, less emphasis has been placed on the final polymer particle morphology. In this work we studied the preparation of silica nanospheres (SN)/polypropylene (PP) nanocomposites by the *in situ* polymerization method using two routes: in route 1 the nanoparticles were added together with the catalytic system (rac-Et(Ind)$_2$ZrCl$_2$)/(MAO) directly into the reactor, and in the route 2 the metallocene rac-Et(Ind)$_2$ZrCl$_2$ was supported on silica nanospheres pretreated with (MAO). The effect of these different preparation procedures on the final polymer properties, the dispersion of nanoparticles in the PP, and on polymer particle morphology was studied.

2. Experimental

2.1. Materials. The metallocene catalyst, rac-ethylenebis (indenyl) zirconium (rac-Et(Ind)$_2$ZrCl$_2$) (Aldrich) was used as the propene polymerization catalyst, and MAO (Witco) as cocatalyst. Propylene was deoxygenated and dried by passage through columns of Cu catalyst (BASF) and activated molecular sieves (13X), respectively. All manipulations were carried out in an inert nitrogen atmosphere using standard Schlenk techniques.

Silica nanospheres (SN) were synthesized using the sol-gel method as reported previously [24].

2.2. Metallocene Catalyst Supported on MAO-Treated Silica Nanospheres (Cat/MAO/SN). The nanoparticles were calcined for 4 h at 450°C in order to control the OH groups on the silica surface. One gram of nanospheres was placed in contact with 4 wt% MAO (0.88 mL) and then contacted with metallocene (rac-Et(Ind)$_2$ZrCl$_2$) in toluene for 3 h at 60°C. This method has been reported previously [16].

2.3. Propene Polymerization Reactions

2.3.1. Homogeneous Polymerization. Polymerization reactions were performed in a slurry system using a 1 L Büchi glass reactor. Toluene, MAO, and propene were added to the reactor, followed by the addition of metallocene catalysts. For each experiment 1.2×10^{-5} mol of metallocene catalyst and 10.4 mL of MAO ([Al]/[Zr] = 1000) were used. The final volume of the solution in the reactor was 500 mL. The polymerization reaction was carried out at 60°C and 2 bar propene for 30 min, while stirring at 1000 rpm.

The polymerization was terminated by the addition of acidified methanol (10% HCl, 20 mL). The polypropylene product was recovered by filtration, washed, and then dried at room temperature. Catalytic activity was expressed as the mass of polypropylene (PP) produced per unit time per mol of Zr and per-unit pressure (kg·mol^{-1}·bar^{-1}·h^{-1}).

2.3.2. Polymerization in the Presence of SN (Route 1). Polymerization in the presence of SN was carried out using the same reaction conditions as those used in the homogeneous polymerization (neat). The polymerization was performed by first adding toluene, then MAO solution, and the SN (dispersed in toluene) into the reactor and mixing for 2 min. The SN were precontacted with MAO in the reactor to decrease the population of catalyst-deactivating OH groups on the silica surface. The catalyst solution was then added and mixed for 2 min and finally saturated with propene. 2 wt% loads of nanospheres were used.

2.3.3. Polymerization on Silica Nanosphere-Supported Metallocene Catalyst (Route 2). Metallocene catalyst supported on MAO-treated silica nanospheres (Cat/MAO/SN) was used for heterogeneous polymerizations. It was used under the same conditions and according to the procedure described above. Heterogeneous polymerizations were carried out by first adding toluene and 10.4 mL MAO to the reactor, followed by the silica nanosphere-supported catalyst (Cat/MAO/SN), mixing for 5 min, and finally saturating with propene for 30 minutes.

2.4. Characterization. Al and Zr content in the supported catalyst was measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) on a Perkin Elmer P-400 instrument.

The viscosimeter molecular weight (Mv) was calculated from intrinsic viscosities determined in decahydronaphthalene (decaline) at 135°C using a Viscosimatic-Sofica viscometer. The Mv values were obtained from the Mark-Kuhn-Houwink equations.

The melting temperature and enthalpy of fusion of the neat and nanocomposite PP samples were measured by differential scanning calorimetry (DSC) on a TA Instruments DSC 2920. Percent crystallinity of the polymer was calculated using the enthalpy of fusion of an ideal polypropylene having 100% crystallinity (207 J/g) as reference [26].

TABLE 1: Results of propene polymerization in the presence of SN used as support of the metallocene catalyst.

Process	Zr (%) (fixed)	Mv (Kg·Mol^{-1})	Tm (°C)	Tc (°C)	χ (%)	ρ (g/cm^3)	m^a (%)	SN content (%)
Pure PP	—	16	125	92	31	0.25	92	—
Route 1	—	16	126	95	33	0.28	91	2.0
Route 2 Cat/MAO/SN	0.45	12	126	97	34	0.30	91	2.0

Mv: Molecular Weight; Tm: Melting temperature, χ: Crystallinity percentage, ρ: Apparent density, Polymerization conditions: mol Zr: 1.2×10^{-5}; Al/Zr: 1000; polymerization temperature: 60°C, Pressure: 2 bar. m: The percentage of dyads, [a]Determined by ^{13}C-NMR.

Tacticity was determined by ^{13}C nuclear magnetic resonance spectra (^{13}CNMR) recorded on a Varian Inova 300 instrument operating at 75 MHz.

Polymer apparent density was measurement in a test tube by measuring a given volume of the polymer and then weighing it.

Polymer particle morphology was examined by scanning electron microscopy (SEM) on a Tesla BS 343A SEM instrument. The dispersion of the silica nanospheres in the composites was analyzed by TEM on a JEOL 1011 microscope operated at 100 Kv.

3. Results and Discussion

The SiO$_2$ nanoparticles synthesized by the sol-gel method presented spherical morphology with diameters of ca. 80–100 nm observed by TEM, as reported in previous work [24, 27].

The PP properties obtained by the homogeneous system (pure PP), routes 1 and 2, are shown in Table 1. The molecular weight of the PP obtained by route 1 did not show any change; however the PP obtained by the heterogeneous system (route 2) decreased by 25% in comparison with the pure PP. The decrease of the molecular weight can be due either an increasing of chain transfer [28] or a decreasing of the chain propagation rate. When support systems are used for propene polymerization, during the prepolymerization stage the polymer form a regular thin layer around the particles, give a diffusion limitation of the monomer to the particle surface resulting in a decrease of the molecular weight [10].

The metallocene (rac-Et(Ind)$_2$ZrCl$_2$) has C$_2$ symmetry with homotopic sites; isotactic polypropylene can be obtained. The tacticity of polypropylene was calculated by ^{13}C NMR and the percentage of dyads (m) is also presented in Table 1. All the polymers were isotactic (m = 92%) and the stereoregularity is not affected by the presence of the nanospheres. The (rac-Et(Ind)$_2$ZrCl$_2$) metallocene is characteristic of a number of small irregular peaks in the polymer as chain based on 2,1 and 1,2 insertions of polypropylene monomer [29].

3.1. Characterization of the Nanocomposite Polymers. The polymers obtained by routes 1 and 2 presented a slight increase in crystallinity and crystallization temperature compared with pure PP (Table 1). The increase in crystallization
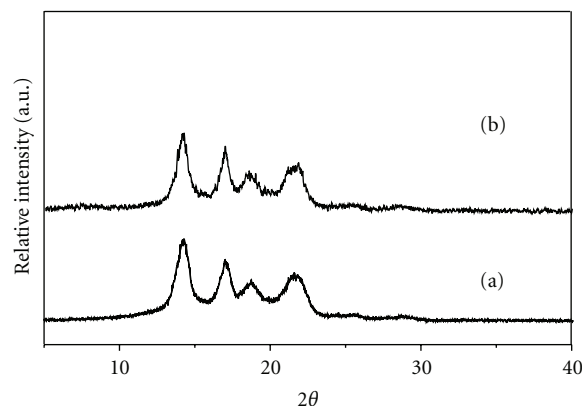

FIGURE 1: XRD patterns of (a) Pure PP and (b) PP obtained by route 2 (PP/Cat/MAO/SN).

temperatures in the presence of the nanospheres is an expression of the nucleating effect of SN [30–32].

The melting temperature of the PP obtained by both routes is comparable with that of pure PP. The apparent density of the heterogeneous system (route 2) is slightly higher than pure PP, showing a positive effect for using nanospheres as support (route 2); it can be related with the increase of the percent crystallinity.

Figure 1 shows the XRD patterns of pure PP and PP obtained by route 2. The use of the support system did not show a change in the crystalline monoclinic α form of PP, as shown by diffractions peaks at 2θ = 14, 16.9, 18.6, and 21.7°, corresponding to the (110), (040), (130), and (111) crystal planes of isotactic PP [33]. The same results were found for PP obtained by route 1.

3.2. Polymer Particle Morphology and Dispersion. Figure 2 shows the SEM images of pure PP and PP obtained by routes 1 and 2. Pure PP shows aggregated particles without morphological control, but when PP was made by routes 1 and 2 there was a replicating phenomenon, with some polymer particles showing a spherical morphology of about 5 μm of diameter. This behavior was more pronounced when nanospheres were obtained by route 2. The polymer particle morphology produced by the nanosupport system had a behavior similar to microsilica particles used as support, in which the replication phenomenon takes place. Fink et al. [10] and Zheng et al. [34] suggested that the morphology
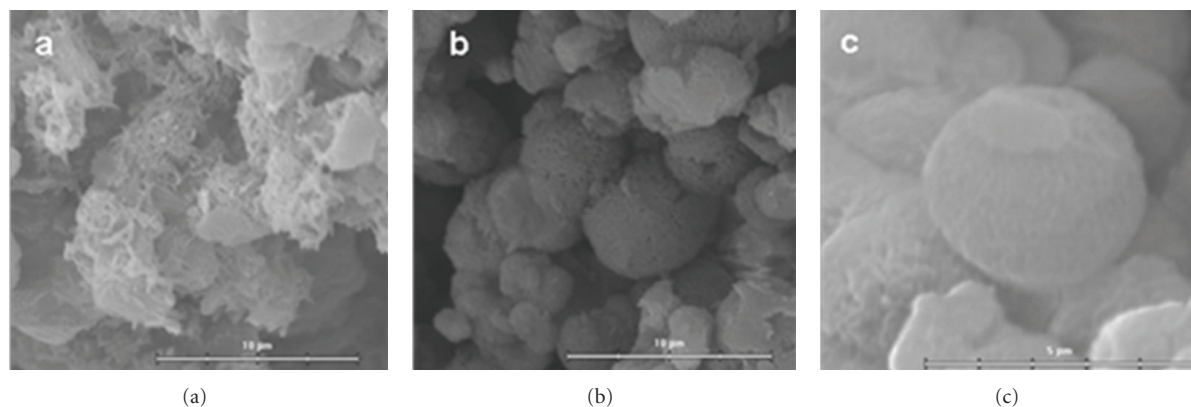
(a)   (b)   (c)

FIGURE 2: SEM image of the (a) Pure PP, (b) PP obtained by route 1 and (c) PP obtained by route 2 (PP/Cat/MAO/SN).

(a)   (b)
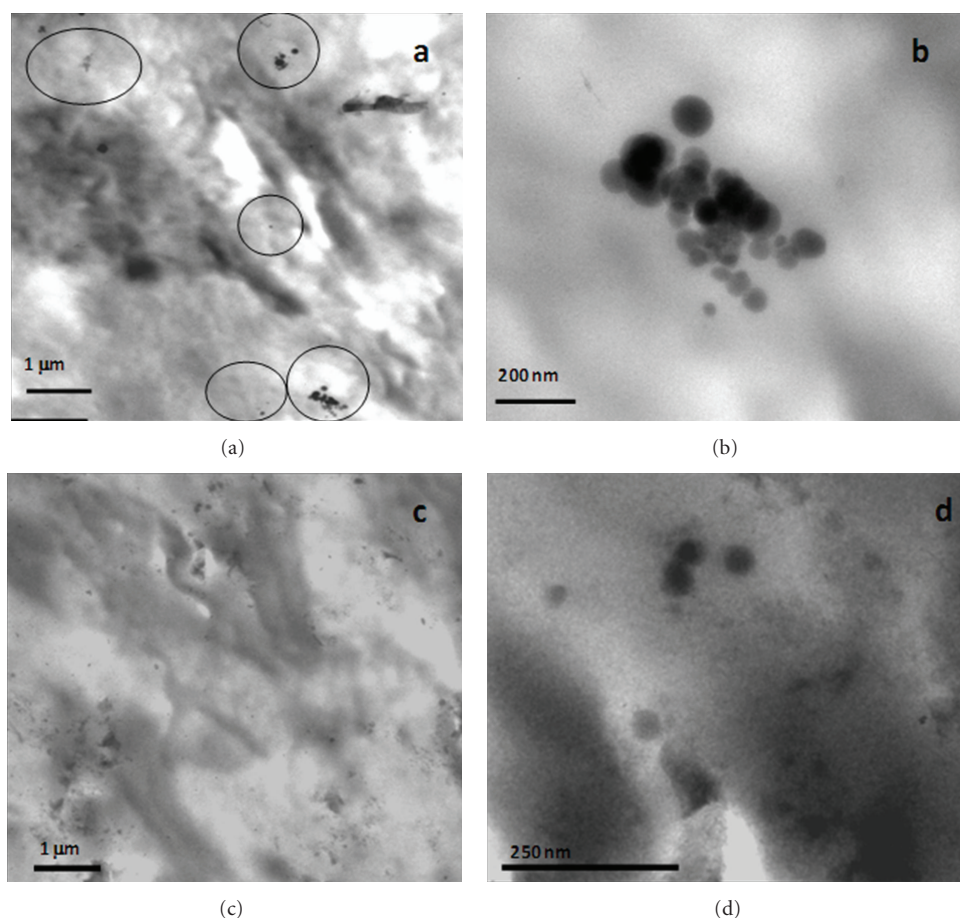

(c)   (d)

FIGURE 3: TEM images of (a) PP/SN nanocomposites obtained by route 1 at 1 μm, (b) PP/SN nanocomposites obtained by route 1 at 200 nm (c) PP/SN nanocomposites obtained by route 2 at 1 μm, and (d) PP/SN nanocomposites obtained by route 2 at 250 nm.

control of the polymer is not only caused by the support, but also by its fragmentation and the resulting distribution of catalyst and cocatalyst on the support during polymerization.

TEM images of PE/SN nanocomposites prepared by *in situ* polymerization using the metallocene catalyst supported on silica nanospheres are presented in Figure 3. The

nanoparticles (2 wt%) in general are well distributed in the polymer matrix, and only small aggregations can be seen in certain regions, and in PP obtained by route 2 an improvement is seen in the distribution of the nanoparticles in the polymer matrix.

The mechanical properties of the polymers could not be measured because the PP obtained with this metallocene

catalyst has a low molecular weight and the polymer is too fragile.

4. Summary

PP nanocomposites were prepared by *in situ* polymerization by two routes where the nanoparticles were added directly into the reactor or used as support. An important point was the improvement of the PP particle morphology by both routes, with nanosphere morphology replicated in the final polymer particles. This phenomenon was more pronounced for PP obtained by route 2.

The polypropylene obtained in the presence of nanospheres had slightly higher percent crystallinity and crystallinity temperature compared with pure PP. In general, the dispersion of the nanoparticles improved for PP obtained when the support system was used (route 2).

Acknowledgments

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