



# An efficient approach to the preparation of polyethylene magnetic nanocomposites



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## ABSTRACT

In the present work, a new method is developed for the preparation of polyethylene magnetic nanocomposites by *in situ* polymerization. Carbon nanotubes (CNTs), synthesized by the chemical vapor deposition method using ferrocene as the precursor and catalyst and silica (SiO<sub>2</sub>) as the support, were used as fillers and compared with a commercial CNT. The synthesized nanofillers had iron magnetic particles encapsulated in CNTs. The fillers were well dispersed into the polyethylene matrix, as evidenced by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs. Even for a very low filler concentration of 0.9 wt%, the presence of magnetic nanoparticles changed the diamagnetic nature of the polymer matrix to a ferromagnetic one. The thermal properties showed that the polymeric matrix did not change their properties significantly.

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## 1. Introduction

Polymer matrices filled with inorganic nanoparticles (NPs) with improved mechanical properties, thermal stability, flame retardancy, chemical resistance, and electrical conductivity represent an area of growing scientific interest [1,2]. Carbon nanotubes (CNTs) were first reported in 1991 by Iijima [3]. Apart from its status as a conventional filler, the attractive mechanical thermal and electrical properties, high flexibility [4], and low mass density [5] of CNTs have gained attention in various fields of research, such as chemistry, physics, material science, and electrical engineering [6–9]. Treacy et al. [10] found that the average Young's modulus of isolated CNT reaches 1.8 TPa. Theoretical and experimental results have confirmed that single-wall CNTs demonstrate a high tensile modulus and tensile strength [11,12]. Wong et al. [13] determined the mechanical properties of multi-walled carbon nanotubes (MWNTs) using atomic force microscopy; these researchers established that they can be characterized by a very high toughness. In 1994, Ajayan et al. [14] reported on polymer nanocomposites using CNTs as filler for the first time. Earlier works used carbon

black, silica, clays, and carbon nanofibers (CNFs) as fillers. In electromagnetic induction shielding, nanotubes have significant advantage over the conventional nanofillers used in the manufacture of multifunctional polymer composites [7,15].

In recent years, the use of CNTs as a reinforcing material for polymer has received enormous attention [6,16–18]. However, the dispersion of CNTs in the polymer matrix has to be taken into consideration to transfer the exceptional properties of CNTs to a polymeric material. The homogenous dispersion of CNTs throughout a polymer matrix is difficult to achieve because there must be considerable interaction between the polymer chain and the CNTs. Their small size and large surface area, as well as the delocalization of  $\pi$  electron subject the CNTs to van der Waals forces, all enhance aggregation [19–21]. An important issue is the compatibility of non-polar polymer matrices and CNTs to induce strong interaction between a polymer phase and filler, and consequently, to produce the efficient reinforcement of composites. In contrast, in the case of polar matrices, the problem seems easier to overcome; Zhang et al. [22,23] presented good results using nylon-6. Applying the same route, however, Tang et al. [24] and Bhattacharyya et al. [25] were unable to achieve significant dispersion of CNTs in polyolefin matrices due to the low compatibility of their apolar nature, which results in CNT aggregation. A number of

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methods in the literature have been reported for the dispersion of CNTs in polymer matrices, for example, solution blending, melt mixing, and *in situ* polymerization [13,26–28]. This last method, where the filler is introduced during the polymerization reaction, is one of the most attractive routes to produce nanocomposites. This technique is known to be more effective in obtaining homogeneous dispersions of filler as compared to other conventional melt mixings.

Both academic and industrial researchers are extremely interested in exploring multifunctional magnetic polymer nanocomposites. These materials can potentially be used in many fields, for example, as microwave absorber, magnetic recording materials, energy storage devices, magnetic sensors, and for drug delivery [29]. The physical or chemical dispersion of magnetic elements, such as iron [30,31], cobalt [32,33], and nickel [34,35], into a polymer matrix can be carried out through the following approaches: *in situ* polymerization [36,37], surface-initiated polymerization [38,39], solution blending [40,41], ball milling [42], surface wetting [43], ion exchange [44], and melt blending [45,29]. Iron is one of the most traditionally used magnetic elements [46], and the magnetic performance of iron NPs has recently attracted a great deal of attention. The synthesis routes of iron NPs from soluble precursors in solutions include chemical reduction [47,48] and thermal [49,50] or sonochemical decomposition [51]. Similar to the conventional CNTs, iron NPs also tend to aggregate due to van der Waals forces, high surface energy, and large specific area. To efficiently disperse and control the particle growth, dispersants or surfactants are added during the fabrication of NPs in solution [50,51]. For instance, Burke et al. [50] carried out several sophisticated steps to produce polymer-Fe nanocomposites in the presence of ammonia and polymer (polyisobutylene, polyethylene, and polystyrene) grated with tetraethylenepentamine from the decomposition of  $\text{Fe}(\text{CO})_5$ . Similarly, Tannenbaum et al. [52] reported an iron oxide nanocluster ( $\gamma\text{-Fe}_2\text{O}_3$ ) from the thermal decomposition of  $\text{Fe}(\text{CO})_5$ , where the synthesis process also involves complicated steps.

One of the most significant disadvantages of iron NPs is their easy oxidation. A recent study showed that the encapsulation of magnetic nanoparticles in CNTs could solve this problem [53,54]. Ferrocene [ $\text{Fe}(\text{C}_2\text{H}_5)_2$ ] is a feasible organometallic compound used as an alternative to produce CNTs that does not require high temperature and acts both as a precursor and a catalyst of synthesis [55,56]. More recently, Osorio et al. [57,58] optimized the synthesis of CNTs with ferrocene using silica nanopowders with different surface areas as a substrate. The results showed that it is possible to control the final magnetic properties, that is, the composition of iron-containing phases in CNTs, by varying the temperature and dwell time of synthesis.

Our research group have been extensively working on synthesizing polyolefin nanocomposites using *in situ* polymerization. Recently, we prepared polyethylene–graphite nanosheet (PE-GNS) and isotactic polypropylene–graphite nanosheet (iPP-GNS) nanocomposites and obtained homogenous dispersions of the filler in the polymer matrix [59–64]. The present work aims to obtain nanocomposites of polyethylene iron encapsulated in carbon nanotubes (PE-CNTFe) through *in situ* polymerization using metallocene [ $(n\text{BuCp})_2\text{ZrCl}_2$ ] as a catalyst and methylaluminoxane (MAO) as a co-catalyst. The characterization of the nanocomposites and their magnetic properties were also studied.

## 2. Experimental

### 2.1. Materials

All compounds sensitive to air and moisture (*i.e.*, the catalyst

and co-catalyst) were manipulated under deoxygenated dry argon using the standard Schlenk and vacuum line techniques. CNTs were acquired from BAYER<sup>®</sup>. Toluene was distilled with metallic sodium and benzophenone. MAO (Witco, 10 wt% Al solution in toluene) and metallocene catalyst bis(*n*-butyl)cyclopentadienylzirconium dichloride ( $(n\text{-BuCp})_2\text{ZrCl}_2$  (Sigma Aldrich) were used as received.

### 2.2. Carbon nanotube synthesis

Two types of CNTs were used in this work: Commercial CNTs were acquired from BAYER<sup>®</sup>, and synthetic CNTs containing iron were synthesized using the method reported in Refs. 57 and 58. The characterization of the CNT-Fe by TEM can be seen in reference 58 as well as in the Supplementary Data.

### 2.3. Fabrication of polymer nanocomposites

The CNTs were stirred with 15 wt% of MAO over 30 min in toluene. The polymerization reactions were performed in a 300 mL reactor equipped with mechanical stirring at a controlled temperature. Toluene was used as solvent, MAO as co-catalyst (Al/Zr = 1000) and  $(n\text{-BuCp})_2\text{ZrCl}_2$  as catalyst ( $5 \times 10^{-6}$  mol). All the reactions were carried out at 25 °C with a constant ethylene pressure of 3 bar over 0.5 h. The CNTs that were previously treated with MAO were introduced to the reactor as filler using a changeable quantity under inert atmosphere. The obtained polymer was washed with 10 vol% of HCl in ethanol solution and dried until it reached a constant weight.

### 2.4. Characterization of polymer nanocomposites

Transmission electron microscopy (TEM) analyses were performed using a JEOL 1011 microscope operating at 120 kV. Samples were prepared *via* the deposition of a solution drop on a copper grid of 300 mesh covered with amorphous carbon. Scanning electron microscopy (SEM) was carried using a Phillips XL30 microscope operating at 20 kV. Samples were prepared by deposition on an aluminum stub and coating with gold.

The molecular weights were obtained with a Waters Alliance GPC 2000 instrument equipped with three Styragel HT-type columns (HT3, HT5, and HT6E). 1,2,4-Trichlorobenzene was used as solvent, with a flow rate of 1 ml/min and a temperature of 135 °C. The columns were calibrated with polystyrene standards.

The magnetic characterization of the CNTs was performed using an EZ9MicroSense vibrating sample magnetometer (VSM) at room temperature with a magnetic field (*H*) ranging from –20 kOe to +20 kOe. Dynamic mechanical analysis (DMA) were obtained using a DMA analyzer (TA Instruments model Q800). The samples were analyzed in single-cantilever mode at a frequency of 1 Hz and a strain level of 0.1% in the temperature range of –140 °C to 120 °C.

Differential scanning calorimetric (DSC) analyses were performed using a Perkin-Elmer differential calorimeter (model DSC Q20) operating at a heat rate of 10 °C/min and a temperature range from 0 to 180 °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 (293 J/g was used for 100% crystalline material). Thermogravimetric analysis (TGA) was performed on a SDT Q600 thermal analyzer Q20 (TA Instruments) at a scanning rate of 20 °C/min from 0 °C to 800 °C.

## 3. Results and discussion

Polymerizations of ethylene were performed in the presence of commercial CNT and of synthesized iron NPs encapsulated in CNTs (CNT-Fe). The catalytic activities of these reactions are listed in

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