



# Synthesis and characterization of polypropylene/iron encapsulated carbon nanotube composites with high magnetic response at room temperature



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## ABSTRACT

Magnetic and conducting polypropylene (PP) polymer nanocomposites with different loadings of synthetic carbon nanotubes (CNT-Fe) were fabricated by *in-situ* polymerization. Chemical vapor deposition was used as the synthetic route for carbon nanotube (CNT) synthesis, in which high-surface-area silica (SiO<sub>2</sub>) acts as the support and ferrocene as the precursor and catalyst. Scanning and transmission electron microscopy analyses evidence the homogenous dispersion of the filler in the polymer matrix. It was found that, with the addition of 3.8 wt.% of the filler, the insulating PP matrix changes to a semiconductor. The magnetic properties of the nanocomposites were investigated using a vibrating sample magnetometer. The addition of 0.8 wt.% CNTs results in ferromagnetic behavior in the diamagnetic polymer matrix and high coercivities at room temperature. The thermal properties were investigated by thermogravimetric analysis and differential scanning calorimetry. Results show an increase in the maximum degradation, crystallization, and melting temperatures of the nanocomposites as compared with neat PP.

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## 1. Introduction

Inorganic–organic composite materials are becoming increasingly important because of their remarkable properties, which can be attributed to the synergism between the properties of their components. There are several routes to prepare these materials, with the most important one perhaps being the incorporation of inorganic components in organic polymers. These materials have attracted the attention of the researchers owing to the significant changes in their mechanical, thermal, electrical, and magnetic properties, compared to pure organic polymers [1]. Polymer nanocomposites demonstrate remarkable enhancement in some properties with a very low amount of addition of fillers such as exfoliated nanosilicate layers, carbon nanotubes (CNTs), and graphite nanoplatelets. However, for the effective performance of

these fillers, the strong interfacial adhesion between the nanofiller and polymer matrix and the homogenous dispersion of the filler in the polymer matrix are imperative [2].

The discovery of carbon nanotubes in 1991 by Iijima [3] has opened a new area of research on the structure, properties and applications of this unique material. In 1994, the first polymeric nanocomposite using CNTs as the filler was reported by Ajayan et al. [4]. The exceptional combination of the mechanical, electrical, and thermal properties of the CNTs make them excellent candidates to alternate or balance the conventional nanofillers in the manufacture of multifunctional polymer nanocomposites [5]. The reinforcing behavior of CNTs in a polymer matrix has also generated a lot of research interest in the past two decades [6]. However, to confer the special properties of CNTs to the polymer matrix, the uniform dispersion of CNTs in the polymer matrix is required, which is difficult. The delocalization of  $\pi$  electrons, small size of CNTs, and large surface area result in van der Waals forces, which cause aggregation [7,8]. However, some researchers have demonstrated uniform distribution of the filler using *in situ*

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polymerization [9–12].

Polypropylene (PP) is one of principal polyolefin's with commercial importance because of its cost-effectiveness and intrinsic properties, such as low density, high stiffness, good tensile strength, and inertness toward acids, alkalis, and solvents. PP has been used in many industrial applications, such as packaging materials, textiles, and automotive parts. However, for advanced applications, the physicochemical properties of PP need to be further improved or new functionalities must be introduced [13]. In order to improve the dispersion of CNTs in a polymer matrix, various methods have been employed. Common methods for CNT-filled polymer nanocomposites include melt blending [14–16], solution mixing [17], and *in situ* polymerization [18]. The limitation of the melt blending method is that it does not always yield homogenous dispersion of the nanotubes because of the lack of compatibility [19]. In the case of PP and PE, the use of the solution mixing method becomes impossible since these polymers are soluble in solvents such as xylene and trichlorobenzene above 120 °C, which have considerable health risks [2]. The *in situ* polymerization is the most suitable technique used to achieve uniform dispersion of the filler, when compared to the conventional melt mixing [20].

Both academic and industrial researchers have been paying increased attention to magnetic polymer nanocomposites. Magnetic nanoparticles and nanocomposites have attracted significant scientific and technological interest because of their potential application in the fields of biomedicine, information technology, magnetic resonance imaging, catalysis, telecommunication, and environmental remediation [21–23]. In contrast, magnetic nanoparticles similar to conventional CNTs tend to aggregate in a polymer matrix and reduce the energy associated with high surface area of the nanosized particles [24]. Iron is the conventionally most-used magnetic material [25] and its excellent magnetic performance has recently attracted considerable interest. However, iron nanoparticles have significant disadvantages such as easy oxidation, which must be resolved when using iron NPs as the filler. Some researchers have reported that the encapsulation of magnetic NP in CNTs can resolve this difficulty [26,27]. Bhatia et al. [28] reported the synthesis of multiwall carbon nanotubes by chemical vapor deposition using ferrocene  $[\text{Fe}(\text{C}_2\text{H}_5)_2]$ , an organometallic compound, which acts as both a catalyst and precursor of synthesis and does not require high temperature. Recently, Osorio et al. [29,30] used silica different surface areas as the substrate and ferrocene as the precursor, and optimized the conditions for the CNTs synthesis. They reported that variation in the temperature and dwell time of the synthesis can help tune the final magnetic properties, i.e., the composition of the iron-containing phases in the CNTs.

Our research group is extensively working on synthesizing polyolefin nanocomposites using *in situ* polymerization. Recently, we prepared polyethylene–graphite nanosheet (PE-GNS), isotactic polypropylene–graphite nanosheet (iPP-GNS) nanocomposites, and polyethylene–CNTs–Fe nanocomposites and obtained homogenous dispersions of the filler in the polymer matrix [31–37]. Park et al. [38] reported the synthesis of polypyrrole (PPy)-coated magnetite ( $\text{Fe}_3\text{O}_4$ ) hybrid particles of dual stimuli-response under magnetic and electric fields. The aim of the present work is to prepare nanocomposites of polypropylene iron-encapsulated carbon nanotubes (PP-CNT-Fe) through *in situ* polymerization using metallocenes [*rac*-Ethylene bis (indenyl) Zirconium (*rac*-Et(Ind) $_2$ ZrCl $_2$ )] as a catalyst and methylaluminoxane (MAO) as a co-catalyst in order to obtain a dual stimuli responsive material under electric and magnetic fields. This multifunctional material has the potential to be applied as sensors in medicine and in electronic devices, low-temperature heaters, energy storage devices [39], solar cells, magnetic recording materials [40], magnetic sensors,

[41] and microwave absorbers [42], in the aerospace and automotive industries.

## 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 (Chemtura, 10 wt% Al solution in toluene) as the cocatalyst. Metallic sodium and benzophenone were used for the distillation of toluene, which was used as solvent. The deoxygenating and drying process of propylene was carried out by passage through the columns of Cu catalyst (BASF) and activated molecular sieves (13X). All manipulates were carried out in inert nitrogen atmosphere using standard Schlenk techniques.

### 2.2. Carbon nanotube synthesis

The CNTs containing iron (CNT-Fe) were synthesized by chemical vapor deposition (CVD), using the method reported in Refs. [29,30]. Ferrocene was used as a precursor and high-surface-area silica as a support. The reaction time was approximately 2 min, and the temperature was increased up to 750 °C.

### 2.3. Polymerization reactions

The CNTs-Fe were stirred with 15 wt.% of MAO for 30 min in toluene. The polymerization reactions were carried out in a Buchi glass reactor of 1 L capacity equipped with a mechanical stirrer and thermocouple. First, toluene was introduced as a solvent, and previously treated CNTs-Fe with MAO were used as the filler, followed by addition of the co-catalyst (MAO, Al/Zr = 1000). Subsequently, the system was saturated with propylene gas and, finally, a given aliquot of catalyst [*rac*-Et(Ind) $_2$ ZrCl $_2$ ] ( $5.0 \times 10^{-6}$  mol) solution in toluene was introduced. The reaction was carried out at 25 °C under 2 bar pressure of propylene, with a stirring rate of 1000 rpm for 30 min. The reaction was terminated with the addition of 5% by volume HCl/methanol 10 vol% solution. Finally, the polymer was precipitated with methanol, filtered and washed before dry to constant weight.

### 2.4. Characterization of polymer nanocomposites

Transmission electron microscopy (TEM) analyses were performed using a JEOL 1011 microscope operating at 120 kV. Copper grid of 300 mesh covered with amorphous carbon was used for sample preparation. A drop of the solution was deposited on the copper grid or from ultrathin films (~50 nm) cut under cryogenic conditions with a Leica Ultracut UCT microtome at –70 °C and placed on a grid (polymeric nanocomposites). A Phillips XL30 microscope operating at 20 kV was used for scanning electron microscopy (SEM). Samples were deposited on an aluminum stub and coated with gold.

The molecular weight analyses were carried out using a Waters Alliance GPC 2000 instrument operating with three Styragel HT-type columns (HT3, HT5, and HT6E). At a temperature of 135 °C and 1,2,4-trichlorobenzene with a flow rate of 1 ml/min was used as a solvent. Polystyrene was used as the column calibration standard.

The Fe on the carbon nanotubes was determined by HR-CS GF AAS through direct solid sampling (SS) using a contraA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany). The samples were directly weighed, without any prior preparation step, on pyrolytically coated graphite tubes. A pre-adjusted pair of tweezers, which is

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