

Research Article

Mechanical Properties of Polyethylene-Carbon Nanotube Composites Synthesized by *In Situ* Polymerization Using Metallocene Catalysts

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The influence of multiwalled carbon nanotubes (MWCNTs) on the properties of polyethylene prepared by *in situ* polymerization using metallocene catalyst (Cp_2ZrCl_2) in combination with methylaluminoxane has been studied. The MWCNT was incorporated in the polymer matrix adopting a stirring method. Incorporation of MWCNT causes a drop in molecular weight of the polymer along with an increase in number of branches and increase in crystallinity. It was also observed that addition of MWCNT during metallocene-catalyzed polymerization caused a drop in both the dynamic modulus and Young's modulus of polyethylene. But the drop in tensile strength was minimal, and there was an increase in elongation at break along with consequent increase in energy at break.

1. Introduction

Incorporation of nanofillers in a polymer matrix can greatly influence the mechanical properties, thermal stability, flame retardance, barrier properties, electrical properties, and scratch resistance of the nanocomposites [1–6]. The carbon nanotube (CNT) is a promising filler and has attracted a great research interest in the area of polymer nanocomposites since its discovery because of its unique properties [5, 7]. The hydrophilic nature of most inorganic fillers is not compatible with the hydrophobicity of the polyolefins. This results in a weak interfacial adhesion between the polymer and nanofillers, thereby adversely affecting the final properties. Since polyolefin is a nonpolar polymer matrix, a homogeneous dispersion of CNT is difficult. CNTs are stabilized by weak van der Waals forces along with π - π interactions between the tubes which lead to the formation of aggregates. The factors influencing polymer nanocomposite properties include the type of

nanofillers, microstructure of polymers, and nanocomposite preparation techniques like melt mixing, solution blending, and *in situ* polymerization [5–14].

The polymerization filling technique (PFT) was commonly used for Ziegler-Natta and metallocene polymerization with a wide variety of microfillers such as graphite, kaolin, glass spheres, wollastonite, silica, and so on, which lead to an *in situ* polymerization technique in combination with various cocatalysts [4–18]. In PFT, polyethylene (PE) is coated on CNT fillers by a four-step process in which the first one includes anchoring of methylaluminoxane (MAO) cocatalyst to CNT, secondly, addition of catalyst to the activated CNT using MAO, then, ethylene polymerization using the CNT-based catalyst, and finally, precipitation of PE on CNTs as coating. Since the PE chains are growing on the CNT surface, better dispersion is easily achieved by disaggregation. But the above process is time-consuming and needs tedious protocols. The dispersion of CNTs and their interfacial interaction between the polymer matrix and

tubes are the main criteria to improve the mechanical properties [19].

Our aim was to prepare PE-MWCNT nanocomposites by a suitable method and to study the mechanical properties of the obtained nanocomposite using the metallocene (Cp_2ZrCl_2)-catalyzed olefin polymerization in combination with MAO cocatalyst. Recently, we reported a one-pot method, using metallocene catalysts, to control PE-MWCNT nanocomposite morphology by the sonication method [20]. Hereby, we report polymerization activity and polymer properties adopting the stirring method to make the process much easier. The MWCNT was vigorously stirred (1500 rpm) rather than sonication, unlike our previous report [20]. The properties of the polymer nanocomposites are compared with the neat PE obtained by using the same catalyst, but in the absence of CNT.

2. Experimental

2.1. Materials. All experiments were performed under standard conditions. Multiwalled carbon nanotubes (MWCNT) were purchased from Nanostructured and Amorphous Materials, Inc. USA. Catalyst Cp_2ZrCl_2 and other chemicals were purchased from Aldrich Chemicals.

2.2. Synthesis of PE-MWCNT Nanocomposites. Ethylene polymerization was carried out in a round-bottom flask (250 mL RB flask) with an experimental setup containing a magnetic stirrer, a constant temperature bath, and a thermometer. Toluene 80 mL was used as a solvent. Prescribed amount of the catalyst and MWCNT were added under vigorous stirring to the flask. The RB flask (reactor) was allowed to attain desired temperature. Then ethylene was supplied into the reactor after applying slight vacuum. Under ethylene-saturated situation, the cocatalyst was added to start the polymerization. At desired time, the polymerization was stopped by quenching with methanol-containing HCl (10 vol.%) [21, 22]. Excess methanol was used to precipitate and wash the product (PE/MWCNT nanocomposites). It was then dried in vacuum at 60°C. Neat PE was prepared by following the same procedure but without CNT. All polymerization experiments were done at similar conditions to make a better comparison.

2.3. Characterization. Polyethylene's 1H - NMR spectra were recorded in $C_6H_4Cl_2$ at 137°C on the Varian Unity Plus (300 MHz) spectrometer. Two major peaks were observed in the 1H NMR of neat PE, one peak around 0.91 ppm (methyl peak) and another broad one at 1.30 ppm (-CH₂ and -CH₃ peaks). There was no noticeable change in the 1H NMR of nanocomposites. PE branching frequency was determined using 1H NMR data obtained. This was reported as branches/thousand carbons, which was calculated from the ratio of number of -CH₃ groups to the total number of carbons [21]. Transmission electron microscope (TEM) images were obtained using JEOL, JEM 2011 (for high-resolution TEM), and HITACHI H-7600. For TEM experiments, PE-nanocomposite membranes were

carefully prepared using an ultramicrotome at room temperature using a diamond knife. Specimens were embedded on an uncoated copper EM grid, and the analysis was carried out using a Schottky-type field-emission gun operating at 200 kV, equipped with a 4 K×4 K resolution camera. A differential scanning calorimeter (DSC, Perkin-Elmer, model: Pyris 1) was used to determine the percentage of crystallinity. The experiment was carried out at a heating rate of 10°C/min under inert atmosphere. To eliminate the difference in sample history, second scan results were reported. To calculate the absolute crystallinity, the heat of fusion, 290 J/g, of a perfect PE crystal was used. Temperature rising elution fractionation (TREF) analysis (Polymer Char, Spain) was utilized to determine the molecular weight of PE. A light-scattering detector was used, and the experiment was done in 1,2,4-trichlorobenzene [23].

To analyze the mechanical properties, samples were fabricated by melting at 150°C and pressing at 3 atmospheres for 5 minutes. The universal testing machine (Instron model 5560) is used to perform tensile tests according to ASTM D 638-03 standard. An average value of five measurements was calculated. A dynamic mechanical analyzer (DMA, TAQ-800, TA instruments) was used to study the dynamic mechanical behavior of materials. The instrument was operated in tensile mode for all experiments under 1 Hz frequency and 5°C/min heating rate.

3. Results and Discussion

The Cp_2ZrCl_2 catalyst, activated by cocatalyst MAO, showed good polymerization activity towards the ethylene monomer with MWCNT as filler [20]. On the addition of MWCNT, the catalytic activity did not show any significant change when compared to the control, (polymerization reaction without CNT) which indicates that the metal complex does not have any effect on the CNT dispersion in +polymer matrix. Ethylene polymerization was conducted with vigorous stirring to improve the dispersion of CNT in the matrix. Figure 1 shows the stress-strain curve, and Table 1 shows mechanical properties of the polyethylene and nanocomposite.

The crystallization behavior of nanocomposites prepared by the zirconocene catalyst under vigorous stirring was influenced by the addition of MWCNT (Table 1). The crystallinity increased from 51.2% for a neat polymer to 74.7% for the nanocomposite. Kim et al. have reported a similar observation [24, 25]. The crystallinity of polymer nanocomposites increased with increase in the concentration of MWCNT. It is noted that PE monomers are vertically grown from the CNT surface, and they have large surface-to-volume and aspect ratio. They have reported that very high concentration of MWCNT reduced the total crystallinity of the nanocomposites, because a large interface region will be created between the PE monomer and MWCNT which forms an amorphous phase that may interfere with the crystal growth [24]. The T_m value has reduced from 134 to 130°C for nanocomposites, and the branching value showed an increase to 9 when compared to neat PE which showed only

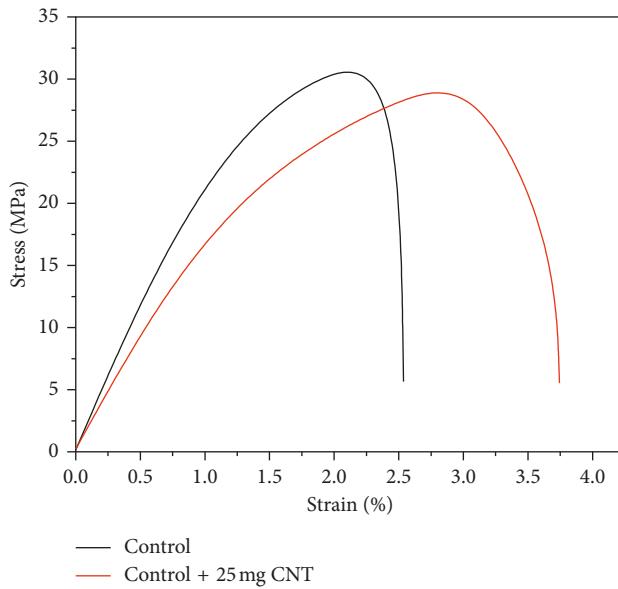


FIGURE 1: Stress-strain plots of the polymer composite and control (neat PE).

4 branches/1000 carbons (Table 1). Chain branching can be correlated with the melting behavior of the PE. Lower melting point of a polymer is due to a decrease in the lamellar crystal structure thickness by an increase in short chain branching of the polymer. The presence of CNT also causes reduction in molecular weight of polymer as compared to the neat PE (control experiment, Table 1). Reduction in molecular weight indicates that CNT adversely affects the polymerization in certain stages.

The effect of CNT on polymer nanocomposite properties prepared by the sonication method has been reported in our previous work [20]. An increase in crystallinity was observed when sonication was performed on the CNT. A similar phenomenon was observed in the present study with the stirring method. The difference when compared to our previous work is in the morphology, wherein the nanocomposite prepared with the stirring method showed the absence of any special morphology as indicated by the TEM results in Figure 2.

The TEM images in Figures 2(a) and 2(b) clearly show the difference in the morphology of neat PE and nanocomposite, respectively. There is no uniform “shish-kebab” morphology like our previous report [20], but it is evident that CNT is coated by PE which might restrict chain mobility. Recently, a shish-kebab nanohybrid structure was reported for polyethylene terephthalate-MWCNT composites by the melt-processing method [26].

The variation in the storage modulus with temperature was studied as shown in Figure 3 for neat PE and the polymer nanocomposite. Incorporation of CNT causes a fall in the storage modulus of PE at all temperatures. The decrease in the storage modulus of the composites is believed to be due to lower molecular weight. Results of stress-strain measurements are also summarized in Table 1. In contrary to the reports, on enhancement in mechanical properties

TABLE 1: Mechanical properties of PE and PE/MWCNT nanocomposite.

Parameters ^a	Neat PE	Composite
$M_w^b \times 10^3$	70.9	67.4
$X^c(\%)$	51.2	74.7
Branches ^d /1000 C	4	9
Tensile strength (MPa)	31.6	30.1
Young's modulus (MPa)	201	132
Elongation (%)	2.5	3.7
Energy at break (J/m ²)	55.05	76.87

^aPolymerization conditions: catalyst (Cp_2ZrCl_2) = 14 μ mol, CNT = 2.5 wt.%, time = 30 minutes, toluene = 80 mL, (Al)/(M) = 750, temp. = 30°C, stirring at 1500 rpm, and activity is in the order of 10^6 g-PE/mol-Zr h bar. ^bDetermined by TREF analysis using a light-scattering detector. ^cDetermined by DSC measurements. ^dDetermined by NMR analysis.

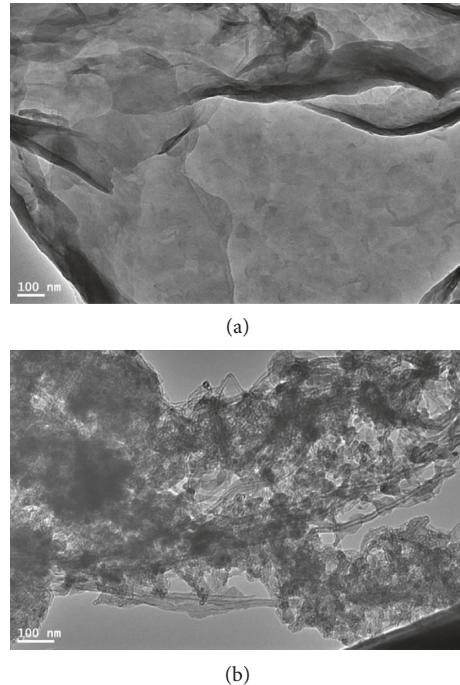


FIGURE 2: TEM images of PE obtained by Cp_2ZrCl_2/MAO with 2.5 wt.% CNT (b) and control (a).

for CNT-filled polyolefin prepared by melt mixing [25–27], a fall in the mechanical properties was found for the polyethylene nanocomposites prepared by the stirring method. This indicates that even though the stirring method is a very convenient one, the complete dispersion of CNT is not achieved.

Incorporation of CNT in the polymer matrix under vigorous stirring caused a decrease in Young's modulus of the PE composite while a marginal fall was observed for tensile strength value. According to Kim et al., binding of CNT caused a hindrance for the free movement of PE chains in the molten state [25]. A preferential entanglement of PE chains with neighbour PEs on the same CNT surface is possible than their interaction with PE molecules from other CNTs, which results in a weak interface between PE and CNT and fall in mechanical properties [25].

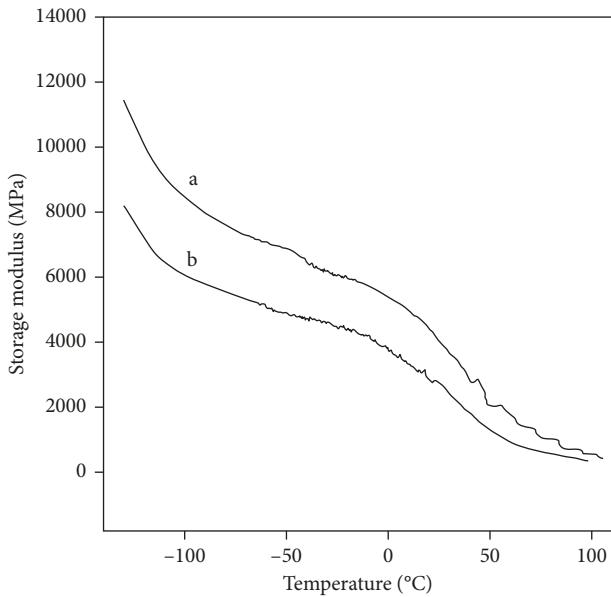


FIGURE 3: DMA analysis of polymer nanocomposites with 2.5 wt.% CNT (b) compared with the control (a).

4. Conclusions

The PE/MWCNT nanocomposite was prepared by the one-pot synthesis method using Cp_2ZrCl_2 in toluene followed by the activation with the MAO-adopting stirring method. Incorporation of MWCNT along with Cp_2ZrCl_2 during polymerization caused a drop in both the dynamic modulus and Young's modulus of the resulting polymer. Even though a minimal drop in tensile strength was observed, there was an increase in elongation at break along with a consequent increase in energy at break.

Data Availability

The data sets used for the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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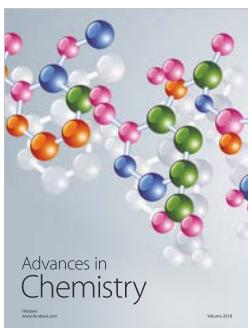
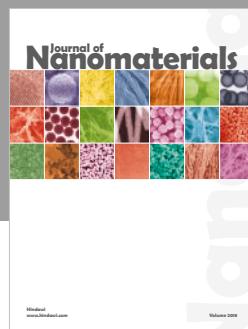
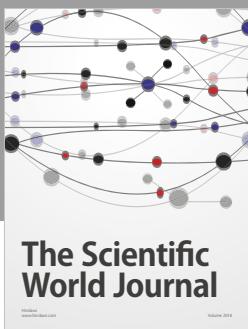
Supplementary Materials

NMR figures for the neat PE and PE nanocomposites are given as supplementary materials. (*Supplementary Materials*)

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