Effects of Multiwall Carbon Nanotubes on the Thermal and Mechanical Properties of Medium Density Polyethylene Matrix Nanocomposites Produced by a Mechanical Milling Method

M. Noroozi, S.M. Zebarjad
Department of Material Science and Engineering, Engineering Faculty, Ferdowsi University of Mashhad, Mashhad 91775-1111, Iran

Medium-density polyethylene/multiwall carbon nanotube (MDPE/MWCNT) nanocomposites were produced by a mechanical milling method using a high-energy ball mill. The MDPE and MWCNTs were added to the ball mill at a constant 20:1 weight ratio of ball/powders and milled for 10 h to obtain polyethylene matrix nanocomposites reinforced with 0.5, 1, 2.5, and 5 weight percent of MWCNTs. To clarify the role of both MWCNT content and milling time on the morphology of MDPE, some nanocomposite samples were investigated by using a scanning electron microscope. To evaluate the role of milling on the microstructure of the nanocomposites, very thin films of MDPE/MWCNTs were prepared and studied by transmission electron microscopy. Thermal behavior of these nanocomposites was investigated by using differential scanning calorimetry (DSC). Standard tensile samples were produced by compression molding. The dependence of the tensile properties of MDPE on both milling time and MWCNT content was studied by using a tensile test. The results of the microscopic evaluations showed that the milling process could be a suitable method for producing MDPE/MWCNT nanocomposites. The addition of carbon nanotubes to MDPE caused a change in its morphology at constant milling parameters. The results of the DSC tests showed that the crystallization temperature of MDPE increased as MWCNTs were added, although no dependency was observed as milling time increased. Crystallization index changed from 50 to 55% as MWCNT content increased from 0 to 5%. The results of the tensile tests showed that both the Young's modulus and the yield strength of MDPE increased as MWCNTs were added. J. VINYL ADDIT. TECHNOL., 16:147–151, 2010. © 2010 Society of Plastics Engineers

Correspondence to: S. Zebarjad; e-mail: Zebarjad@um.ac.ir
DOI 10.1002/vnl.20221
Published online in Wiley InterScience (www.interscience.wiley.com).

INTRODUCTION

Mechanical milling and mechanical alloying are techniques originally developed in the late 1960s for the solid-state processing of metals. Mechanical alloying is widely used in the metals industry for producing composite metal powders with fine microstructures [1, 2]. According to traditional terminology, when two or more metals are mechanically alloyed, a new phase with a different composition is formed at the interface of the two initial phases. As applications for this technique expanded to blending polymers and producing coatings, the terminology was borrowed from the metals industry, with a different meaning. In the case of polymers and ceramics, the new meaning simply implied an improved dispersion of phases or the creation of a uniform coating without the formation of a new phase [3].

Ball mills consisting of a motor, vial, and balls are used in the mechanical alloying process. Several different ball mill configurations exist, but two key parts are common to all configurations: the vial and balls. During mechanical milling, powders are placed in the vial with two or more metallic or ceramic balls. The motor of the mill vigorously turns the vial, a process resulting in high-energy impacts between the balls and the material. These impacts trap material between the balls or between a ball and the vial wall with each turn. As milling occurs, the particles are repeatedly fractured, deformed, and fused together. This process of repeated fracturing and cold-welding causes a refinement in microstructure with milling time. The result is a two-phase lamellar microstructure with an interlamellar distance dependent on total milling energy [2–8].

Total milling energy can be manipulated by changing the ratio of the total ball mass to the powder mass (charge ratio), milling temperature, ball mill design, ratio of the diameter of the balls to the internal diameter of the cylindrical vial, or milling time. The milling temperature can be critical because of its effect on both the material brittleness and thermally aided diffusion across interfaces [1–3].

On the basis of our literature review, there is little literature concerned with the properties of polymer nanocomposites produced by the mechanical milling process and the other processes investigated by others. For example, McNally [9] blended polyethylene and MWCNTs with a mini-twin-screw extruder. The ultimate tensile strength and elongation at break of the nanocomposites decreased with the addition of MWCNTs. The temperature of crystallization (T_c) and the crystalline region were modified by incorporating MWCNTs. Tang et al. [10] melted mechanically mixed HDPE/CNTs and observed an increase in stiffness, peak load, and work to failure for the nanocomposite films as MWCNT content increased. Ruan et al. [11] showed that the presence of MWCNTs in nanocomposites could lead to a 150% increase in strain energy in comparison to that of pure ultra-high-molecular-weight polyethylene (UHMWPE) film at similar draw ratios. This increase was accompanied by an increase of 140% in ductility and up to a 25% increase in tensile strength. Wang et al. [12] reported that the mechanical and thermal properties of UHMWPE/CNT fibers prepared by gel spinning and ultradrawing methods were improved compared to those of pure UHMWPE fiber. Zou et al. [13] fabricated HDPE/CNT nanocomposites by using the screw extrusion and injection techniques. They found that a critical MWCNT concentration of around 1.0 wt% gave HDPE matrix nanocomposites with increased mechanical properties. According to our literature survey, it seems that the production of PE/MWCNTs by the ball milling method has not been paid attention to in more detail. Thus the main goal of the current research was the production of polyethylene nanocomposites reinforced with different multiwall carbon nanotube contents by using ball milling and investigation of their microstructure and their thermal and mechanical properties.

METHODS

Materials

Medium-density-polyethylene (MDPE) granules (melting point 127°C, MFI 2.4 g/10 min, density 0.937 g/cm^3) were purchased from Scoopa Co., Korea. Figure 1 shows the SEM micrograph taken from the MDPE powders. It can be seen that the average particle size is about 50 microns. Multiwall carbon nanotubes with a purity higher than 95% were produced via a chemical vapor deposition technique and were supplied by the Iran Research Institute of the Petroleum Industry with an average diameter of about 10 nm and a length of about 0.5–2 mm. Figure 2 shows the TEM micrograph of these multiwall carbon nanotubes.

Milling

A high-energy ball mill 70 mm in diameter with steel balls of different diameters was employed to blend MDPE powder with 0.5, 1, 2.5, and 5 wt% of MWCNTs at a constant 20:1 weight ratio of ball/powders for 10 h of milling time. To avoid excess heating, milling was interrupted after each hour for about 15 min.

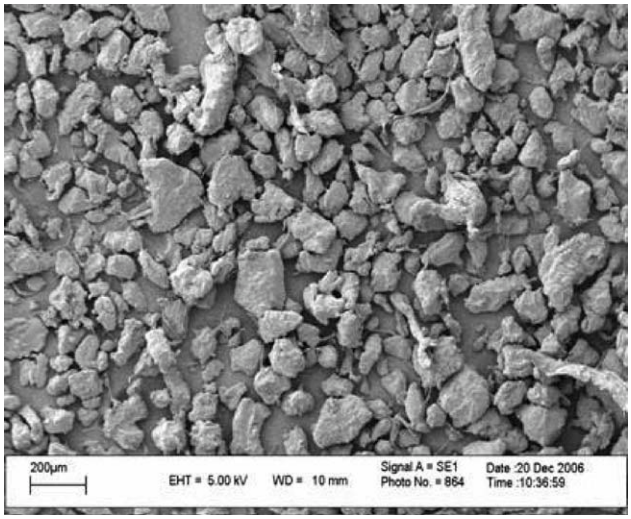


FIG. 1. SEM micrograph of medium-density polyethylene before milling.

Microscopic Evaluation

In order to clarify the role of both MWCNT content and milling on the morphology of MDPE, some ball-milled nanocomposite samples were investigated by using a scanning electron microscope (LEO 1450 VP). Also, to evaluate the role of milling time on the microstructure of these nanocomposites, a very thin film of MDPE/

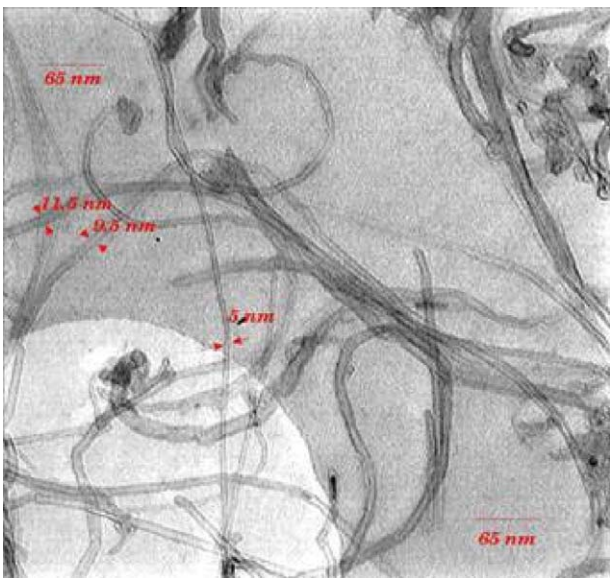


FIG. 2. TEM micrograph of the carbons nanotube used. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

 DOI 10.1002/vnl

MWCNTs was prepared and studied by transmission electron microscopy (LEO 912 AB).

Thermal Properties

Thermal properties of nanocomposites were measured by differential scanning calorimetry (DSC) performed with a Perkin-Elmer DSC-7 instrument. The mass of the samples used varied between 2 and 4 mg. The samples were put in an aluminum crucible and crimped with a small press. They were heated first at a rate of 10°C/min from room temperature to 150°C and held at this temperature for 10 min. The samples then were cooled to room temperature at 10°C/min. A second heating run was performed at the same rate through the full melting range.

Tensile Sample Preparation

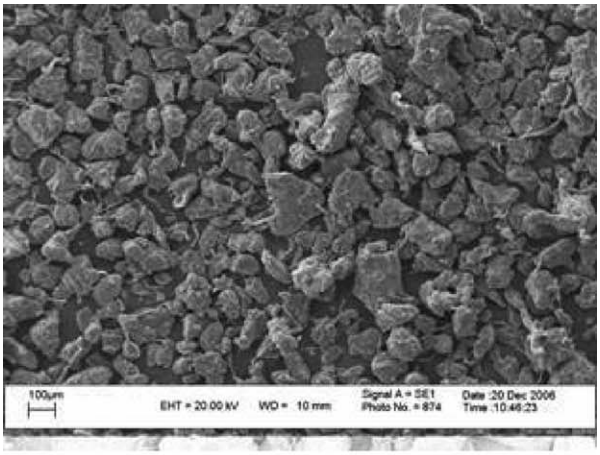
In order to evaluate the mechanical properties of the MDPE and its nanocomposites, standard tensile samples were produced by compression molding. The mold could produce dog-bone-shaped samples according to ASTM D678. They were prepared at 110°C under a constant pressure of about 40 kg/cm^2 applied for 20 min.

Tensile Tests

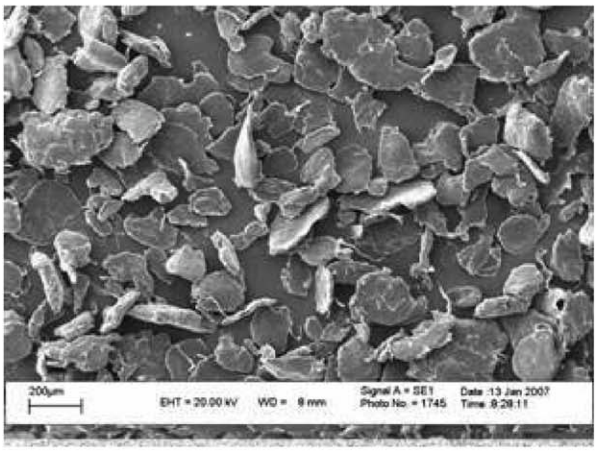
Tensile tests of the dog-bone-shaped samples were conducted by using a Zwick Z150 tensile apparatus. The tests were done at room temperature with a crosshead speed of 5 mm/min. At least 3 samples were tested for all materials, including MDPE and its nanocomposites, and the average values are reported.

RESULTS AND DISCUSSION

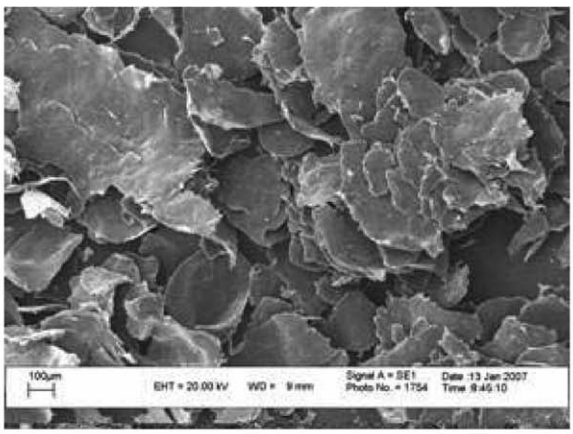
Figure 3a–3c show the SEM micrographs taken from pure MDPE and MDPE/0.5%CNT and MDPE/1%CNT nanocomposites after 10 h of milling. As is seen, at constant milling parameters (ball/powder ratio and milling time), addition of carbon nanotubes to MDPE caused its morphology to change. This change occured because the thermal conductivity of the CNTs was so much higher than that of the pure medium-density polyethylene that it led to a dominant cold-weld mechanism during milling. In fact, the temperature experienced by the polyethylene particles during milling was very important in determining the nature of the final powder shape. It was reported that more than 90% of the mechanical energy imparted to the powders during milling is transformed into heat that raises the temperature of the powders [14]. Increasing temperature makes polyethylene powders soft and finally melts them locally. On the other hand, the polyethylene powder particles can cold-weld together because of ball collisions. The presence of carbon nanotubes inside polyethylene powders leads to dispersion of the heat produced due to the larger milling area. As a matter of fact, under



(a)



(b)



(c)

FIG. 3. SEM micrographs of MDPE/CNT nanocomposites produced after 10 h of milling (a) 0%CNT, (b) 0.5%CNT, and (c) 1%CNT.

the same milling conditions, the melted zone in polyethylene/MWCNT powder is much bigger than that of neat polyethylene.

Figures 4a and 4b show transmission electron microscopy (TEM) micrographs obtained at different magnifications from a MDPE/MWCNT nanocomposite after 10 h

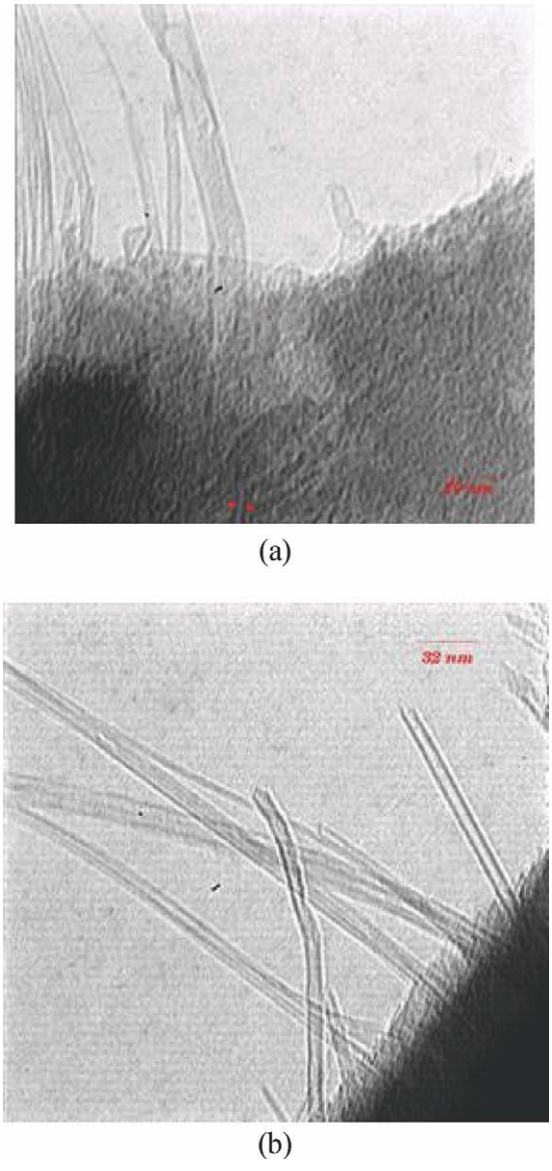


FIG. 4. TEM micrographs of MDPE/1%CNT nanocomposite at different magnifications. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of milling. As can be seen, the multiwall carbon nanotubes are dispersed inside the medium-density polyethylene, a result which proves that the nanocomposites can be produced by using the milling method.

Figure 5 compares the morphologies of neat MDPE and the MDPE/1%MWCNT nanocomposite. Both samples were milled for 10 h under similar milling conditions. As is clear in Fig. 5, cold-welding of the MDPE nanocomposite is much more extensive than that of the neat MDPE. This difference is attributed to the increased thermal conductivity of neat MDPE when CNT is added to it.

Thermal properties were also investigated by DSC. Table 1 lists the DSC characteristics of MDPE and the MDPE/MWCNT nanocomposites. The percentages of crystallinity of MDPE and its nanocomposites were calculated as

$$X_C(\text{MDPE}) = \Delta H^*(\text{MDPE})/\Delta H_0(\text{MDPE}) \quad (1)$$

$$X_C(\text{Nanocomposite}) = \Delta H^*(\text{Nanocomposite})/\Delta H_0(\text{MDPE}) \quad (2)$$

where ΔH^*(MDPE) is the apparent enthalpy of fusion per gram of MDPE in the nanocomposite, ΔH_0(MDPE) is the heat of fusion of 100% crystalline MDPE, taken as 293 J/g as proposed by another researcher [9], and ΔH^*(Nanocomposite) is the apparent enthalpy of fusion per gram of the nanocomposite. The relationship between ΔH^*(Nanocomposite) and ΔH^*(MDPE) as well as that between X_c (MDPE) and X_c (Nanocomposite) can be obtained from Eqs. *3* and *4*, respectively,

$$\Delta H^*(\text{MDPE}) = \Delta H^*(\text{Nanocomposite})/W(\text{MDPE}) \quad (3)$$

$$X_C(\text{MDPE}) = X_C(\text{Nanocomposite})/W(\text{MDPE}) \quad (4)$$

where W(MDPE) is the weight fraction of MDPE in the nanocomposites.

It seems that the addition of MWCNTs to MDPE had no significant effect on the melting temperature of MDPE. In fact, the small fluctuation of melting temperature

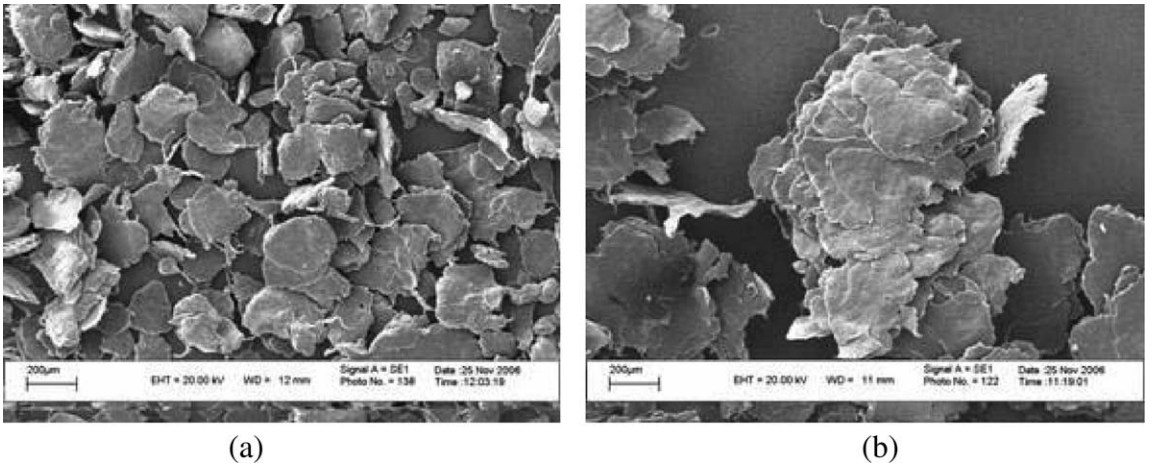


FIG. 5. Comparison of powder morphology after milling: (a) neat MDPE, (b) MDPE/1%MWCNT.

TABLE 1. Thermal properties of MDPE and MDPE/MWCNT nanocomposites after 10 h of ball milling.

Material	T_m (°C)	ΔH_m (j/g)	T_c (°C)	ΔH_c (j/g)	X_c
PE	128.2	148	113.5	−141	51
PE-0.5%MWCNT	127.8	147	114.4	−135	52
PE-1%MWCNT	127.8	151	111.9	−136	52
PE-2.5%MWCNT	127.5	158	114.8	−141	55
PE-5%MWCNT	127.8	152	115.2	−136	55

observed as the amount of MWCNT increased is within the typical experimental accuracy for these types of measurements. However, an increase in crystallization temperature (T_c) clearly would indicate that crystallization started earlier in the filled nanocomposites than in the unfilled MDPE. In fact, the temperature of crystallization (T_c) was raised by about 2°C for the nanocomposite with 5 wt% of MWCNTs. This result was obtained because the MWCNTs acted as a nucleating agent in the matrix. The degree of crystallization of all of the nanocomposites [X_C (Nanocomposite)] increased. On the otherhand, the change in crystallinity is completely opposite to that reported by other researchers [9, 11]. The exact reason for the difference is that some of the volume in the nanocomposites was occupied by MWCNT particles. Moreover, the increase of nucleating sites due to MWCNTs was more effective and could affect the crystallinity. It is clear that at the higher weight percentages of MWCNTs, the crystalline index did not change because of agglomeration of the MWCNTs.

Table 2 shows the mechanical properties of MDPE and the MDPE/MWCNT nanocomposites. Both the yield strength and the Young's modulus of the nanocomposites are higher than those of neat MDPE. The interesting result found in the current study is that the promotion of both the yield strength and the Young's modulus of MDPE due to the addition of MWCNTs is much higher than that obtained via the conventional methods used by other investigators. For example, McNally [9] reported that adding 10% of MWCNTs to PE caused an increase of about 15% in yield stress. However, in our research, a 20% improvement in yield stress and a 27.5% increase in the Young's modulus of MDPE resulted from the presence of just 5% of MWCNTs. This observation proves that the distribution of MWCNTs inside the matrix caused by the ball-milling process is better than that achieved with conventional methods.

CONCLUSIONS

The main goal of the current research was the fabrication of MDPE/MWCNT nanocomposites by using a ball-milling method and the investigation of their thermal and mechanical properties. The results are summarized as follows:

TABLE 2. Mechanical properties of PE and PE/MWCNT nanocomposites after 10 h of ball milling.

Material	Young's Modulus (GPa)	Yield stress (MPa)	Consumed Energy up to 7% strain (N mm)
PE-MWCNT (0%)	0.44	15.91	4700
PE-MWCNT (0.5%)	0.42	16.34	4729
PE-MWCNT (1%)	0.48	16.19	5040
PE-MWCNT (2.5%)	0.55	18.37	5182
PE-MWCNT (5%)	0.56	19.02	5537

- The milling process can be a suitable method for producing MDPE/MWCNT nanocomposites.
- Addition of carbon nanotubes to medium-density polyethylene causes a change in its morphology at constant milling parameters.
- The increases in both yield strength and Young's modulus of MDPE due to the addition of MWCNTs are much higher than those achieved by using conventional methods.

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