Characterization of Carbon Nanotube-reinforced Polyethylene Nanocomposite Produced by Cryogenic Ball-milling Process

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ABSTRACT

The feasibility of using the cryogenic ball-milling process as an environmentally friendly method to produce polymer/CNT nanocomposites was investigated. Linear Low density Polyethylene was used as the matrix material, and 1wt % of Multi-walled carbon nanotubes was used as reinforcement; the influence of the milling time and balls size was evaluated. The morphology of the nanocomposite, and the degree of dispersion of the MWCNTs were studied using SEM, visual inspection and light transmission microscopy; ropes as well as aggregates of MWCNTs were observed, and wetting of the nanotubes by the matrix was also evidenced. An increase of up to 28% in the elastic modulus (determined by tensile testing) with respect to the matrix, was obtained. DSC analysis showed evidence of increase in the degree of crystallization, a result of the nucleating capability of the CNTs in the matrix.

Keywords: Carbon nanotubes, nanocomposites, cryogenic ball milling, mechanical properties.

INTRODUCTION

Any polymer composite where a fiber is used as reinforcement should fulfill some basic requirements so that a significant enhancement in the properties of the matrix can be achieved. First, the aspect ratio (the ratio of the length to the diameter of the fiber) has to be large, second the fiber has to form an intimate contact with the matrix, so when stress is applied, it can be efficiently transferred from the matrix to the reinforcement, third the strength of the fiber has to be much greater than the strength of the matrix, and finally the fiber has to be well dispersed and distributed throughout the matrix. [1]. Carbon nanotubes fulfill most of the reinforcement criteria described above. The combination of high aspect ratio, small size, very low density, and more importantly, excellent physical properties, such as extremely high mechanical strength and stiffness, high electrical and thermal conductivity, make carbon nanotubes (CNTs) perfect candidates as ideal reinforcing fillers in high strength, lightweight polymer nanocomposites with high performance and multi-functions.

Besides the filler properties and geometry (i.e. aspect ratio), other factors to be considered when analyzing the enhancement of the mechanical properties in nanocomposites are: degree of dispersion, distribution and alignment, as well as polymer-CNT interactions and interface characteristics.

CNTs tend to form bundles or ropes, which then form highly entangled and stable aggregates. In order to produce a good polymer/CNT nanocomposite, one in which a significant enhancement of the properties of the matrix is achieved, it is necessary to break the CNT aggregates at least into isolated bundles or ropes; however, the ideal nanocomposite will have individual CNTs uniformly distributed throughout the matrix. A good dispersion and distribution will result in a more efficient stress transfer and in a more uniform stress distribution, avoiding stress concentration.

The objective of the present work was to evaluate the efficiency of the cryogenic mixing process to produce Polyethylene/MWCNTs nanocomposites with enhanced mechanical properties. The mechanical properties of the nanocomposites and unfilled matrix were determined by tensile testing, and the change in elastic modulus was compared with matrix was has been reported in the literature by other authors.

It is worth pointing out at this stage, that the cryogenic device used in work could only operate at cryogenic temperatures. Hence, it was not the goal of the authors to compare the results with measurements made at room temperatures using the same device; it was simply one of the several devices the authors have been using in their efforts to obtain the best procedure for efficient mixing of nanoparticles with polymeric matrices. Another device that is currently being used by the authors for declustering of carbon nanotubes is the magnetic assisted impact coating device, by Aveka Inc.; the study is being conducted at room temperature, and the results will be published at a later stage.

EXPERIMENTAL

Materials

The nanocomposites were prepared using as the matrix, Linear Low Density Polyethylene (LLP8555.25) supplied by Exxon Mobil. The LLDPE was used in powder form with the average particle diameter of 378 μm (determined in dry state using laser diffraction particle size analyzer, Beckman Coulter LS230). MWCNTs, purchased from Cheap Tubes Inc., used as reinforcement, were said to be of 95 wt% purity with outside diameter in the range 20-30 nm and length 10-30 m. The CNTs were incorporated into the matrix as received; no surface treatment or further purification was performed.

Sample Preparation

The mixing of the LLDPE powder with 1wt% of MWCNTs was done in batches of 1.5 g, at liquid nitrogen temperatures, using a cryogenic milling device (6850 Freezer/Mill from SPEX CertiPrep Group). The mixing action of the apparatus results only from the movement of metallic balls inside four vials, due to the magnetic field generated by the coil surrounding the vials.

The influence of the mixing time and ball size on the mechanical properties of the nanocomposites was studied. The two ball sizes used were 1/2″ and 3/16″ in diameter; in order to keep the mass ratio of material to balls constant at 3/50 throughout the study, 3 large balls or 58 small balls were used. The total mixing times were 12, 18, 24 and 30 minutes. The following parameters were kept constant: frequency at 10 Hz, 10 minutes of pre-cooling, and 2 minutes of cooling or rest between every 3 minutes of continuous milling.

Nanocomposites Characterization

The morphology of the recovered, cryogenically mixed PE/MWCNT powder, was evaluated using Scanning Electron Microscopy (SEM) (*LEO 1530vp*). The homogeneity of the nanocomposites was investigated by light transmission microscopy of thin films; the films were prepared by melting the nanocomposites between glass slides using a hot plate, set at 200°C. The optical micrographs were acquired with a Nikon microscope (model Eclipse E200) using an objective lens with 4x magnification.

In order to evaluate the mechanical properties of the nanocomposites, the recovered material was compression molded at 150°C and 2000psi (using a *CAVEN* press). Rectangular test specimens of 40x10mm and 0.5mm thick were cut from sheets of 40x50mm and 0.5mm thick.

The tensile tests were performed using an Instron universal testing machine (Instron 5567); with a 500N load cell, crosshead speed of 30mm/min, and initial distance between grips of 20mm. Five specimens of each sample were tested. It is important to note that even though the dimensions of test specimens did not fulfill any particular standard (ASTM or ISO), all the calculations were done using ASTM D638 standard as a reference.

The actual content of MWCNTs in the nanocomposites was determined through Thermogravimetric analysis (TGA) using a TA Instrument (model Q50); about 7mg of each sample was heated at 10°C/min from room temperature to 550°C. The specimens were held in Aluminum pans, and the system was purged with nitrogen.

RESULTS AND DISCUSSION

Morphology of the nanocomposites

SEM inspection of the mixed powder recovered from the cryogenic ball miller showed that the CNT aggregates were broken into smaller aggregates, and ropes. Figure 1 shows, at two levels of magnification, a characteristic SEM image of cryogenically mixed powder using large balls for 12min. Even though small aggregates of nanotubes can be observed at both magnification levels (Figure 1), at the higher magnification (Figure 1b), ropes of MWCNTs can be seen attached to a LLDPE particle. Since the nanotube ropes are fused into the PE particle and the CNTs were coated by the polymer (as demonstrated in previous work by the authors [1]), it can be concluded that through cryogenic ball-milling it is possible to achieve good wetting of the filler.

Through optical microscopy (Figure 2), small CNT aggregates were observed, but their sizes decreased with increasing mixing time. For a longer mixing time better dispersion and distribution was obtained (see Figure 2b, for example).

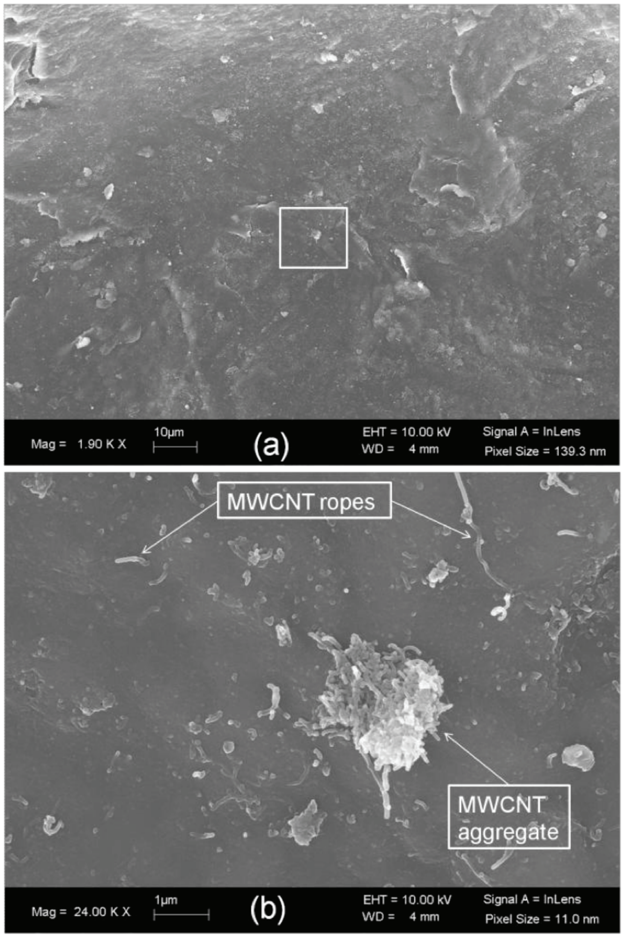

Figure 1: SEM images of the PE/MWCNT cryogenically mixed powder using 1/2” for 12min. (b) is a magnification of the boxed region in (a).

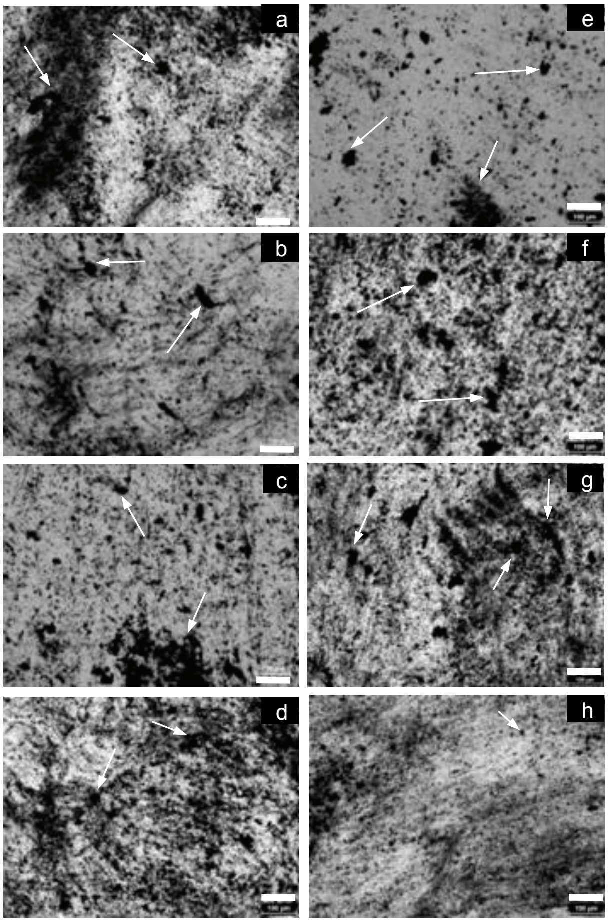

Figure 2: Optical micrographs of the nanocomposites cryogenically mixed using large balls for: (a) 12min, (b) 18min, (c) 24 min, (d) 30 min, and small balls for: (e) 12min, (f) 18min, (g) 24 min, and (h) 30 min. The scale bar in all the images is 100µm, the arrows indicate aggregates.

Mechanical properties of the nanocomposites

In order to indentify the influence that the mixing parameters have on the mechanical properties of the nanocomposites, normalized value of the tensile properties were determined according to the following expression:

$$Y_N \quad \frac{Y}{1\;\text{[redacted]}_{T}} \qquad (1)$$

Where Y_N is the normalized tensile property, Y is the nominal value (measured values of E: Elastic modulus, or σ_y: yield strength) and φ_{CNT} is the volume fraction of MWCNTs calculated from the mass fraction determined through TGA (densities of PE and the CNT used were 0.936 g/cm^3 and 2.1 g/cm^3, respectively; values reported by suppliers).

Figures 3 and 4 show the normalized values of the yield strength (σ_{yN}), and elastic modulus (E_N) as a function of the mixing time and ball size.

Even though the SEM images show good wetting of the nanotubes by the LLDPE, the presence of agglomerated CNTs limits the stress that can be transferred from the matrix to the filler; therefore the yield strength of the nanocomposites was not significantly improved by incorporating 1wt% of MWCNTs (see Figure 3). On the other hand, the yield strain of the nanocomposites tends to be lower than the yield strain of the unfilled LLDPE (results not shown due to space constraints), because CNTs are more rigid than the polymeric matrix, they restrain the deformation of the matrix [2].

Figure 3 shows that the elastic modulus of the nanocomposites is increased between 8 and 28% with respect to the matrix. The enhancement in Young's modulus results not only from the mechanical reinforcement that CNTs impart, but also from a higher degree of crystallinity, which was demonstrated through DSC analysis in previous work [1]. However, as it can be seen in Figure 3, there is no clear correlation between the Young's modulus and the mixing time; which can be attributed to the presence of CNT aggregates of different sizes and shapes (Figure 2), causing the aspect ratio of the filler to be less than expected. This will affect not only the mechanical properties of the filler but also how it interacts with the matrix [3].

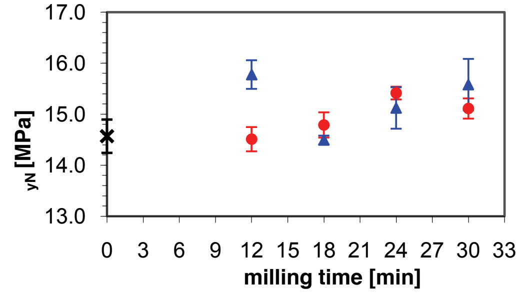

Figure 3: Normalized yield strength (σ_{yN}) as a function of the mixing time for: × unfilled LLDPE a LLDPE/1wt%MWCNTs cryogenically mixed using ▲ large balls, and ● small balls.

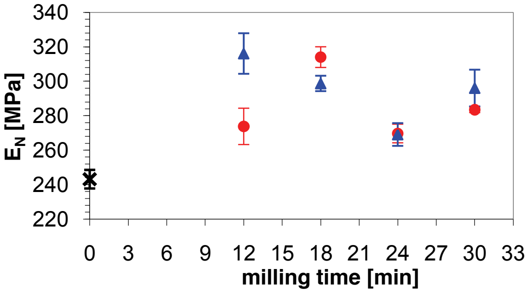

Figure 5: Normalized elastic modulus (E_N) as a function of the mixing time for: × unfilled LLDPE, and LLDPE/1wt%MWCNTs cryogenically mixed using ▲ large balls, and ● small balls.

The change in elastic modulus of the cryogenically mixed nanocomposites was compared to experimental values reported in the literature by other authors. Figure 5 shows a summary of the change in elastic modulus as a function of the content of nanotubes for different Polyethylene grades reinforced with MWCNTs. From the information presented in

Figure 5, it can be seen that even though CNT aggregates are still present in the cryogenic mixed nanocomposites, the elastic modulus enhancement obtained is, in many cases, superior to what has been reported by other authors. The sample preparation methods used by these authors are summarized below.

Gorrasi et al. [4] produced LLDPE/MWCNTs nanocomposites, by centrifugal ball milling in solid state at room temperature. The MWCNTs used had diameters of 10-15nm and length up to 10μm. They observed a 20% increase in elastic modulus by incorporating 1 and 2 wt% of MWCNTs.

Xiao et al. [5] studied the mechanical properties of LDPE reinforced with MWCNTs with diameters ranging between 10 and 20nm, and lengths between 1and 5μm. The nanocomposites were prepared through mechanical mixing at 140°C. The results of their tensile tests showed that the elastic modulus increases with the nanotube content.

Kanagaraj et al. [6] studied the mechanical properties of injection molded tensile specimens of HDPE/MWCNT nanocomposites. The nanotubes were functionalized with chemical groups such as carboxyl, carbonyl, and hydroxyl, through acid treatment. The mixing was done in water; pellets of HDPE were added to an aqueous suspension of the MWCNTs, which was heated and magnetically stirred to produce coated polymer pellets. The results of tensile tests show that the elastic modulus increases linearly with increasing MWCNTs contents.

Wang et al. [7] prepared nanocomposites of UHMWPE and functionalized MWCNTs (with diameter of 20-40nm and length of 0.5-50μm) through solution mixing. The mechanical properties were determined in tension using gel spun fibers. They reported an increase in elastic modulus of between 5 and 14%, with respect to the unfilled matrix, depending on the content of MWCNTs.

Ruan et al. [8] reported 38% increase in modulus with respect to the matrix of hot-drawn films of nanocomposites, consisting of UHMWPE reinforced with 1 wt% of MWCNTs The specimens were prepared through solution mixing.

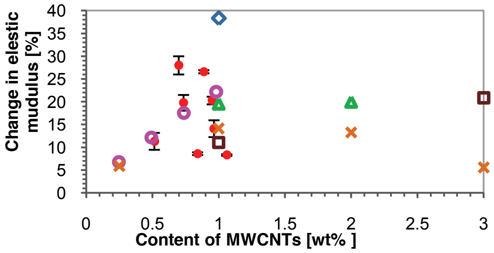

Figure 4: Change in Elastic modulus as a function of CNT content. ● LLDPE-MWCNTs cryogenically mixed, △ LLDPE-MWCNTs energy ball milling [4], □ LDPE-MWCNTs mechanical mixing [5], HDPE-MWCNTs (functionalized) [6], × UHMWPE-MWCNTs (functionalized), ▮UHMWPE-MWCNTs hot-drawn films [8]

By comparing the change in elastic modulus with respect to the matrix, for different PE/MWCNTs nanocomposites, it is possible to conclude that (1) for similar content of CNTs, fuctionalization of the nanotubes does not significantly improve the reinforcement capability of the nanotubes, (2) as the nanotube content is increased the elastic modulus tends to be higher, and (3) by using the cryogenic ball milling device to mix the nanocomposites it is possible to achieve greater enhancement in elastic modulus than other reported methods, even at a lower level of nanotube concentration

CONCLUSIONS

The cryogenic ball-milling process allows production of PE/CNT nanocomposites with enhanced elastic modulus. When compared to other techniques it was evident that the increase in modulus that can be achieved through cryogenic mixing is superior to what has been reported in the literature.

Acknowledgments

This work was funded by the National Science Foundation (Award: CMMI-0802947). The authors acknowledge the collaboration of Dr. Edward Dreizin and Dr. George Collins.

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