USING MAGNETIC IMPACT COATING TECHNIQUE TO PREPARE CARBON NANOTUBE-REINFORCED POLYMER NANOCOMPOSITES

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ABSTRACT

The efficiency of using the dry coating process to produce polymer/CNT nanocomposites with improved mechanical and thermal properties was evaluated. A Linear Low density Polyethylene (LLDPE) in a powder form was used as the matrix material. The polymer powder was mixed with 0.25wt%, 0.5wt% and 1wt% of MWCNTs by the simultaneous deagglomerating and coating actions of the magnetic assisted impact coating device; the influence of the nanotube concentration and coating time on the mechanical properties and homogeneity of the nanocomposites were evaluated. The mechanical properties were determined in tension, and the morphology and homogeneity of the mixture were investigated through scanning electron microscopy (SEM). Significant increases in elastic moduli and strengths were observed with respect to the unfilled matrix material.

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-function applications. These excellent physical properties of carbon nanotubes were exploited, by reinforcing linear low density polyethylene with various concentrations of multi-walled carbon nanotubes (MWCNTs), using a magnetic impact coating (MAIC) device [2]. The principle of operation of the MAIC equipment is relatively simple; the powder (host and guest particles) and the magnets are placed together in the device chamber (see Figure 2), then an oscillating magnetic field fluidizes the powders by rotational and translational movement of the magnets [3]. The collision between the host and guest particles with the magnets and chamber walls leads to deagglomeration of the guests and subsequent coating.

The objective of the present work was to evaluate the efficiency of using the dry coating process, to produce homogeneous polymer/CNT nanocomposites with superior mechanical properties, and to study the influence of the CNT concentration and the MAIC processing time on the mechanical properties and homogeneity of the nanocomposites. The mechanical properties of the nanocomposites and unfilled matrix were determined by tensile testing, and the change in elastic modulus and tensile strength were compared with those of the unfilled polymer.

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 µm.

Sample Preparation

The MWCNTs were incorporated to the matrix as-received; that is, the nanotubes were not deagglomerated prior mixing, and no surface treatment or further purification was performed. The morphology of the nanotubes as-received can be seen, at two levels of magnification, in the SEM images shown in Figure 1. The LLDPE (grade LL8555.25) was mixed with 0.25, 0.50 and 1 wt% of MWCNTs in batches of 5g through dry coating, using the MAIC device from Aveka shown in Figure 2. The powder (LLDPE and MWCNTs) and the magnets are placed together inside a glass jar in the device chamber, and then an oscillating magnetic field fluidizes the powders by rotational and translational movement of the magnets. The collision between the host (i.e. LLDPE) and guest particles (i.e. aggregates of MWCNTs) with the magnets and jar walls leads to deagglomeration of the guests and subsequent coating of the host particles.

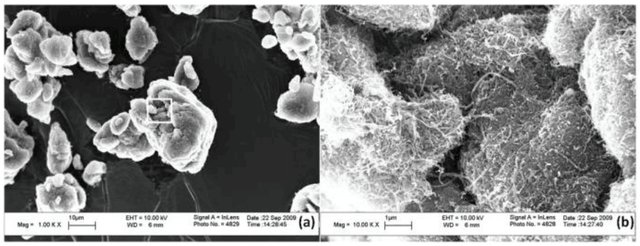

Figure 1: SEM images of the MWCNTs as-received; (b) is a higher magnification of the region inside the box in (a).

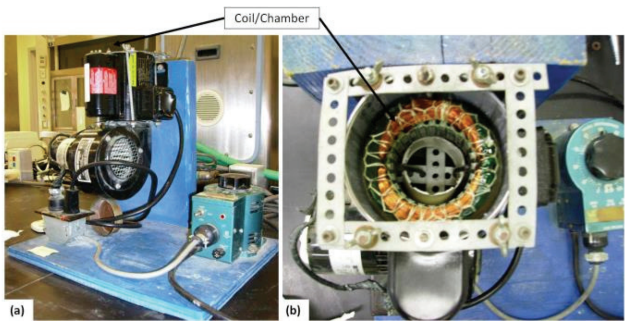

Figure 2: Photographs of the MAIC device by Aveka Inc. (a) General view and (b) detail of the coil/chamber.

The magnets used had particle size between 800 and 1400 µm (see Figure 3), the mass ratio of magnets to material was held constant at 2:1 throughout the study. The input voltage was also kept constant at 140V/70%, and the processing times used were: 10, 20 and 30 minutes.

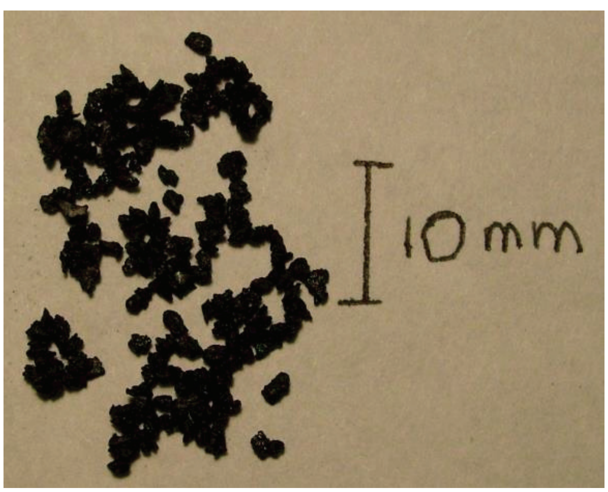

Figure 3: Photograph of the magnetic balls used for dry coating and mixing.

Nanocomposites Characterization

The morphology of the powder recovered from the MAIC was evaluated through SEM (LEO 1530vp). A small amount of the recovered material was stuck through double side carbon tape to the SEM stub, and coated with carbon.

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 40mmx10mm and 0.5mm thick were cut from sheets of 40mmx50mm 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

Figure 4 shows the SEM images of the mixtures containing 1wt% and 0.25wt% of MWCNTs. From these images it can be seen that for 10min of mixing time a discrete coating was obtained for both concentrations of nanotubes (4a and 3d). However, after 30min of mixing time, the mixture containing 0.25wt% of MWCNTs Figure 4f) shows that the CNTs are mostly forming aggregates on top of a LLDPE particle; while the mixture containing 1wt% of MWCNTs (Figure 4c) has continuous coating of nanotubes, but also some aggregation and some cracks along the coating layer can be seen.

The homogeneity of the nanocomposites was investigated by light transmission microscopy of the compression molded plates. The micrographs were acquired with a Nikon microscope (model Eclipse E200) using an objective lens with magnification 4x. The micrographs are presented in Figure 5. From these micrographs it can be concluded that aggregates of MWCNTs are present for all processing times and concentrations. However, the sizes of the aggregates tend to decrease as the processing time is increased.

It is interesting to note that contrary to what was observed in the SEM images of the LLDPE/0.25wt% MWCNTs mixtures, the micrograph of these nanocomposites show an improvement of the homogeneity of the nanocomposites as the processing time increases. The difference may indicate that during the dry coating process some of the nanotubes could be penetrating the polymer particles; therefore, to better understand the dry coating process and the influence of the process parameters on the quality of the mixtures it is necessary to develop a test method that would enable the investigator to observe and analyze a cross section of the particles after dry coating and mixing.

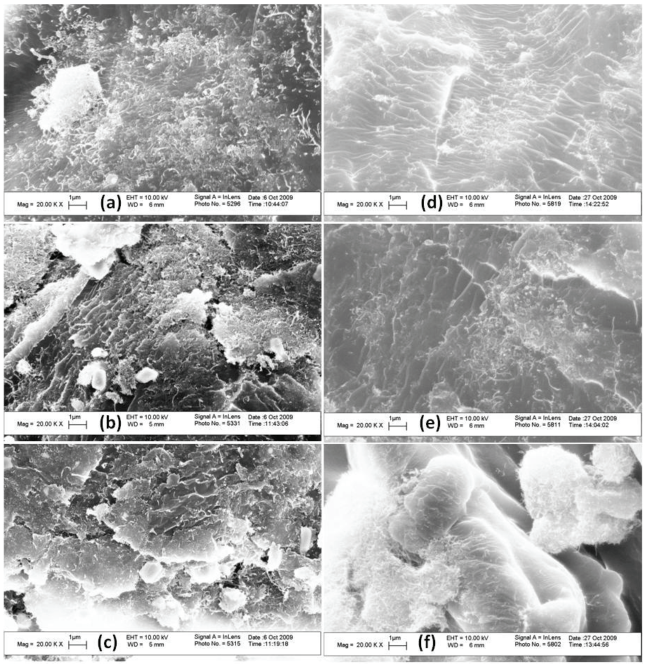

Figure 4: SEM images of the powder recovered from the MAIC. Mixture of LLDPE/1wt% and processing times: (a) 10min, (b) 20min and (c) 30min. Mixture of LLDPE/0.25wt% and processing times: (d) 10min, (e) 20min and (f) 30min.

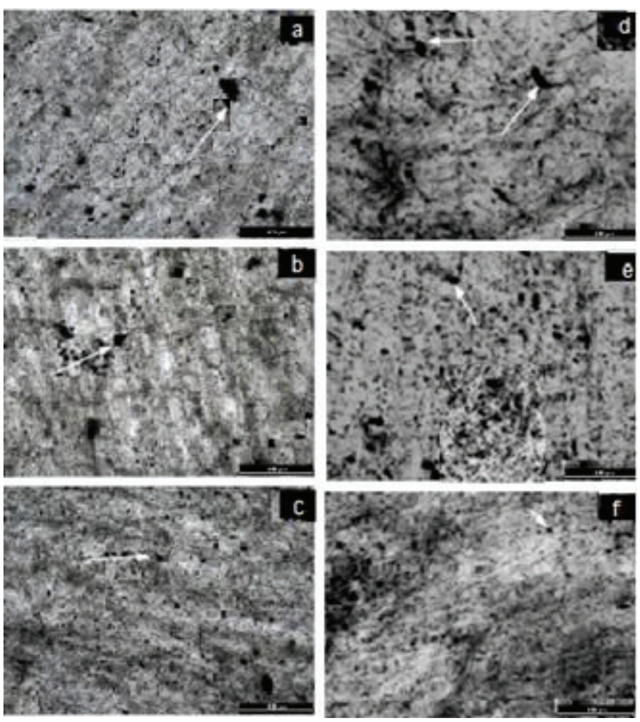

Figure 5: Optical micrographs of the nanocomposites (1wt% MWCNTs) obtained from magnetic assisted impact mixing: (a) 12min, (b) 18min, (c) 24 min, (d) 30 min, and small balls for: (e) 12min, (f) 18min, (g) 24 min, and (h) 30 min. The scale bar in all the images is 500μm, the arrows indicate aggregates.

Mechanical properties of the nanocomposites

Figures 6 and 7 show the values of the maximum stress (σ_{max}), and elastic modulus (E) as a function of the mixing time for various concentrations of MWCNTs, respectively. The maximum stress is essentially the yield strength of the nanocomposite. Figure 7 shows that the elastic modulus of the nanocomposites is increased between 17% and 37% 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 7, there is only a marginal 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 5), 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 [4].

Even though the SEM images show good wetting of the nanotubes by the LLDPE, the presence of some 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 6). 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 [5].

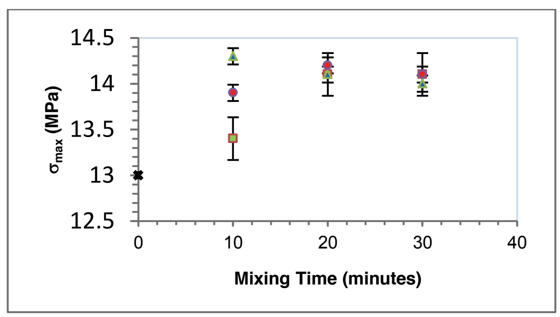

Figure 6: Maximum stress as a function of MAIC processing time for the nanocomposites containing: ● 1wt%, ▲ 0.5wt and ■ 0.25wt% of MWCNTs. The elastic modulus of the unfilled LLDPE (x) is also shown as reference.

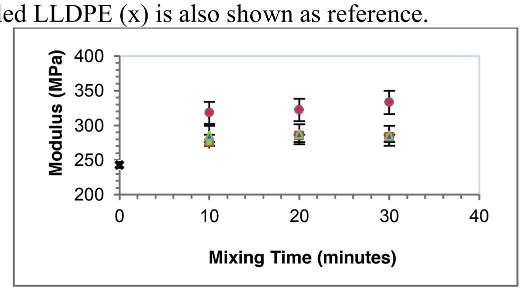

Figure 7: Elastic modulus as a function of MAIC processing time for the nanocomposites containing: ● 1wt%, ▲ 0.5wt and ■ 0.25wt% of MWCNTs. The elastic modulus of the unfilled LLDPE (x) is also shown as reference.

The change in elastic modulus of the magnetic-assisted mixed nanocomposites was compared to experimental values reported in the literature by other authors. Figure 8 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 8, it can be seen that even with some CNT aggregates still present in the magnetic impact-assisted 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. [6] 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. [7] 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. [8] 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. [9] 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. [10] 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.

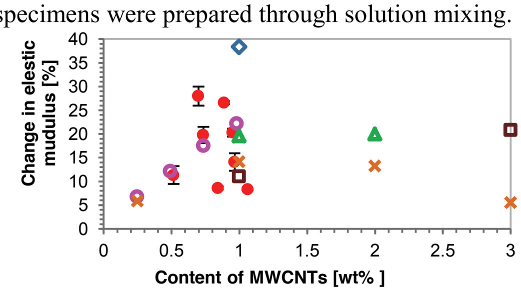

Figure 8: Change in Elastic modulus as a function of CNT content. ● LLDPE-MWCNTs magnetic impact-assisted mixed, Δ LLDPE-MWCNTs energy ball milling [6], □ LDPE-MWCNTs mechanical mixing [7], O HDPE-MWCNTs (functionalized) [8], x UHMWPE-MWCNTs (functionalized), ◊UHMWPE-MWCNTs hot-drawn films [10]

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 magnetic–assisted impact coating method 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 magnetic-assisted impact coating and mixing process allows production of PE/CNT nanocomposites with enhanced dispersion of carbon nanotubes in the matrix material, and a subsequent increased elastic modulus. When compared to other techniques it was evident that the increase in modulus that can be achieved through MAIC mixing process is superior to what has been reported in the literature.

Acknowledgments

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