Properties of Carbon Nanotubes/Linear Low Density Polyethylene Nanocomposites Fabricated by Cryogenic Ball-Milling

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ABSTRACT

Cryogenic ball-milling process was used to produce Polyethylene/CNT nanocomposites; containing 1wt% of Multi-walled carbon nanotubes. Through tensile testing an increase of up to 28% in elastic modulus was observed with respect to the matrix. The morphology of the nanocomposite, and the degree of dispersion of the MWCNTs were studied using SEM and light transmission microscopy. Both MWCNT ropes and aggregates were observed; also wetting of the nanotubes by the matrix was observed.

Keywords: Carbon nanotubes; Mechanical properties, Thermal properties; Thermogravimetric analysis (TGA); Cryogenic ball-milling.

INTRODUCTION

Carbon nanotubes (CNTs) as any other nanomaterial are characterized by very high surface energy, caused by their high surface area to volume ratio; hence, these materials are thermodynamically driven to reduce this energy. CNTs also 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.

Numerous researchers have been trying to develop optimal methods to break these aggregates in order to produce a nanocomposite with well dispersed nanofillers. Some of the methods that are currently being used can be grouped into the following categories: melt mixing [1], solution mixing [2], in-situ polymerization [3], and dry state mixing [4-6].

Melt mixing has been widely used in the industry to mix polymers with several additives. However, melt mixing is not a very efficient method to incorporate CNTs into polymers; high melt viscosity limits the technique to low concentrations of CNTs [7]. It has also been observed that as the aggregates break, the melt viscosity increases significantly [8].

Solution mixing consists of mixing together in a common solvent, a polymeric solution and a CNT powder (a surfactant may be used to improve the dispersion) followed by precipitation or film casting [7, 9]. This method has some disadvantages: residual solvent (or surfactant) can act a plasticizer for the matrix, altering the properties of nanocomposites [10], CNT reagglomeration may occur during solvent evaporation [7, 9], and environmental concerns regarding solvent emissions have to be considered.

When in-situ polymerization is used, the CNTs are dispersed into a monomer solution, followed by the polymerization reaction.

Unlike solution mixing and in-situ polymerization, dry state mixing can be considered an environmentally friendly process, since there are no solvent emissions or residues to be discarded. Some of the dry state mixing methods that have been reported in the literature include solid-sate mechanochemical pulverization in a pan mill [11], solid-state shear pulverization process (SSSP) [12], dry coating [13], and cryogenic mixing [14].

In the present work, linear low density polyethylene (LLDPE) was cryogenically mixed with multi-walled carbon nanotubes (MWCNTs), and the morphology, mechanical properties, and thermal properties of the nanocomposites were evaluated, using several characterization techniques. 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.

EXPERIMENTAL

Materials

The nanocomposites were prepared using as the matrix, Linear Low Density Polyethylene 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. The CNTs were incorporated into the matrix as received; no surface treatment or further purification was performed.

Sample Preparation

The LLDPE powder and 1wt % of MWCNTs were mixed in batches of 1.5g in a cryogenic milling device (*6850 Freezer/Mill* from *SPEX CertiPrep Group)*; at liquid nitrogen temperature.   The milling action of this apparatus was produced by back and forward movement of metallic balls inside the steel vials due to a magnetic field generated by the coil surrounding the vials. It is important to point out that only the balls move inside the vials; neither the coil nor the vials move during the entire milling cycle.

The influence of the total milling time, and the ball size, on the quality of the nanocomposites was investigated. Two ball sizes were used: 1/2" and 3/16" diameter. The mixing was carried out under liquid Nitrogen or cryogenic temperatures, with total milling times of 12, 18, 24, and 30 minutes. The following parameters were kept constant: frequency at 10 Hz, 10 minutes of pre-cooling, and 2 minutes cooling or repose between every 3 minutes of continuous milling. The recovered material was compression molded into sheets of 40x50mm and 0.5 mm thick at 155°C and about 14 MPa.

Nanocomposite characterization

Optical Microscopy and Scanning Electron Microscopy

The extent of dispersion of the CNTs in the LLDPE was evaluated at different levels of magnification (i.e. visual inspection, optical microscopy and SEM). The morphology and degree of mixing of the recovered powder and the corresponding compression molded sheets were evaluated by visual inspection. 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 micrographs were acquired with a Nikon microscope (*model Eclipse E200*) using an objective with 4x magnification. Scanning electron microscopy (SEM) (*LEO 1530*vp) was used to obtain more detailed information on the morphology of the powder recovered from the mill.

Tensile testing

The tensile tests were performed using an Instron universal testing machine (*Instron 5567*), with a 500N load cell, and crosshead speed of 30mm/min. The test specimens used were rectangular strips of 40x10mm and 0.5mm thickness cut from compressed molded sheets, the initial distance between grips was 20mm. Five specimens of each sample were tested.

Fractography

The neck region near the fracture surface was evaluated using Polarized Light Microscopy. The micrographs were acquired with a Nikon microscope (model Eclipse E200) using and objective lens with magnification of 4x and 10x.

Thermal analysis

The crystallization and melting behavior of the unfilled polymer and the nanocomposites were evaluated under non-isothermal conditions by differential scanning calorimetry (DSC); a TA Instrument DSC (model *Q100)* was used. Aluminum pans were used as specimen holders, and the system was purged with nitrogen.   All the samples were subjected to cooling and heating scans at 10°C/min from 30°C to 200°C; to erase the thermal history of the material the system was kept at 200°C for 3 min, after the first heating.

The onset degradation temperature of the unfilled polymer and the nanocomposites was determined by thermogravimetric analysis (TGA); tests conditions are described in detail in the following section.

Thermogravimetric analysis

The actual CNT content in the nanocomposites was determined using a TA Instrument TGA (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 [14]), it can be concluded that through cryogenic ball-milling it is possible to achieve good wetting of the filler by the polymer.
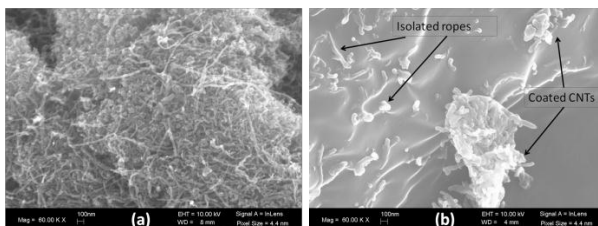

Figure 1: SEM images. (a) as-received CNTs, and (b) LLDPE/ 1 wt% CNT cryogenically mixed powder with large balls for 24min.

Fractography results

Birefringence, observed with polarized light microscopy, was used to compare differences in orientation near the fracture surface of the tested nanocomposites and unfilled polymer.

Birefringence results from differences in the velocity of light as it travels through a specimen. In the case of polymeric materials, the velocity of light propagation strongly depends on the interactions between the electromagnetic wave and the bounding electrons; therefore, birefringence is not uniform

and it is often seen as colored fringes as a result of residual stresses and/or molecular orientation. When an external stress is applied the polymer chains are oriented, the bonds are stretched or the bond angles distorted, making the presence of colored fringes more pronounced [15].

Figure 2 (a, b, c), shows the fracture region of the unfilled and filled LLDPE; from this micrograph it is possible to conclude that the highest orientation of the polymer occurs along the boundaries of the fracture surface, where the difference in fringe colors is more intense.

Figure 2c shows that fracture of the test specimen starts at CNT agglomerates. Also from this micrograph it is possible to see that high orientation of the matrix is observed only in the regions closest to the aggregates. By comparing the birefringence near the fracture surface of the unfilled polymer (Figure 2a) and the nanocomposite fabricated by cryomilling (Figure 2b, c), one can conclude that the cryogenically mixed nanocomposites have the highest orientation or residual stresses near the fracture surface; a consequence of good adhesion between the nanotubes and the matrix material.
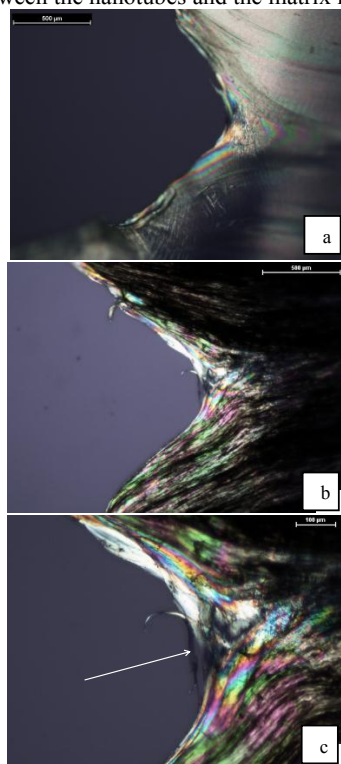

Figure 2: Polarized light micrograph of the fracture surface of unfilled LLDPE (a), and LLDPE/1wt% MWCNTs cryogenically mixed with small balls for 18min (b and c); the arrow indicates MWCNTs aggregate, (c) is a magnification of the fractures region shown in (b).

Mechanical properties of the nanocomposites

In order to identify 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:

$$Y_N = \frac{Y}{1 - \varphi_{CNT}} \qquad (1)$$

Where Y_N is the normalized tensile property, Y is the nominal value (measured values of E: Elastic modulus) 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).

Figure 3 shows that the elastic modulus of the nanocomposites is increased between 8 and 28% with respect to the matrix material. 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 [14]. 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, 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 [7].
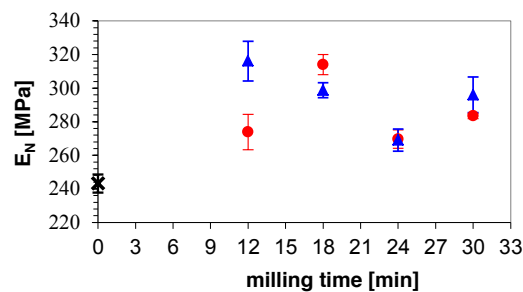

Figure 3: Normalized elastic modulus (E_N) as a function of the mixing time for: × unfilled LLDPE, and LLDPE/1wt%MWCNTs cryogenically mixed using ▲ large balls, and ● small balls.

Thermal properties

A summary of the thermal properties is presented in Table 1. The main change in the thermal properties was observed in the crystallization enthalpy (ΔH_c); all the nanocomposites have higher ΔH_c than unfilled LLDPE, with increases between 5 and 12%. This is associated with increase in the degree of crystallinity.

Figure 4 shows a set of cooling thermograms. The crystallization peaks of the nanocomposites shifted toward higher temperatures with respect to the unfilled LLDPE; an average increase of 3.7±0.4°C in the onset crystallization temperature ($T_{c,onset}$), and 3.2±0.2°C in the peak crystallization temperature ($T_{c,p}$) were observed. This clearly indicates that the CNTs are acting as heterogeneous nuclei for the matrix, thus allowing the crystallization process of the LLDPE to start at higher temperatures.

No significant variation in the onset degradation temperatures was observed, following incorporation of 1wt% of MWCNTs in LLDPE when compared with the unfilled LLDPE.

Table 1 Summary of thermal properties.

Sample	$T_{c,onset}$ [°C]	$T_{c,p}$ [°C]	ΔH_c [J/g]	$T_{m,onset}$ [°C]	$T_{m,p}$ [°C]
LLDPE	115.1	112.8	146.53	122.6	126.5
PE1S12	118.4	115.9	160.93	121.6	127.1
PE1S18	119.1	116.1	163.59	121.9	127.5
PE1S24	119.2	116.2	156.22	121.4	127.0
PE1S30	119.2	115.9	158.34	121.6	127.1
PE1L12	118.6	115.7	160.28	122.0	127.4
PE1L18	118.2	116.0	156.25	122.5	127.4
PE1L24	119.0	116.0	153.40	122.8	127.3
PE1L30	119.1	115.8	156.77	122.0	127.3

*PE1xy denotes 1 wt% CNT-filled nanocomposites; where x=ball size (Small or Large), and y=milling time (in minutes)
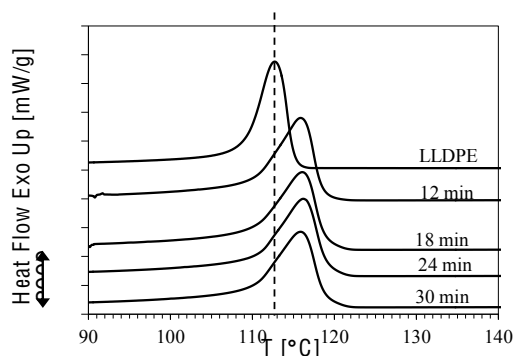

Figure 4: Cooling thermograms performed at 10°C/min for un filled LLDPE, and cryogenically mixed nanocomposites with small balls for 12min, 18min, 24min and 30min.

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

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