

MANUFACTURE OF CNT REINFORCED POLYMER COMPOSITES USING NANOFIBERS CONTAINING CNTS

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ABSTRACT

The electrospinning process has been recognized as a viable method to disperse and align nanoparticles within fibrous polymer matrix, however electrospun mats solely cannot be used for structural components. In this study, electrospun mats containing CNTs, which were prepared by electrospinning of solutions of nylon 6 and multiwalled carbon nanotubes (MWNTs), were consolidated into solid composites by a hot pressing. To validate an idea that nanofibers can be utilized as a dispersion media of CNTs for advanced polymer composites, Raman spectroscopy was carried out for the nanofiber mats and revealed that MWNTs were dispersed in nanofibers and furthermore aligned along the fiber axis. Due to the well dispersed and aligned CNTs in nanofibers, the mechanical properties of the nanocomposites manufactured from electrospun nanofiber mats were improved.

1. INTRODUCTION

Among many nanoscale materials, carbon nanotube (CNT), discovered by Japanese scientist Sumio Iijima, have drawn much attention due to its outstanding material properties such as mechanical, thermal, electrical, and magnetic properties [1], for example, its modulus (\sim TPa) is far higher than that of carbon fibers (200-800 GPa) [2]. However, these superior properties have not been realized in macroscale due to its entanglement and aggregation tendency.

Many attempts have been made to overcome the aggregation problem and to transfer the exceptional mechanical properties of the nanoscale materials to the macroscale properties of the bulk materials. These includes (1) Optimal Physical Blending – using high power dispersion (including sonication and stirring), compatibilizer, polymer-assisted melt blending, and surfactants. (2) In-situ Polymerization – attaching CNTs to polymers' surfaces. (3) Chemical Functionalization – purifying CNTs, cutting CNTs for disentangling, using activation treatments and chemical functionalization of CNTs. (4) Numerous alignment methods: ex-situ alignment, force field-induced alignment, magnetic field-induced alignment, electrospinning-induced alignment, and liquid crystalline phase-induced alignment [3]. In this study, the electrospinning process was chosen to manufacture CNT reinforced polymer nanocomposites. This process involves applying a high voltage to a polymer solution in a syringe and producing a fine jet of liquid from the tip of the needle when the polymer solution overcomes surface tension due to the electric force [4]. The formed jet undergoes a uniaxial stretching by whipping instability, which reduces the fiber diameter from micron size to nanometer size. The electrical and mechanical forces in the electrospinning are driving CNTs to disperse and align in nanofibers, which will resolve the aggregation problem of CNTs.

In this study, nanofibers produced by electrospinning were used as carriers of CNT particles, i.e., these intermediate nanofibers containing CNTs were used to manufacture nanocomposites.

2. EXPERIMENTAL

Materials

In this study, Nylon 6 was chosen as the matrix material of nanocomposites and provided from a company (Kolon) in Korea. Multi-walled carbon nanotubes (MWNTs) from NanoKarbon inc were used as received. The purity of MWNTs was over 85%. Formic acid was then used to make solutions of Nylon 6 and MWNTs. The concentration of Nylon and MWNTs in solution was fixed to be 10 wt%. Five solutions were prepared to produce nanofibers containing MWNTs by varying MWNT content of 0, 1, 2, 3 and 4 wt%, respectively, with respect to the Nylon content.

Electrospinning and composites fabrication

The solutions were then sonicated for several hours to disperse MWNTs in them prior to the electrospinning. After the sonication process, all solutions were electrospun into nanofiber mats with a fixed process condition: voltage = 20kV, tip-to-collector distance = 8-12 cm, and rate of flow = 0.5ml/hour. The nanofibrous mats were consolidated into nanocomposites by hot pressing at 20°C higher than the melting temperature of the Nylon used. The hot process melts nanofibers which form continuous matrix phase in composites.

Characterization: SEM, Raman spectroscopy, DSC, and mechanical tests

The nanofibers mats were firstly examined using SEM (Jeol JSM-6700F, high resolution) to observe nanofibers in electrospun mats. To investigate the distribution of MWNTs in the nanofibers, Raman spectroscopy was carried out using an instrument (T64000, HORIBA). The microstructural change of the Nylon matrix during the thermal process was analyzed using DSC thermogram, which was obtained by heating the nanocomposites from 0 to 300 °C with a heating rate of 10°C/min. Finally the mechanical properties of the nanocomposites were characterized using Instron-5543.

3. RESULTS AND DISCUSSION

Dispersion and alignment of MWNTs in nanofibers

Figure 1(a) shows the morphology of MWNTs used in this study. The average diameter of MWNTs was approximately 75nm. In Figure 1(b) to (f) SEM photographs of electrospun nanofiber mats were shown, from which the average diameter of nanofibers were measured. Since the average diameters of nanofibers were similar to or less than that of MWNTs (see Figure 2), it can be deduced that each nanofiber can contain only 1 MWNT along the fiber axis if MWNTs was embedded in the fibers.

The Raman spectrums of both MWNT and the nanocomposites were shown Figure 3. Two typical (first-order) Raman peaks were observed at around 1365cm⁻¹ (D peak) and 1585cm⁻¹ (G peak). The ratio of two peak intensity was reduced as MWNT contents increased. This may be due to the alignment of MWNT in nanofibers during the electrospinning, which can be explained as follows.

It is known that the D peak is related to the breaking of symmetry caused by structural disorders, such as in-plane substitution heteroatoms, vacancies, grain boundaries, and so on, while the G peak is relevant to in-plane tangential stretch vibration mode (E_{2g}) of

the graphite sheet [5]. Raman peaks are attributed to phonon of materials. Phonons are constrained on Brillouin zone which is a function of atomic geometry. As such the reduction and addition of peak intensity without chemical reaction means the change of geometry. Therefore the reduction of the ratio I_D/I_G can be considered as the reduction of structural disorders, i.e., MWNT alignment along the fiber axes.

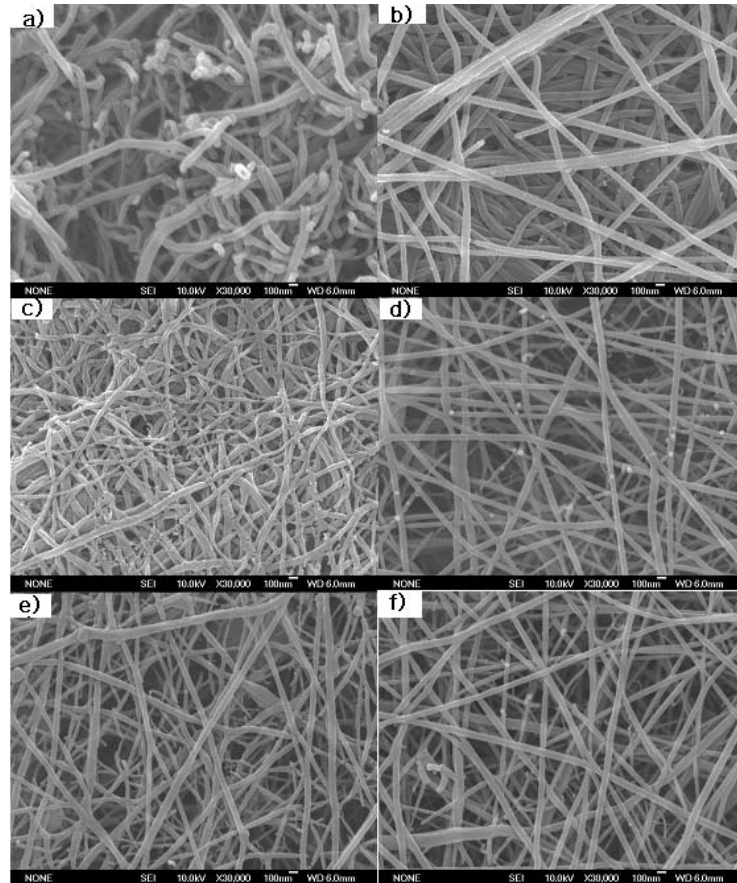


Figure 1: SEM photographs: a) MWNTs and b-f) nanofiber mats with MWNT content of 0, 1, 2, 3 and 4wt%, respectively.

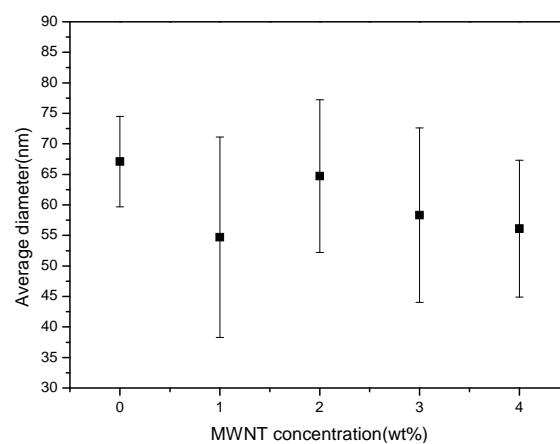


Figure 2: The average diameter of MWNT/Nylon nanofibers with respect to the concentration (0, 1, 2, 3 and 4wt%).

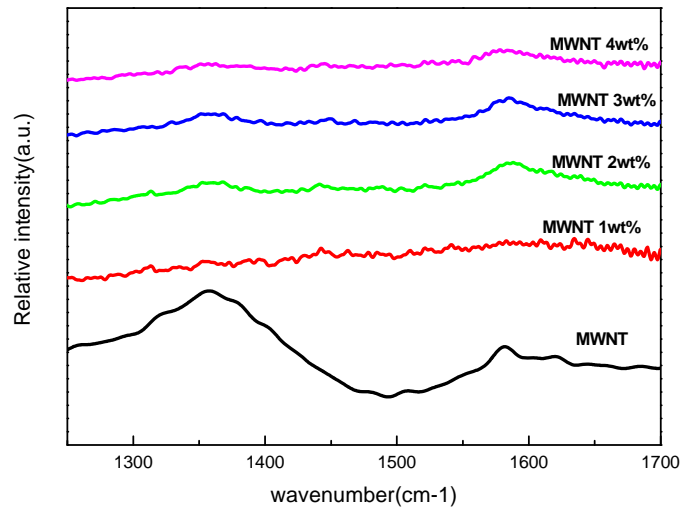


Figure 3: Comparison of the D and G-band region in the Raman spectra.

Table 1: The ratio of two characteristic peaks (I_D/I_G) according to MWNT contents.

sample	MWNT	MWNT 1wt%	MWNT 2wt%	MWNT 3wt%	MWNT 4wt%
I_D/I_G	1.17	-	0.91	0.91	0.97

Micro-structural change of Nylon matrix during the hot pressing

DSC thermogram of MWNT nanocomposites was shown in Figure 4. There was little change in the melting temperature of MWNT nanocomposites. The neat resin (Nylon) exhibits multiple melting endotherms corresponding to melting of the γ and the α phase crystals, however the α phase is the dominant phase. As the MWNT loadings increases, the structure transforms from the α phase to the γ phase, resulting in approximately equal mixture of both crystal phase. Further CNT loading was found to transform the structure to γ phase dominant one. This result is consistent with the fact that electrospinning favors the less stable phase [6]. On the other hand, it is known that the α phase is the thermodynamically stable phase, and consists of sheets of hydrogen-bonded chains, while the γ phase is the least stable phase, and arise from random hydrogen bonding between parallel chains [7]. In this regard, it can be deduced that the mechanical performance of the matrix in the nanocomposites may deteriorate with MMT loading, however the mechanical performance of the nanocomposites will be determined by the load-carrying capacity of MWNTs because the matrix in composites functions load transfer to the reinforcement.

Mechanical properties

Mechanical properties of MWNT were examined by carrying out tensile tests, and a typical stress-strain curve was shown in Figure 5. It is clear that MWNT loading in the polymer matrix increased the initial stiffness and also tensile strength to an extent, however the breaking strain decreased.

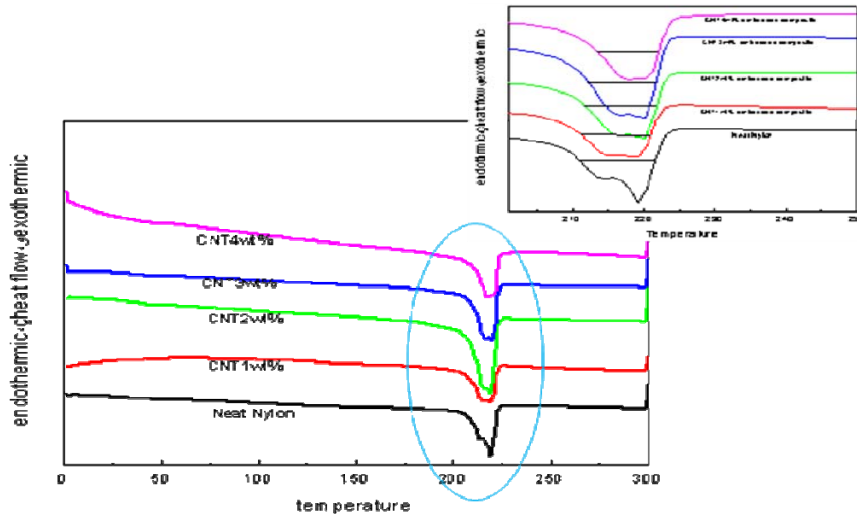


Figure 4: DSC thermograms of Nylon and Nylon /MWNT nanocomposites.

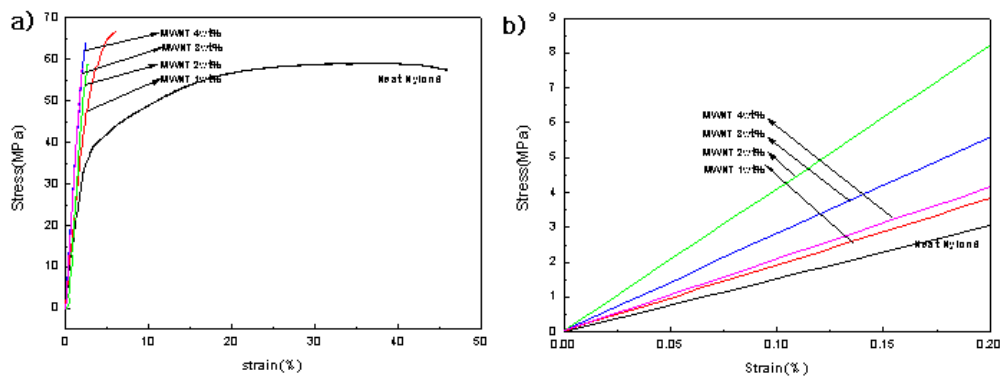


Figure 5: Typical stress-strain curve of Nylon and MWNT nanocomposite: (a) overall and (b) small deformation behavior.

The initial stiffness was compared in Figure 6 (a), showing that MMTs increased the modulus of the nanocomposites significantly. The maximum stiffness was achieved in a nanocomposite with MWNT content of 2wt%. On the other hand, the tensile strength was not improved much due to the weak interaction of MMTs with Nylon molecules (see Figure 6(b)), however its maximum was observed again at the MWNT concentration of 2wt%. The breaking strain was reduced significantly. This mechanical behavior of nanocomposites can be explained by two factors: aggregation and adhesion. The aggregation of nanoparticles deteriorates a capability of the load transfer from the matrix to nanofillers because the load transfer of a region without interfacial resins rely on only interactions between nanofillers, e.g., van der Waals force for MWNTs, which is weaker than the interaction between polymer molecules. Therefore nanocomposites with aggregated fillers show the decreased mechanical properties, even small deformation characteristic such as the initial modulus. On the other hand, the tensile strength of nanocomposites is affected by the adhesion of nanofillers to polymer molecules. If the adhesion is not strong enough to transfer load from the matrix to the nanofillers within large deformation regime, even good dispersion of nanofillers in polymer matrix cannot ensure the improvement of the tensile strength. As a result, it can be tentatively concluded that the MWNTs was dispersed well through electrospun

nanofibers, however no treatment on MWNTs brought out their weak adhesion with surrounding polymer molecules, resulting in the decreased tensile strength.

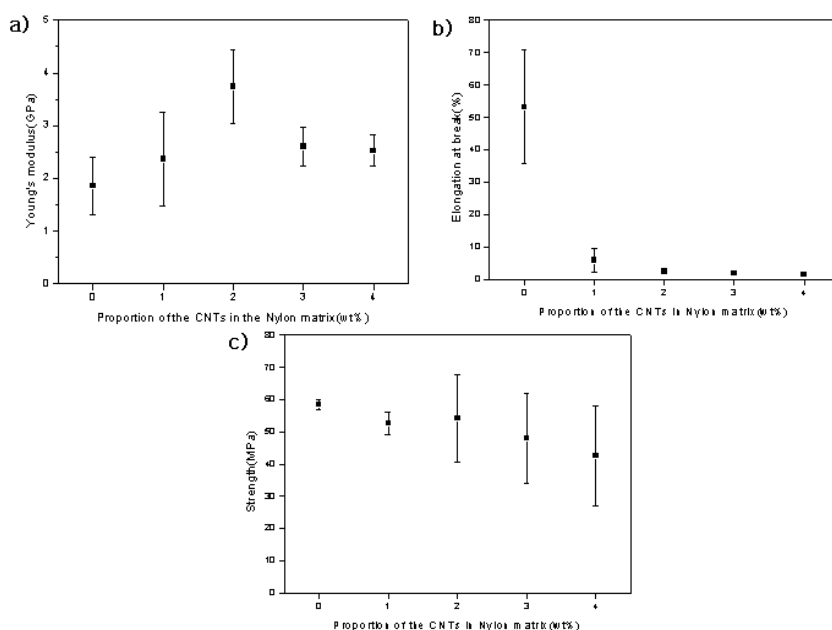


Figure 6: Mechanical properties of MWNT nanocomposites according to MWNT contents: (a) initial modulus, (b) breaking strain and (c) tensile strength.

4. SUMMARY

Many attempts have been made to realize the outstanding properties of CNT in macro-scale through its polymer composites; however commercialization has been delayed due to its aggregation problem in polymer matrix. In this work the electrospinning process were employed to overcome this problem. For this, polymer solutions with CNTs were prepared using a sonication process. Due to its electrical and mechanical forces, the electrospinning of the solutions produced nanofibers containing CNTs which were dispersed and aligned along the fiber axis. This dispersion and alignment was confirmed by Raman spectroscopy of the nanofiber mats. Using a hot press, the electrospun mats were consolidated to solid nanocomposites, whose mechanical properties were characterized. It was observed that the initial modulus of the nanocomposites was improved significantly, while their tensile strength was not improved much. Further study has been centered on the electrospinning of polymer solutions with functionalized CNTs, which will validate an idea that nanofibers can be utilized as a dispersion media of CNTs for advanced polymer composites.

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