Fabrication of MWNTs/nylon conductive composite nanofibers by electrospinning


School of Advanced Materials Science and Engineering, Center for Nanotubes and Nanostructured Composites, SungKyunKwan University, Suwon, 440 736, Republic of Korea

Available online 12 October 2006

Abstract

MWNT/nylon 6, 6 composite nanofibers were fabricated using an electrospinning method, and the electrical properties were examined as a function of the filler concentration. Initially, the pristine, purified MWNTs were treated with a 3:1 mixture of concentrated H2SO4/HNO3 to introduce carboxyl groups onto the MWNT surface. The carboxylated MWNTs were then treated with thionyl chloride and an ethylenediamine solution for amide functionalization. FT-IR spectroscopy was used to examine the functionalization of the MWNTs. Nylon 6, 6 is readily soluble in formic acid. Therefore, the amide functionalized MWNTs were dispersed in formic acid. The solution remained stable and uniform for more than 40 h. –NH2 termination of the MWNTs improved the dispersion stability of the MWNTs in formic acid. The MWNTs-suspended in a solution of nylon 6, 6 in formic acid was electrospun to obtain the nanofibers. The electrical properties of the nanofibers were examined as a function of the filler concentration. The results showed that the I–V properties of the nanofiber sheet improved with increasing filler concentration.

Keywords: MWNT; Electrospinning; Composite; Nylon

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention on account of their unique mechanical and electrical properties. These properties find applications in a wide variety of electrical devices and materials. There are many reports of composites of CNTs with a polymer for use in many devices [1–4]. Several parameters can affect the properties of the CNT composites, such as the filler dispersion, orientation and interfacial bonding [5]. Electrospinning is a novel and efficient tool for producing nanotube–polymer composites. Composites fabricated by electrospinning can be used to assemble fibrous polymer sheets with fiber diameters ranging from the nm to μm range. The electrospinning set-up consists of a bipolar high voltage source, a syringe injector coupled to a needle (to carry the polymer fluid from the syringe to the spinneret) and a conducting collector to obtain randomly orientated or aligned nanofibers. In the electrospinning process, high strength, low weight and low porosity can be achieved along with tailored surface functionality, depending on the polymer type and polymer nanofibers with a wide range of properties, such as electrical conductivity [6–10]. These properties make the polymer nanofibers a good candidate for a wide variety of applications. Several studies have focused on conducting polymer composite nanofibers using CNTs as the filler. However, the degree of dispersion of CNTs in the composite matrix is the key issue. Generally, a stable and uniform suspension of nanotubes in the polymer is required to obtain a fine dispersion, which can be achieved using various types of surfactants, such as sodium dodecyl sulfate and triton-X [11]. However, this approach is problematic due to the need to remove and separate the surfactants from the solution, which can lead to undesired effects.

Nylon has good chemical resistance and stability. However, the degree of dispersion of the MWNTs in an as prepared nylon solvent is poor, and there are few reports on the electrospinning of MWNTs/nylon composites. This study fabricated MWNTs/nylon nanofiber composites using an electrospinning technique. Formic acid was used as the solvent due to the fine dispersion stability of the MWNTs and good solubility of nylon. The electrical properties of the MWNTs/nylon nanofibers were examined as a function of the filler composition. This paper reports the –NH2 functionalized carboxylated MWNTs dispersed in a nylon solution prepared in
formic acid, the electrospinning of MWNTs/nylon nanofibers and the electrical characterization of the spun mat.

2. Experimental

Nylon 6, 6 (Sigma Aldrich) was used as the matrix material for the nanofiber and multi-walled nanotubes (MWNTs, Iljin Nanotech Co., Ltd., diameter ∼15–25 nm), which were grown by chemical vapor deposition (CVD). To obtain a uniform dispersion, the raw MWNTs were first functionalized [12] by sonicating a suspension of MWNT in a sulfuric and nitric acid solution (95% H2SO4: 65% HNO3 =3:1) for ∼4–7 h. After the acid treatment, the functionalized MWNTs were collected on a PTFE (polytetrafluoroethylene) membrane (pore size ∼1 μm). The acid treated MWNTs were neutralized by thorough rinsing the collected nanotubes with deionized water 3 times, followed by drying at ∼90 °C under atmospheric conditions.

The amine group was attached to the functionalized MWNTs through a synthetic route using thionyl chloride (SOCl2) followed by ethylenediamine. 0.5 g of the acid treated MWNTs was dispersed by sonicating a suspension of MWNT in 200 ml of SOCl2 for 5 min. The mixture was refluxed for 24 h at 50–70 °C, filtered, and washed with anhydrous tetrahydrofuran (THF) to remove any unreacted SOCl2. The filtrate was stirred in 200 ml of ethylenediamine for 3 days at 50–70 °C and filtered through a 1 μm membrane. After filtration, the residue was washed with anhydrous ethyl alcohol to remove the residual ethylenediamine [13]. The functionalized MWNTs were then dried at ∼70 °C under atmospheric conditions. Fourier transform infrared (FT-IR) spectroscopy (Bruker IFS-66/S) was used to characterize the functionalized MWNTs.

The functionalized MWNTs were dispersed in formic acid by sonication for 1–3 h. Nylon was then added and heated to allow for dissolution until the viscosity of the solution reached its optimum level. The nylon concentration in the formic acid ranged from 10 to 15 wt.%. A dispersed MWNTs/nylon solution with a nanotube concentration ranging from 1 to 20 wt.% was obtained using this process.

The MWNTs/nylon solution was spun into fibers using an electrospinning system (Nanofiber Co, Korea). Fig. 1(a) shows a schematic diagram of the electrospinning process.

A syringe was filled with a MWNTs/nylon solution and transferred at a flow rate of 0.1–0.5 ml/h. The electrospin fibers were collected on a metal collector or a glass plate. The inner diameter of the syringe needle was 0.25 mm and the distance between the needle and the rotating drum collector was 7–12 cm. The potential difference between the MWNTs/nylon solution loaded needle and the collector was 15–20 kV.

The MWNTs/nylon nanofibers obtained were coated with a conducting platinum coating and their textural morphology was examined by environment scanning electron microscopy (ESEM: XL30 ESEM-FEG, Philips) and transmission electron microscopy (TEM: JEM 3010, JEOL). The nanofiber samples for the ESEM studies were prepared on an aluminum plate, whereas they were spun directly onto a TEM-copper-grid for TEM analysis.

The electrical properties of the MWNTs/nylon nanofibers were examined as a function of the filler content. The MWNTs/nylon nanofibers were sprayed on the ITO coated glass for a 3 min period. The thickness of the nanofiber sheet was found to be ∼1 μm. The metal coated glass electrode with area of ∼0.25 cm² was placed on the MWNTs/nylon fiber sheet sprayed on the ITO glass. Fig. 1(b) shows a schematic diagram of the analysis.

3. Results and discussion

The dispersion of the CNTs in the polymer composites is the key issue. There are several methods for dispersing the CNTs in polymer solvents. Typically, an acid treatment is used to disperse...
the CNTs in solvents such as DMF, NMP, and water. It was reported that the acid treated MWNTs could be well dispersed in DMF [14]. The superior dispersion of the acid treated MWNTs in DMF can be explained by the strong coulombic attraction interaction between the positively charged amide groups (–NR$_2$) and the negatively charged MWNTs in the DMF suspension [14,15]. An aqueous solution is a good solvent for dispersing acid treated MWNTs. Acid treated MWNTs have functional groups such as carbonyl, hydroxyl, and carboxyl, which contain oxygen. Therefore, an interaction between the acid treated MWNTs and water molecules is increased and an electrostatic repulsive force is induced between the MWNTs. As a result, the inter-tube dispersion is very efficient. A dispersion of MWNTs in an aqueous solution can be improved using these two interactions. The electrostatic repulsive force between MWNTs has a maximum point when the solution has a pH of 7 [16]. MWNTs dispersed in aqueous solution can be precipitated when the pH of the solution is varied to a pH lower or higher than pH 7. Formic acid was used as a solvent in this study because the nylon is soluble in formic acid.

Fig. 2 shows the FT-IR spectra for (a) the pristine MWNTs, (b) carboxylic functionalized MWNTs and (c) amide functionalized MWNTs. The peak at $\sim 1631$ cm$^{-1}$ was assigned to the C–C stretching vibration mode associated with sidewalls of the MWNTs. After the acid treatment of the MWNTs, an additional peak was observed at $\sim 1712$ cm$^{-1}$, which was assigned to the C=O stretch of the carboxyl group. However, after the amine treatment of the carboxylated MWNTs, the 1712 cm$^{-1}$ peak disappeared and a new peak at $\sim 1577$ cm$^{-1}$ was observed. This was assigned to the in-plane N–H molecular vibrations of the amine group [17]. It is believed that a substitution reaction occurs and a –NH group replaces the –OH group of the carboxylated MWNTs after amide functionalization to form the –CO–NH functional group.

Fig. 3 shows images of the dispersion of carboxylated MWNTs and the amide functionalized MWNTs in the formic acid solution (sonication $\sim 30$ min). The bottle on the left side contained carboxylic functionalized MWNTs and the bottle on the right side contained amide functionalized MWNTs. (a) Initial status and (b) after 44 h.

Fig. 4 shows images of the dispersion of carboxylated MWNTs and the amide functionalized MWNTs in the formic acid solution. The bottle on the left side contained carboxylic functionalized MWNTs and the bottle on the right side contained amide functionalized MWNTs. (a) Initial status and (b) after 44 h.

Fig. 3. Images of the MWNTs dispersed in a formic acid solution (sonication $\sim 30$ min). The bottle on the left side contained carboxylic functionalized MWNTs and the bottle on the right side contained amide functionalized MWNTs. (a) Initial status and (b) after 44 h.

The solution flow rate was 0.4 ml/h.

Fig. 4. SEM images of the (a) only nylon fibers with a 15 wt.% nylon solution, (b), (c) and (d) are TEM images of the MWNTs/nylon composite nanofibers with 2 wt. %, 10 wt.%, and 20 wt.% of MWNTs in the nylon fibers respectively. All the samples were electrospun at 18 kV with a needle and a collector distance of 10 cm. The solution flow rate was 0.4 ml/h.
acid solution in (a) initial stage and (b) after 44 h. The figure shows that, the amide functionalized MWNTs were more stable in formic acid than the carboxylated MWNTs. Although, both had good dispersion properties during the initial stage, the amide functionalized MWNTs dispersion was stable for more than 40 h. In contrast, during the same period of time, the carboxylated MWNTs agglomerate, precipitated and settle to the bottom of the solution. For the acid treated MWNTs, it appears that the molecular interactions between the acid molecules and carboxyl group (on the surface of the MWNTs) are weaker than the coulombic attraction between the positively charged amide groups (–NR₂) and the negatively charged MWNTs in DMF suspension. Furthermore, the electrostatic repulsive force between the acid treated MWNTs in formic acid was also weak because of low pH. However, for the amide functionalized MWNTs, the amine terminated MWNTs have stronger interaction with the formic acid molecules than the carboxylated MWNTs. Hence, amide functionalized MWNTs showed better stability in formic acid than carboxylated MWNTs.

MWNTs/nylon nanofibers were obtained using the mixed solution of MWNTs and nylon by electrospinning. SEM and TEM were used to examine the morphology of the nanofibers obtained. Fig. 4(a) shows the SEM images of the nylon nanofibers showing that the spun nanofibers were oriented randomly in the non-woven mat. The diameter of the nanofibers was ~150–200 nm. Fig. 4(b), (c), and (d) shows the TEM images of the MWNTs/nylon spun nanofibers containing 2, 10 and 20 wt.% MWNTs, respectively. The TEM images show that the fibers containing MWNTs increase in density with increasing wt.% of the MWNTs in the nylon 6, 6 fibers. In another experiment, a fluid blocked the outlet spinneret as a result of the high concentration of MWNTs in the fluid.

Fig. 4(a) shows a typical I–V characteristic of the nanofiber composite mat containing 10 wt.% and 20 wt.% MWNTs. In the I–V measurement, the contact resistance was neglected and the measurements were carried out for different MWNT concentrations. The I–V characteristics of the nanofiber mat showed a non-ohmic behavior. Fig. 5(b) gives a plot of the MWNT loading in the nylon 6, 6 fibers as a function of current (A). It can be seen that, there was no significant variation in the current up to ~6 wt.% loading in the fiber. However, at ~10 wt.% MWNTs, the current was ~0.15 and ~0.68 mA at an applied voltage of ~5 and 10 V, respectively. The current increased from 0.59 mA to 1.77 mA with increasing MWNT loading in the fiber from 10 wt.% to 20 wt.%. The observed increase in current suggests that theCNT loading boosts the electron conduction path. Moreover, there is the possibility of “bridging” between the nylon phases with increasing carbon nanotube loading. As a result the effective concentration of charge carrier increases which, in effect, reduces hopping distance of conduction electron and favors percolation phenomenon. The MWNTs incorporated in the nylon/MWNTs composite nanofibers with different concentrations were confirmed by TEM (Fig. 4(b–d)). The nylon/MWNTs composite nanofibers containing 20 wt.% MWNTs contained more closely packed MWNTs. The close packing of MWNTs with covalent interlocking with the matrix allows electron charge transfer from the matrix to the loaded MWNTs through chemical bonding between the filler and the matrix. For MWNTs in nylon 6, 6 nanofibers, charge can be transferred from the nylon matrix to the MWNTs through the chemical bonding between the nanotubes and matrix. As a result, the MWNTs can facilitate electron transport and increase the electrical conductivity of the nanofibers [18].

4. Conclusion

Non-woven mats of nylon nanofibers loaded with MWNTs were fabricated using an electrospinning process. Formic acid was used as the solvent. No surfactants were used to help functionalize the MWNTs. Moreover, the –NH₂ terminated carboxylated MWNTs dispersion was stable for more than 40 h compared with the carboxylated nanotubes. The observed improvement in the –NH₂ functionalized MWNTs was attributed to the strong intra-molecular forces that overcome the inter-tube coulombic attraction. The filler concentration was varied from 0 to 20 wt.% and the I–V characteristics were examined. The I–V characteristics were found to be non-ohmic and improved with increasing filler concentration in the nylon nanofiber. This increase was attributed to the enhancement of the electron conduction process by MWNT loading.

Acknowledgements

This research was supported by the Ministry of Industry and Energy of the Korean government and KOSEF through the
CNNC, grant (0401-DD2-0161), one of the technical development program of the Materials, and grant no. RT104-03-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy.

References