Anisotropic electrical conductivity of MWCNT/PAN nanofiber paper

Eun Ju Ra, Kay Hyeok An, Ki Kang Kim, Seung Yol Jeong, Young Hee Lee *

Department of Physics, Center for Nanotubes and Nanostructured Composites (CNNC), Sungkyunkwan Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Jangangu chonchondong, Suwon 440-746, Republic of Korea

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Abstract

The electrospinning process has been used successfully to fabricate the multiwalled carbon nanotubes (MWCNTs)-embedded polyacrylonitrile (PAN) nanofiber paper. The diameters of nanofibers decreased with increasing CNT concentration. We found large anisotropic electrical conductivity, i.e., the electrical conductivity of the carbonized nanofiber paper along the spinning direction was about three times larger than that normal to the spinning direction, in good contrast with observations that the carbonized PAN nanofiber paper without CNTs did not reveal anisotropy in electrical conductivity. This proves that CNTs in PAN nanofiber were preferentially aligned along the nanofiber axis, in excellent agreements with transmission electron microscopy observations.

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1. Introduction

Polymer nanofiber papers have been fabricated using an electrospinning process that produces nanofibers from an electrically charged jet of polymer solution or polymer melts. The nanofiber diameters range from 40 nm to 2 \( \mu \)m, depending on the polymer types, bias voltage, viscosity of the solution, and so on [1]. One advantage of nanofibers is the high specific surface area developed by creating pores on the nanofiber surface [2,3]. Mechanical strength of an individual nanofiber is also expected to be enhanced with decreasing diameters [4]. This material has been widely applied to filters [5], scaffolds [6], protective clothing [7], and sensors [8].

Polyacrylonitrile (PAN) has been widely used to fabricate nanofibers owing to their easy carbonization process. PAN nanofiber papers can be used directly for electrode materials after stabilization and carbonization, which cannot be realized in other types of polymers. Another advantage of the carbonized PAN nanofiber is that the nanofiber surface can be modified and functionalized by activation process under different ambient conditions [3].

In spite of significant improvements in specific surface area of the carbonized PAN nanofibers, several drawbacks of polymer nanofibers are still present. For instance, the electrical conductivity of polymer nanofiber paper is an order of \( \mu \)S/cm, although this value relies on types of polymers [9]. Despite the fact that the electrical conductivity of an individual PAN nanofiber after carbonization is 4.9 S/cm [10], the electrical conductivity of the carbon nanofiber paper is expected to be low due to the sparse network of the nanofibers. For this reason, CNT/PAN composite has been introduced recently [11,12]. The multiwalled carbon nanotubes (MWCNTs)/PAN (20/80) composite papers without carbonization possess electrical conductivities of up to 0.5–1.0 S/cm at ambient temperature. However, the PAN-based carbon nanofibers are often required in many applications, which accompany inevitably stabilization and carbon-
ization process. For instance, the PAN-based carbon nanofiber papers have been directly used for supercapacitor electrodes, where high capacitance of 173 F/g at 10 mA/g was obtained but the power density was poor due to large electrical resistivity of the PAN-based carbon nanofibers [13]. Higher electrical conductivity is always desired to have high capacitance and high power density in supercapacitors [14]. This is the main reason to introduce CNTs in PAN nanofibers. While CNT/PAN nanofibers were prepared in organic solvent, CNT/poly(ethylene oxide) (PEO) was electrospun in water with additional surfactant [15]. Although CNT alignment was observed inside nanofiber in the latter, this material cannot be carbonized for electrodes.

In this Letter, we have studied characteristics of MWCNT/PAN composite papers after stabilization and carbonization process. The electrical conductivity was significantly enhanced with increasing MWCNT concentration. In particular, the conductivity reached about 35 S/cm at 10 wt% of MWCNT concentration after carbonization at 1000 °C, about ten times the pure PAN nanofiber paper. In addition, we will also describe the correlation between structural and mechanical properties.

2. Experimental

The MWCNTs used in this study were the CVD-grown material produced at Iljin Co. The diameters of MWCNTs were about 20 nm with typical length of a few μm. This sample was refluxed in 3 M nitric acid and stirred at 110 °C for 5 h to attach functional groups of carboxyl and hydroxyl groups [16]. MWCNTs were then dried after rinsing by distilled water. PAN and N,N-dimethylformamide (DMF) were purchased from Aldrich Chemical. The prepared MWCNT was immersed in 36 g of DMF and sonicated for 10 h in a bath-type sonicator (Hwashin Technology Co. 400 W). MWCNTs were homogeneously dispersed and stable having a dark ink-like appearance without being precipitated for several hours. PAN of about 4 g was then dissolved in MWCNT-dispersed DMF solution with different concentrations of 0.5, 2.5, 5.0, 7.5, and 10.0 wt%. This polymer solution was used for electrospinning.

The electrospinning technique is based on electrostatic forces drawing a jet of the polymer solution, which experiences high extension due to an electrostatically driven bending instability forming thin nanofibers [17]. The experimental setup used for the electrospinning process is shown in Fig. 1. A power supply (NT-PS-35 K, NTSEE, Korea) with variable high voltage (maximum voltage of 35 kV) was used for the electrospinning process. The electrospun fiber was collected by attaching it to the aluminum foil wrapped on a metal drum with a diameter of 15 cm rotating at 1000 rpm. The bias voltage was fixed at 20 kV, regardless of the MWCNT concentration. The electrospun fiber paper was stabilized at 280 °C with a ramping rate of 1 °C/min for 1 h in air and then carbonization was performed at 800, 900, and 1000 °C for 1 h under Ar atmosphere.

The nanofiber morphology was analyzed by using scanning electron micrograph (SEM: JSM6700F, Zeol) and transmission electron microscopy (TEM: JEM2100F, Zeol). Raman spectra were obtained using an excitation energy of 514 nm at 10 mW (RM1000-InVia, Renishaw). The electrical conductivity was measured by four-probe method at room temperature and ambient condition.

3. Results and discussion

3.1. Morphology of nanofibers

Fig. 1a shows a schematic of the electrospinning method. The polymer solution was ejected from the syringe pump by the bias voltage applied between syringe and collector drum. The polymer jet follows basically the field lines formed between two electrodes and is spread over the drum surface. The electric current in the jet lines also plays an important role in determining

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Fig. 1. (a) A schematic of electrospinning apparatus and (b) SEM image of partially aligned nanofibers that are electrospun. The arrow indicates the winding direction of nanofibers.
the diameter of nanofibers [18]. Nanofibers formed on the surface of collector drum were preferentially oriented along the winding direction, as shown in Fig. 1b. The degree of orientation could be evaluated by the electrical conductivity, as will be discussed below.

Fig. 2 shows SEM images of the nanofiber paper obtained with different MWCNT concentrations after stabilization and carbonization. The pure PAN nanofibers in Fig. 2a were straight with a smooth surface and an average diameter of about 300 nm. The nanofibers became curlier and more corrugated with increasing MWCNT concentrations. This is closely related to the morphology of MWCNTs embedded in PAN nanofibers in Fig. 3a,b. Some MWCNTs were even exposed to the outer surface of nanofibers, as shown in Fig. 2e. We note that MWCNTs embedded in PAN nanofiber were mostly aligned along the nanofiber axis, as shown in Fig. 3b. MWCNTs were preferentially aligned along the electric field line during injection, making them align along the nanofiber axis, in good agreements with the previous report [15]. We note that some beads were formed (Fig. 3c) particularly at high MWCNT concentration. More beads were formed, when the dispersion of MWCNTs was poor even at low MWCNT concentration. This suggests that the control of dispersion in polymer solvent is a crucial factor in increasing nanotube concentration in host polymer nanofiber. Fig. 3d shows an example of the aggregated MWCNTs embedded in the nanofiber, when nanotubes were not well dispersed at 2.5 wt% of MWCNT concentration. Although MWCNTs seemed to be well dispersed by sonication in DMF, some of the long nanotubes were entangled to each other, forming an agglomerate in this case.

One intriguing point is that the nanofiber diameters were reduced with increasing MWCNT concentrations, as shown in Fig. 2. The diameter of the PAN nanofiber decreased rapidly by adding small amount of MWCNT concentration, as shown in Fig. 2f. The diameters of MWCNT/PAN kept decreasing gradually with further increasing MWCNT concentration. This reduction in diameters originates from the enhanced conductivity of the polymer solution with additional MWCNTs. This allows large electric current during electrospinning and induces large charge accumulation in the solution jet, resulting in strong electrostatic repulsion among jet sprays. This repulsive force easily overcomes the surface tension of the jet to reduce diameters of the polymer nanofibers [18].

3.2. Raman spectra

Raman spectra provide information on the crystallinity of the graphite-based materials [19]. Fig. 4 shows Raman spectra of the MWCNT/PAN nanofibers at an MWCNT concentration 5.0 wt% as a function of carbonization temperature. When the overlapped D- and G-band were deconvoluted by using mixed Gaussian–Lorentzian curves, the best curve fitting was obtained with three bands at 1573–1591 cm$^{-1}$ (G-band), 1343–1354 cm$^{-1}$ (D-band), and 1462–1497 cm$^{-1}$ ($D_0^0$-band, associated with amorphous sp$^2$-bonded carbons or interstitial defects) [20–22]. The D- and G-peak positions...
Fig. 3. (a) SEM image of the protruded MWCNTs at the edge, (b) TEM image of the MWCNT oriented inside PAN fiber, (c) SEM image of the MWCNT/PAN nanofiber paper at an MWCNT concentration of 5 wt% and a circular bead and (d) TEM image of the aggregated MWCNTs inside the nanofiber.

Fig. 4. Raman spectra of MWCNT/PAN nanofibers at an MWCNT concentration of 5.0 wt% as a function of carbonization temperature: (a) 800; (b) 900 and (c) 1000 °C. The intensity ratio ($R$) for MWCNT/PAN nanofibers and crystalline domain size ($L_a$) of (d) carbonization temperature at an MWCNT concentration of 5.0 wt% as a function and (e) MWCNT concentration.
were almost independent of the carbonization temperature. It is well known that \( R \)-value, the intensity ratio of the D-band to the G-band, depends on both the degree of graphitization and the alignment of the graphitic planes. The \( R \)-value is also sensitive to the ratio of concentration of graphite edge planes and/or crystal boundaries to standard graphite planes. The lower the \( R \)-value, the larger the amount of sp\(^2\) clusters that exist in the sample. The \( R \)-values of MWCNT/PAN nanofibers decreased with increasing carbonization temperature (Fig. 4d). This strongly indicates the transformation of disordered carbons into graphitic carbons during carbonization process. The sample crystallinity can be quantified by an empirical formula, where the crystallite domain size \( L_a \) (nm) of graphite is obtained by \( L_a = 4.4/R \) [22]. Using this equation, \( L_a \) was enhanced from 4.21 to 4.93 nm with increasing carbonization temperature, as shown in Fig. 4d. The \( R \)-value was abruptly reduced by introducing 0.5 wt% of MWCNTs in the PAN nanofiber, as shown in Fig. 4e. This was mainly attributed to the reduction of the PAN weight (~30 wt%) after carbonization. The strong G-band of MWCNTs, which is a characteristic of sp\(^2\) hybridization, reduced the \( R \)-value. This is in excellent agreement with the previous report that the \( R \)-value was saturated at an MWCNT concentration of about 5 wt% [23].

3.3. Electrical conductivity

Since the potential application of MWCNT/PAN nanofiber paper is electrodes of supercapacitors and fuel cells, carbonization process is prerequisite prior to applications. Carbonized pure PAN nanofiber papers have in general electrical conductivity of a few S/cm, much larger than that (a few \( \mu \)S/cm) of polymer nanofibers without carbonization [11,12]. Since MWCNTs have superb electrical properties, we expect a better electrical conductivity in MWCNT/PAN nanofibers. As observed in Fig. 1b, the PAN nanofibers were aligned preferentially along the winding direction. We measured the electrical conductivity parallel and perpendicular to the winding direction (or fiber axis) by the four-point probe method. The electrical conductivity of the pure PAN nanofiber paper is 0.2–0.5 S/cm, depending on the carbonization temperature, as shown in Fig. 5. Carbonization at high temperature slightly increased the electrical conductivity due to the reduction of sp\(^3\) bonds. No significant conductivity change between perpendicular and parallel directions (Fig. 5) was observed in pure PAN nanofibers in spite of some preferential alignment along the winding direction. The electrical conductivity as a function of MWCNT concentration in terms of carbonization temperature is also shown in Fig. 5. The electrical conductivity of the MWCNT/PAN nanofiber papers was enhanced more appreciably at higher carbonization temperature with increasing MWCNT concentration. This is strongly correlated with Raman spectra, where the relative ratio of graphitic sp\(^2\) (corresponding G-band in Raman spectra) to the insulating sp\(^3\) (D-band) was increased with increasing carbonization temperature and MWCNT concentration. Since MWCNTs are aligned preferentially along the nanofiber axis and provide good conducting pathways, we expect a higher conductivity along the nanofiber axis. The gradual increase of the conductivity in both directions suggests that the percolation limit was not reached even at 10 wt% of MWCNT concentration. This value is relatively larger than the typical CNT concentration for percolation limit of the bulk polymer [24,25]. This could be attributed to the insufficient dispersion of MWCNTs in our sample or a characteristic of nanofibers. The parallel component of
the electrical conductivity of the MWCNT/PAN nanofiber paper was significantly larger than that of perpendicular component by a factor of about three, regardless of the MWCNT concentration, as shown in Fig. 5c. We note that the anisotropy at 800 °C is close to one, independent of MWCNT concentration. The resistivity of PAN nanofiber can be expressed by \( \rho = \rho_{\text{PAN}} + \rho_{\text{CNT}} \). In this case, the resistivity of PAN nanofibers bridged among MWCNT networks is dominant due to the insufficient heat treatment, whereas the resistivity of nanotubes is negligible. Therefore, no significant anisotropy is expected, similar to the pure PAN nanofiber network. At high carbonization temperature, the resistance of the PAN nanofiber is significantly reduced and thus \( \rho_{\text{CNT}} \) prevails the resistance of the network, invoking the anisotropic conductivity. In such a case, the effective length of the MWCNT network along the perpendicular direction will be longer than that along the parallel direction [26].

### 4. Conclusion

We have prepared MWCNT/PAN nanofiber papers by using electrospinning method. The paper was further stabilized and carbonized at different temperatures. We found that the diameters of MWCNT/PAN nanofibers decreased with increasing MWCNT concentration, which was attributed to the enhanced electrical conductivity of the polymer solution at high MWCNT concentration. We also found that the electrical conductivity of the carbonized MWCNT/PAN nanofiber papers is highly anisotropic, i.e., the conductivity parallel to the winding direction is about three times higher than that perpendicular to the winding direction at 2.5 wt% of MWCNT concentration. We also proved that the D-band in Raman spectra is strongly correlated to the electrical conductivity of the composite.

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### References