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Controlled Nanofiber Composed of Multi-Wall Carbon Nanotube/Poly(Ethylene Oxide)

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We have successfully fabricated poly(ethylene oxide) (PEO) nanofibers containing embedded multi-wall carbon nanotubes (MWCNTs). An initial dispersion of the MWCNTs in distilled water was achieved using sodium dodecyl sulfate. Subsequently, the dispersion was decanted into a PEO solution, which enabled separation of the MWCNTs and their individual incorporation into the PEO nanofibers on subsequent electrospinning. Initially, the carbon nanotube (CNT) rods were randomly oriented, but owing to the sink-like flow in the electrospinning wedge, they became gradually oriented along the streaming direction, in order that oriented CNTs were obtained on entering the electrospun jet. Individual MWCNTs became embedded in the nanofibers, and were mostly aligned along the fiber axis. Evidence of load transfer to the nanotubes in the composite nanofiber was observed from the field-emission scanning electron microscopy, transmission electron microscopy and conductivity data.

Keywords nanofiber, electrospinning, multi-wall carbon nanotube, poly(ethylene oxide), composite

Introduction

Since the observation by Iijima (1), many researchers have reported on polymer composites containing carbon nanotubes (CNTs). These materials have revolutionary mechanical, optical, and electrical properties (2, 3). Carbon nanotubes have a unique molecular structure, a very high aspect ratio, extraordinary mechanical strength, and flexibility, all of which can be directly measured using transmission electron microscopy (TEM) (4). These properties make them ideal reinforcing fibers in nanocomposites.

Carbon nanotube-reinforced composites have been investigated as flame retardants (5), for improved electrical conductivity and electrostatic charging behaviors (6, 7), as optical emitting devices (5), and for lightweight, high-strength composites. For the above reasons, they are ideal candidates for developing functional and structural polymer/CNT composites (8). However, CNTs have rarely been used as reinforcing inclusions in a polymer matrix, mainly because it is difficult to achieve an efficient dispersion. This difficulty arises from the non-reactive surface character of CNTs. To

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achieve the full reinforcing potential of MWCNTs, they must be well dispersed and exhibit good interfacial strength with a matrix. In an oriented system, CNT orientation is also important to achieve a high modulus (9).

Recently, Vigolo and co-workers (10, 11) have developed a technique to spin carbon nanotubes directly from an aqueous dispersion containing sodium dodecyl sulfate (SDS). This dispersion was injected into a rotating solution of poly(ethylene oxide) (PEO), whereby the shear forces induced a degree of alignment. Replacement of the SDS adsorbed on the CNTs by PEO aggregated the CNTs. Another way of achieving dispersion is electrospinning, and a polymer solution that is electrospun is often highly elongated. We have previously used electrospinning (12) to embed carbon nanotubes in a polymer matrix to form a composite nanofiber in which the individual CNTs could be discerned. The purpose of this work was to electrically characterize the above composite nanofibers, and PEO nanofibers incorporating multi-wall carbon nanotubes (MWCNTs) were fabricated using the electrospinning process.

Experimental

Preparation of the Solutions

The MWCNTs used in the preparation of the dispersions were purchased from ILJIN Nanotech Inc., Korea. The MWCNTs were dispersed in distilled water using an SDS dispersing agent in concentrations in the range 0.1–3 wt%. All the dispersions were sonicated for a period of 1 h at a frequency of 20 kHz using a Fisher sonic dismembrator Model 550 (Fisher Scientific, UK). The resulting dispersions were homogeneous and stable, and had a dark, ink-like appearance. Aqueous poly(ethylene oxide) (Aldrich Chemical Co., USA) molecular weight = 100,000 g/mol) was mixed with an ethanol/water mixture to give 20 wt% solution, and this was added to the MWCNTs/surfactant dispersion to form a viscoelastic spinnable solution.

Electrospinning

Our electrospinning apparatus consisted of a syringe pump (KD Scientific, USA), a metal needle, a grounded target (covered with aluminum foil), and a high voltage supply (Nano Technics, Korea). In the electrospinning process, a polymer solution is held at the end of a capillary tube by surface tension, and is subjected to an electric field that induces an electric charge on the liquid's surface. Mutual charge repulsion induces a force that is directly opposite to the surface tension. As the intensity of the electric field increases, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as a Taylor cone (13). When the electric field reaches a critical value, where the repulsive electric force can overcome the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Since this jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber, which deposits randomly on a collecting metal drum. Thus, continuous fibers can be laid to form a non-woven fabric. Our solutions were electrospun from a 10 mL syringe with an 18 gauge needle at an operating voltage of 15 kV. The distance between the needle tip and the collecting plate was 15 cm, and the feed rate was 6 $\mu\text{L}/\text{min}$. Electrospinning was carried out for periods of 5 s.

Electrical Conductivity Measurements

The electrical conductivity of the electrospun fibers was measured using a digital multi-meter (Model 34401A, Agilent, USA). The conductivity of the solutions was measured using a pair of vertical parallel electrode rods.

Field Emission Scanning Electron Microscopy

The surface morphology of the electrospun fibers was observed using field-emission scanning electron microscopy (SEM, Model 6330F, JEOL, JAPAN), and the diameter of the electrospun fibers was determined from the microphotographs obtained.

Transmission Electron Microscopy

Samples were prepared for transmission electron microscopy (TEM) analysis by direct deposition of the electrospun nanofibers onto a copper grid coated by a porous carbon film. The samples were investigated using a low electron dose imaging and an acceleration voltage of 200 kV in a Model JEM-1010 TEM (JEOL, Japan).

Results and Discussion

The compositions of the dispersions and processing solutions are summarized in Table 1. The stability of nanofiber dispersions within the polymer solutions was reflected in the observation that the suspension with the higher nanofiber loading (~ 3 wt%) appeared homogeneously black. The dispersion of carbon nanofibers in the polymer matrix is largely influenced by their degree of dispersion in the solvent. In our study, the surfactant SDS was used as an agent to improve the dispersion of the nanofibers in the solvent. The surfactant was coated onto the nanofiber surface, which prevented the dispersed nanofibers from re-agglomerating because of the steric repulsion occurring between the surfactant-coated nanofibers. Using this assumption, we concluded that the degree of dispersion of the nanofibers, before they were put into the matrix, was a significant factor in obtaining a homogeneous and stable composite. Our results are in good agreement with a study on the dispersion of carbon nanotubes within a polymer matrix.

Table 1
The solution parameters used in the electrospinning process

	MWCNTs dispersion (% (w/w))+ 1% (w/w) SDS	PEO solution	Composition of the electrospinning solution
1	0.5	20 wt% PEO in	87.5% PEO + 12.5 MWCNTs (w/w)
2	1	ethanol/water (6:4)	87% PEO + 13 MWCNTs (w/w)
3	2		86.5% PEO + 13.5 MWCNTs (w/w)
4	3		86% PEO + MWCNTs (w/w)

The electrical conductivity of the PEO/MWCNTs/SDS solutions is shown in Figure 1. These were two orders of magnitude difference between the conductivities of the solutions containing 0 and 1.0 wt% MWCNTs, where the conductivity of the solutions increased dramatically. We estimated the percolation threshold (14) of the PEO/MWCNTs/SDS solutions was midway between the abrupt change in the conductivity, i.e., at about a concentration of 0.5 wt%. The percolation phenomenon is related to the insulator-conducting phase transition of conductive-insulating composites. In a composite obtained by compaction of a mixture of a conducting powders and an insulating solution, if the volume fraction of the conducting powder is lower than the critical value, the composite behaves as an insulator. As the volume fraction approaches the critical value, the composite undergoes an insulator-conducting phase transition, at which the electrical conductivity of the composite changes abruptly by several orders of magnitude. This is attributed to the formation of clusters of conducting powder spanning the composite. The critical value is often referred to as the percolation threshold.

Figure 2 shows the ejected electrospinning solution jet from the needle tip. The pictures shown in Figure 2 were taken using a 1/500 s shutter speed employing a Nikon Model D-70 digital camera (Nikon, Japan). The electric potential, denoted by the distance between the capillary tip and the collection screen, was adjusted so that a stable jet was obtained, as shown in Figure 2(a). However, as shown in Figure 2(b), the jet of PEO/MWCNTs was short and oscillated wildly. The incorporation of MWCNTs into a polymer improves electrical conductivity, and so the electrical conductivity increased with increasing MWCNTs content, i.e., the charge repulsion of the liquid surface increased so that the repulsive force easily overcame the surface tension of the liquid.

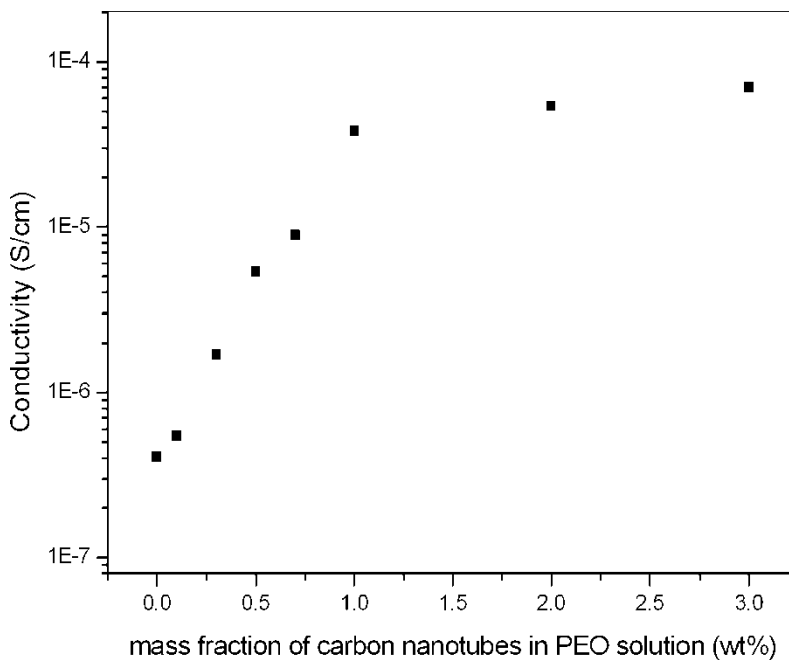


Figure 1. Electrical conductivity of PEO/SDS solutions according to concentration of MWCNTs.



(a)



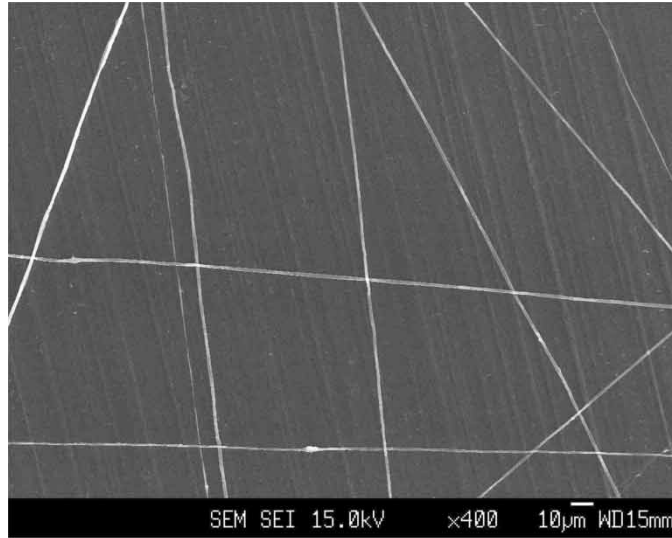
(b)

Figure 2. The ejected electrospinning solution jet with adjusted electric potential: (a) PEO and (b) PEO/MWCNTs/SDS.

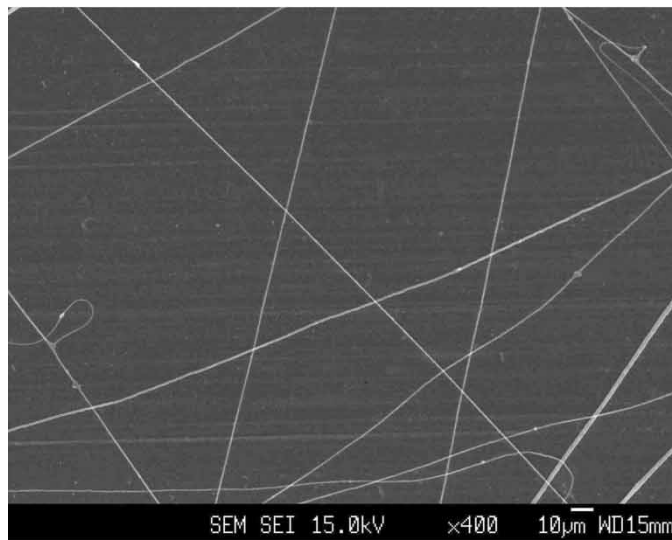
Figure 3 shows SEM images of the electrospun fibers. Figure 3(a) shows PEO fibers that did not contain any MWCNTs. Figures 3(b), (c), and (d) show electrospun fibers from PEO solutions with designated MWCNTs contents of 1, 2, and 3 wt%, respectively. The all of parameters of electrospinning process which are deposition time, applied voltage, feed rate, and tip-to-collector distance were fixed except the concentration of MWCNTs. Figure 3 shows the widening of distribution of fibers with increasing MWCNTs content. In addition, the distribution of fibers gradually widened as the electrical conductivity increased. The electrical charge induced on the liquid surface

and the MWCNTs by the electric field meant that mutual charge repulsion led to the formation of a force that was directly opposed to the surface tension.

The distribution of number of deposited fibers according to concentration of MWCNTs is shown in Figure 4. The number of electrospun fibers increased according



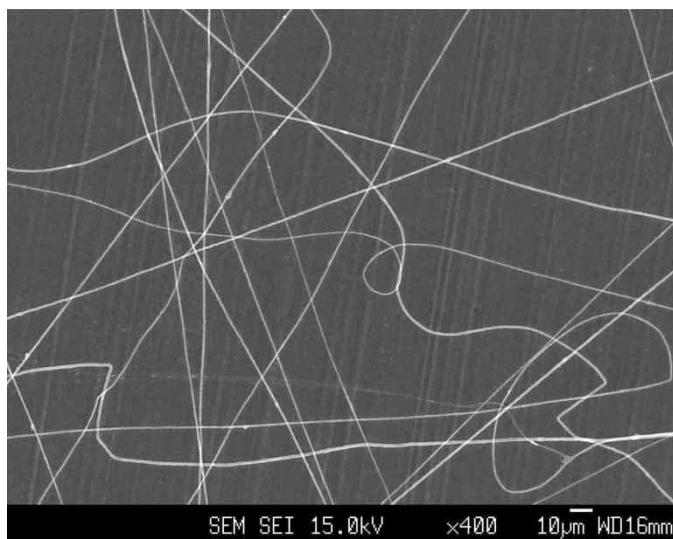
(a)



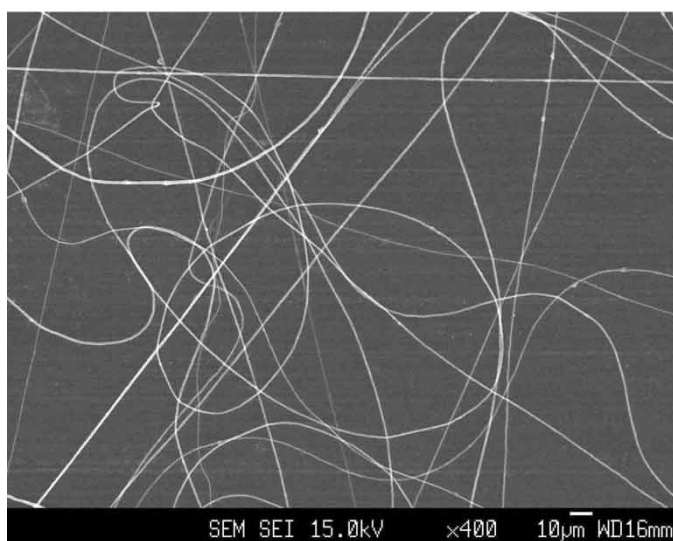
(b)

Figure 3. SEM images of electrospun fibers obtained from 20 wt% PEO solutions with different MWCNTs concentrations: (a) 0, (b) 1, (c) 2, and (d) 3 wt%.

(continued)



(c)



(d)

Figure 3. Continued.

to the increase in concentration of MWCNTs. The number of fibers at a MWCNTs concentration of 3 wt% was about three times the number of fibers at a MWCNTs concentration of 0 wt%. This was caused by the increase in repulsive charge from the increase in MWCNTs concentration. The increased repulsive force more easily overcame the surface tension of the liquid, which explains why the jet broke up earlier for higher concentration of MWCNTs.

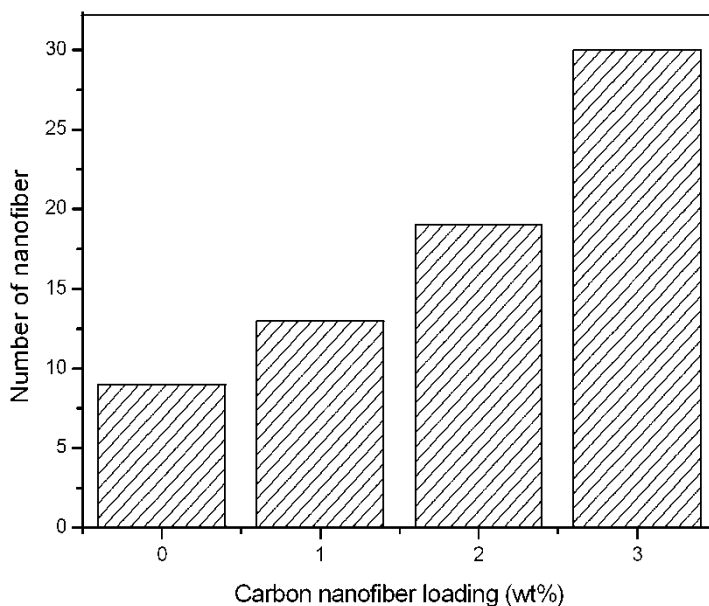


Figure 4. The distribution of number of deposited fibers with various concentration of MWCNTs.

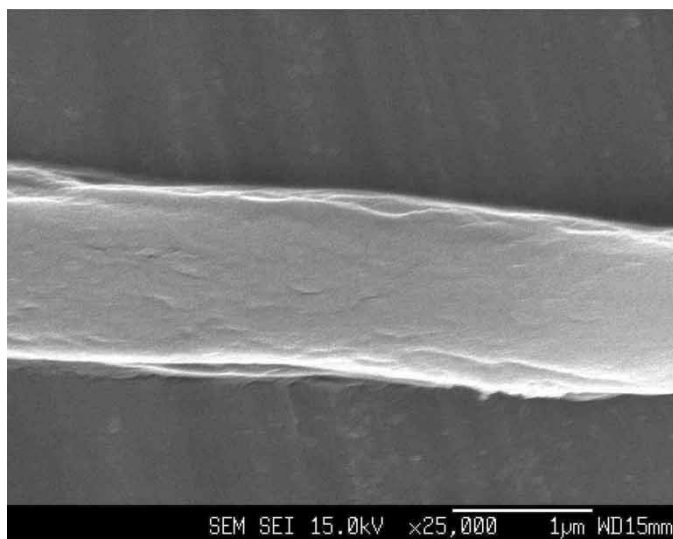
Figure 5 shows SEM images of the electrospun fibers produced from PEO/MWCNTs solutions having the concentrations listed in Figure 3. These SEM images show the difference in fiber diameter of the electrospun fibers as a function of the concentration of MWCNTs. At each MWCNTs concentration, the thinnest electrospun fiber diameter was 1.35, 0.7, 0.4, and 0.28 μm , respectively. The increased electrical conductivity reduced electrospun fiber diameter and increased repulsion, and so the jet was more easily broken up than at low concentrations of MWCNTs.

The MWCNTs/PEO dispersion was electrospun and directly deposited onto both TEM grids and the flat collector. In many regions of the electrospun nanofibers, the embedded nanotubes appeared to be well oriented along the fiber axis. Some examples of such nanofibers are shown in Figure 6 for nanotubes dispersed using SDS. In Figure 6, it can be seen that the nanotubes were oriented along the fiber axis and that the MWCNTs were well stretched by the electrospinning process.

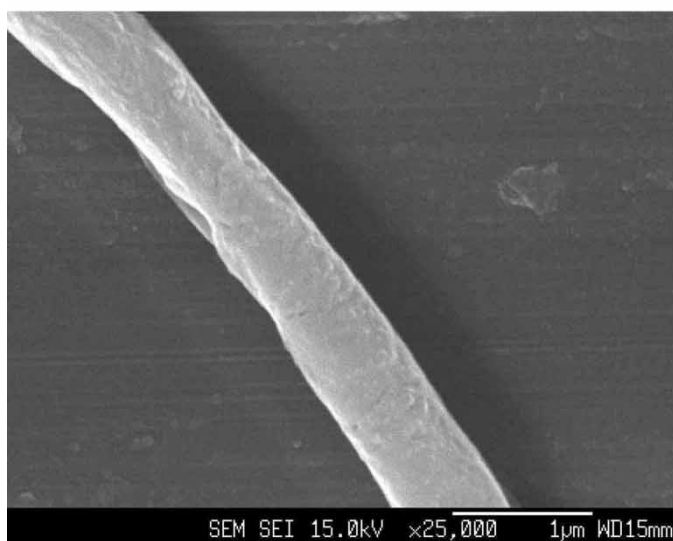
The MWCNTs was well dispersed using our system, and the resulting fibers had an improved electrical conductivity. Electrospinning of the solutions made this possible.

Conclusions

The electrospinning process was used to embed MWCNTs in a polymeric matrix to form composite nanofibers. An initial dispersion of MWCNTs in water was achieved using amphiphilic SDS molecules. This dispersed the MWCNTs and allowed for their individual incorporation into PEO nanofibers on subsequent electrospinning. The focus of this work was on the improvement of the electrical conductivity of these composite nanofibers. We observed that the percolation threshold of the electrical conductivity of



(a)

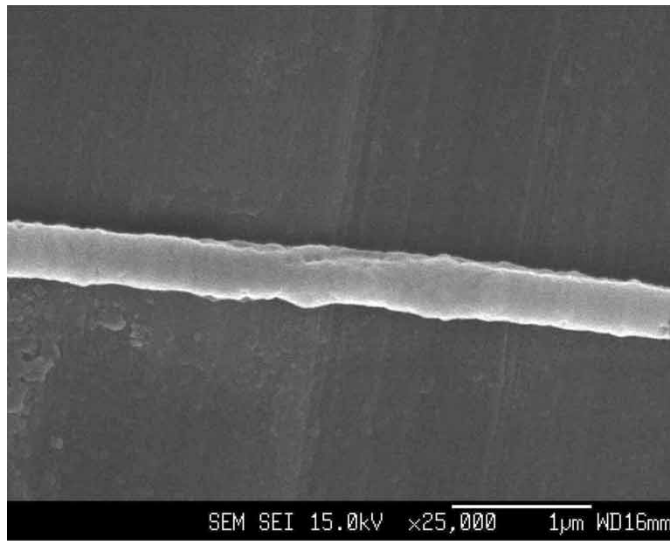


(b)

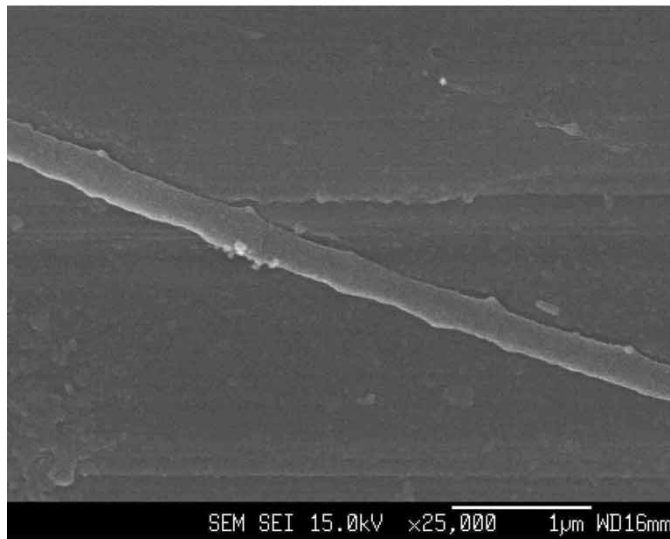
Figure 5. SEM images of nanofibers obtained from 20 wt% PEO solutions with different MWCNTs concentrations: (a) 0, (b) 1, (c) 2, and (d) 3 wt%.

(continued)

the PEO composites occurred at a MWCNTs concentration of 0.5 wt%. The distribution of fibers and the repulsive charge increased gradually after high electrical conductivity was achieved. TEM images indicated that the MWCNTs were embedded in the nanofibers as



(c)



(d)

Figure 5. Continued.

individual components mostly aligned along the fiber axis. SEM images showed that the size distribution and diameter of the electrospun fibers was improved by the increased electrical conductivity.



(a)



(b)

Figure 6. TEM images of oriented MWCNTs in MWCNTs/PEO/SDS nanofibers: (a) 0.5 wt% MWCNTs, (b) 2 wt% MWCNTs.

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