Single-Walled Carbon Nanotubes Embedded in Oriented Polymeric Nanofibers by Electrospinning

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The electrospinning process was used successfully to embed single-walled carbon nanotubes (SWCNTs) in a poly(ethylene oxide) (PEO) matrix, forming composite nanofibers. Initial dispersion of SWCNTs in water was achieved by the use of an amphiphilic alternating copolymer of styrene and sodium maleate. The resulting dispersions were stable, having a dark, smooth, ink-like appearance. For electrospinning, the dispersions were mixed with PEO solution in an ethanol/water mixture. The distribution and conformation of the nanotubes in the nanofibers were studied by transmission electron microscopy (TEM). Oxygen plasma etching was used to expose the nanotubes within the nanofibers to facilitate direct observation. Nanotube alignment within the nanofibers was shown to depend strongly on the quality of the initial dispersions. Well-dispersed and separated nanotubes were embedded in a straight and aligned form, while entangled nonseparated nanotubes were incorporated as dense aggregates. X-ray diffraction demonstrated a high degree of orientation of the PEO crystals in the electrospun nanofibers with embedded SWCNTs. This result is in pronounced distinction to the detrimental effect of incorporation of multiwalled carbon nanotubes on polymer orientation in electrospun nanofibers, as reported previously.

Introduction

Realization of the unique properties of carbon nanotubes (CNTs)1−2 in technological applications is yet a formidable challenge which attracts significant efforts. Bulk production of CNTs often results in a dense entangled network of nanotube bundles. Thus, separation of CNT bundles, their dispersion, and their alignment are elementary crucial steps for many applications, such as electronic devices, electron emitters, nanocomposite materials, and macro fibers.3−4 Among several approaches to align nanotubes,5−8 the electrospinning technique was recently used to incorporate CNTs in a polymeric matrix to form composite nanofibers,9−12 combining the benefits of nanofibers14 with the merits of carbon nanotubes. Due to the sink flow and the high extension of the electrospun jet, it is expected to align the nanotubes during the electrospinning process as was also predicted by a mathematical model.13 However, the distribution and alignment of the nanotubes in the nanofibers are strongly associated with the quality of the nanotube dispersion prepared before addition of the spinable polymer solution. Previous work showed that well-separated and regular smooth-shaped multiwalled carbon nanotubes (MWCNTs) were incorporated as individual elements mostly aligned along the nanofiber axis. Conversely, irregular nanotubes were poorly aligned and appeared curled, twisted, and entangled. It is also suggested15 that the nanofiber diameter, the interaction between the spun polymer and the nanotubes and wetting ability are important factors affecting the alignment and distribution of the nanotubes. This was demonstrated by the difference in the alignment of single-walled carbon nanotubes (SWCNTs) in polyacrylonitrile (PAN) and polylactic acid (PLA) nanofibers.

The present work is a continuation of the previous report on MWCNTs embedded in polymer nanofibers.13 We aim to incorporate SWCNTs into PEO nanofibers by the electrospinning process. SWCNTs are much smaller and uniform in shape and size, compared to MWCNTs; hence, they are expected to be embedded in a more regular form. On the other hand, their stronger tendency to bundle up into coiled aggregates introduces a pronounced difficulty. Therefore, special attention is given to the dispersion process, essential for successful alignment of the nanotubes by the electrospinning process. Structural analysis of the composite nanofibers in terms of the distribution and orientation of both the nanotubes and the polymer matrix is studied.
The linear velocity in the tapered edge rotating disk with a tapered edge rotating at a speed of 500 rpm, nanofibers were obtained in a converging electric field on a substrate at an electric field strength of 0.6 KV/cm. Oriented ropes of the nanotubes were embedded in the nanofibers by electrospinning in a controlled environment vitrification system (CEVS) at 50 W and 10 cm³/min oxygen volumetric flow rate. The exposure time ranged from 30 to 120 s.

**Experimental Section**

**Carbon Nanotubes and Dispersions.** As-produced SWCNTs purchased from Carbolex were used for preparation of the dispersions. SWCNTs were dispersed in milli-Q water using, as the dispersing agent, an alternating amphiphilic copolymer of styrene and maleic anhydride generally named as polysoap (PSSsty). The maleic anhydride group was neutralized by boiling the solution in 0.1N NaOH for 2 h to form carboxylate groups. The dispersion of 0.2% (w/w) SWCNT and 1% (w/w) PSSty (Table 1) was sonicated for 1 h in a 43 kHz Delta D2000 sonicator. The resulting dispersions were homogeneous and stable, having a dark ink-like appearance.

**Solutions for Electrospinning.** Solutions of PEO (MW = 60 kDa, Aldrich Chemical Co., Inc.) in ethanol/water mixture were added to the SWCNT/polysoap dispersion in order to achieve viscoelastic, spinnable solutions. The PEO served also as the polymeric matrix of the electrospun nanofibers in which the nanotubes are embedded after solvent evaporation. The compositions of the dispersions and processing solutions are summarized in Table 1.

**Electrospinning.** The electrospinning process was conducted at room temperature in air using air backpressure of 5 mbar pressurizing the solution out of a syringe 0.5 mm in diameter at an electric field strength of 0.6 KV/cm. Oriented ropes of the nanofibers were obtained in a converging electric field on a rotating disk with a tapered edge rotating at a speed of 500 rpm (the linear velocity in the tapered edge was V = 8.8m/s).17,18

**Plasma Etching.** As sample preparation for electron microscopy, the composite nanofibers were etched by reactive ion etching (RIE) process using oxygen as the reactive gas. The oxygen plasma is known to be adequate for etching organic materials.19,20

**High-Resolution Scanning Electron Microscopy (HRSEM).** The specimen for high-resolution scanning electron microscopy (HRSEM) were prepared by direct deposition of the electrospin nanofibers onto a piece of silicon wafer. The micrographs were obtained using a LEO Gemini 982 high-resolution SEM (HRSEM) at an acceleration voltage of 2–4 kV and a sample–detector distance of 1–2 mm.

**Transmission Electron Microscopy (TEM).** Nanofibers for TEM analysis were prepared by electrospinning directly onto a copper grid coated by a holey carbon film. Nanotube dispersions were imaged by cryo-TEM of vitrified thin films prepared in a controlled environment vitrification system (CEVS)21 and subsequently using an Oxford Instruments CT-3500 cryo-specimen holder and transfer system. Images were obtained using low-electron-dose imaging and an acceleration voltage of 120 kV in a Philips CM 120 TEM and were recorded with a Gatan MultiScan 791 CCD camera, using the Gatan Digital Micrograph 3.1 software package.

**X-Ray Diffraction.** X-ray diffraction patterns of oriented ropes collected on a rotating disk were recorded on flat film (Kodak MX125) in a Warhus vacuum camera with 0.025 in. pinholes (Blake), using Ni-filtered Cu Kα radiation from a sealed-tube generator (Philips PW1730). Both the nanofiber axis and the photo film were perpendicular to the X-ray beam. The sample–detector distance was 5.31 cm for wide-angle diffraction. Exposure time was about 50 h.

**Results and Discussion**

The SWCNT/PEO dispersion was electrospun and directly deposited either onto TEM grids placed on the flat collector or around the rotating wheel to collect a rope of oriented nanofibers. The first attempts to image carbon nanotubes within the nanofibers proved to be very difficult.

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**Table 1. Parameters of Solutions Used in the Electrospinning Process**

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<th>Dispersions</th>
<th>Solvent Composition</th>
<th>Electrospinning Composition</th>
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<tr>
<td>SWCNTs dispersion</td>
<td>40:60 (v/v) ethanol:water</td>
<td>electrosprning solution composition</td>
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<tr>
<td>0.2% (w/w) SWCNT</td>
<td>6% (w/w) PEO</td>
<td>50% (w/w) PEO solution dispersion</td>
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<tr>
<td>1% (w/w) PSSty</td>
<td></td>
<td>50% (w/w) SWCNT dispersion</td>
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Figure 1. HRSEM of nanofiber before etching (a) and after 60 s (b), 90 s (c), and 120 s (d) etching at 50 W and 10 cm³/min oxygen.
due to the low contrast between the polymeric matrix and the nanotubes and to the small diameter of the nanotubes relative to the nanofibers. Consequently, RIE was used to selectively etch the polymer matrix. HRSEM images of the nanofibers before and after plasma etching, shown in Figure 1, demonstrate the detrimental effect of long-time etching on the nanofibers' surfaces, finally resulting in dramatic distortion of the fiber.

TEM micrographs of the composite nanofibers are shown in Figure 2. In the top image (Figure 2a), vague traces of SWCNTs due to the low contrast between PEO matrix and the nanotubes are observed along the nanofiber axis. However, after intermediate-time plasma etching, which reduces the nanofiber thickness without damaging the carbon nanotubes, the SWCNTs are clearly exposed as shown in Figure 2b, revealing several SWCNTs well centered and aligned along the nanofiber axis. At the left bottom corner of the image, a cluster of catalyst and amorphous carbon is also observed.

A cryo-TEM micrograph of the original nanotube dispersion prior to the addition of the PEO solution is presented in Figure 3. It is evident that the nanotubes are well separated either individually (thin arrow) or as thin bundles (thick arrow), imaged as thicker threads containing no more than 3–4 nanotubes. Entangled clusters of nanotube bundles are not observed in this image. However, a few small clusters could be found occasionally after viewing many images.

It is important to note that the electrospinning process can handle even dispersions of poor quality, but the alignment and distribution of nanotubes embedded in the nanofibers will be directly affected. For example, Figure 4a shows an image of a dispersion in which the amount of the nanotubes was increased 5-fold while the amount of the polysoap dispersant remained unchanged, resulting in insufficient coverage of the nanotubes' surface. The dispersion in this case is rather poor, with many bulbs consisting of catalyst particles surrounded by amorphous carbon and anchored nanotubes and thicker bundles.
Hence, these bulbs are embedded in the nanofiber as such (Figure 4b) and cannot be unraveled by the electrospinning process.

X-ray diffraction patterns from ropes of electrospun nanofibers are shown in Figure 5. Nanofibers containing only PEO (Figure 5a) exhibit a characteristic fiber pattern of the common monoclinic unit cell, as was described in our previous work. The sharp equatorial reflections indicate that the PEO crystals are oriented with the chain axis preferentially aligned along the nanofiber axis. The degree of orientation can be evaluated by the azimuthal breadth of the first equatorial reflection (120) by calculating the full width at half-maximum (fwhm), which is presented in Table 2. Upon the addition of SWCNTs, the PEO orientation remains mostly unaffected (Figure 5b). The slight difference in the values of the degree of orientation may be attributed to the difficulty in precise measurement of the fwhm. Yet, as can be clearly qualitatively observed, the orientation remained generally unchanged. Here, the thin and well-aligned nanotubes do not disturb the crystalline structure of the PEO. No trace of diffraction from carbon nanotubes could be observed in the composite nanofiber pattern.

Conclusions

The electrospinning process was successfully used to embed SWCNTs in a polymeric matrix, forming composite nanofibers. Initial dispersion of SWCNTs in water was achieved by the use of an amphiphilic alternating copolymer of styrene and sodium maleate. To image the nanotubes within the polymer nanofibers, oxygen plasma etching was used at optimal conditions for adequate reduction of nanofiber thickness and exposure of the nanotubes. The conformation of the nanotubes within the nanofibers was strongly correlated to the quality of the initial dispersion. Well-dispersed and separated nanotubes were embedded in a straight and aligned form, while entangled nonseparated nanotubes were incorporated as dense aggregates. The high degree of orientation of PEO crystals was not significantly affected by the well-aligned SWCNT, which is in pronounced distinction to the detrimental effect of MWCNTs incorporation, as was previously reported. The significant features of these composite nanofibers, particularly their reinforcement by oriented individual or small-bundle SWCNTs, while maintaining a high degree of polymer orientation, may yield interesting performance, which is a subject of further studies.

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<table>
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<th>nanofiber composition</th>
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<td>PEO</td>
<td>14</td>
</tr>
<tr>
<td>PEO/PSSty/SWCNT</td>
<td>20</td>
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Table 2. Degree of Orientation of PEO in the Nanofibers

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Figure 5. X-ray diffraction of (a) PEO nanofiber and (b) PEO/SWCNT/PSSty nanofiber.