Fabrication of Water-Soluble Polyaniline/Poly(ethylene Oxide)/Carbon Nanotube Electrospun Fibers

Yen-Wen Lin, Tzong-Ming Wu

Department of Materials Science and Engineering, National Chung Hsing University, Taichung, Taiwan 402

ABSTRACT: Ultrafine electrospun fibers of water-soluble polyaniline (PANI)/poly(ethylene oxide) (PEO) and multi-walled carbon nanotubes with attached carboxylic groups (c-MWCNTs) were successfully prepared by an electrospinning technique. Water-soluble PANI can be fabricated by a direct sulfonation of emeraldine salt form of PANI, which has been treated with chlorosulfonic acid in an inert solvent. The morphology and fiber diameter of water-soluble PANI/PEO/MWCNT fibers revealed that the composite fibers had a diameter ranging between 181 and 217 nm, with a general uniform thickness along the fibers. The X-ray diffraction data of these composite fibers were similar to those of PANI/PEO fibers, indicating the c-MWCNT is uniformly distributed in PANI/PEO matrix.

The mechanical property of 5 wt % PANI/PEO/MWCNT composite fibers was about three times in magnitudes higher than that of PANI/PEO samples. The conductivity of 5 wt % PANI/PEO/MWCNT composite fibers at room temperature is three orders in magnitude higher than that of PANI/PEO specimens. These results demonstrate that the addition of a small number of c-MWCNTs to a PANI/PEO matrix can form a conducting network in well dispersed composite fibers, thus increasing their electrical conductivity. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polyaniline; carbon nanotubes; electrical properties; electrospinning

INTRODUCTION

Intrinsically conducting polymers (ICPs) have recently received considerable attention due to their superior electrical properties.[1–3] Among ICPs, polyaniline (PANI) is one of the most frequently investigated because of its good processability, environmental stability, and reversible control of conductivity both by protonation and by charge-transfer doping.[4,5] Therefore, PANI can be widely used in various applications, such as in light-emitting diodes, biosensors, secondary batteries, and protection against corrosion.[6–12] However, the major drawback of PANI is its insolubility in common organic solvents and its infusibility at melt-processing temperatures which is associated with the stiffness of the PANI backbone and the hydrogen-bonding interactions between the imine and amino groups.

It is well-known that the fabrication of polymer nanofibers can provide a high surface area for a given mass or volume. Hence, synthesis and processing of controlled one-dimensional nanostructures of polymer is the subject of extensive research, going from the direct synthesis of nanofibers or precisely defined block copolymers,[13–18] to the nanopatterning using lithography methods or self-assembly templates.[19–22] Among these techniques, electrospinning has rapidly achieved popularity as a simple and quick method for generating nanofibers of polymers. The process involved the application of a strong electrostatic field between a capillary, connected to a tank containing a polymer solution, and a ground collector. Since the PANI is insoluble in common organic solvents, it will limit the fabrication of PANI nanofibers. One method to improve the solubility of PANI is to introduce the protonic acid into the PANI chains, leading to counterion-induced processability.[23,24] Another study involves the copolymerization of aniline with its derivatives and the introduction of substituents at the N sites or onto the backbone of PANI, to enhance the solubility of PANI.[25–27] According to those studies, PANI has been fabricated with better processability and can be soluble in various common organic solvents. Nevertheless, such synthesized PANIs are not soluble in water.

In this study, we report the fabrication of water-soluble conductive nanofibers of PANI using the electrospinning technique. The water-soluble PANI is synthesized by a direct sulfonation of emeraldine

salt form of PANI that has been treated with chlorosulfonic acid in an inert solvent. But the water-soluble PANI contained low viscosity due to the difficulty of chain entanglement of polymer backbone, the addition of a spinable polymer to assist the formation of fiber is applied in this work. Polyethylene oxide (PEO) was chosen as the spinable polymer since it is known to be easily electrospun and relatively soluble in water. The conductivity of water-soluble PANI/PEO composite nanofibers would be significantly decreased since PEO is not conductive material. Carbon nanotubes (CNTs) have recently attracted considerable interest because of their unique structural, mechanical, and electronic properties.[28–30] The addition of CNTs to a polymer remarkably improves the electrical and mechanical properties of the neat polymer matrix.[31,32] Therefore, multi-walled carbon nanotube (MWCNT) was selected as an electronic and mechanical enhancement. This article will present an exhaustive morphological study and conductivity of the PANI/PEO/MWCNT nanofibers. Raman spectroscopy, X-ray photoelectron spectrometer, and electron microscopy are employed to characterize the structure and morphology of the resulting PANI/PEO/MWCNT composite fibers.

Scheme 1 Schematic drawing of total reaction of water-soluble PANI/PEO/MWCNT composites.

EXPERIMENTAL

Preparation of water-soluble PANI/PEO/MWCNT composite fibers

PEO with $M_w = 600,000$ g/mol were purchased from Aldrich (New York). The MWCNTs used in this work were prepared by ethylene chemical vapor deposition using Al_2O_3-supported Fe_2O_3 catalysts. The diameter of MWCNTs is about 15 nm and the purity of MWCNTs is higher than 95%. The as-prepared MWCNTs were treated in a 65% HNO_3 solution using a reflux process for 4 h, which produced the carboxylic acid functional groups at the defect sites and thus improved the solubility of MWCNTs in solution. The resultant MWCNTs were washed thoroughly with deionized water until the pH value is at about 6, and then the sample was filtered and dried in a vacuum at 60°C for 24 h. Various weight ratios of MWCNTs were dissolved in 50 mL of water and ultrasonicated for 1 h to form the stable dispersion.

Water-soluble PANI was prepared by a sulfonation process of emeraldine salt of PANI with chlorosulfonic acid. For the fabrication of emeraldine salt form of PANI, a chemical oxidation of aniline with ammonium persulfate in $1.0M$ HCl solution was performed. The resulting PANI in emeraldine salt form was dissolved in 50 mL of 1,2-dichloroethane (DCE) at 80°C. Certain amount of the chlorosulfonic acid diluted with 5 mL of DCE was added dropwise into the dispersion liquid, and then the reaction was held for 1 h. The produced chlorosulfonated PANI was separated by filtration, immersed in 50 mL of water, and heated at 60°C for 1 h with stirring to promote its hydrolysis. At the same time, the MWCNT dispersion and PEO was poured into water-soluble PANI aqueous solution with constant mechanical stirring at a reaction temperature of 60°C for 4 h. Therefore, the PANI/PEO/MWCNT composite was synthesized by the solution mixing procedure. In

TABLE I
The Weight Percent, Viscosity, and Tensile Modulus of Water-Soluble PANI/PEO/MWCNT Composite

Sample	PANI content (g)	PEO content (g)	c-MWCNT content (g)	Viscosity (cP)	Tensile modulus (MPa)
PANI/PEO	0.2	0.6	0	613.3 ± 55.0	8.2
1 wt % PANI/PEO/MWCNT	0.2	0.6	0.008	631.2 ± 48.9	16.3
3 wt % PANI/PEO/MWCNT	0.2	0.6	0.024	668.0 ± 57.1	18.5
5 wt % PANI/PEO/MWCNT	0.2	0.6	0.04	661.2 ± 56.3	23.6

Figure 1 Photographs showing the aqueous dispersion stability of (a) water-soluble PANI/PEO and water-soluble PANI/PEO/MWCNT composites containing (b) 1 wt % c-MWCNTs, (c) 3 wt % c-MWCNTs, and (d) 5 wt % c-MWCNTs.

order to enhance the water evaporation, several amount of ethanol was added into the PANI/PEO/MWCNT solution. The schematic drawing of total reaction is shown in Scheme 1. Table I summarizes the weight ratio and viscosity of PANI/PEO/MWCNT materials.

The water-soluble PANI/PEO/MWCNT solution was stored in a 2.5-mL syringe with a 22-gauge needle, which was mounted on an infusion pump and a rate of 0.1 mL h^{-1} was set; smaller rate turned into an unstable jet. The spinning direction was from the left to the right. A voltage of 10 kV was applied to the needle by a high voltage power supply; this value was chosen because the fibers showed good homogeneity at this voltage. A flat piece of aluminum foil, placed 15 cm away the capillary tip, was used to collect the electrospun fibers.

Characterization of PANI/PEO/MWCNT composite fibers

The molecular structures of the resulting PANI/PEO/MWCNT composite fibers were measured by Raman and XPS spectroscopies. Raman spectra were analyzed with a TRIAX 550 Jobin-Yvon monochromator equipped with a liquid nitrogen cooled charge coupled device detector, using a He-Ne laser operating at 633 nm as the excitation source. The Raman signals were collected through a long-working dis-

tance ×50 objective. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI 5000 Versa Probe X-ray photoelectron spectrometer with the incident radiation consisting of Mg Kα X-ray and the takeoff angle fixed at 45°. The XPS spectra were fitted using Gaussian curves. The morphology of all samples was characterized by field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). FESEM measurements were conducted at 3 kV using a JEOL JSM-6700F field-emission instrument. HRTEM experiments were performed on a JEOL JSM-2010 instrument with an accelerating voltage of 200 kV. The samples for HRTEM images were prepared by casting a drop of the sample suspended in ethanol on a copper grid covered with carbon. X-ray diffraction (XRD) scans of these specimens were performed using a 3 kW Rigaku D/MAX 2000 diffractometer equipped with the Cu Kα radiation in the reflection mode. Silicon powder (325 meshes) was used as a standard sample for evaluation of the instrumental broadening, for which we assumed Gaussian profiles. The silicon peak at $2\theta = 28.48°$ had an integral half-width of 0.142°.[33] The electrical conductivity at room temperature of PANI/PEO/MWCNT composite fibers was measured by a four-probe method using a programmable direct-current voltage/current generator. Mechanical properties were tested using an Instron model 5544. Samples were prepared according to ASTM standard D4762-04.

RESULTS AND DISCUSSION

Figure 1 presents photographs of vials of the fabricated water-soluble PANI/PEO/MWCNT composite in the mixture of water and ethanol solution. The fabricated water-soluble PANI/PEO/MWCNT composites remained dispersed in the mixture of water and ethanol solution for at least 1 week; neither sedimentation nor aggregation of water-soluble PANI was observed in these samples. These results suggest that the modification by sulfonation adds
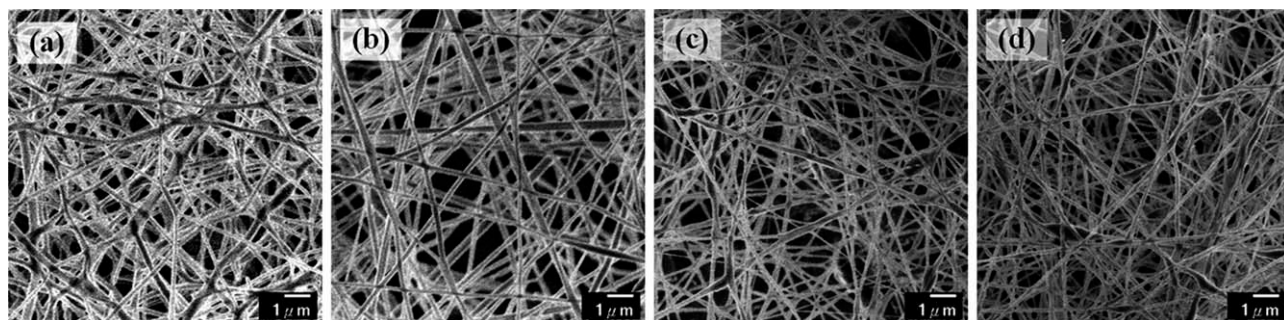

Figure 2 FESEM images of (a) water-soluble PANI/PEO and water-soluble PANI/PEO/MWCNT composites containing (b) 1 wt % c-MWCNTs, (c) 3 wt % c-MWCNTs, and (d) 5 wt % c-MWCNTs.
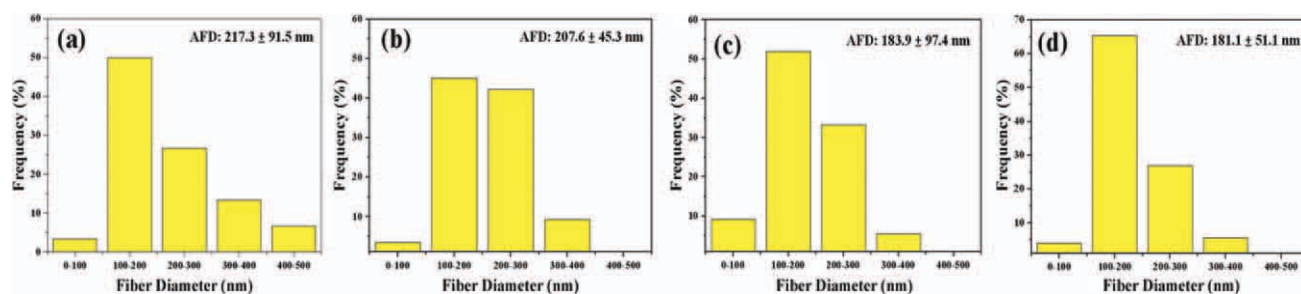
Figure 3 Histograms of the fiber diameter distribution of (a) water-soluble PANI/PEO and water-soluble PANI/PEO/MWCNT composites containing (b) 1 wt % c-MWCNTs, (c) 3 wt % c-MWCNTs, and (d) 5 wt % c-MWCNTs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

—SO_3H groups to the polymer chains and thus improves the water-solubility of the PANI. Both carbon nanotube modified with carboxylic acid groups and PEO are water-soluble. Therefore, all data shown in Figure 1 are completely soluble in the mixture of water and ethanol solution.

The morphological study of the electrospun composite fibers was characterized using electron microscopy. Figure 2 shows typical FESEM images of water-soluble PANI/PEO/MWCNT composite fiber with various MWCNT contents. For the PANI/PEO samples, the continuous and bead-free fiber can be fabricated. With the addition of 1 wt % MWCNT, similar morphology can be obtained. By adding more MWCNT into the PANI/PEO solution, the fiber diameter obtained for each composition with the same experimental parameters could be moderately decreased. In all cases, the process with addition of MWCNT into water-soluble PANI/PEO specimens was very stable and fibers could be collected continuously for long times. The histograms of the fiber diameter distributions of the above samples are displayed in Figure 3. As it can be seen, the fibers were obtained with quite uniform size distributions. The average fibers' diameter is significantly reduced with increasing content of MWCNT. The average diameter of PANI/PEO is about 217 nm and can be decreased to 181 nm with the content of MWCNT up to 5 wt %. The morphology of PANI/

PEO/MWCNT materials can be observed using TEM, which is shown in Figure 4. From this TEM image, it is clearly seen that the MWCNT is individually distributed in the composite fibers, implying that MWCNTs do not aggregate during the solution mixing and spinning procedure. The modification of MWCNT with carboxylic acid groups can induce structural arrangement for the formation of PANI/PEO nanostructure during the electrospinning process. Additionally, the MWCNT distributed inside the PANI/PEO matrix can enhance the conductivity of composite fibers.

The structure of fabricated PANI/PEO/MWCNT composite fibers can be further identified by XRD method. Figure 5 shows the XRD data for the PANI/PEO/MWCNT composite fibers. For comparison, the XRD data of MWCNT is also shown in this figure. The XRD peaks from MWCNT were observed at $2\theta = 25.9°$, corresponding to the (002) reflection of the graphite-like structure.[34] Meanwhile, there are two XRD peaks at $2\theta = 19.2$ and $23.2°$ for PANI/PEO sample, corresponding to the (120) and (032) reflections of the PEO structure. No crystalline peak of water-soluble PANI was obtained because the water-soluble PANI was amorphous. The XRD data of these PANI/PEO/MWCNT composite fibers yield similar traces compared to those from the PANI/PEO samples, indicating that no additional structural order had been introduced into the
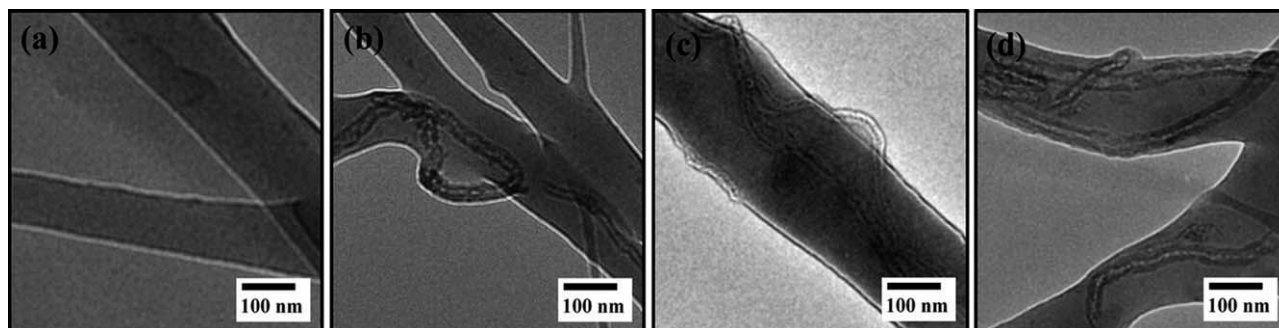

Figure 4 TEM images of (a) water-soluble PANI/PEO and water-soluble PANI/PEO/MWCNT composites containing (b) 1 wt % c-MWCNTs, (c) 3 wt % c-MWCNTs and (d) 5 wt % c-MWCNTs.
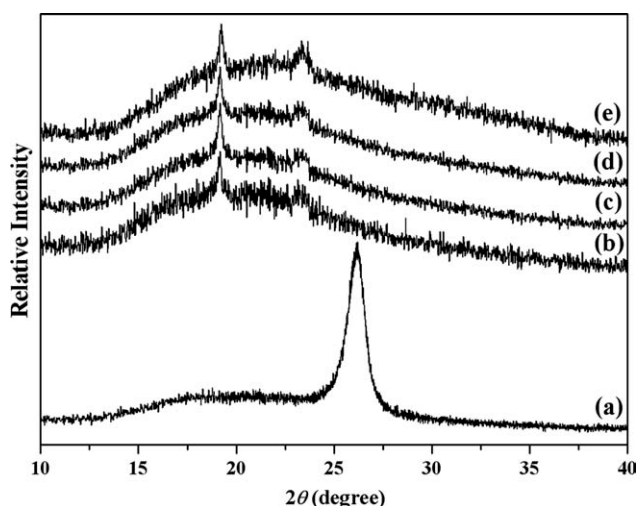
Figure 5 XRD data of (a) c-MWCNT, (b) water-soluble PANI/PEO and water-soluble PANI/PEO/MWCNT composites containing (c) 1 wt % c-MWCNTs, (d) 3 wt % c-MWCNTs, and (e) 5 wt % c-MWCNTs.

composite fibers. The crystallinity and crystallite size of PANI/PEO/MWCNT composite fibers were very close to that of PANI/PEO samples. This result demonstrates that the MWCNT was encapsulated within the PANI/PEO matrix, suggesting that the outer layer of the composite fibers was almost the same as that of PANI/PEO materials.

In order to confirm the interaction between the water-soluble PANI/PEO and c-MWCNTs, XPS analysis was used to characterize the intrinsic redox state and doping level of PANI/PEO/MWCNT composite fibers. Figure 6 presents the XPS spectra of the PANI/PEO/MWCNT composite fibers with different c-MWCNT contents at room temperature. The XPS data of these PANI/PEO/MWCNT composite fibers show similar tendency as compared to those from the PANI/PEO samples, suggesting that the doped state of PANI/PEO and PANI/PEO/MWCNT is very similar. Further narrow scans were taken of the elemental regions to provide more information about the chemical nature of each element and are summarized in Table II. The S/N ratio was very close to 0.4, indicating that every five aniline units (or average) contained two sulfonate substituents. Figure 7 shows the Raman spectra of PANI/PEO/MWCNT composite fibers. For comparison, the figure also includes the c-MWCNT spectrum, which exhibits two strong peaks at 1570 and 1320 cm^{-1}. These Raman spectra are almost the same as those of PANI/PEO and PANI/PEO/MWCNT composite fibers. The characteristic peak at 1570 cm^{-1} is attributed to the in-plane vibrations of the graphitic wall and the disorder-induced peak at 1320 cm^{-1} may originate from defects in the graphitic structure.[35] The spectra of PANI include two characteristic peaks

at 1165 and 1325 cm^{-1}, which are assigned to C—H bending and C—N stretching of the cation radical species (C—N$^{\bullet+}$), respectively. According to a previous investigation,[36] the degree of doping was proportional to the ratio of intensity of C—N$^{\bullet+}$ stretching to that of C—H bending vibrations. The calculated $I_{C-N^{\bullet+}}/I_{C-H}$ increases from 1.28 for water-soluble PANI/PEO specimens to 1.58 for 5 wt % c-MWCNT-containing PANI/PEO/MWCNT composite fibers, suggesting that the degree of protonic acid doping increases with the content of c-MWCNTs.

The electrical conductivities of water-soluble PANI/PEO/MWCNT composite fibers were measured using the standard four-probe method. The room-temperature conductivities of c-MWCNTs and water-soluble PANI/PEO specimens were approximately 16.0 and 6.2 × 10^{-9} S/cm, respectively. Meanwhile, adding 1 wt % c-MWCNT to water-soluble PANI/PEO dramatically increased its conductivity at room temperature from 6.2 × 10^{-9} S/cm to 8.4 × 10^{-7} S/cm. Increasing the c-MWCNT content further slightly increased the conductivity at room temperature from 8.4 × 10^{-7} S/cm for 1 wt % c-MWCNT-containing water-soluble PANI/PEO/MWCNT composite fibers to 3.3 × 10^{-6} and 9.0 × 10^{-6} S/cm for 3 wt % and 5 wt % c-MWCNT-containing PANI/PEO/MWCNT composite fibers, respectively. The conductivity of 5 wt % PANI/PEO/MWCNT composite fibers at room temperature was about three orders in magnitudes higher than that of PANI/PEO samples. These results show that a small number of c-MWCNTs can efficiently form a better conducting network in the PANI/PEO/MWCNT composite fibers, improving the
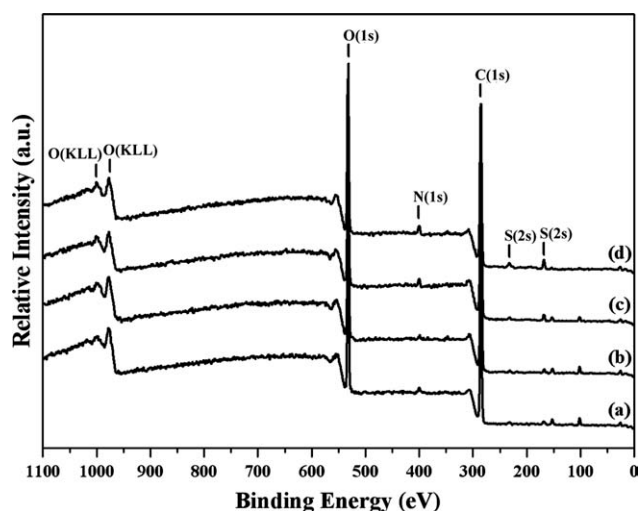

Figure 6 XPS data of (a) water-soluble PANI/PEO and water-soluble PANI/PEO/MWCNT composites containing (b) 1 wt % c-MWCNTs, (c) 3 wt % c-MWCNTs, and (d) 5 wt % c-MWCNTs.

TABLE II
The Chemical Nature of Each Element for PANI/PEO/MWCNT Sample was Obtained Using XPS

Peak	PANI/PEO	1 wt % PANI/PEO/MWCNT	3 wt % PANI/PEO/MWCNT	5 wt % PANI/PEO/MWCNT
C 1s	68.3%	69.4%	71.3%	68.9%
O 1s	30.0%	28.6%	25.3%	28.0%
N 1s	1.2%	1.4%	2.4%	2.2%
S 2p	0.5%	0.6%	1.0%	0.9%
S/N ratio	0.42	0.43	0.42	0.41

electrical conductivity. The mechanical properties of water-soluble PANI/PEO/MWCNT composite fibers were measured using the tensile test method. The tensile modulus of water-soluble PANI/PEO specimens was approximately 8.2 MPa. Meanwhile, adding 1 wt % c-MWCNT to water-soluble PANI/PEO dramatically increased its mechanical properties from 8.2 MPa to 16.3 MPa. Increasing the c-MWCNT content further slightly increased the tensile modulus from 16.3 MPa for 1 wt % c-MWCNT-containing water-soluble PANI/PEO/MWCNT composite fibers to 18.5 and 23.6 MPa for 3 wt % and 5 wt % c-MWCNT-containing PANI/PEO/MWCNT composite fibers, respectively. The mechanical property of 5 wt % PANI/PEO/MWCNT composite fibers was about three times in magnitudes higher than that of PANI/PEO samples. These results show that a small number of c-MWCNTs can efficiently enhance the mechanical property of PANI/PEO/MWCNT composite fibers.
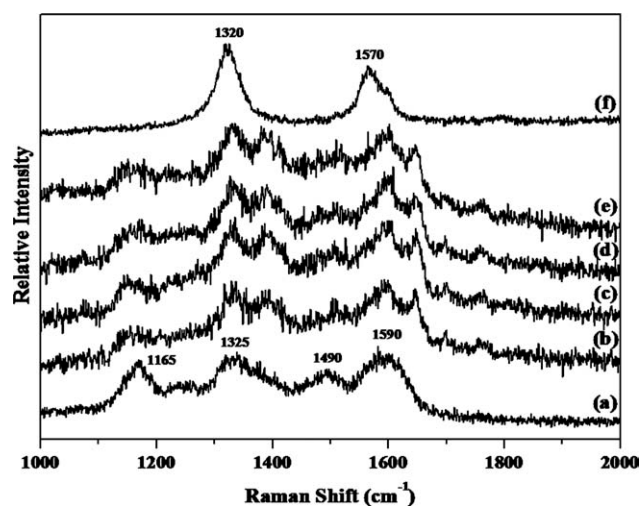

Figure 7 Raman spectra of (b) water-soluble PANI/PEO and water-soluble PANI/PEO/MWCNT composites containing (c) 1 wt % c-MWCNTs, (d) 3 wt % c-MWCNTs, and (e) 5 wt % c-MWCNTs. Raman spectra of (a) water-soluble PANI and (f) c-MWCNT are also shown in this figure.

CONCLUSIONS

Ultrafine electrospun fibers of water-soluble PANI/PEO and MWCNTs with attached carboxylic groups (c-MWCNTs) were prepared by an electrospinning technique. The morphology and fiber diameter of water-soluble PANI/PEO/MWCNT fibers revealed that the composite fibers had a diameter ranging between 181 and 217 nm, with a general uniform thickness along the fibers. The XRD data of these composite fibers were similar to those of PANI/PEO fibers, indicating the c-MWCNT is uniformly distributed in PANI/PEO matrix. The mechanical property of 5 wt % PANI/PEO/MWCNT composite fibers was about three times in magnitudes higher than that of PANI/PEO samples. The conductivity of 5 wt % PANI/PEO/MWCNT composite fibers at room temperature is three orders in magnitude higher than that of PANI/PEO specimens. These results demonstrate that the addition of a small number of c-MWCNTs to a PANI/PEO matrix can form a conducting network in well dispersed composite fibers, thus increasing their electrical conductivity.

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