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SHORT COMMUNICATION

Electrically conducting electrospun silk membranes fabricated by adsorption of carbon nanotubes

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Abstract We present a simple method of obtaining electrically conducting electrospun silk non-woven membranes consisting of nanofibers with multi-walled carbon nanotubes (MWCNTs) adsorbed on their surface. Nanofibrous membranes with fibroin diameters of 460±40 nm were formed from aqueous *Bombyx mori* fibroin solution by electrospinning. The MWCNTs adhered well to the surface of the highly porous silk nanofibrous membranes when Triton X-100 was used as the surfactant for the dispersion of the MWCNTs in aqueous media. The electrical conductivity of the membranes was 2.4×10^{-4} S/cm due to the presence of the MWCNTs on their surface. In addition, the strong interaction between the MWCNTs and nanofibers keeps them from separating each other, even after ultrasonication. The combination of the high conductivity of the membranes and the simple process used to fabricate them could lead to significant advances in the development of new materials, such as electromagnetic interference shielding or electrostatic dissipation membranes.

Keywords Silk fibroin · Carbon nanotubes · Electrical conductivity · Electrospinning · Membranes

Introduction

Electrical conductivity is one of the most important properties of polymeric materials for applications including electromagnetic interference (EMI) shielding for electronic devices and electrostatic dissipation [1]. The typical electrical conductivity of polymers, however, ranges from 10^{-14} to 10^{-17} S/cm. To improve their electrical conductivity, polymeric materials have been composed with carbon fillers such as carbon fibers, carbon black, synthetic graphite [1], and carbon nanotubes (CNTs) [2–5]. Among these different materials, CNTs have attracted the most attention since their discovery by Ijima [6], due to their unique structure and outstanding mechanical, electrical, and thermal properties [2–6].

Electrospinning offers an alternative approach to protein fiber formation that can potentially generate very fine fibers [7, 8]. This is a useful feature given the potential role of these types of fibers in certain applications, such as membranes. Electrospinning has been utilized to generate nanometer diameter fibers from various polymers. Silk is a well-described natural fiber produced by the silkworm *Bombyx mori*, which has been used in the form of threads in textiles for thousands of years [7]. Recent interest in the use of reprocessed silks, for example, as proteins in biotechnological materials and in biomedical applications, originates from the unique mechanical properties of these fibers as well as their biocompatibility [8]. Recently, CNT-filled nanofibrous membranes have been produced by electrospinning to improve their performance characteristics [9, 10]. In the present study, we improved the electrical conductivity of silk nanofibrous membranes for EMI shielding or electrostatic dissipation by the incorporation of CNTs.

Experimental

Materials

Cocoons of the *B. mori* silkworm silk were kindly supplied by Boeun Traditional Sericulture Farm, South Korea. Poly

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(ethylene oxide) (PEO) with an average molecular weight of 9×10^5 g/mol (Aldrich) was used for blending with the silk fibroin.

Preparation of aqueous *B. mori* fibroin solution

The cocoons were boiled for 30 min in a 0.02 M aqueous solution of Na_2CO_3, and the silk fibroin was obtained by rinsing thoroughly with water to extract the glue-like sericin proteins. The spinning solution was prepared by dissolving the silk fibroin in 9.3 M LiBr solution at 60 °C, yielding a 20% (w/v) solution. This solution was dialyzed in water for 48 h. The final concentration of the aqueous silk solution was about 8.0 wt%. The aqueous silk solution was blended with 5.0 wt% aqueous PEO solution, which generated a 7.5 wt% silk/PEO solution.

Preparation of nanofibrous silk membranes

Electrospinning was performed using the same procedure as that described in a previous study [7, 8]. The capillary tube was connected to a syringe filled with 10 ml of the silk/PEO blend solution. The flow rate was 0.02 ml/min, and the voltage was gradually increased to 12.0 kV (E=0.6 kV/cm). The nanofibrous membranes obtained from the silk/PEO blend solution were crystallized in methanol for 10 min, and then washed with water for 48 h at 37 °C to extract the PEO from the membranes.

Preparation of MWCNT dispersion

The CNTs used in this study were MWCNTs (JEIO, Korea), which were synthesized via a thermal chemical vapor deposition (CVD) method. To remove the impurities (such as metallic catalysts) from the MWCNTs, they were treated with 3 M HNO_3, followed by refluxing them in 5 M HCl. The purified MWCNTs were dispersed in pure water (0.5 mg/ml) containing 0.3 wt% Triton X-100 (non-ionic). Ultrasound was then applied using an ultrasonic generator (Kyungill Ultrasonic, Korea) with a nominal frequency of 28 kHz and a power of 600 W.

Characterizations

The electrospun silk fibroin membranes were dipped into a MWCNT dispersion bath for 60 s, rinsed briefly (60 s) in deionized water, and then dried under vacuum conditions (Fig. 1). Images of the electrospun fibers before and after the adsorption of the MWCNTs were obtained with a field emission gun scanning electron microscope (FESEM S-4200, Hitachi). The electrical conductivities of the MWCNT-adsorbed silk membranes were measured by a four-probe method using a picoameter with an internal voltage source (487, Keithley, USA) and an impedance analyzer (4284 A, HP, USA). A Surface Science model SSX-100 X-ray photoelectron spectrometer (XPS) was used to analyze the surface of the silk membranes to estimate the surface density of silk versus PEO. Survey scans (spot, 1,000 μm; resolution, 4; window, 1,000 eV) were performed using a flood gun (charge neutralizer) setting of 5 eV and nickel wire mesh held over the sample to prevent the charging of the sample surface.

Results and discussion

To increase the viscosity of the aqueous silk solution (8 wt%), PEO (MW 900 K) was added at a ratio of 4/1 (silk/PEO wt/wt). The viscosity and surface tension of the pure silk solution (8 wt%) were not high enough to maintain a stable drop at the end of the capillary tip. However, the addition of PEO to the silk solutions generated a viscosity and surface tension suitable for electrospinning. As the potential difference between the capillary tip and the aluminum foil counter electrode was gradually increased, the drop at the end of the capillary tip elongated from a hemispherical shape into a cone shape. The morphology and diameters of the electrospun fibers were examined using SEM (Fig. 2). The silk/PEO blend solution produced fine uniform fibers with an average fiber diameter of 460±40 nm, which was determined by counting 100 individual fibers from the SEM images using an image analyzer software. The individual electrospun fibers appeared to be randomly distributed in the non-woven

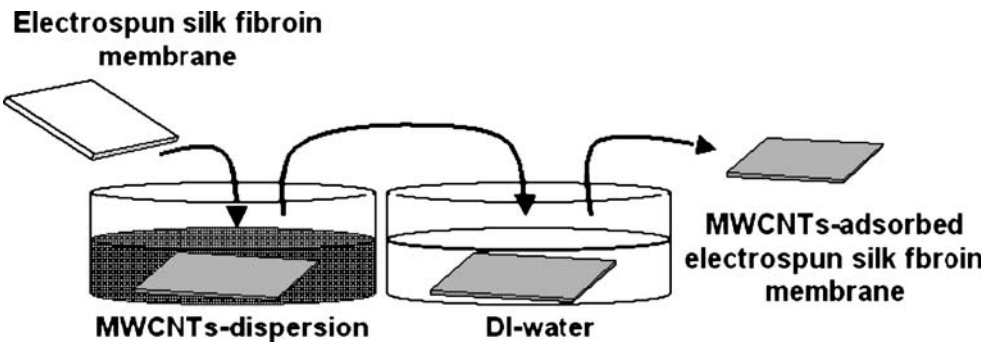

Fig. 1 Scheme showing the simple process used for producing the MWCNT-adsorbed electrospun non-woven silk membranes

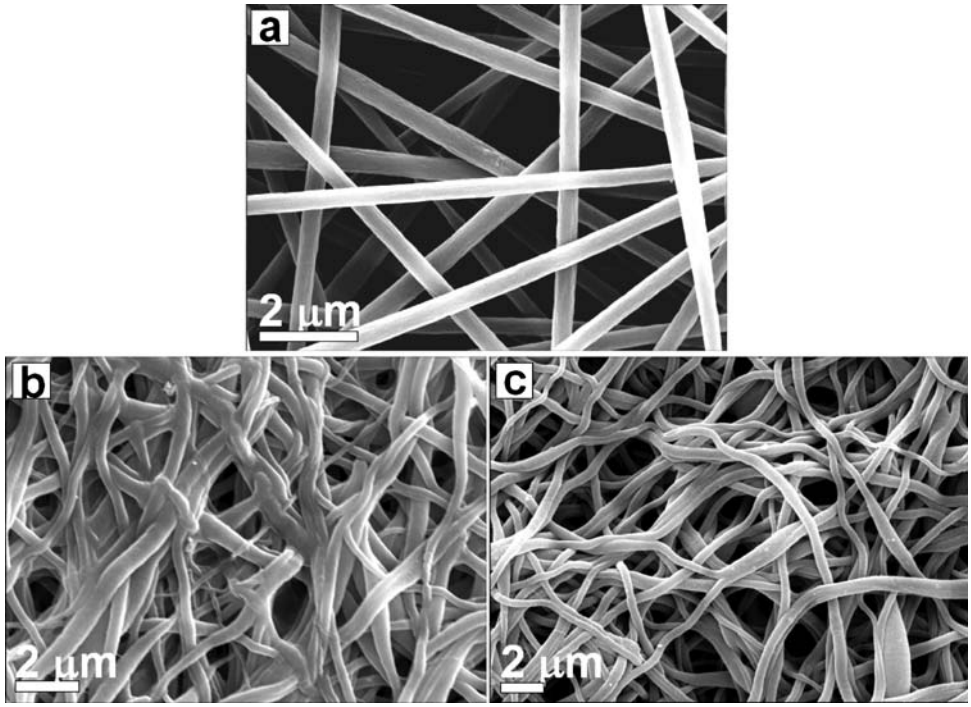

Fig. 2 SEM image of the electrospun silk nanofibers obtained from the silk/PEO (80:20 wt%) solution. **a** As-electrospun fiber; **b** methanol-treated electrospun fiber; **c** PEO-extracted electrospun fiber

mat. The electrospun mats were treated with methanol to render them insoluble in water. Note that the structure of the fibroin in the as-spun fibers is mostly random coil and the contact with methanol induces crystallization of the electrospun silk fibers or the cast films obtained from the regenerated silk fibroin solutions [7, 8]. After methanol treatment, the structure changed to predominantly beta-sheet. The surface composition of the mats before and after the methanol treatment was determined by XPS (Table 1). The ratio of the N_{1s} peak to that of the C_{1s} peak for the mat was 0.23 before the methanol treatment. After the methanol treatment, the N_{1s}/C_{1s} ratio increased to 0.29 due to the solubility of PEO in methanol. When the PEO was extracted from the mat at 37 °C in water for 2 days, the N_{1s}/C_{1s} ratio increased to 0.32 and remained at this value after 7 days. Therefore, all of the PEO had been extracted after 2 days. The SEM images of the electrospun fibers after methanol treatment shows the roughness of the fiber surfaces due to the phase separation between silk fibroin and PEO and the extraction of the PEO in water (Fig. 2).

We used a surfactant that facilitates the dispersion of the MWCNTs in aqueous media in an attempt to prevent the MWCNTs from aggregating due to the substantial van der Waals interaction between them. Triton X-100 surfactant was employed to disperse the purified MWCNTs, and in this case, homogenous black ink-like solutions were obtained after ultrasonication (Fig. 3a). The SEM image (Fig. 3b) shows the MWCNTs cast on the silicon wafer with a high degree of dispersion. This indicates that the MWCNTs are dispersed individually in the aqueous solution containing the surfactant. To adsorb the MWCNTs on the electrospun silk nanofibrous membranes, an aqueous dispersion of the MWCNTs containing Triton X-100 (0.3 wt%) was employed.

High resolution SEM images of the nanofibrous membranes obtained after dip-coating them in the aqueous

Table 1 High-resolution XPS results from the electrospun silk/PEO blend surfaces

Element	O_{1s}		N_{1s}		C_{1s}		N_{1s}/C_{1s}
	Binding energy (eV)	Atomic %	Binding energy (eV)	Atomic %	Binding energy (eV)	Atomic %	
BM	530.9	24.2	398.6	14.3	284.6	61.5	0.23
AM	530.9	24.6	398.8	17.0	284.6	58.4	0.29
EX	530.8	24.3	398.4	18.2	284.6	57.5	0.32

BM Before methanol treatment, *AM* after methanol treatment, and *EX* after PEO extraction in water for 2 days

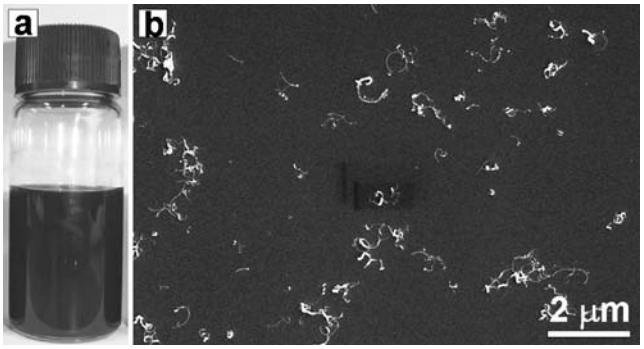

Fig. 3 **a** Aqueous MWCNT dispersion and **b** SEM image of the MWCNTs spin coated on the silicon wafer

MWCNT dispersion containing Triton X-100 during 300 s are shown in Fig. 4. The MWCNTs were densely adsorbed on the surface of the nanofibers only, maintaining their high porosity. The color of the non-woven membranes was changed from white to gray due to the presence of the MWCNTs in the membranes (Fig. 4). Even after the sonication of the

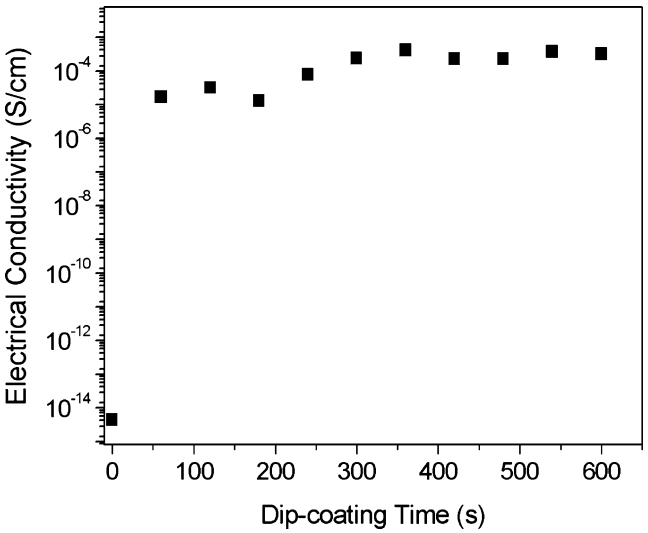

Fig. 5 Electrical conductivity of MWCNT-adsorbed silk fibroin membranes

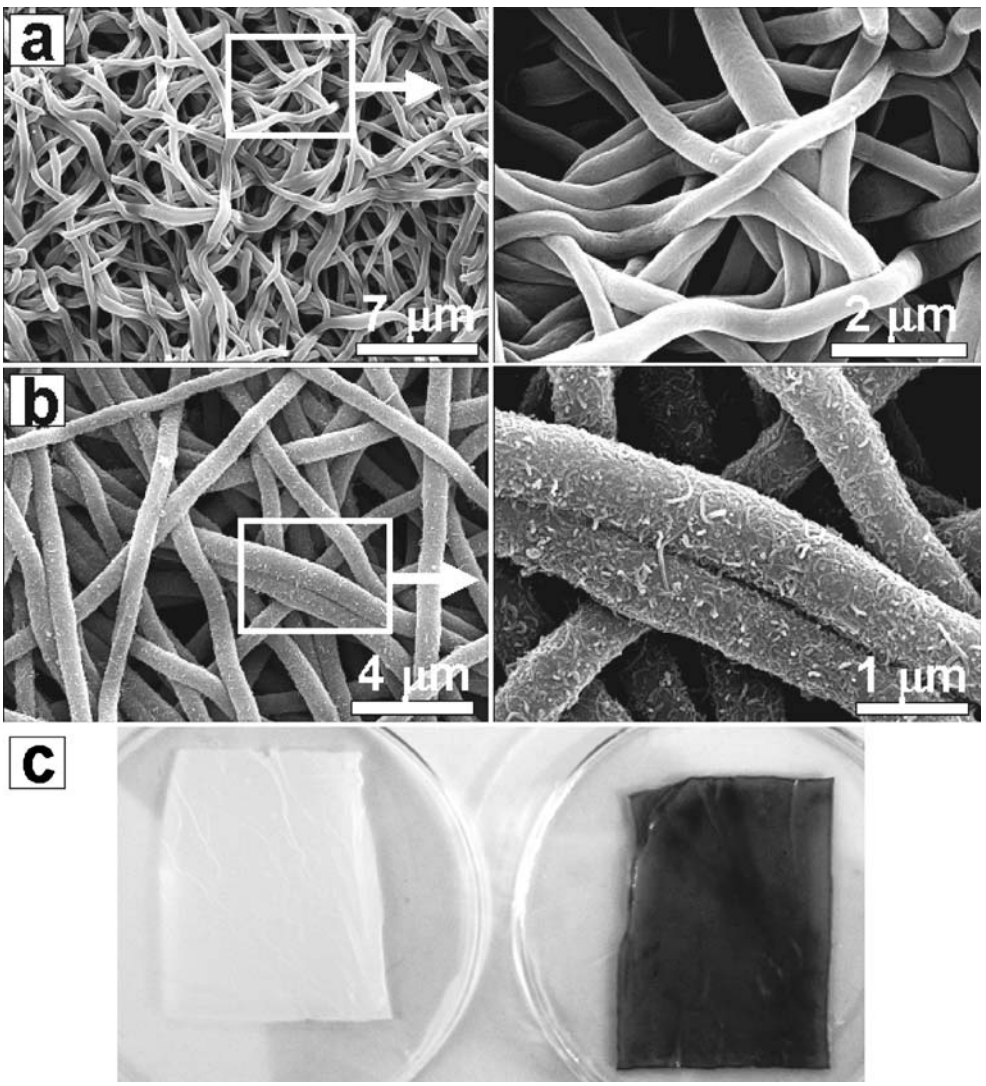

Fig. 4 SEM images of the crystallized and PEO-extracted silk fibroin nanofibers: **a** before and **b** after the adsorption of the MWCNTs and **c** images of the non-woven silk fibroin membrane (*left*) and the MWCNT-absorbed non-woven silk fibroin membranes (*right*)

MWCNT-adsorbed membranes for 10 min, a significant amount of MWCNTs remained on the surface of the nanofibers. This implies that the MWCNTs were not just deposited on the nanofiber surface, but that there was a strong interaction between the MWCNTs and the silk fibroin, causing them to be tied to each other. It is interesting to monitor the change in the electrical conductivity of the MWCNT-adsorbed membranes. The conductivity of the MWCNT-adsorbed silk membranes was 2.4×10^{-4} S/cm at room temperature, while the electrical conductivity of pure silk membranes was 4.4×10^{-15} S/cm. It should be noted that, in our systems, an MWCNT dispersion with only a low concentration (0.5 mg/ml) was utilized to produce these highly conducting polymeric membranes due to the presence of the MWCNTs on the surface of the nanofibers. We also varied the dip-coating time of the silk membranes in the MWCNT dispersion to investigate the conductivity dependence. However, electrical conductivity of the electrospun silk membranes was found to be approximately $\sim10^{-4}$ S/cm, regardless of the dip-coating time as shown in Fig. 5. This indicates that the adsorption rate of MWCNTs on the surface of the individual electrospun silk fibers is high due to the interaction between the oxidized MWCNTs and the fibroins containing peptide groups [10–13].

Conclusions

The electrical conductivity of the electrospun *Bombyx mori* silk nanofibrous membranes was improved by the incorporation of the multiwalled carbon nanotubes (MWCNT) in aqueous media. The membranes were produced from a blend of an aqueous silk fibroin solution and aqueous PEO solution, followed by the electrospinning of the blend solution. PEO with a molecular weight of 900,000 was blended with the silk fibroin to improve its processability and then extracted in water after the crystallization of the silk fibroin in methanol. The membranes were then dipped into an aqueous dispersion of the MWCNTs containing Triton X-100 surfactant to adsorb them on the surface of the silk fibroin nanofibers. Interestingly, the MWCNTs-adsorbed silk fibroin nanofibrous membranes show a large increase in their electrical conductivity (from $\sim10^{-15}$ to $\sim10^{-4}$ $S\cdot cm^{-1}$), which was measured by a four-probe method at room temperature. This value indicates their possible use in applications such as electromagnetic interference shielding and electrostatic dissipation.

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References

1. Clingerman ML, Weber EH, King JA, Schulz KH (2003) J Appl Polym Sci 88:2280
2. Zhang WD, Shen L, Phang IY, Liu T (2004) Macromolecules 37:256
3. Vigolo B, Penicaud A, Coulon C, Sauder C, Pailler R, Journet C, Bernier P, Poulin P (2000) Science 290:1331
4. Harris PJF (2004) Int Mater Rev 49:31
5. Jin H-J, Choi HJ, Yoon SH, Myung SJ, Shim SE (2005) Chem Mater 17:4034
6. Iijima S (1991) Nature 354:56
7. Jin H-J, Fridrich SV, Rutledge GC, Kaplan DL (2002) Biomacromolecules 3:1233
8. Jin H-J, Chen J, Karageorgiou V, Altman GH, Kaplan DL (2004) Biomaterials 25:1039
9. Sung JH, Kim HS, Jin H-J, Choi HJ, Chin I-J (2004) Macromolecules 37:9899
10. Kim HS, Jin H-J, Myung SJ, Kang M, Chin I-J (2006) Macromol Rapid Commun 27:146
11. Gao J, Itkis, ME, Yu A, Bekyarova E, Zhao B, Haddon RC (2005) J Am Chem Soc 127:3847
12. Saran N, Parikh K, Suh D-S, Munoz H, Kollar H, Manohar SK (2004) J Am Chem Soc 126:4462
13. Yoon SH, Jin H-J, Kook M-C, Pyun YR (2006) Biomacromolecules 7:1280