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Multiwalled Carbon Nanotubes-Embedded Electrospun Bacterial Cellulose Nanofibers

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Multiwalled carbon nanotubes (MWCNTs) were embedded in electrospun bacterial cellulose (BC) nanofibers, which were prepared using an electrospinning method. In this study, Gluconacetobacter xylinum BRC5 *was employed to produce a hydrogel-like bacterial cellulose (BC) sheet. BC was difficult to process in the solution stat because of the large concentration of intra- or inter-molecular hydrogen bonds. In this study, an ionic liquid, 1-allyl-3-methyl-imidazolium chloride, was used to dissolve BC. To form BC nanofibers, 5 wt% BC solutions both with and without MWCNTs were electrospun. Scanning electron microscopy and transmission electron microscopy showed that the MWCNTs were embedded and well aligned along the fiber axis. The crystalline polymorph transformed from cellulose I (pristine BC) to cellulose II (electrospun regenerated BC fibers). Moreover, the tensile strength and modulus of the MWCNT-embedded electrospun BC nanofibers increased by approximately 290% and 280%, respectively. Additionally, the thermal stability and electrical conductivity of the MWCNT-embedded electrospun BC nanofibers also increased compared to pristine BC.*

Introduction

The nomenclature "cellulose" was first given in 1839 in a report by A. Payen as constituting the cell walls of higher plants [1]. Cellulose is the most common organic polymer, and is considered to be an almost inexhaustible source of raw material to meet the increasing demand for environmentally friendly and biocompatible products [2]. Cellulose is prepared mainly from wood pulp but can also be produced in a highly hydrated form by some bacteria (for example, *Acetobacter, Rhizobium, Agrobacterium*, and *Sarcina*), known as bacterial cellulose (BC) [3]. The BC used in this study was an ex-cellular product of the bacterium, *Gluconacetobacter xylinum BRC5*, and has an ultrafine structure and unique properties, such as high mechanical strength, thermal stability, high degree of swelling, high crystallinity and biocompatibility (non-pyrogenic, Non-toxic) [4]. Compared to other cellulose forms, BC has excellent chemical purity, which is its most important feature. Other forms of

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cellulose normally contain hemicelluloses and lignin, the removal of which is inherently difficult. In addition, numerous new applications of BC take advantage of its biocompatibility in areas, such as the formation of cellulose composites with synthetic polymers and biopolymers [5–8]. Therefore, preparing regenerated BC materials is a great challenge.

Although individual strands of cellulose are no less hydrophilic or more hydrophobic than other soluble polysaccharides, the tendency to form crystals through intra- and intermolecular hydrogen bonding makes it completely insoluble in water and most common organic solvents. Therefore, there has been considerable interest in the development of an effective solvent system for cellulose dissolution. Several solvent systems have been reported, including *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) [9–10], *N*-methylmorpholine-*N*-oxide (NMMO) [11], NaOH/urea aqueous solution [12] and some molten salt hydrates [13]. However, the technologies currently employed in cellulose processing are not environmentally friendly, high energy costs and uncontrolled (such as NMMO system [14]) or ineffective in dissolving BC. Therefore, there is a need for an effective and eco-friendly solvent system.

In 2002, a new type of solvent system, ionic liquids (ILs), which can dissolve large amounts of cellulose, was reported [15]. ILs are believed to be an ideal solvent not only because they can dissolve a broad range of biomaterials, particularly lignin and lignocelluloses, but also due to their thermal stability, electrochemical stability, low vapor pressure, non-volatility, non-flammability, electric conductivity, liquid over a wide range of temperatures etc. These characteristics make ILs green solvents for cellulose. Another important property is the miscibility with water, for example, 1-alkyl-3-methylimidazolium salts are miscible with water at 25°C. This behavior offers an extraordinary benefit for solvent extraction or product separation processes. Therefore, ILs would be an effective solvent for BC dissolution.

Carbon nanotubes (CNTs) are one of the most exciting new materials since their discovery in 1991 by Iijima [16]. CNTs are long, slender fullerenes, in which the walls of the tubes are hexagonal carbon (graphite structure) often capped at each end. CNTs are promising fillers in polymer matrixes to prepare CNTs-reinforced composite materials on account of their exceptionally high aspect ratio, elastic modulus and high axial strength [17]. A number of studies have focused on the development of a new class of high-performance polymer composites with nanotubes as a reinforcement or filler. Polymer composite applications are quite intuitive because of their relative flexibility of fabrication, ability to tailor the composite properties through a wide range of polymers, and the ubiquity in which the polymers permeate our daily lives.

Recently, nanofibrous mats have been exploited for their high surface-to-volume ratio. In addition, three basic approaches to the fabrication of nanofibrous structure mats have emerged: self-assembly, electrospinning and thermally-induced phase separation. Among these three methods, electrospinning is one of the simplest and most effective methods for producing micro/nanofibrous nonwoven mats [18–19]. Up to now, this method has been used in many synthetic and natural biopolymers to prepare the ultra-thin fibrous mats. Moreover, these nonwoven mats have applications in filtration, protective clothing and biomedicine. However, electrospinning of some natural biopolymers, such as cellulose, is still a challenge.

In this study, a regenerated BC solution was prepared from a nonvolatile room temperature ionic liquid (RTIL) solvent, 1-allyl-3-methyl-imidazolium chloride

(AMIMCl). However, the viscosity of the solution (5 wt%) was so high and the thermal stability and non-volatility made it unsuitable for electrospinning. Therefore, a co-solvent, dimethylsulfoxide (DMSO), was added to improve the spin-ability of the blended solution [20]. This study examined the properties of the multi-walled carbon nanotube-embedded, electrospun-regenerated BC nanofibers (electrospun MWCNTs/BC nanofibers) obtained from the acid-treated multi-walled carbon nanotube (MWCNTs)-blended BC/AMIMCl solution. To our knowledge, this is the first report of the electrospinning of MWCNTs-embedded BC nanofibers from an ionic liquid solution system.

Experimental Procedure

Materials

The MWCNTs (purity, 95%; supplied by Iljin Nanotech, Korea) were synthesized by thermal chemical vapor deposition (CVD). AMIMCl (≥97.0%) was purchased from Aldrich. DMSO, as the co-solvent, was obtained from DC Chemical Co., Ltd., Sulfuric acid (H_2SO_4 98%, DC chemical co. Ltd., Korea) and nitric acid (HNO_3, 70%, DC chemical co. Ltd., Korea) were purchased and used as received.

Preparation of Purified and Functionalized MWCNTs

The pristine multi-walled carbon nanotubes were acid-treated to remove the impurities, such as the metallic catalysts. The multi-walled carbon nanotubes were suspended in a mixture of H_2SO_4 and HNO_3 (3:1, vol/vol) and heated to 60°C under reflux for 3 h. The MWCNTs were then diluted with 400 mL deionized water and vacuum filtered through a polytetrafluoroethylene membrane with a pore size of 0.45 μm. The solid was washed with deionized water until the pH of the rinsing water reached pH 7, and then dried in a vacuum oven at 25°C for 2 days. It should be noted that these acid treatments can reduce the length of the multi-walled carbon nanotubes and introduce functional groups to their surfaces, such as carboxylic acid and hydroxyl groups.

Biosynthesis of Bacterial Cellulose Hydrogels

The BC pellicle was synthesized by *Gluconacetobacter xylinum* BRC5. Briefly, the bacterium was cultured on Hestrin and Schramm (HS) medium composed of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.5% (w/v) bacto-peptone, 0.27% (w/v) disodium phosphate, and 0.115% (w/v) citric acid. All the cells used to synthesize the BC hydrogels were pre-cultured in a test tube for 3 days until the activity of the bacteria reached a maximum. The cells were then inoculated into a 500 mL Erlenmeyer flask containing 100 mL of the HS medium. The flasks were incubated statically at 30°C for 2 weeks. The fabricated BC hydrogels were purified by immersing them in a 0.25 M aqueous sodium hydroxide (NaOH) solution for 48 h at room temperature. The bacterial cellulose hydrogels were neutralized by repeated washing with deionized water. The purified bacterial cellulose hydrogels were stored in deionized water at 4°C until needed.

Preparation of the Regenerated Cellulose Solution

The BC hydrogels were first dried using a lyophilization method in a freeze-dryer (IP3 Jouan, France) for several days. The freeze-dried BC was cut into small pieces and stored in a vacuum oven at 25°C for at least 3 h prior to use. A 5 wt% BC/AMIMCl solution was prepared by dissolving the appropriate amount of cellulose in AMIMCl. The mixture was then stirred at 70°C until the cellulose had dissolved completely. The BC/AMIMCl solution was mixed with DMSO (1:2, mass ratios) to adjust the viscosity of the solution system and stirred gently for several hours at room temperature. Finally, homogeneous transparent amber BC/AMIMCl/DMSO was obtained [21].

Electrospinning

The spinning solution was prepared by adding 0.02 wt% MWCNTs to the BC/AMIMCl/DMSO system. The homogeneous system was then prepared by intense stirring for a further 3 h. Electrospinning was performed, as described in previous studies [22]. A high voltage electric field was generated by a power supply (ES100P-5 W, Gamma High Voltage Research, Inc., Ormond Beach, FL) and the applied voltage was set to $25 \sim 30$ kV. A 5 ml syringe connected a capillary tube was filled with the MWCNTs/BC/AMIMCl/DMSO solution. The solution was injected at a flow rate of $30 \sim 50$ µl/min. The tip-to collector distance was 20 cm. A special rotating drum collector, which was first used to make the orientated nanofibers was prepared by organizing parallel copper wires with a 1 cm spacing between them [23]. The rotation speed was fixed at 300 rpm. The nanofibrous membranes obtained from the composite solution were coagulated in ethanol overnight at room temperature, and then washed several times with ethanol. Long time dialysis by deionized water was performed until the solvents were removed. Finally, a vacuum oven was used to dry and remove the resident solvents remaining in the BC/MWCNTs mats. In order to compare with the MWCNTs-embedded, regenerated BC electrospun nanofibers, regenerated BC nanofibers without MWCNTs reinforcement were also prepared using the same method described above.

Characterization

The morphology of the electrospun nanofibers were examined by field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi, Japan) equipped with an energy dispersive X-ray analyzer (EMAX, EX-350, Horiba, Japan) at an accelerating voltage of 15 kV. Prior to analysis, the samples were pre-coated with a homogeneous Pt layer by ion sputtering (E-1030, Hitachi, Japan). Transmission electron microscopy (TEM) was performed using a Philips CM 200 unit operated at an acceleration voltage of 100 kV.

The functional groups of the MWCNTs and the structure of the electrospun BC and MWCNTs/BC nanofibers were confirmed using Fourier transformed infrared spectroscopy (FT-IR, VERTEX 80 v, Bruker Optics, Germany). X-ray diffraction (XRD, DMAX-2500, Rigaku, Japan) was performed using a diffractometer with reflection geometry and CuK_{α} radiation (wavelength, $\lambda = 0.154$ nm) operated at 40 kV and 100 mA. The data was collected at a scan speed of 1°/min within a range of scattering angles (2θ) from 5° to 60°.

The thermoproperties of the lyophilized pristine BC, electrospun BC and MWCNTs reinforced BC was analyzed using a thermal gravimetric analyzer (TGA, Q50, TA instruments, UK) from room temperature to 800°C at a heating rate of 15°C/min under a nitrogen atmosphere.

The tensile properties of the electrospun BC and BC/MWCNTs fiber mats were determined at room temperature using a universal test machine (UTM, Instron 5565, INSTRON, USA). The tensile strength per cross-sectional area (kg/mm^2) and the ratio of the relative elongation to the initial sample length at break (%) were determined by observing the stress–strain curves using the same weight of each sample for comparison. The thickness of the mats was measured with a micrometer (Mitutoyo, Japan).

The electrical resistance of the samples was measured using a surface resistance measuring device (Hiresta-up MCP-HT 450, Mitsubishi chemical corporation, Japan) with a large probe (MCP-HTP15) attached.

Results and Discussion

The electrospun MWCNTs/BC nanofibers and regenerated BC nanofibers were obtained by electrospinning. FE-SEM (Figs. 1(a, b)) showed that the electrospun MWCNTs/BC nanofibers and regenerated BC nanofibers contained continuous smooth surfaces and with a diameter of $200 \sim 500$ nm. This suggests that the MWCNTs were coated with the BC layer, indicating good adhesion between the MWCNTs and BC. Aggregation and MWCNTs extrusion sections also existed on the surface of the fibers but infrequent (Fig. 1(b), upper right). Fiber aggregation

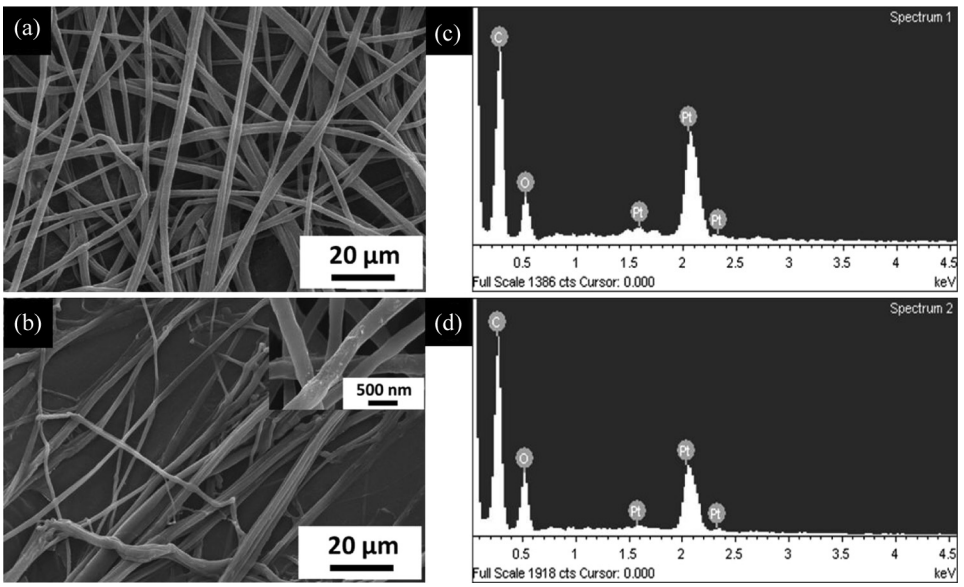

Figure 1. FE-SEM images of the electrospun regenerated BC fibers without and with MWCNTs embedded, respectively (a, b), and a higher magnification image of the electrospun MWCNTs/BC nanofibers (upper right). The EDXA spectrum of the electrospun regenerated BC fibers without and with MWCNTs embedded, respectively (c and d).

Table 1. Elementary analysis of the electrospun regenerated BC nanfibers and electrospun MWCNTs/BC nanofibers

Sample	C %	O %	Content of MWCNTs (%)
Electrospun regenerated BC nanfibers	44.71	41.23	0
Electrospun MWCNTs/BC nanofibers	44.89	29.43	0.41

was also observed, which was attributed to the inherent properties of the room temperature ionic liquid used as a solvent, such as stability, low vapor pressure and non-volatility. Aggregation occurred at the collector before coagulation in ethanol. Figures 1(c, d) shows the EDXA spectrum of the electrospun regenerated BC fibers without and with the MWCNTs embedded, respectively. The MWCNTs content in cellulose was calculated using the results from elemental analysis, as shown in Table 1. The MWCNTs content in the regenerated fibers was approximately 0.41 wt%, which is in agreement with the content (0.4 wt%) calculated from the quantity of materials.

The internal structural details of the electrospun MWCNTs/BC nanofibers were examined by TEM (Fig. 2). The MWCNTs were embedded and well aligned along the fiber axis (Figs. 2(a, b)). On the other hand, the aggregation and extrusion of MWCNTs were also observed in the TEM images (Figs. 2(c, d)), which is in agreement with the FE-SEM images (Fig. 1(b), upper right).

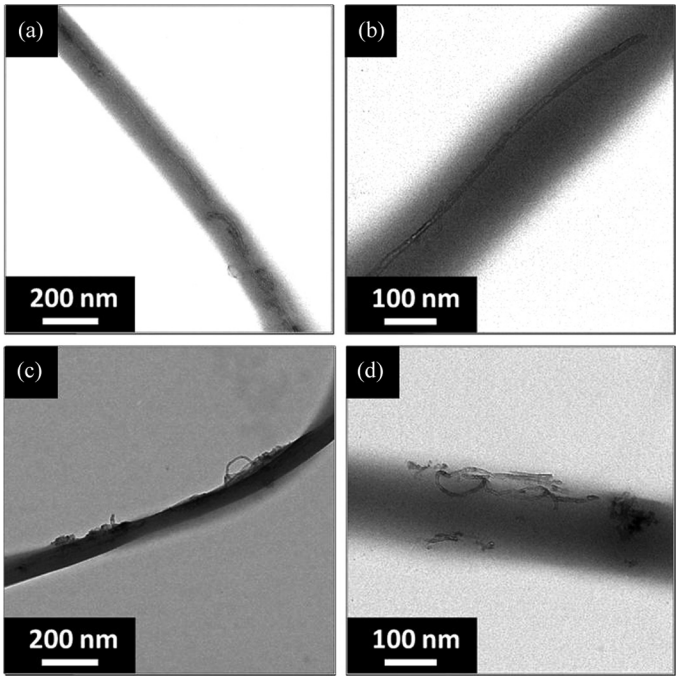

Figure 2. TEM images of the electrospun MWCNTs/BC nanofibers (a, c) and a higher magnification image (c, d).

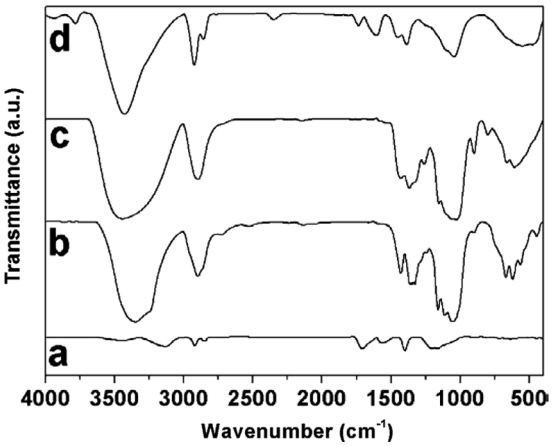

Figure 3. FT-IR spectra of acid-treated MWCNTs (a), pristine BC (b), electrospun regenerated BC fibers (c) and electrospun MWCNTs/BC nanofibers (d).

Figure 3 shows the FT-IR spectra of the MWCNTs (after acid treatment) (Fig. 3(a)), pristine BC (Fig. 3(b)), electrospun regenerated BC fibers (Fig. 3(c)) and electrospun MWCNTs/BC nanofibers (Fig. 3(d)). The peaks at 1712 and 1565 cm^{-1} suggest the presence of the carboxyl and carboxylate groups on the surface of the MWCNTs after the acid treatment (Fig. 3(a)) [24].

The broad and strong peaks located at 3000 to 3500 cm^{-1} were assigned to the vibrations in the concentration of O–H groups in cellulose. The trend of the curves (Figs. 3(b, c and d)) was indicated by a shift in the band of the O–H vibration of the regenerated cellulose to a higher frequency. This suggests the splitting of hydrogen bonds. Moreover, there was a shoulder peak at 3238 cm^{-1} in the pristine BC curve, which indicated a cellulose I_α structure [21]. This peak disappeared in the regenerated BC samples, and was independent of the addition of MWCNTs.

The peaks in FT-IR curve of the electrospun MWCNTs/BC nanofibers (Fig. 3(d)) at 1646 cm^{-1} were assigned to unsaturated C–C bonds [25]. This confirmed the presence of MWCNTs in the regenerated BC fibers. FT-IR suggests that the pristine BC contains the cellulose I_α structure. After dissolution by the RTILs, the cellulose I_α structure also disintegrated with the disruption and breaking of the intra- and intermolecular hydrogen bonds. Simultaneously, the crystallinity of the electrospun MWCNTs/BC nanofibers increased due to the embedding of MWCNTs. This suggests that the thermal stability and mechanical properties may be increased further.

The XRD patterns in Figure 4 show that the pristine BC (Fig. 4(a)) had a cellulose I structure (characteristic peaks at $2\theta = 14.0°(101)$, $16.5°(10\bar{1})$, $22.3°(002)$) [26], while the electrospun regenerated BC fibers (Fig. 4(b)) and electrospun MWCNTs/BC nanofibers (Fig. 4(c)) had mainly a cellulose II structure (characteristic peak 2θ at approximately $2\theta = 12.0°(101)$, $20.0°(10\bar{1})$ (shoulder peak), $21.5°(002)$). The small peak at 25.6° indicates a graphite-liked structure (002) [27]. XRD confirmed that a cellulose I (pristine BC) to cellulose II (electrospun regenerated BC fibers) crystalline polymorph transformation had occurred. A previous study reported that a mostly amorphous structure was achieved from regenerated

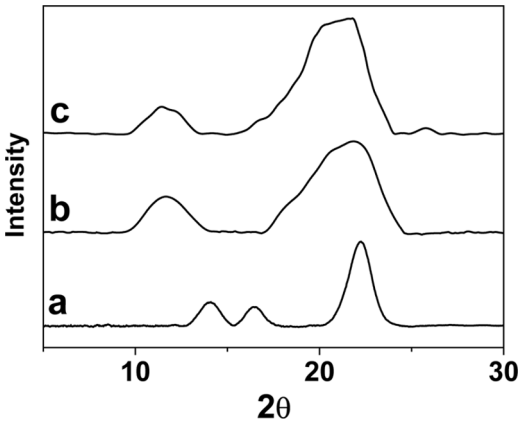

Figure 4. XRD pattern of the pristine BC (a), electrospun regenerated BC fibers (b) and electrospun MWCNTs/BC nanofibers (c).

cotton linters using a similar method [20]. This was attributed to the rapid coagulation of the regeneration process at a 60% relative humidity. Therefore, coagulation begins in the early stages of the electrospinning process. This limits re-crystallization of the cellulose chains, which can explain the more separated fibers.

The thermal-degradation of the pristine BC, electrospun regenerated BC fibers, and electrospun MWCNTs/BC nanofibers in a nitrogen atmosphere were measured and plotted (Fig. 5). The TGA curves showed that the degradation temperatures of the pristine BC (Fig. 5 dot line), electrospun regenerated BC fibers (Fig. 5 solid line) and electrospun MWCNTs/BC nanofibers (Fig. 5 dash line) begin at approximately 203°C, 237°C and 260°C, respectively. This increasing trend appears to be due to the crystalline polymorph transformation and orientation as well as to the embedded MWCNTs. On the other hand, TGA was found to be an unsuitable method for determining the amount of MWCNTs in the composites because the BC charred after burning at temperatures up to 600°C and did not decompose completely [28].

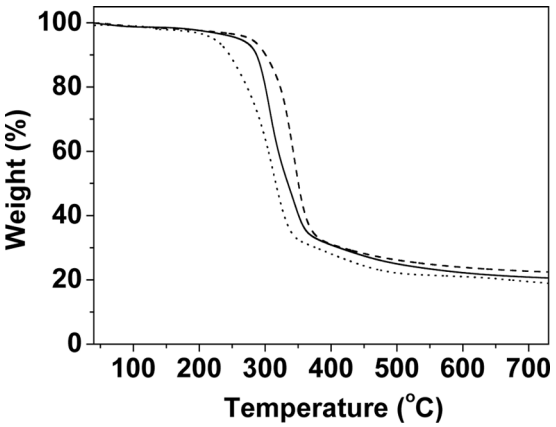

Figure 5. Thermo-gravimetric analysis traces of the pristine BC (dot line), electrospun regenerated BC fibers (solid line), and electrospun MWCNTs/BC nanofibers (dash line).

Table 2. Tensile properties of the pristine BC and electrospun MWCNTs/BC nanofibers

Specimen	Tensile stress at break (standard) (MPa)	Tensile strain at break (standard) (%)	Modulus (GPa)
Pristine BC	93.6 ± 9.9	5.5 ± 0.9	5.3 ± 0.3
electrospun MWCNTs/ BC nanofibers	247.4 ± 8.1	4.4 ± 1.5	14.3 ± 0.9

Carbon nanotubes are promising fillers in polymer matrixes to increase their mechanical properties on account of their high aspect ratio, modulus and strength [17,29]. Tensile testing was carried out in a Krebs solution at a cross head speed of 0.1 mm/min. Table 2 shows the mean tensile stress and strain at break from at least 5 samples. The average modulus was also calculated (Table 2). From the UTM data, the tensile strength and Young's modulus of the composite increased by approximately 290% and 280%, respectively. This can be explained by the dispersion and orientation of the MWCNTs loading in the composite fibers assisting the cellulose matrix in sustaining a high strength and modulus. Accordingly, the addition of a small amount of MWCNTs enhanced the mechanical properties of the MWCNTs incorporated BC nanofibers.

The electrical conductivity of the pristine BC, electrospun-regenerated BC fibers and electrospun MWCNTs/BC nanofibers were measured at room temperature. The electrical conductivity of the electrospun regenerated BC fibers (2.28×10^{-13} S/cm) was similar to that of the pristine BC (2.42×10^{-14} S/cm), while the electrospun MWCNTs/BC nanofibers increased to 1.95×10^{-8} S/cm. This was attributed to the incorporation of well-embedded and aligned MWCNTs in the regenerated BC fibers during electrospinning.

Conclusion

In this study, MWCNTs-embedded electrospun, regenerated BC nanofibers were spun successfully from a MWCNTs-blended regenerated BC solution containing an ionic liquid, AMIMCl, as the solvent. FE-SEM showed that the regenerated nanofibers had a smooth and continuous surface. Well-dispersed and aligned MWCNTs were observed in the cellulose nanofibers by TEM. A crystalline cellulose I (pristine BC) to cellulose II (electrospun regenerated BC fibers) polymorph transformation was detected by FT-IR and XRD. Moreover, the crystallinity of the composite fiber was increased by the MWCNTs embedded in the regenerated BC nanofibers. In addition, there was a interaction between the BC and MWCNTs, which increased the thermal and mechanical properties as well as the electrical conductivity. Compared to other natural materials reinforced with MWCNTs, such as MWCNTs-embedded electrospun-regenerated silk nanofibers [22], this regenerated composite fiber might have potential medical, mechanical and electrical applications, and be a precursor for the production of cellulose-based carbon fibers.

Acknowledgment

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References

[1] Ring, G. J. F. (1982). In: *Cellulose and Other Natural Polymer System*, Brown, R. M. (Ed.), Plenum Press: New Youk, 299.
[2] Klemm, D., Heublein, B., Fink, H.-P., & Bohn, A. (2005). *Angew. Chem. Int. Ed.*, *44*, 3358.
[3] Jonas, R. & Farah, L. F. (1998). *Polym. Degrad. Stabil.*, *59*, 101.
[4] Iguchi, M., Yamanaka, S., & Budhiono, A. (2000). *J. Mater. Sci.*, *35*, 261.
[5] Kakugo, A., Gong, J. P., & Osada, Y. (2007). *Cellulose Communications*, *14*, 50.
[6] Phisalaphong, M., Suwanmajo, T., & Sangtherapitikul, P. (2008). *J. Appl. Polym. Sci.*, *107*, 292.
[7] Jiang, H., Wang, Y., Jia, S., Huang, Y., He, F., & Wan, Y. (2007). *Key Eng. Mater.*, *923*, 330–332.
[8] Phisalaphong, M., Suwanmajo, T., & Tammarate, P. (2008). *J. Appl. Polym. Sci.*, *107*, 3419.
[9] Masson, J. F. & Manley, R. S. J. (1991). *Macromolecules*, *24*, 6670.
[10] Wang, M., Zhu, P., Zhao, X., & Dong, Z. (2008). *Hecheng Xianwei*, *37*(6), 20.
[11] Biganska, O. & Navard, P. (2005). *Biomacromolecules*, *6*, 1948.
[12] Zhou, J. & Zhang, L. (2000). *Polym. J.*, *32*, 866.
[13] Hattori, K., Cuculo, J. A., & Hudson, S. M. J. (2002). *Polym. Sci., Part A: Polym. Chem.*, *40*, 601.
[14] Cai, J., Zhang, L., Zhou, J., Qi, H., Chen, H., Kondo, T., Chen, X., & Chu, B. (2007). *Adv. Mater.*, *19*, 821.
[15] Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). *J. Am. Chem. Soc.*, *124*, 4974.
[16] Iijima, S. (1991). *Nature*, *354*, 56.
[17] Schadler, L. S., Giannaris, S. C., & Ajayana, P. M. (1998). *Appl. Phys. Lett.*, *73*, 3842.
[18] Kim, G. H., Min, T., Park, S. A., & Kim, W. D. (2008). *Bioinsp. Biomim.*, *3*, 016006.
[19] Riboldi, S. A., Sadr, N., Pigini, L., Neuenschwander, P., Simonet, M., Mognol, P., Sampaolesi, M., Cossu, G., & Mantero, S. (2008). *J. Biomed. Mater. Res. A*, *84A*, 1094.
[20] Xu, S., Zhang, J., He, A., Li, J., Zhang, H., & Han, C. C. (2008). *Polymer*, *49*, 2911.
[21] Zhang, H., Wu, J., Zhang, J., & He, J. (2005). *Macromolecules*, *38*, 8272.
[22] Kang, M., Chen, P., & Jin, H.-J. (2009). *Curr. Appl. Phys.*, *9*, S95.
[23] Katta, P., Alessandro, M., Ramsier, R. D., & Chase, G. G. (2004). *Nano Lett.*, *4*, 2215.
[24] Chen, C. C., Chen, C. F., Chen, C. M., & Chuang, F. T. (2007). *Electrochem. Commun.*, *9*, 159.
[25] Roman, M. & Winter, W. T. (2004). *Biomacromolecules*, *5*, 1671.
[26] Kim, C. W., Kim, D. S., Kang, S. Y., Marquez, M., & Joo, Y. L. (2006). *Polymer*, *47*, 5097.
[27] Kim, D. B., Jo, S. M., Lee, W. S., & Pak, J. J. (2004). *J. Appl. Polym. Sci.*, *93*, 1687.
[28] Ishida, O., Kim, D.-Y., Kuga, S., Nishiyama, Y., & Malcolm Brown, R. (2004). *Cellulose*, *11*, 475.
[29] Andrews, R., Jacques, D., Minot, M., & Rantell, T. (2002). *Macromol. Mater. Eng.*, *287*, 395.