Regenerated bacterial cellulose/multi-walled carbon nanotubes composite fibers prepared by wet-spinning

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ABSTRACT

Regenerated bacterial cellulose (BC) and regenerated bacterial cellulose/multi-walled carbon nanotubes (BC/MWCNTs) composite fibers were prepared by wet-spinning of a regenerated BC and BC/MWCNTs solution dissolved in dimethylacetamide/lithium chloride, and coagulated with ethanol. Field emission scanning electron microscopy and transmission electron microscopy showed smooth continuous fibers with well-dispersed MWCNTs. The chemical structure of the specimens was analyzed by Fourier transform infrared spectroscopy. The results obtained by using a universal testing machine indicated that the mechanical properties of the fibers were enhanced considerably by reinforcement with MWCNTs. There was an approximate 430% increase in the modulus of the regenerated BC/MWCNTs composite fibers, compared with the original pristine BC. Moreover, the electrical conductivity of the regenerated BC/MWCNTs (1.0 wt%) composite fibers was 1.7×10^{-10} S/cm.

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1. Introduction

Carbon nanotubes (CNTs), which were first discovered by Iijima in 1991 [1], have attracted considerable attention on account of their high aspect ratios (>1000) and unique mechanical, thermal, electrical, magnetic and optical properties. In some special applications, such as space exploration, high-performance lightweight structural materials are required, which can be developed by adding CNTs to polymers or other matrix materials. Moreover, although graphite is a semi-metal, CNTs can be either metallic or semi-conducting, due to the presence of topological defects from the fullerene-like end caps in the CNTs (pentagons in a hexagonal lattice). Therefore, the physico-mechanical properties of CNTs are dependent upon their dimensions, helicity or chirality. The synthesis, structures, properties and applications of CNTs have been studied extensively [2–5]. These properties make CNTs excellent reinforcing agents for polymers. It has been recognized that the reinforcing efficiency of CNTs strongly depends on their dispersion and orientation, as well as on the interfacial strength of the CNTs/polymer matrix when preparing polymeric nanocomposites filled with CNTs [6–8]. An effective approach for achieving these requirements is to functionalize nanotubes with polymers that are identical or structurally similar to matrix polymers [9].

Cellulose is a polydisperse linear polyglucan that forms a hydrogen-bonded supermolecular structure. It is one of the most abundant biopolymers on Earth and a major component of plants. Many different types of cellulose can be found in plants, seaweed or microorganisms. Among these, bacterial cellulose (BC) is a specific product of the primary metabolism. Cellulose is synthesized by bacteria belonging to the genera *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina* [10]. The BC used in this study was produced by *Gluconacetobacter xylinum* BRC5. One of the most important features of this BC is its chemical purity, which distinguishes this cellulose from that from plants, which is usually associated with hemicelluloses and lignin, the removal of which is inherently difficult. Because of the unique properties resulting from the ultrafine structure, BC can be converted into cellulose derivatives (ethers and esters) and regenerated materials (fibers, films, food casings, membranes, sponges, etc.) [11]. Moreover, many new functional cellulose materials are being developed over a broad range of applications in paper, textiles, and food casings, and as a biomaterial in cosmetics and medicine [12–15]. Therefore, the preparation of regenerated BC materials is a significant and necessary challenge.

However, it is difficult to dissolve cellulose in water and most common organic solvents because of its large proportion of intra-

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and inter-molecular hydrogen bonds. Thus far, only a limited number of solvent systems have been found to dissolve cellulose, e.g., N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) [16,17], N-methylmorpholine-N-oxide (NMMO) [18], NaOH/urea aqueous solution [19], some molten salt hydrates [20,21], such as Li-ClO$_4 \cdot$ 3H$_2$O, and some aqueous solutions of metal complexes [22,23]. Lately, NMMO has been used to produce cellulose fibers, leading to a new class of man-made cellulose fibers with the generic name of Lyocell [24]. However, the NMMO/cellulose/H$_2$O system has some disadvantages, such as uncontrolled thermal stability (a runaway reaction), high evaporation costs (energy cost), and a high tendency of fibrillation of the Lyocell fibers. In addition, these solvent systems are ineffective in dissolving the bacterial cellulose used in this study. The DMAc/LiCl system is an optimal solvent with appropriate solubility and relatively low cost.

In this study, multi-walled carbon nanotubes (MWCNTs) were introduced into a regenerated BC solution, which was prepared by dissolving BC in a DMAc/LiCl system. Composite fibers were then prepared by the wet-spinning of the mixture into ethanol (extra pure) as a coagulation bath. The morphology of the composite fibers was observed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The structure transformation was monitored by Fourier transform infrared (FTIR) spectroscopy. The mechanical properties and electrical conductivity were characterized by using a universal testing machine (UTM) and a multimeter, respectively. The morphological investigation showed that the MWCNTs were wrapped in or covered by a BC layer and well dispersed and aligned within the BC matrix, indicating good adhesion between the MWCNTs and BC. This was attributed to various interactions between the BC and MWCNTs, such as hydrogen bonding. As a result, the compatibility and strong interactions between the MWCNTs and BC significantly enhanced the dispersion and mechanical properties of the BC matrix.

2. Experimental procedure

The bacterial cellulose pellicle was synthesized from *Gluconacetobacter xylinum* BRC5 in Hestrin and Schramm medium [25]. Briefly, *Gluconacetobacter xylinum* pd-5 was obtained from Yonsei University and used to produce the bacterial cellulose pellicles. The bacterium was cultured on Hestrin and Schramm (HS) medium consisting 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 were precultured in a test tube containing a small cellulose pellicle on the surface of the medium, and 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 cellulose pellicles were dipped into 0.25 M NaOH for 48 h at room temperature to eliminate the cells and components of the culture liquid. The pH was then reduced to 7.0 by repeated washing with distilled water. The purified cellulose pellicles were stored in distilled water at 4 °C to prevent drying [1]. BC was dried in a freeze-dryer (IP3 Jouan, France) for 3 days.

Dimethylacetamide (DMAc) and lithium chloride (LiCl) were purchased from Aldrich, USA. The cellulose was dissolved in DMAc/LiCl system by using a previously reported method [9]. The resulting regenerated BC solution was approximately 4 wt%. The regenerated BC/MWCNTs solution was prepared by adding 1 wt% acid-treated MWCNTs (treated with 3 M HNO$_3$ and 1 M H$_2$SO$_4$ at 60 °C for 24 h) to the regenerated BC solution with constant stirring for more than 3 h to obtain a homogeneous mixture.

The regenerated BC fibers and regenerated BC/MWCNTs composite fibers were spun from the spinning solution by using dry-jet wet-spinning. The spinning solutions were extruded at a speed of 2 mL/min through a spinneret into a coagulating bath. The fibers were then washed with distilled water, wound around a polypropylene centrifugal tube, and dried in an oven at 60 °C.

Images of the regenerated fibers were taken by field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan). The fibers were frozen in liquid nitrogen, fractured immediately, and vacuum-dried. The fracture surface of the fibers was also investigated. The internal structure of the regenerated BC/MWCNTs composite fibers was examined by TEM (CM200, Philips, Netherlands). Ultrathin slices were obtained from the regenerated BC/MWCNTs composite fiber samples imbedded in an epoxy resin by ultra-microtoming under cryogenic conditions.

The acid-treated MWCNTs were well mixed with potassium bromide (KBr) powder and pressed into a small pellet. The BC membrane without MWCNTs and the BC regenerated fibers with and without MWCNTs were dried at 60 °C. The pristine BC, regenerated BC fibers and regenerated BC/MWCNTs composite fibers were analyzed by FTIR spectroscopy on a VERTEX 80 V (Bruker, USA) equipped with a high-sensitivity DiGiTect detector in absorption mode with a resolution of 0.15 cm^{-1} in the range of 4000–400 cm^{-1}.

The mechanical properties of the specimens were measured using by a universal testing machine (UTM, Instron 5565, INSTRON, USA) at a crosshead speed of 0.1 mm/min at room temperature.

The electrical conductivity of the composites was determined by measuring the volume conductivity (S/cm), which corresponds to the resistance expressed, by using a two-probe method.

3. Results and discussion

The regenerated BC and regenerated BC/MWCNTs composite fibers with a 1.0 wt% MWCNTs loading were fabricated by using a dry-jet wet-spinning process, which is described elsewhere [9,26]. Both the regenerated BC fiber and the regenerated BC/MWCNTs composite fibers showed a continuous smooth surface (Fig. 1a and b; SEM images of the regenerated BC fibers are not shown) with a diameter of 21 and 43 μm, respectively. Fig. 1c and d shows cross-sectional SEM images of the regenerated BC fibers and regenerated BC/MWCNTs composite fibers. With a 1.0 wt% MWCNTs loading, Fig. 1d suggests that the MWCNTs were wrapped in or covered by the BC layer, indicating good adhesion between the MWCNTs and BC.

TEM was used to examine the internal structural details of the regenerated BC/MWCNTs composite fibers. From Fig. 2, it is evident that the MWCNTs were embedded and aligned along the fiber axis by using the wet-spinning process. Furthermore, the MWCNTs were well dispersed within the BC matrix.

Fig. 3 shows FTIR spectra of the acid-treated MWCNTs, pristine BC, regenerated BC fibers, and regenerated BC/MWCNTs composite fibers. The peaks at 1715 and 1561 cm^{-1} indicate carboxylic acid and carboxylate groups on the surface of the MWCNTs, respectively (Fig. 3a) [27]. The bands at 2854 and 2921 cm^{-1} were assigned to CH$_2$ stretching. The peak at 3450 cm^{-1} was attributed to the presence of hydroxyl groups (–OH). All these peaks suggest the oxidation of MWCNTs by concentrated acid. The pristine BC IR spectrum (Fig. 3b) shows two anisotropic vibrations at 1158 and 1052 cm^{-1}, which were assigned to the C–O–C vibration between the glucose rings and coupled C–O vibration, respectively. The peak at 3360 cm^{-1} was assigned to the presence of hydroxyl groups.

The FTIR spectra of the pristine BC and regenerated BC fiber (Fig. 3b and c) was similar, indicating that no chemical reaction had occurred during the dissolution and coagulation processes of the BC. A new peak at 899 cm^{-1}, belonging to the C–O stretching vibration in the amorphous region, was observed in the regenerated cellulose fibers. A characteristic O–H broad vibration band
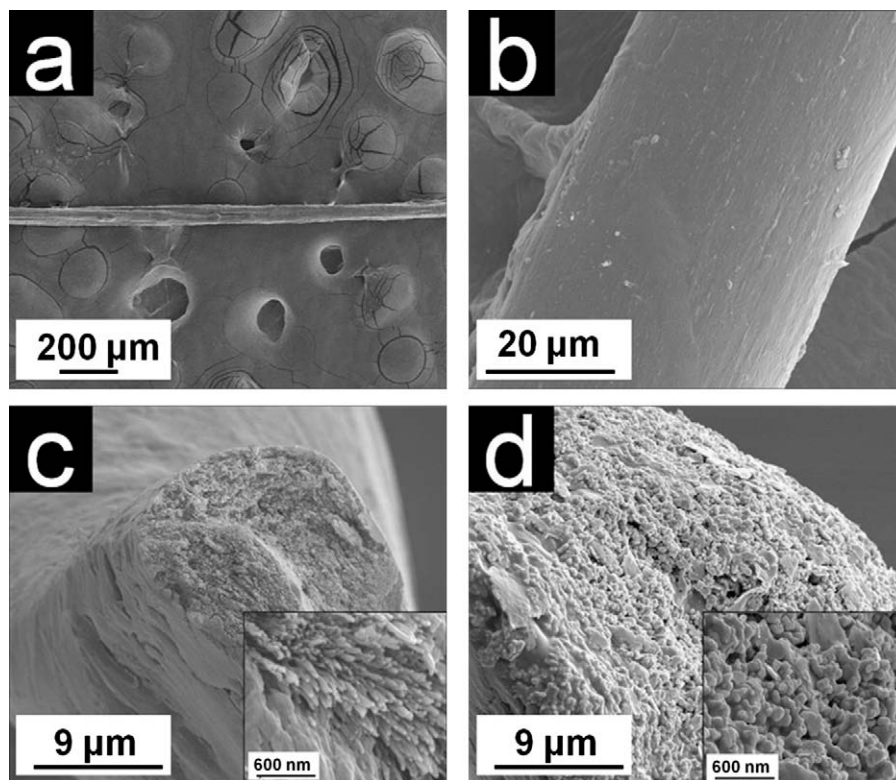
Fig. 1. SEM images of the regenerated BC/MWCNTs composite fibers (a and b), and the cross-sectional fracture and the enlarged cross-sectional fracture of a regenerated BC fiber (c) and regenerated BC/MWCNTs composite fiber (d).
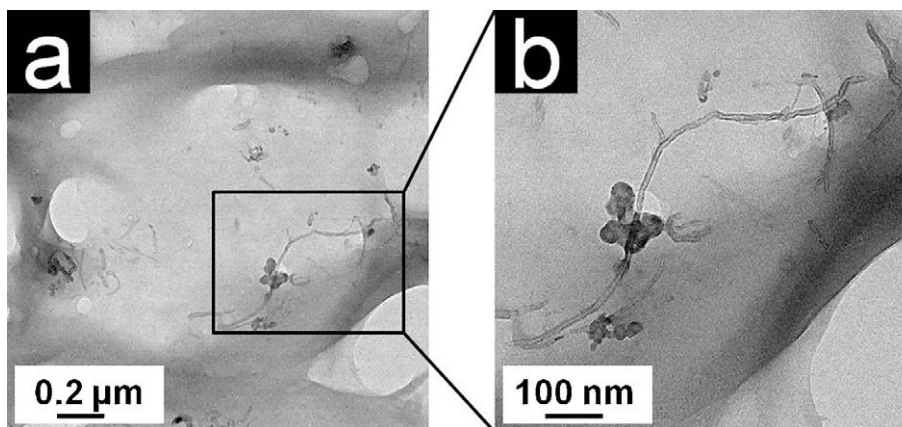

Fig. 2. TEM images of the regenerated BC/MWCNTs composite fibers (a), and enlarged image (b).

for BC was located in the range of 3000–3500 cm^{-1}. The band of the O–H vibration of the regenerated BC shifted from 3356 cm^{-1} to a higher frequency 3436 cm^{-1}, which might be evidence of some hydrogen bond splitting [28,29]. Fig. 3c and d shows the FTIR spectra of the regenerated BC fiber and regenerated BC/MWCNTs composite fibers. Compared with the regenerated BC fibers, the regenerated BC/MWCNTs composite fibers showed a doublet peak around 1720 cm^{-1} due to the incorporation of acid-treated MWCNTs.

The enhanced modulus of the composites due to the incorporation of either single walled carbon nanotubes or MWCNTs has been reported [30,31]. In this study, tensile testing was carried out in Krebs solution with a cross speed of 0.1 mm/min. Fig. 4 shows the stress/strain diagrams of the tensile test. Young's modulus of

the pristine BC, regenerated BC fiber, and regenerated BC/MWCNTs composite fibers was 7.3, 29.2, and 38.9 GPa, respectively. Young's modulus of the regenerated BC fibers and regenerated BC/MWCNTs composite fibers was approximately 300% and 430% higher than that of the pristine BC, respectively. In addition, the regenerated BC/MWCNTs (1.0 wt%) composite fibers showed a 33% increase in the modulus compared with the regenerated BC fibers. This is because the MWCNTs loading in the composite fibers enabled the cellulose matrix to sustain a high modulus. A similar result was reported by Zhang et al. [26].

The electrical conductivity of the regenerated BC/MWCNTs composite fibers was measured by using a two-probe method at room temperature. The electrical conductivity of the regenerated BC/MWCNTs composite fibers increased rapidly with the addition
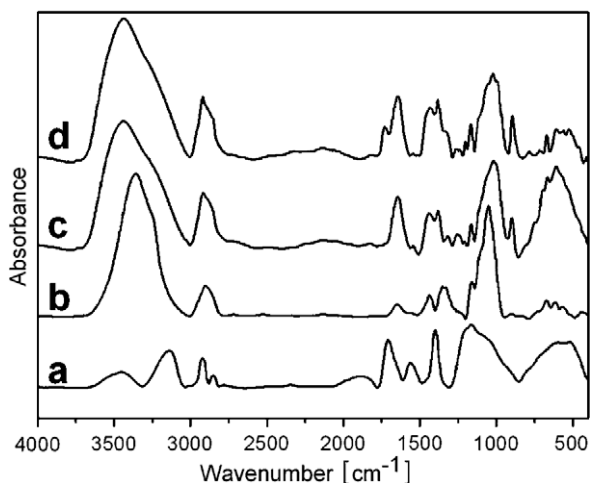
Fig. 3. FTIR spectra of (a) acid-treated MWCNTs, (b) pristine BC fiber, and (c) regenerated BC fiber, and (d) regenerated BC/MWCNTs composite fibers.
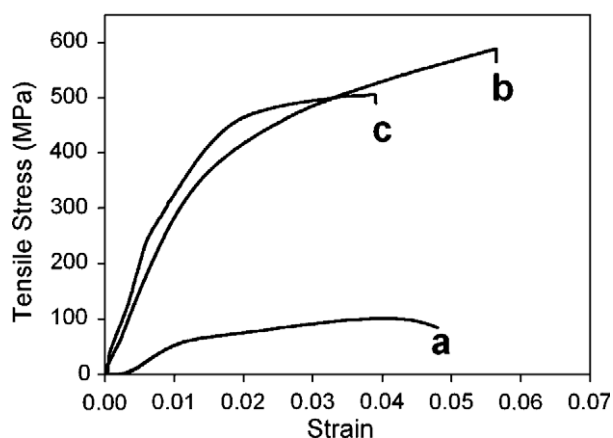

Fig. 4. Stress/strain diagrams of (a) pristine BC, (b) regenerated BC fiber, and (c) regenerated BC/MWCNTs composite fibers.

of MWCNTs (2.5×10^{-16} S/cm (0 wt%) to 1.7×10^{-10} S/cm (1.0 wt%)). This was attributed to the incorporation of well-dispersed and aligned MWCNTs in the regenerated BC/MWCNTs composite fibers during the dry-jet wet-spinning process.

4. Conclusion

Regenerated BC/MWCNTs composite fibers were successfully spun from regenerated BC/MWCNTs solutions by using a dry-jet wet-spinning process. Well-dispersed and aligned MWCNTs were observed in the cellulose fibers by TEM. There was good adhesion between the BC and MWCNTs in the regenerated BC/MWCNTs composite fibers. This report provides a simple and effective method for preparing regenerated BC/MWCNTs composite fibers with a significant increase in modulus (38.9 GPa) and electrical conductivity. Compared with other natural materials reinforced with CNTs, such as regenerated silk materials containing or coated with CNTs [32], this regenerated composite fiber might have medical, mechanical and electrical applications and may be a precursor for the production of cellulose-based carbon fibers.

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