

Preparation and Properties of Bacterial Cellulose/Alginate Blend Bio-Fibers

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ABSTRACT

LiOH/urea/thiourea aqueous systems have been successfully applied to the dissolution of bacterial cellulose (BC) and alginate (AL) to prepare blend fibers. Morphology, compatibility and mechanical properties of the blend fibers were investigated by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and tensile tests. The analyses indicated a good miscibility between alginate and bacterial cellulose, because of the strong interaction from the intermolecular hydrogen bonds. The mechanical properties of BC/AL blend fibers were significantly improved by introducing bacterial cellulose.

INTRODUCTION

Biopolymers have been considered as alternatives for non-biodegradable petroleum-based polymers because of their abundance, renewability, low cost, and good biodegradability. Cellulose is the most abundant natural biopolymer on the earth, synthesized by plants, algae and also some species of bacteria. Unlike cellulose from plants, bacterial cellulose (BC) is chemically pure and free of lignin and hemi-cellulose. BC has high crystallinity and a high degree of polymerization. Plant-derived cellulose and BC have the same chemical composition but different structures and physical properties. The BC network structure comprises cellulose nanofibrils 3-8 nm in diameter, and the crystalline regions are normal cellulose I. The specific properties such as the nanometric structure, unique physical and mechanical properties together with its higher purity have lead to a great number of commercial products.¹⁻³

Alginate (AL) is a binary linear hetero polysaccharide containing one, four-linked α -L-guluronic acid and β -D-mannuronic acid, and has been widely used in the field of controlled release, ion exchange, and in the vapor-permeation membrane-separation technique.⁴ Alginate can be transformed into the most widely used water-soluble

form, sodium alginate, through the incorporation of sodium salt. However, because of its highly hydrophilic character due to both of its carboxyl and hydroxyl groups, the mechanical strength of the AL materials in the wet state is very weak to limit its application.

In our laboratory, solubility of cellulose in LiOH/urea/thiourea aqueous solution has been studied, and regenerated cellulose fibers were prepared successfully from cotton linters.⁵ In this study, we attempted to prepare blend fibers from bacterial cellulose and alginate using the aqueous LiOH/urea/thiourea as co-solvent. To the best of our knowledge, this type of blend fiber was first prepared in this work.

EXPERIMENTAL

Materials

The bacterial cellulose used in our experiments was purchased from Hainan YIDA Food Industry Co. (China). Sodium alginate was purchased from the Branched Factory of Shanghai Chemical Reagent Co. (China).

Preparation Of Blend Solution

BC was cut into small pieces (0.2X0.2 cm²), dispersed in the aqueous solvent (LiOH: urea: thiourea: H₂O=4.6:10:4.5:80.1, ratio by weight), and stirred for 5 min at room temperature to obtain a BC slurry. The slurry was then cooled to -20°C in a freezer and held at -20°C until it became a solid frozen mass for 12 h. The frozen solid was then allowed to thaw and was stirred extensively at room temperature to obtain clear BC solution (I). Certain amounts of sodium alginate were dissolved in LiOH/thiourea/urea aqueous solution at room temperature to obtain alginate solution (II). The total concentration of solid biopolymers in the solution was controlled to be 6 wt%. A mixture of I and II with weight ratio 80:20 was stirred at room temperature for 10 min and then filtered and

degassed at 10°C by centrifuging. The final composition of the fibers in relative weight components of alginate and BC was 20:80.

Preparation Of Novel Blend Fibers

A laboratory scale wet-spinning apparatus was used to prepare the blend fibers, as schematically shown in Figure 1. The spinning dope I, II and blend solution were introduced into the cylinder at room temperature, respectively. A pressure of 0.1 MPa was applied to the spinning dope to extrude it into coagulation bath using a spinneret of 12 orifices, the orifice diameter (d) was 0.1 mm. The 10 wt % H₂SO₄ aqueous solution was selected as the coagulation bath. The temperature of the coagulation bath was preset for 20°C. The apparent jet stretch ratio (the ratio of the take-up velocity to the dope extrusion velocity) was 90 %, the fibers were subsequently washed in water at boil and further drawn up, while the post-drawing ratio was adjusted as 120 %. After spinning and washing thoroughly, the regenerated bacterial cellulose fibers (RBC), regenerated alginate fibers (RAL), blend fibers(BC/AL) were gradually dried by a heating roller (surface temperature 65-80°C) and wound on a spool.

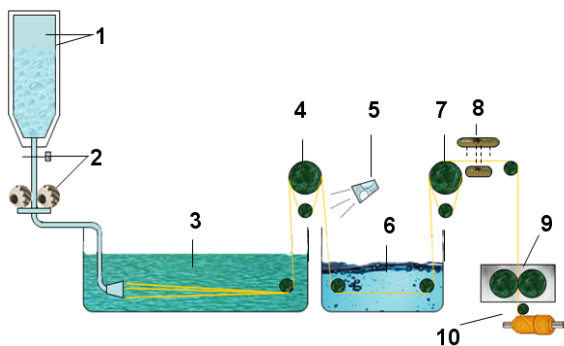


FIGURE 1. Sketch of multifilament spinning machine:1-A pressure extruder with a stainless cylinder having cooling jacket; 2-gauging device; 3-coagulation bath(10 wt% H₂SO₄ aqueous solution, 20°C); 4-Nelson-type roller; 5-water spray device; 6-washing bath(hot water, 50°C); 7-post drawing roller; 8-post treatment device (finishing oil bath); 9-heating roller;10-take-up device.

Characterization

The FTIR spectrums (4000-400 cm⁻¹) of blend fibers were recorded using a Nicolet 410 spectrometer with a resolution of 4 cm⁻¹ and 128 scans per sample. The fiber was frozen in liquid nitrogen, snapped immediately, and vacuum-dried. SEM characterization was performed by using a JEOL JSM-5600LV microscope, at an acceleration voltage

of 10 kV and 15 mm working distance. The stress-strain experiments were made using a universal tensile tester (XQ-1, Donghua University, China). According to ASTM D2256-80, the fibers samples were conditioned for 24 h in standard atmosphere before testing of the dry mechanical properties of the fibers. However, the wet mechanical properties of the fibers were tested after the fibers were immersed in the distilled water at 20°C for 3 minutes. The gauge length was 20 mm and the tensile speed was 5 mm/minute. The pre-tensile forces of dry fibers and wet fibers were determined to be 0.08cN/dtex and 0.04cN/dtex according to their linear densities, respectively. The tester gave stress, strain, tensile curve and their averages from the sixty observations automatically. All the experiments were made at an atmospheric condition of 20°C and relative humidity 60 %.

RESULTS AND DISCUSSION

Infrared (IR) spectroscopy is useful for studying hydrogen bonding and miscibility because the strength of the hydrogen bond and the fraction of hydrogen-bonded groups can be directly investigated from the spectra. The IR spectra of the blend fibers and are shown in Figure 2.

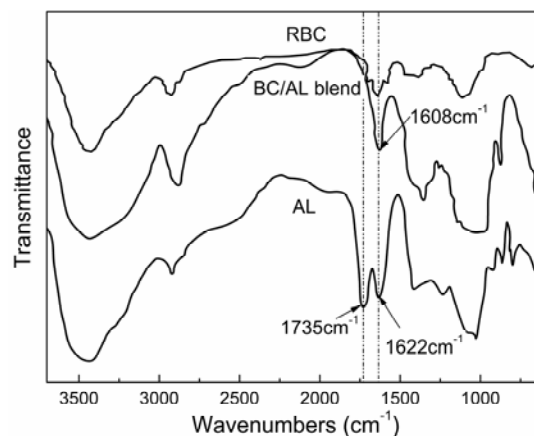


FIGURE 2. The FTIR spectra of regenerated bacterial cellulose (RBC), alginate (AL) and BC/AL blend fibers.

The stretching vibration of hydroxyl groups in the RBC, BC/AL, and AL appears at 3000–3600 cm⁻¹. The -OH stretching-vibration bands of the blend fibers were broadened and shifted to a lower wave number compared to RC and AL, indicating that a stronger hydrogen bond occurred between RC and AL. The strong band of AL at 1622 cm⁻¹ was

assigned to the carboxyl group, while the carboxyl group bands for BC/AL shifted from 1622 to 1608 cm^{-1} , indicating the specified intermolecular hydrogen bonds between -OH of BC and C=O of AL forms. The band at 1735 cm^{-1} for AL belongs to C=O in AL, but disappeared in the blend fibers. This difference would also be derived from specified interaction between the hydroxyl group of cellulose and carboxyl group of AL. Similar observations were previously discussed in the preparation of cotton cellulose/AL blend membranes.⁶

It is well known that the mechanical properties of fibers, especially the blend fibers are strongly dependent on their morphologies and, therefore, the control of the morphology of polymer blend is

extremely important for the tailoring of the final product properties. The SEM micrographs of blend fibers are shown in *Figure 3*. The BC/AL blend bio-fibers showed a circular shape with fairly regular size along the fiber axis. However, the micro void can be seen in the cross-section of the blend fibers, which can be considered as the evidences of partly phase separation. Here, we proposed that, in the blend solution, alginate partly destroyed the interaction between solvent and BC chains by a much stronger interaction between carboxyl groups of AL and then the exposed hydroxyl groups of BC prompted the formation of a new physical crosslinking network with a bigger pore size than that of pure regenerated cellulose itself (*Figure 3-c*).

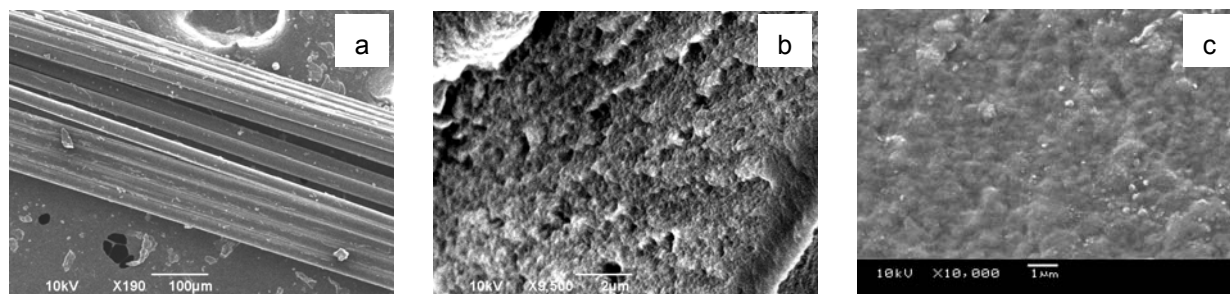


FIGURE 3. SEM images of (a) the surface, (b) cross-section of the BC/AL blend fibers and (c) cross-section of the RBC fibers.

The presence of alginate in the cellulose-alginate composite could enhance the molecular motion of cellulose in the blend and perturbed the strong hydrogen bond of pure cellulose resulting in the reduction in mechanical strengths. It can be found from *Table I* that the BC/AL blend fibers were a little weaker than regenerated cellulose fibers under either dry or wet state. As we know that alginate materials was mechanically weak and much weaker under wet state, the mechanical properties of the blend fibers of alginate with bacterial cellulose were obviously stronger than alginate materials, which is another indicator for the strong intermolecular hydrogen bonding between two polymers in the blends. The effect of alginate content on the mechanical properties of the BC/AL blend fibers was similar to those previously observed in the blend membranes of BC and alginate blend in NaOH/urea,⁷ cellulose cuoxam with alginate,⁸ and cotton cellulose and alginate blend in NaOH/urea aqueous solution.⁹

TABLE I. Mechanical properties of bacterial BC/AL blend fibers and pure RBC fibers.

Fibers and their states		Tensile Strength (cN/dtex)	Elongation at Break (%)
BC/AL	Dry state	1.57±0.24	10.8±1.1
blend fibers	Wet state	0.91±0.37	14.4±2.1
RBC fibers	Dry state	1.83±0.13	11±1.6
	Wet state	1.04±0.27	15.4±2.3
RAL fibers	Dry state	1.21±0.22	8.3±1.2
	Wet state	0.54±0.13	4.4±2.1

CONCLUSION

Novel blend bio-fibers of bacterial cellulose/alginate were prepared in LiOH/urea/thiourea aqueous solvent by coagulating with 10 wt % H_2SO_4 aqueous solution for the first time. The blend fibers of 20 wt % AL and 80 wt % BC demonstrated a homogeneous structure with a certain level of miscibility of the blend. The FTIR spectra displayed the specified interaction between the hydroxyl group of BC and the carboxyl group of AL. The values of tensile strength and

elongation at break for the blend bio-fibers reached 1.57 cN/dtex and 10.8%, respectively. The mechanical properties of the blend fibers were slightly improved compared to those of the pure AL materials. To this end, BC/AL blend fibers have great potential as new regenerated biodegradable fibers with structural and physic-mechanical properties comparable to those of pure regenerated cellulose fibers. Its biomedical application can be expected, especially for the tissue engineering scaffold.

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