CELLULOSE CHEMISTRY AND TECHNOLOGY

PREPARATION OF CELLULOSE/CHITIN BLEND BIO-FIBERS *VIA* DIRECT DISSOLUTION

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The paper proposes a novel way for preparing cellulose/chitin blend fibers from a NaOH/thiourea/urea aqueous solution by direct dissolution. The structure, miscibility and properties of the blend fibers were investigated in detail. It was demonstrated that cellulose and chitin showed a good miscibility in blend fibers. The thermal stability of the blend fibers was higher than that of pure cellulose fibers, due to the strong interaction between the cellulose and chitin molecules. However, the blend fibers displayed slightly lower tensile properties than those of pure regenerated cellulose fibers, which was attributed to the partial damage of the cellulose crystalline region, caused by chitin addition. Additionally, SEM measurements evidenced a rather smooth and homogeneous morphology of the blend fibers.

Keywords: biopolymers, cellulose/chitin, direct dissolution, blend fibers, properties

INTRODUCTION

With the increase of worldwide environmental pollution caused by non-biodegradable polymers, research on biodegradable polymers is both necessary and valuable, supporting global sustainability and helping to solve the petroleum crisis and environmental problems. Cellulose is the most abundant organic biodegradable substance in the living world and a potential feedstock in the future for chemicals instead of oil.[1,2] It is renewable, but it cannot be dissolved in common solvents or melt before thermal degradation.

Chitin is the most important natural polysaccharide occurring in crustaceous shells or in cell walls of fungi. It has gained much attention for biomedical applications, due to its biocompatibility and restorative properties.[3,4] Its crystalline structure, resulted from intra- and intermolecular hydrogen bonds, is responsible to a great extent for its thermal and chemical stability. However, the poor solubility in most organic solvents restricts its utilization.

As generally known, cellulose fibers are moisture-absorbent, comfortable, while chitin fibers are biostatic, inflammation-diminishing, odor-resistant, odor-preventing and itch-resistant.[5] Therefore, the combination of cellulose with chitin seems to be an attractive task. Bochek *et al.*[6] analyzed the macromolecular interactions in chitin/cellulose blend solutions, in which dimethylacetamide/ lithium chloride was used as a solvent, and found out that the macromolecules of the two polymers showed partial compatibility. Phonwong *et al.*[7] prepared chitin/cellulose blend films in which dimethylacetamide/lithium chloride was used as a solvent. Zhang *et al.*[8] prepared cellulose/chitin blend membranes from NaOH/thiourea aqueous solutions and investigated the morphology and structure of the blend membranes. Undoubtedly, the blend bio-fibers composed of cellulose and chitin should have a great potential as biological materials. However, it is only the viscose/chitin xanthate blend fibers prepared by the viscose method that have been cited[9-13] until now. Nevertheless, the viscose technology induces the well-known problem of environmental pollution.

Dissolving cellulose and chitin into the blend solution is an important way for fiber preparation, since there is almost no loss of raw materials. The present study attempts at preparing cellulose/chitin blend fibers from a NaOH/thiourea/urea aqueous solution, which is able to dissolve cellulose directly and appears as a green solvent.[14] There follows a description of the method adopted for fiber preparation and fiber characterization in terms of mechanical properties, macro-molecular structure and surface morphology.

EXPERIMENTAL

Materials

The cotton linter pulps were supplied by Shanghai Cellulose Pulp Factory, China. The viscosity-average molecular weight ($\overline{M}_\eta$) of the pulps, determined by viscometry in cadoxen, was of 8.56×10^4. The pulps were shredded into powder, and dried in a vacuum oven at 70 °C for 24 h before dissolution. A commercial chitin from crab shell, provided by AK Biotech Co, Ltd (Shandong, China), showed[15] a 91% degree of acetylation (*DA*) from the nitrogen content, calculated by equation (1):

$$DA = 1 - [(W_C / W_N - 5.14)/1.72]\times 100\% \qquad (1)$$

where W_C/W_N is the carbon-to-nitrogen mass ratio.

Preparation of the mixture solution

A 5 wt% cellulose solution was prepared by dissolving cotton linter in 8 wt% NaOH/6.5 wt%, thiourea/8 wt% urea aqueous solution, as described in a previous work.[14] A chitin solution in 10 wt% NaOH aqueous solution was prepared according to Hirano's method.[16] 40 g of chitin powder were immersed into 154 mL 46 wt% NaOH in an ice bath, for about 6 h. After being stirred and frozen at -5 °C for 24 h, the resulted product was thawed and stirred extensively at room temperature, after which the chitin solution was obtained, with a 3.5 wt% concentration.

The chitin solution was mixed with the cellulose solution to obtain a mixture solution containing 10 wt% of W_{chitin}, according to literature.[8] Subsequently, the resulted solution was stirred at room temperature for 30 min and degassed at 10 °C by centrifugation.

Preparation of blend fibers

A laboratory scale wet-spinning apparatus was used to prepare blend fibers, as schematically shown in Figure 1. The mixture solution was introduced into the cylinder at room temperature. A pressure of 0.1 MPa was applied to the spinning dope, to extrude it into a coagulation bath using a spinneret with 12 orifices. The 12.5 wt% H_2SO_4/10 wt% Na_2SO_4 aqueous solution was selected as a coagulation bath at the temperature of 20 °C. The apparent jet stretch ratio (the ratio of take-up velocity to the dope extrusion velocity) was of 90%. The fibers were subsequently washed in boiling water and then drawn out, while the post-drawing ratio was adjusted to 120%. After spinning and washing thoroughly, the blend fibers were gradually dried by a heating roller (surface temperature 65-80 °C) and wound on a spool.

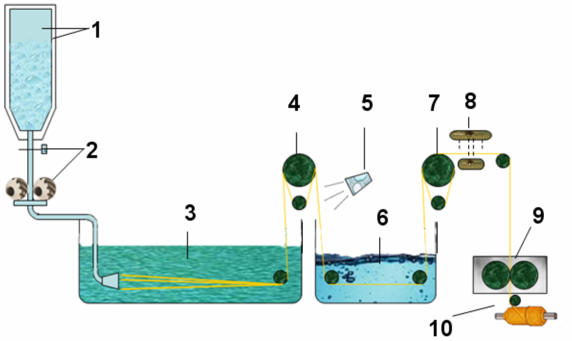

Figure 1: Set-up of a multi-filament spinning machine

1 – pressure extruder with a stainless cylinder equipped with a cooling jacket; 2 – gauging device; 3 – coagulation bath; 4 – Nelson-type roller; 5 – water spray device; 6 – washing bath; 7 – post-drawing roller; 8 – post-treatment device; 9 – heating roller; 10 – take-up device

Characterization

The Fourier transform infrared (FTIR) spectra (4000-400 cm^{-1}) of blend fibers were recorded on a Nicolet 410 spectrometer with a resolution of 4 cm^{-1}. The test specimens were prepared by the KBr-disk method. The thermal properties of the blend fibers were measured on the Model STA-449C differential scanning calorimeter DSC (NETZSCH Company), at a heating rate of 10 °C/min under N_2 atmosphere. The morphology of the blend fibers was characterized on a JEOL JSM-5600LV scanning electron microscope (SEM). Wide angle X-ray diffraction (WAXD) measurement of the blend fibers was conducted on an X-ray diffractometer (Rigaku/Dmax-B, Japan) with Cu-Kα, at 40 kV and 50 mA. X-ray diffraction patterns were recorded in a range of 2θ, from 5 to 40°. The fibers' degree of crystallinity (χ_c) was calculated according to the peak separation method. The tensile properties of the fibers were measured on a tensile testing machine provided by Chang-Zhou Textile Machine Co. Ltd (Changzhou, China), according to ASTM D2256-80.

RESULTS AND DISSCUSSION

Structure of blend fibers

Figure 2 shows the FTIR spectra of chitin, cellulose fibers and chitin/cellulose blend fibers. As to the spectrum of chitin powders, the peaks located at 1652, 1555 and 1310 cm^{-1} were assigned to amides I, II and III, while the broad bands appearing at 3266 and 3455 cm^{-1} were attributed to the -NH and -OH stretching vibration bands of chitin, respectively.[8] Compared to the chitin and regenerated cellulose fibers, the -NH stretching band of chitin disappeared in the blend fibers and the -OH stretching band became larger, implying a strong interaction between cellulose and chitin, attributed mostly to intermolecular hydrogen bonding. The -OH group of cellulose and the -NHCO- group of chitin interacted with each other, which makes the C=O stretching bands shift to a lower frequency, resulting in the disappearance of the -NH absorbed band. This strong intermolecular hydrogen bonding reflects a certain level of miscibility of the blend fibers.

Thermal properties of blend fibers

Figure 3 plots the DSC heating curves of the regenerated cellulose fibers, chitin powder, as well as of the cellulose/chitin blend fibers. One may observe that the two pure regenerated fibers reveal a distinct endothermic peak at 325 and 215 °C, which is the result of the decomposition of glucopyranose rings of cellulose and of chitin, respectively. Compared to cellulose, a melting endothermic peak appears for chitin at 218 °C, as well as an endothermic peak of thermal decomposition for cellulose at 378 °C. The decomposition of the glucopyranose rings of the blend fibers shifted to a higher temperature (378 °C), indicating that the thermal stability of the blend fibers was enhanced with the import of chitin.

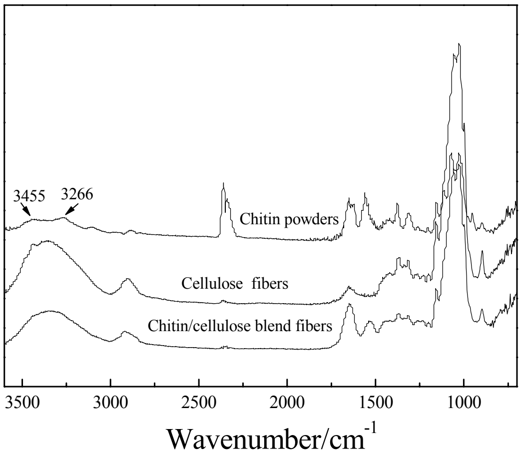

Figure 2: FTIR spectra of chitin, cellulose fibers and cellulose/chitin blend fibers

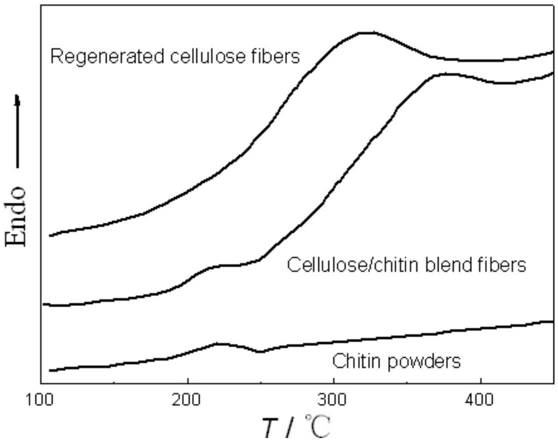

Figure 3: DSC heating curves of regenerated cellulose fibers, chitin powders and cellulose/chitin blend fibers

The upward shift of the degradation peak also suggests that the blends exhibit good miscibility, which contributed to the interaction of the hydrogen bonding between cellulose and chitin. Nishioka *et al.*[17] proved that the difference in thermal decomposition was correlated with the miscibility of two components.

Tensile properties of blend fibers

Table 1 lists the tensile properties of the cellulose/chitin blend and cellulose fibers. Both tensile strength and elongation at break of the blend fibers with 10 wt% chitin were slightly lower than those of the cellulose fibers. A possible explanation is that the addition of a small amount of chitin interferes with the orientation and crystallization of cellulose macromolecules, which generally determine the tensile properties of the fibers. The drop in the tensile properties of the cellulose fibers with the addition of chitin was also present in viscose/chitin xanthate blend fibers.[12,13]

Figure 4 illustrates the WAXD curves of the cellulose/chitin blend fibers and cellulose fibers. The observation was made that the blend fibers exhibit a typical cellulose II crystalline form in which the peaks at 2θ = 11.8°, 19.8° and 21° correspond[18] to the ($\overline{110}$), (110) and (200) planes, which surely means that the cellulose crystal form is not disturbed by the blending process. Nevertheless, as seen in Table 1, the degree of crystallinity (χ_c) of the blend fibers is lower than that of the cellulose fibers, indicating that crystallization of the cellulose macromolecules gets lower with the import of chitin. Possibly, the strong interaction between chitin and cellulose macromolecules results in the partial damage of the original cellulose crystalline region. Therefore, the tensile properties of the blend fibers decrease correspondingly.

Table 1
Tensile properties of cellulose/chitin blend fibers and cellulose fibers

Samples	Tensile strength (MPa)	Elongation at break (%)	χ_c (%)
Cellulose/chitin blend fibers	256.01 ± 20.72	8.7 ± 2.2	55.0 ± 2.1
Cellulose fibers	267.84 ± 39.95	12.0 ± 1.9	61.0 ± 2.4

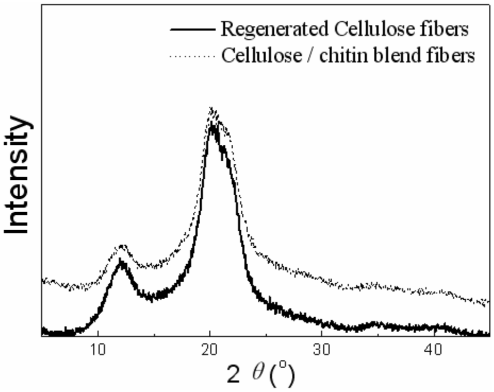

Figure 4: WAXD curves of cellulose/chitin blend fibers and cellulose fibers

Morphology of blend fibers

The present study evidences a good miscibility of cellulose with chitin for the blend fibers, similar results being also reported through morphological observations made on the fracture surfaces of the blend fibers.[10,12,13] Figure 5a shows the SEM photographs of the surfaces of the prepared blend fibers. Comparatively with pure regenerated cellulose fibers (Fig. 5b), one may observe that the surface of the blend fibers is not so smooth as that of the regenerated cellulose fibers, exhibiting a homogeneous morphology and no obvious splits, which is indicative of a good miscibility and blend homogeneity between cellulose and chitin, at a composition ratio of 9/1 by weight.

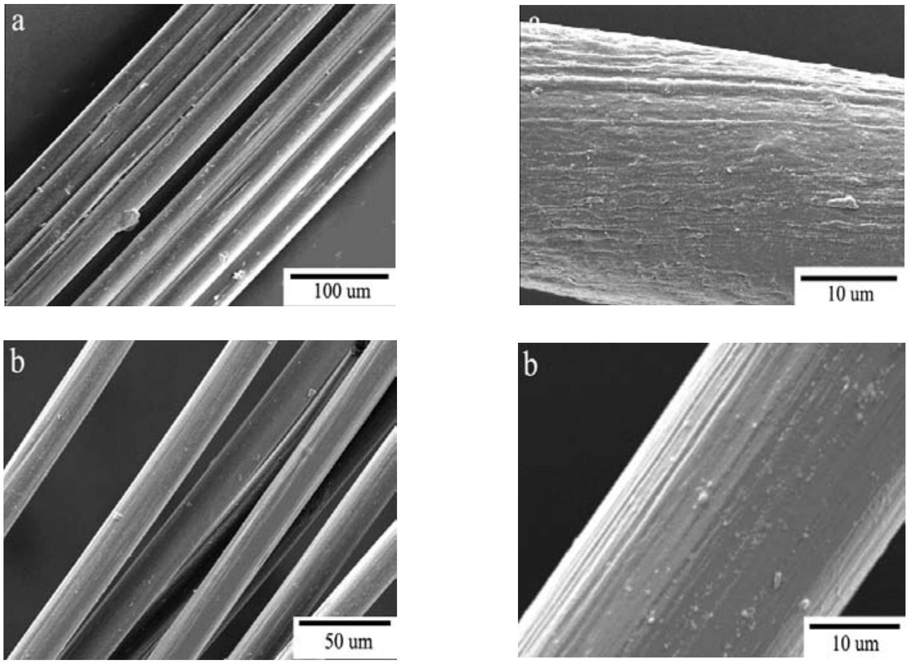

Figure 5: SEM photographs of the (a) surfaces of the prepared blend fibers and (b) regenerated cellulose fibers

CONCLUSIONS

Regenerated cellulose/chitin blend fibers were prepared directly from cellulose and chitin, in a 8 wt% NaOH/6.5 wt% thiourea/8 wt% urea aqueous solution. The strong intermolecular interaction between chitin and cellulose molecular chains grants their good miscibility. The import of chitin in the cellulose fibers can improve their thermal stability, compared to that of pure cellulose fibers. However, the tensile properties of the blends were slightly deteriorated with the addition of chitin, because the import of chitin partly destroys the crystalline region of the cellulose macromolecules. At a chitin content of 10 wt%, the average tensile strength and elongation at break of the blend fibers were of 1.73 cN/dtex and 8.7%, respectively. The blend fibers display a fibrillar nature and homogeneous blend properties. As a conclusion, the biodegradable cellulose/chitin blend fibers with good mechanical properties and compatibility combine the beneficial characteristics of the individual components, which makes them available for biomedical applications.

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