Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Fan, Lihong , Du, Yumin , Zhang, Baozhong , Yang, Jianhong , Cai, Jun , Zhang, Lina and Zhou, Jinpin(2005) 'Preparation and Properties of Alginate/Water-Soluble Chitin Blend Fibers', Journal of Macromolecular Science, Part A, 42: 6, 723 — 732

To link to this Article: DOI: 10.1081/MA-200058635

URL: http://dx.doi.org/10.1081/MA-200058635

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 42:723–732, 2005

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1081/MA-200058635

Preparation and Properties of Alginate/Water-Soluble Chitin Blend Fibers

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Water-soluble chitin (half-deacetylated chitin) was prepared from chitosan by N-acetylation with acetic anhydride. Alginate/water-soluble chitin blend fibers were prepared by spinning their mixture solution through a viscose-type spinneret into a coagulating bath containing aqueous $CaCl_2$ and ethanol. The structure and properties of the blend fibers were studied with the aids of infrared spectra (IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). structure analysis indicated good miscibility existed between alginate and water-soluble chitin, due to the strong interaction from the intermolecular hydrogen bonds and electrostatic interactions. Best values for the dry tensile strength and breaking elongation were obtained when the water-soluble chitin content was 30 wt%. The wet tensile strength and breaking elongation decreased with the increase of water-soluble chitin content. The introduction of water-soluble chitin in the blend fiber can improve the water-retention properties of the blend fiber compared to pure alginate fiber. The fibers treated with aqueous solution of silver nitrate have good antibacterial activity to Staphylococcus aureus.

Keywords alginate, water-soluble chitin, blend fibers, structure, properties

Introduction

Alginates are linear copolymers of β-(1-4)-linked D-mannuronic acid and α-(1-4)-linked L-guluronic acid units, which exist widely in many species of brown seaweeds. Alginate fibers can be prepared by extruding solutions of sodium alginate into a calcium salt solution bath or an acidic solution to produce the corresponding calcium alginate or alginic acid fibers respectively. Fibers of this type have been used extensively in wound dressing applications, due to their excellent biocompatibility, non-toxicity, and potential bioactivity, offering many advantages over traditional cotton and viscose gauzes. Alginate fibers, typically as a calcium salt, interact with the wound exudates to form a moist gel, as a result of the ion exchange between the calcium ions in the fiber and the sodium ions in the exudates (1). This eliminates fiber entrapment in the wound, which

Received October 2004, Accepted November 2004

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is a major cause of patient trauma during dressing changes. Such gelation provides the wound with a moist healing environment, which promotes healing and leads to better cosmetic repair of the wound (2). This *in situ* generation of a moist healing environment and the consequent high absorbency of the alginate dressings are two of the outstanding properties, which make the alginate dressing one of the most versatile wound dressings available today. In addition, alginate containing dressings have been demonstrated to activate macrophages within the chronic wound bed and generate a pro-inflammatory signal which may initiate a resolving inflammation characteristic of healing wounds (3). Therefore, many commercially available wound dressings contain calcium alginate fibers.

Another type of natural polysaccharide used in wound management products is chitin, and its partially deacetylated derivative, chitosan. Recent observations have suggested that chitin and chitosan can accelerate wound healing (4). Chitin and chitosan have a rigid crystalline structure formed by hydrogen bonding through intra- and intermolecular interactions and do not dissolve in water. The accelerated wound healing effects of chitin and chitosan are not totally effective, due to relatively low interaction between the wounded sites and the healing agents. The half-deacetylated chitin is known to have good water solubility and be more effective as wound healing accelerators than chitin and chitosan (5–7). Silver ions have been found to have antibacterial effects on some microbes. The silver salt is the most effective antimicrobial agent in the treatment of burn patients (8). The antibacterial fibers were obtained by treatement with an aqueous solution of silver nitrate.

In this paper, we prepared water-soluble chitin (half-deacetylated chitin) from chitosan by N-acetylation with acetic anhydride, and the novel bicomponent fibers were prepared through blending alginate and water-soluble chitin. The structure and properties of the blended fibers were studied through infrared spectra (IR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The mechanical properties and water-retention values of the blended fibers were also measured with regard to the different proportions of the two components. The properties of the antibacterial fibers were examined.

Experimental

Materials

Sodium alginate (chemical grade) was purchased from Shanghai Chemical Reagents. Chitosan was supplied by Yuhuan Ocean Biochemistry Co. Ltd, in Zhejiang province in China. The degree of deacetylation (DD), determined by elemental analysis, was 93%. The intrinsic viscosity ($[\eta]$) of the chitosan sample was measured with an Ubbelohde viscometer, and the viscosity-average molecular weight (M_η) was calculated to be 5.0×10^5 with the Mark–Houwink equation (9):

$$[\eta] = 6.59 \times 10^{-3} M_\eta^{0.88} \, (\mathrm{mL/g})$$

All other reagents used were of analytical grade.

Preparation of Water-soluble Chitin (Half-deacetylated Chitin)

Water-soluble chitin was prepared according to our previous work (10). Chitosan (40 g) was dissolved in 10% aqueous acetic acid/methanol, and acetic anhydride (16 g) was added. After stirring at room temperature for 5, acetone was added. The precipitate was collected by filtration. After dialyzing against deionized water for 3 days, the product was vacuum dried at room temperature. The degree of deacetylation (DD) of the product determined by elemental analysis was 48%.

Preparation of Blend Fibers

Water-soluble chitin was dissolved in distilled water to prepare a 4 wt% solution. Sodium alginate was dissolved in distilled water at room temperature to a concentration of 5 wt% and then mixed with the water-soluble chitin. The mixed solutions were vigorously stirred at room temperature for an hour, and filtered under pressure through a 200 mesh filter cloth. The clear filtrate spinning solution was poured into the spinning tank, and degassed under diminished pressure for an hour. After that, the spinning solution was extruded at 25°C from a 30-hole (0.08 mm diameter) viscose-type spinneret into a coagulating bath containing 10 wt% calcium chloride aqueous solution and ethanol to form fibers. The volume ratio of calcium chloride aqueous solution to ethanol was 50/50. The as-spun fibers were washed and stretched (20% stretching ratio) in distilled water, then air-dried to provide fibers. According to the water-soluble chitin contents of 10, 30, 50, and, 70 wt%, the blend fibers were labeled as AW10, AW30, AW50 and AW70, respectively. The pure alginate fiber and water-soluble chitin were coded as AL and WS, respectively.

Antibacterial Treatment of the Fibers

The pure alginate fiber and blend fibers (AL, AW10, AW30, AW50 and AW70) were placed in a treatment bath containing silver nitrate (0.01 wt%) for 10 min, rinsed and dried. The antibacterial fibers were coded as $\mathrm{AL_{Ag}}$, $\mathrm{AW10_{Ag}}$, $\mathrm{AW30_{Ag}}$, $\mathrm{AW50_{Ag}}$, and $\mathrm{AW70_{Ag}}$.

Characterization of Fibers

Infrared spectra (IR) of the sample were recorded with a Nicolet-170SX FTIR (USA). The test specimens were cut into small pieces for preparation of KBr discs. The samples were made thin enough to observe the Lambert-Beer Law. The morphological structure of the blend fiber samples was studied with the Hitachi SX-650 (Japan) scanning electron microscopy (SEM). X-ray diffraction (XRD) patterns of the sample were measured with a Shimadzu Labx-XRD-6000 diffractometer (Japan), using a Cu Kα target at 40 kV and 50 mA. The diffraction angle ranged from 5° to 40°. The crystallinities of the sample were calculated by the following equation (11):

$$\mathrm{X_c = F_c/(F_c + F_a) \times 100\%}$$

where $\mathrm{F_c}$ and $\mathrm{F_a}$ are the areas of crystal and noncrystalline regions, respectively. The tensile strength (σ_b) and the breaking elongation (ε_b) of the fibers were determined on a fiber electron tensile tester (CMT8502, Shenzhen SANS Test Machine Co., Ltd., China). The gauge length was 90 mm and crosshead speed was 50 mm/min. All samples were preconditioned at 20°C and 65% relative humidity for 24 h prior to testing. The water-retention values (WRV) of the fibers were calculated as follows:

$$\mathrm{WRV = (W_1 - W_0)/W_0 \times 100\%}$$

where W_0 denote the original weight (g) of the fiber which was dried at 80°C until a constant weight achieved, W_1 is the weight of fully swollen fiber that was centrifuged at 4000 rev/min for 10 min.

Antibacterial Testing

The shake-flask method was used to evaluate the antibacterial activity of the fibers against *Staphylococcus aureus* (a kind of Gram-positive bacterial inhabitant of colonized or infected wounds) in term of bacterial reduction rate. A 0.5 mL aliquot of a known and fresh culture was added to 70 mL of phosphate-buffered saline (PBS, 0.03 mol/L, pH 7.2–7.4) containing 0.75 g fibers. After the cultivation was shaken (300 rpm) at 37°C for 1 h, 0.5 mL of the obtained mixture was sampled, diluted with PBS, and spread on the nutrient agar (agar, 15 g; peptone, 10 g; beef extract, 3 g; NaCl, 3 g in 1000 mL distilled water, pH 7.0) plate to give the single colonies. After being incubated at 37°C for 24 h, the number of survivors was counted. The number of bacteria in 0.5 mL of fresh culture was also determined by means of this plate-counting method. The bacteria reduction rate (BBR) of each fiber was calculated as follows:

$$\mathrm{BRR} = (\mathrm{N}_1 - \mathrm{N}_2)/\mathrm{N}_1 \times 100\%$$

where N_1 is the average number of colonies before shaken incubation and N_2 is the average number of colonies after shaken incubation.

Results and Discussion

Structure and Morphology

The IR spectra of chitosan (CS) and water-soluble chitin (WS) are shown in Figure 1. The infrared spectrum of chitosan shows the 1597 cm^{-1} amino characteristic peak. The absorption band of amide I at 1656 cm^{-1} was very weak, and this agreed with the high DD (9). In comparison with the chitosan, the water-soluble chitin showed the following major difference. The absorption band of amide I and II at 1654 cm^{-1}, 1562 cm^{-1} were strengthened drastically. The amino characteristic peak at 1597 cm^{-1} was weakened. The latter data suggests the chitosan amino group was acetylated. The IR spectra of the samples of AL, AW10, AW30, AW50, AW70 and WS are shown in Figure 2. The IR spectrum of the alginate showed absorption bands at 3418 cm^{-1} (OH stretching), 1608 cm^{-1} (COO^- asymmetric stretching), and 1421 cm^{-1} (COO^- symmetric stretching). The absorption band at around 3418 cm^{-1} for the blend fibers, concerned with the OH stretching vibration for AL, broadened and shifted to a lower wave number with the introduction of WS. These significant changes indicated the formation of the intermolecular hydrogen bond between alginate and water-soluble chitin. The absorption band at 1608 cm^{-1} for the AL fiber, assigned to the asymmetric stretching vibration of COO^-, shifted to a higher wave number. The absorption band of amino at 1562 cm^{-1} for WS disappeared in the blend fibers, suggesting that electrostatic interaction between the COO^- groups of alginate and amino of WS. Based on the latter evidence, it can be concluded that strong interaction exist between alginate and water-soluble chitin molecules, due to the formation of intermolecular hydrogen bonds and electrostatic interactions.

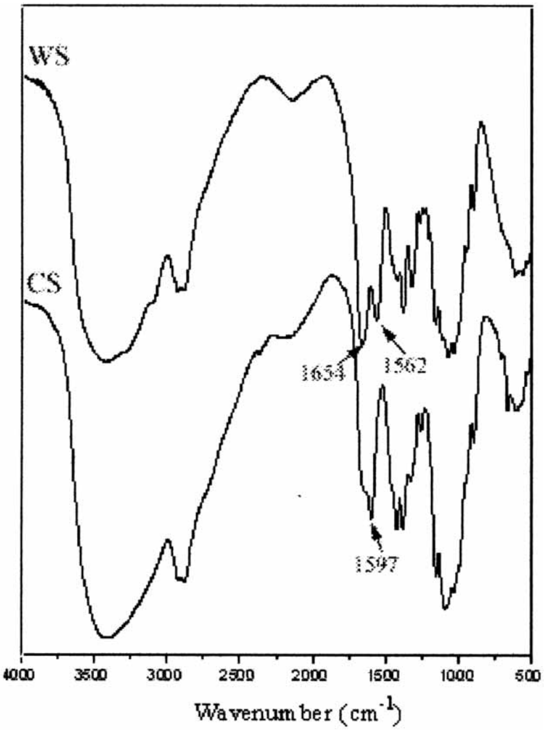

Figure 1. IR spectra of chitosan (CS) and water-soluble chitin (WS).

Figure 3 presents the X-ray diffraction pattern of alginate, water-soluble chitin and their blend fibers. The diffraction of alginate shows typical peaks around 14° and 23° (12). Three typical peaks in $2\theta = 9.5^\circ$, 19°, and 26° were observed for water-soluble chitin. The diffraction intensities of water-soluble chitin at 9.5°, 19°and 26° decreased drastically with increasing alginate content. The diffraction peak of alginate at 14° turned into an irregular wide peak in the blend. The crystallinity was calculated and the order was WS (47%) > AW70 (42%) > AW50 (40%) > AW30 (37%) > AW10 (33%) > AL(30%). It is obvious that the crystallinities of blend fibers increased gradually with the increase of WS, which can be explained that intermolecular interaction destroyed the regularity of WS. The results suggest the good miscibility for the blend fibers. The results also supported the conclusion drawn from IR, i.e., t the good miscibility existing between alginate and water-soluble chitin was due to the strong interaction from the intermolecular hydrogen bonds and electrostatic interactions.

The selected fibers were examined by scanning electron microscopy Figure 4. The surfaces of AW30 and AW50 showed homogeneous morphology, suggesting high miscibility between alginate and water-soluble chitin. The fibers displayed striation along the fiber length, and this agreed with the literature (13).

Mechanical Properties of Fibers

The effect of WS content on the tensile strength of fibers in dry and wet states is shown in Figure 5 and Table 1. The dry tensile strengths of the AW10, AW30, and AW50 were

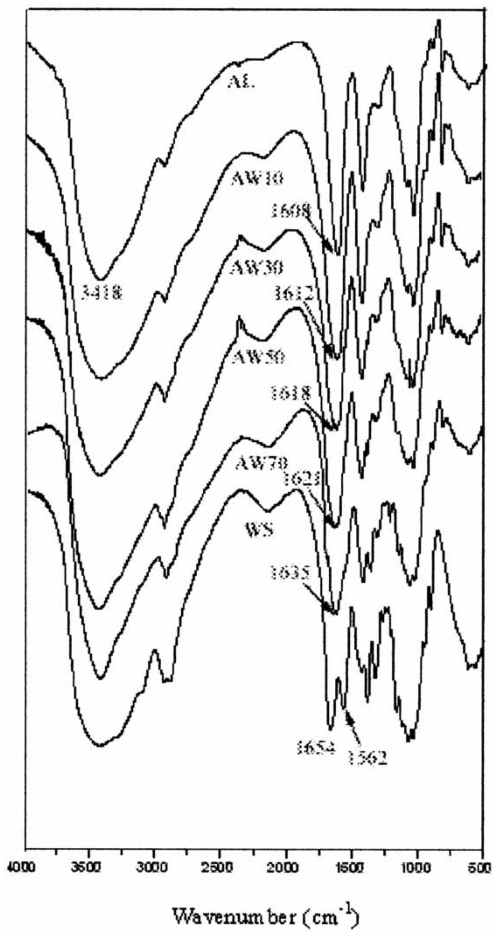

Figure 2. IR spectra of AL, AW10, AW30, AW50, AG70, and WS.

higher than that of pure alginate, and the maximum value was observed at AW30 achieved 12.25 cN/tex. The wet tensile strength decreased with the increase of WS content. Figure 6 shows the breaking elongation of the fibers in dry and wet states. The alteration of breaking elongation expressed a tendency similar to that of the tensile strength. Breaking elongation of the dry fibers of AW10, AW30, and AW50 were higher than that of pure alginate, with the maximum value observed for AW30 having a 23.3% value. Breaking elongations of the blend fibers decreased with the increase of WS content. These results might be attributed to the intermolecular interaction between the two polymers. Thus, controlling blend conditions, blend fibers can obtain better mechanical properties than the pure alginate fiber.

Water-retention Properties

The water-retention properties of the blend fibers are plotted in Figure 7. The water-retention values (WRV) of alginate/water-soluble chitin blend fibers increase with the

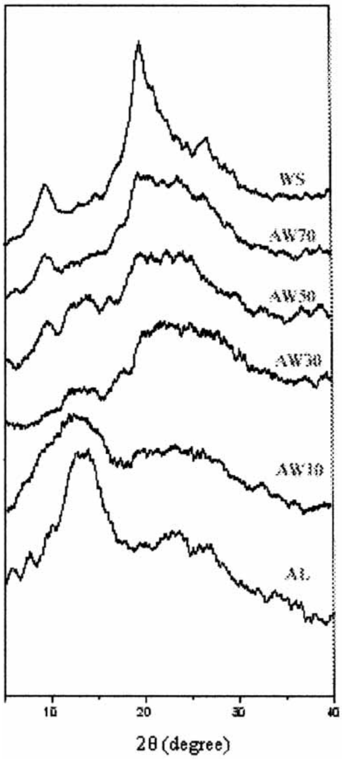

Figure 3. The X-ray diffraction patterns of AL, AW10, AW30, AW50, AW70, and WS.

increasing of water-soluble chitin content. The WRV of the blend fibers were in the ranges of 110–176%, obviously higher than that of pure alginate fiber, which has the lowest values (91%) (Table 1). The improvement in water-retention is due to water-soluble chitin being more hydrophilic than calcium alginate.

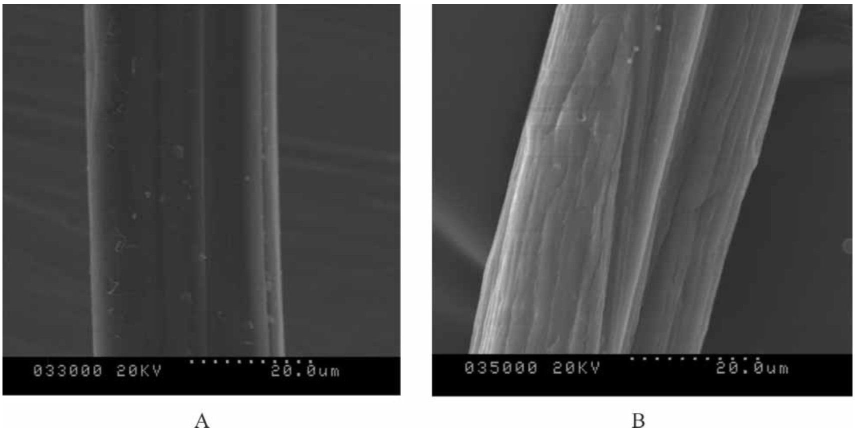

Figure 4. SEM photographs of the blend fibers: (A) surface of AW30, (B) surface of AW50.

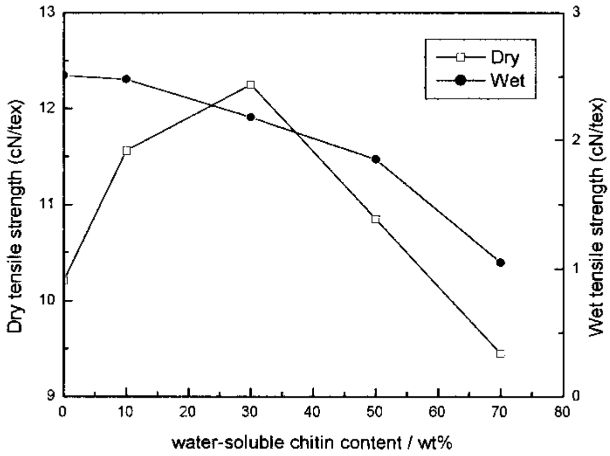

Figure 5. The effect of water-soluble chitin content (wt%) on tensile strength of the fibers.

The mechanical properties and water-retention properties of $AgNO_3$ treated fibers were not significantly different from the untreated fibers (Table 1). The latter implies that the silver ion was more like a coating, not penetrating the alginate-based fibers.

Antibacterial Testing

The antibacterial properties of the fibers were investigated (Table 1) showing that untreated fibers have little antibacterial activity and the fibers treated with $AgNO_3$ have good antibacterial activity toward *Staphylococcus aureus*. It is well known that silver ion has good antibacterial properties. The alginate-base fibers were immersed in silver nitrate solution, and the calcium alginate fiber converted into calcium/silver alginate

Table 1
The properties of the blend fibers

Fiber	The bacteria reduction rate (BBR)	Tensile strength (cN/tex) (dry/wet)	Breaking elongation (%) (dry/wet)	WRV (%)
AL	2.44	10.21/2.51	18.2/42.5	91
AW10	5.78	11.56/2.48	20.4/41.6	110
AW30	6.55	12.25/2.18	23.3/38.4	125
AW50	6.42	10.85/1.85	19.5/35.1	151
AW70	6.88	9.45/1.05	16.4/32.8	176
AL_{Ag}	>99.99	10.32/2.54	18.5/40.5	89
$AW10_{Ag}$	>99.99	11.37/2.50	19.3/39.8	108
$AW30_{Ag}$	>99.99	12.12/2.21	22.3/37.5	132
$AW50_{Ag}$	>99.99	10.91/1.79	17.6/34.3	150
$AW70_{Ag}$	>99.99	9.42/1.04	16.8/31.6	184

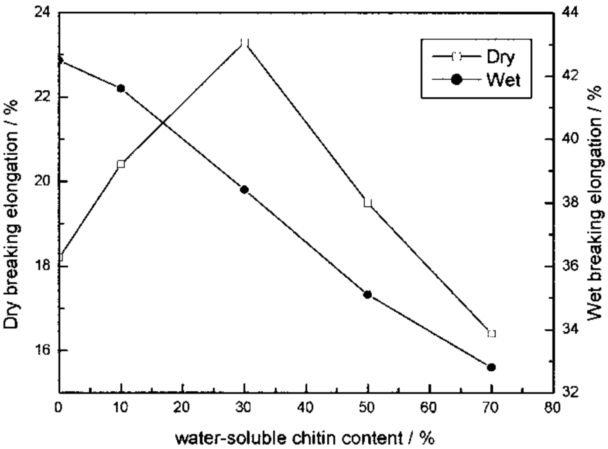

Figure 6. The effect of water-soluble chitin content (wt%) on breaking elongation of the fibers.

fiber. Thus, the treated fiber has good antibacterial activity compared with the untreated fiber.

Conclusions

Alginate and water-soluble chitin blend fibers can be obtained by spinning their solution through a viscose-type spinnet into a coagulation bath containing aqueous $CaCl_2$ and ethanol. The strong intermolecular interaction between alginate and the water-soluble chitin molecule occurs in the blend fibers. There is good miscibility between alginate and the water-soluble chitin molecular, due to the strong intermolecular interaction.

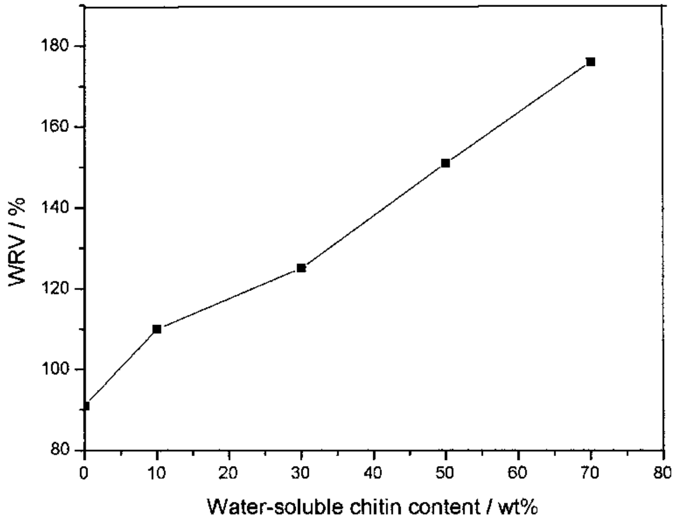

Figure 7. The effect of water-soluble chitin content (wt%) on the WRV of the fibers.

The best values of the dry tensile strength and breaking elongation were obtained when the water-soluble chitin content was 30 wt%. The wet tensile strength and breaking elongation decreased with an increase of WS. The introduction of water-soluble chitin in the blend fiber can improve water-retention properties of blend fiber compared to pure alginate fiber. The $AgNO_3$ treated fibers have good antibacterial activity toward *Staphylococcus aureus*. This novel alginate and water-soluble chitin blend fiber is promising for wound dressing applications.

Acknowledgement

We gratefully acknowledge financial support from the Hubei New Textile Material & Application Key Laboratory (Wuhan University of Science and Engineering) open foundation No. TKL200408.

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