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Preparation and properties of alginate/carboxymethyl chitosan blend fibers

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Abstract

Alginate/carboxymethyl chitosan blend fibers, prepared by spinning their mixture solution through a viscose-type spinneret into a coagulating bath containing aqueous $CaCl_2$, were studied for structure and properties with the aid of infrared spectroscopy (IR), X-ray diffraction (XRD) and scanning electron micrography (SEM). The analyses indicated a good miscibility between alginate and carboxymethyl chitosan, because of the strong interaction from the intermolecular hydrogen bonds. The best values of the dry tensile strength and breaking elongation were obtained when carboxymethyl chitosan content was 30 and 10 wt%, respectively. The wet tensile strength and breaking elongation decreased with the increase of carboxymethyl chitosan content. Introduction of CM-chitosan in the blend fiber improved water-retention properties of blend fiber compared to pure alginate fiber. Antibacterial fibers, obtained by treating the fibres with aqueous solution of *N*-(2-hydroxy)-propyl-3-trimethylammonium chitosan chloride and silver nitrate, respectively, exhibited good antibacterial activity to *Staphylococcus aureus*.

Keywords: Alginate; Carboxymethyl chitosan; Blend fibers; Miscibility; Properties

1. Introduction

Alginate fibers have been extensively used in wound dressing applications due to their excellent biocompatibility, non-toxicity, and potential bioactivity, which can offer 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 exudates (Qin, Agboh, Wang, & Gilding, 1996). This eliminates fiber entrapment in the wound, which is a major cause of patient trauma at dressing change. Such gelation provides the wound with a moist environment, which promotes healing and leads to a better cosmetic repair of the wound (Winter, 1962). 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 (Thomas, Harding, & Moore, 2000). Therefore, many commercially available wound dressings contain calcium alginate fibers.

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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 (Mattioli-Belmonte, Muzzarelli, & Muzzarelli, 1997). Chitin and chitosan have rigid crystalline structures formed by hydrogen bonding intra- and inter-molecularly and do not dissolve in water. Probably the wound healing acceleration effects of chitin and chitosan do not become fulfilled due to relatively low interaction between the wound sites and the healing agents. Carboxymethyl chitosan (CM-chitosan), a water-soluble chitosan derivative, has already been used extensively in a wide range of biomedical applications due to its unique chemical, physical, and biological properties and especially its excellent biocompatibility (Muzzarelli, 1988). Chen, Wang, Liu, and Park (2002) found that CM-chitosan did not restrict normal human skin fibroblasts but impeded keloid fibroblast by inhibiting type I collagen secretion and suggested a role for wound healing in keloid control (Chen et al., 2002).

It is well known that blending is an effective and convenient method to improve the performance of polymer materials. Thus, in the present study, novel bicomponent fibers were prepared from alginate and CM-chitosan. CM-chitosan has a molecular structure similar to that of alginate in terms of its carboxyl groups. This similarity is expected to give high compatibility between these two polymers. For this reason blend fibers were made in the present work. Fibers may have some endogenous antimicrobial activity but silver has a long history of use in medicine as an antimicrobial agent. Silver nitrate is effective antimicrobial agent in the treatment of burn patients (Klasen, 2000). *N*-(2-Hydroxy)-propyl-3-trimethylammonium chitosan chloride (HTCC) can be synthesized from chitosan and glycidyltrimethylammonium chloride (GTMAC) (Nam, Kim, & Ko, 1999), which enhances water solubility and antimicrobial activity of chitosan. In this paper, the fibers were placed in a treatment bath containing an aqueous solution of HTCC and silver nitrate, respectively, to impart antibacterial activity to the fiber. The properties of the antibacterial fibers were examined.

2. Experimental

2.1. Materials and methods

Sodium alginate was purchased from Shanghai Chemical Reagents Company, chemical grade. Chitosan was supplied by Yuhuan Ocean Biochemistry Co. Ltd, in Zhejiang province in China. The degree of deacetylation (DD) as determined by elemental analysis was 0.93, and the molecular weight calculated from GPC was 2.9×10^5. Standard pullulans for GPC were purchased from Showa Deuko, Tokyo, Japan. *N*-(2-Hydroxy)-propyl-3-trimethylammonium chitosan chloride (HTCC) was prepared according to Nam et al. (1999). All of other reagents used are of analytical grade.

2.2. Preparation of carboxymethyl chitosan

Chitosan (10 g) was suspended in 50 wt% NaOH and kept at −20 °C for 16 h. The frozen alkali chitosan was transferred to 2-propanol (100 mL), and chloroacetic acid (10 g) was added in portions. After stirring at room temperature for 2 h, heat was applied to bring the reaction mixture to a temperature of 60 °C for another 2 h. After dialyzing against deionized water for 3 days, the product was vacuum dried at room temperature.

2.3. Preparation of blend fibers

By changing the weight ratio of sodium alginate to CM-chitosan to 9:1, 7:3, 5:5, and 3:7, a series of 1000 mL mixtures of 4 wt% aqueous CM-chitosan and 5 wt% aqueous sodium alginate were vigorously stirred at room temperature for an hour, and filtered through a 200-mesh filter cloth under pressure. The clear filtrate as a spinning solution was degassed in the spinning tank under diminished pressure for an hour. It was then extruded at 25 °C through a 30-hole (0.08 mm diameter) viscose-type spinneret into a coagulating bath containing 5 wt% aqueous calcium chloride. The as-spun fibers were washed and stretched (stretching ratio is 20%) in distilled water, then dried. According to the weight ratio of sodium alginate to CM-chitosan to 9:1, 7:3, 5:5, and 3:7, a series of blend fibers were prepared, labeled as AC10, AC30, AC50, and AC70, respectively. The pure alginate fiber and CM-chitosan were coded as pure alginate and CMCN, respectively.

2.4. Antibacterial treatment of the fibers

The pure alginate fiber and blend fibers (pure alginate, AC10, AC30, AC50, and AC70) were placed in a treatment bath containing 1 wt% aqueous HTCC and 0.01 wt% silver nitrate for 10 min, respectively, rinsed in distilled water and dried at 25 °C. The antibacterial fibers were coded as pure alginate HTCC, $AC10_{HTCC}$, $AC30_{HTCC}$, $AC50_{HTCC}$, $AC70_{HTCC}$, pure $alginate_{Ag}$, $AC10_{Ag}$, $AC30_{Ag}$, $AC50_{Ag}$, and $AC70_{Ag}$.

2.5. Characterization of fibers

Infrared spectra (IR) of samples which had been cut into small pieces for preparation of KBr discs were recorded with a Nicolet-170SX FTIR (Madison, USA). The morphological structure of the blend fiber samples was studied by scanning electron microscopy (SEM) with a Hitachi SX-650 (Tokyo, Japan) machine. X-ray diffraction (XRD) patterns of the sample were measured with a Shimadzu Labx-XRD-6000 diffractometer (Kyoto, Japan), and using a Cu Kα target at 40 kV and 50 mA. The diffraction angle ranged from 5° to 40°. 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 mechanical testing. The water-retention values (WRV) of fibers were calculated as follows:

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

where W_0 denotes the original weight (g) of 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*g* for 10 min.

2.6. Antibacterial testing

A shake-flask method was used to evaluate the antibacterial activity of the fibers against *Staphylococcus aureus* (a Gram-positive bacterial inhabitant of colonized or infected wounds) in term of bacterial reduction rate. Aliquots (0.5 mL) of fresh culture were added to 0.03 M sodium phosphate buffer pH 7.3 (70 mL) containing fibers (0.75 g). After the cultivation was shaken (300 rpm) at 37 °C for 1 h, an aliquot (0.5 mL) was diluted with the sodium phosphate buffer, and spread on nutrient agar (made up from agar, 15 g; peptone, 10 g; beef extract, 3 g; NaCl, 3 g in 1000 mL distilled water, pH 7.0) plates 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 (BRR) of each fiber was calculated as follows:

$$\mathrm{BRR} = (N_1 - N_2)/N_1 \times 100\%,$$

where N_1 and N_2 are the average number of colonies arising from pre- and postincubation cultured samples, requisitely.

3. Results and discussions

3.1. Structure and morphology

The IR spectra of the samples of chitosan, HTCC, and CM-chitosan are shown in Fig. 1. In the infrared spectrum of chitosan, the 1598 cm^{-1} peak corresponds to the amino group. The absorption band of amide I at 1656 cm^{-1} was very weak, and this was comensurate with a high DD (Tang, Du, & Fan, 2003). Compared with chitosan, HTCC shows the disappearance of the NH_2 associated band at 1598 $cm^{-1}$of the N–H bending in the primary amine, and appearance of a new band at 1482 cm^{-1}, which is attributed to the methyl groups

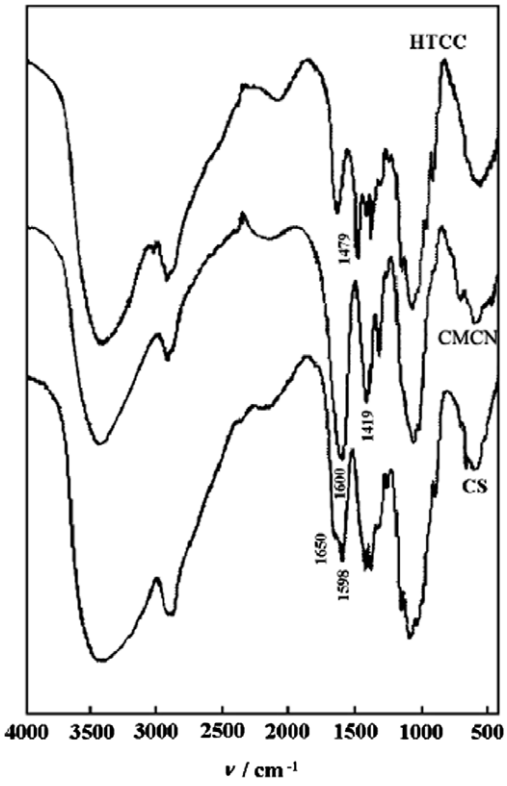

Fig. 1. IR spectrum of chitosan, CM-chitosan (CMCN) and N-(2-hydroxy)-propyl-3-trimethylammonium chitosan chloride (HTCC).

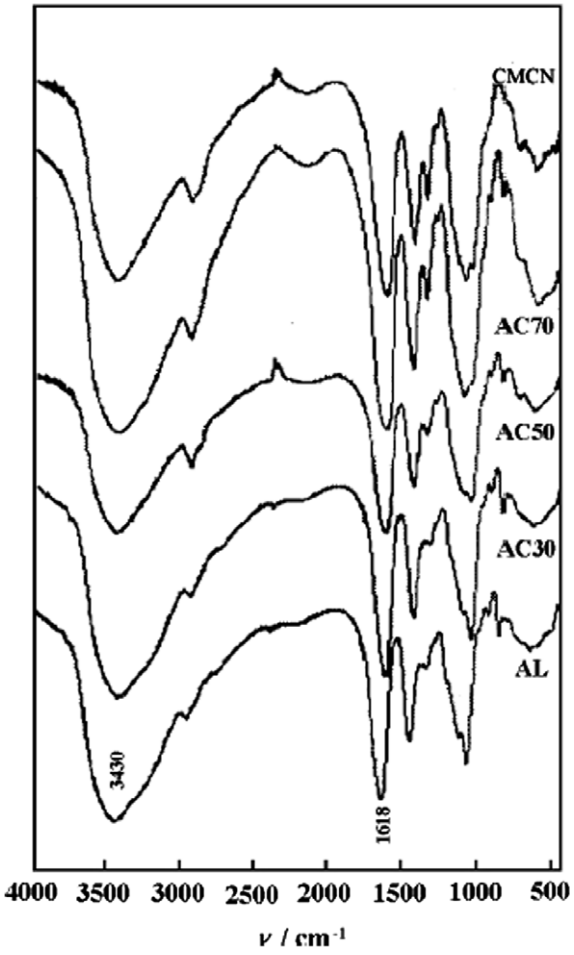

Fig. 2. IR spectra of pure alginate (AL), alginate/CM-chitosan (w/w), 70/30 (AC30), 50/50 (AC50), 30/70 (AC70), and pure CM-chitosan (CMCN).

of the ammonium. This IR spectrum is consistent with the reported spectra (Xu, Du, Huang, & Gao, 2003). CM-chitosan showed the characteristic peaks at 1600 cm^{-1} (COO^- asymmetric stretching) and 1419 cm^{-1} (COO^- symmetric stretching). The absorption bands at 3420 cm^{-1} are ascribable to the stretching vibration of OH and NH group of CM-chitosan.

The IR spectrum of alginate (Fig. 2) showed absorption bands at 3430 cm^{-1} (OH stretching), 1618 cm^{-1} (COO^- asymmetric stretching), and 1421 cm^{-1} (COO^- symmetric stretching). For the blend fibers, the absorption band at around 3430 cm^{-1} concerned with OH stretching vibration for pure alginate broadened and shifted to a low wave number with the increase of CM-chitosan content. The absorption band at 1618 cm^{-1} for pure alginate fiber assigned to the asymmetric stretching vibration of COO^- shifted to a lower wave number. Based upon this evidence, it can be concluded that a certain degree of interaction between alginate and CMCN molecules is due to the formation of intermolecular hydrogen bands.

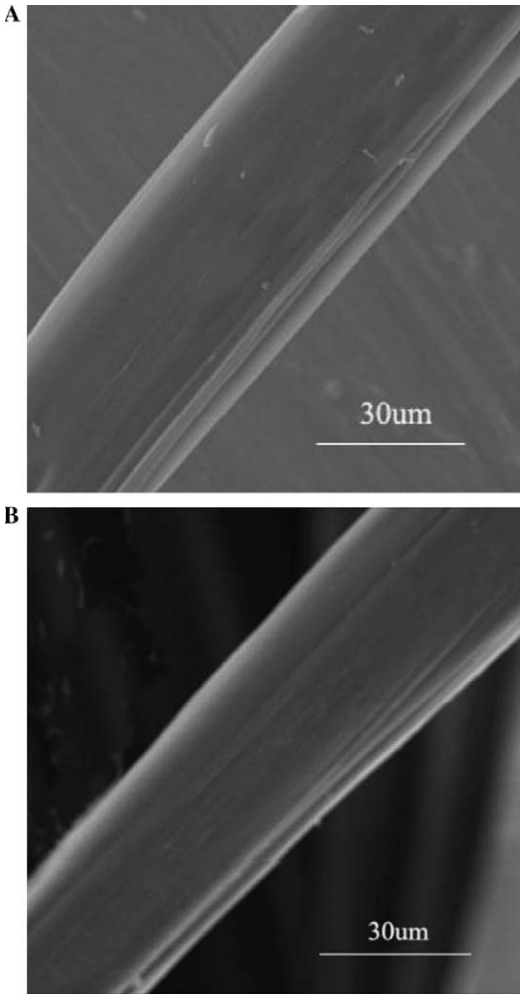

Fig. 3. SEM photographs of blend fibers, alginate/CM-chitosan (w/w), 70/30 (A), 50/50 (B).

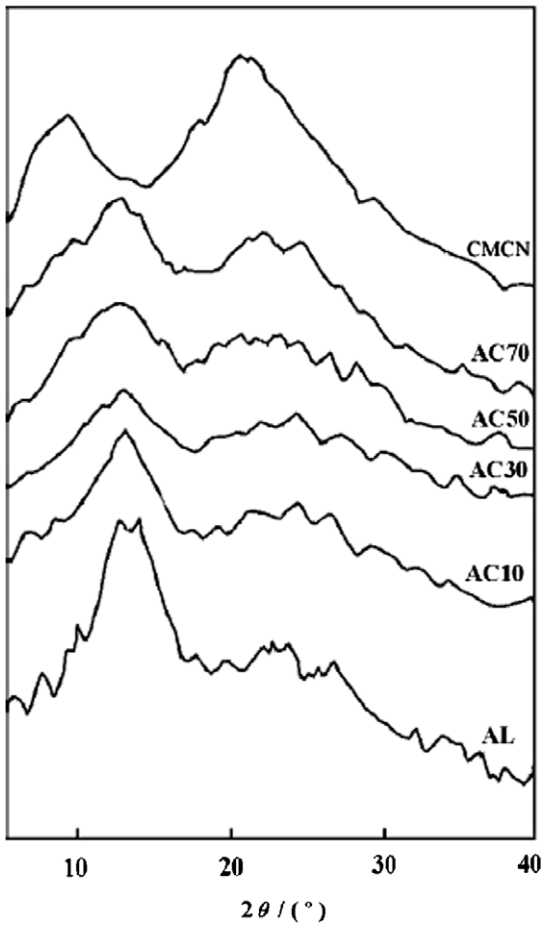

Fig. 4. The X-ray diffraction patterns of pure alginate (AL), alginate/CM-chitosan (w/w), 90/10 (AC10), 70/30 (AC30), 50/50 (AC50), 30/70 (AC70), and pure CM-chitosan (CMCN).

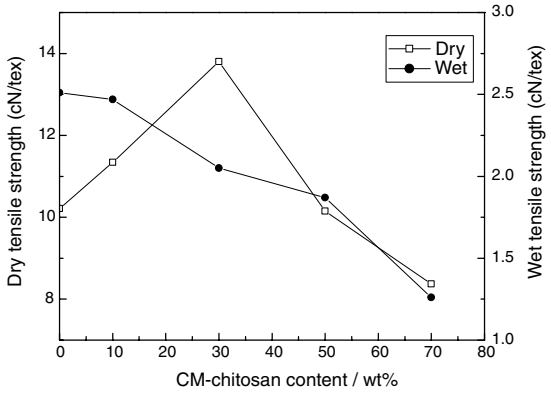

Fig. 5. The effect of CM-chitosan content (wt%) on tensile strength of blend fibers.

The surfaces of the blend fibers were examined by scanning electron microscopy (Fig. 3). The surfaces of samples AC30 and AC50 showed a smooth and homogeneous morphology, suggesting high miscibility and blend homogeneity between alginate and CM-chitosan.

Two typical peaks in $2\theta = 10°$ and 20° were observed for the X-ray diffraction pattern of CM-chitosan (Fig. 4).

Table 1
Properties of alginate and chitosan-alginate fibers

Alginate fiber	Alginate/ CM-chitosan (w/w)	Bacterial reduction rate (%)	Tensile strength (cN/tex) (dry/wet)	Breaking elongation (%) (dry/wet)	Water retention value (%)
Pure alginate	10/0	5.32	10.21/2.51	18.2/42.5	91
AC10[a]	9/1	7.53	11.34/2.47	23.1/41.5	130
AC30[a]	7/3	7.65	13.80/2.05	21.5/40.3	202
AC50[a]	5/5	8.95	10.15/1.87	17.1/39.2	315
AC70[a]	3/7	10.21	8.37/1.26	15.2/36.3	398
Pure alginate treated with HTCC	10/0	89.53	10.31/2.63	22.1/43.5	96
$AC10_{HTCC}$[b]	9/1	88.64	11.15/2.56	23.2/41.5	138
$AC30_{HTCC}$[b]	7/3	90.52	12.64/2.18	21.6/40.3	215
$AC50_{HTCC}$[b]	5/5	87.31	10.06/1.78	16.9/39.2	309
$AC70_{HTCC}$[b]	3/7	86.62	8.02/1.14	15.8/36.3	400
Pure alginate treated with Ag	10/0	>99.99	10.81/2.57	19.1/42.5	89
$AC10_{Ag}$[c]	9/1	>99.99	11.25/2.53	21.6/40.8	128
$AC30_{Ag}$[c]	7/3	>99.99	14.50/2.14	20.4/39.8	214
$AC50_{Ag}$[c]	5/5	>99.99	10.15/1.72	15.8/39.4	331
$AC70_{Ag}$[c]	3/7	>99.99	8.12/1.19	14.5/37.3	387

[a] Fibers untreated.
[b] Fibers treated with HTCC.
[c] Fibers treated with $AgNO_3$.

The diffraction of alginate shows typical peaks around 14° and 23° (Yang, Zhang, Peng, & Zhong, 2000). The diffraction intensities of CM-chitosan at 20° decreased drastically with increasing content of alginate, and the diffraction peak of CM-chitosan at 10° disappeared in the blend, suggesting that intermolecular interaction between two compounds destroyed the crystalline regularity of CM-chitosan. The results suggest good miscibility of the components in the blend fibers. The results also supported the conclusion drawn from SEM and IR that there was good miscibility between alginate and CM-chitosan, due to the strong interaction from the intermolecular hydrogen bonds.

3.2. Mechanical properties of fibers

The effect of CM-chitosan content on the tensile strength of fibers in dry and wet states is shown in Fig. 5 and Table 1. The dry tensile strengths of the AC10 and AC30 were higher than that of pure alginate, and the maximum value was observed at 30% CM-chitosan content which achieved 13.80cN/tex in the dry state. The wet tensile strength of the blend fiber decreased with increase of CM-chitosan content. The increase in tensile strength of this blend fiber can be explained by the presence of some interaction between alginate and CM-chitosan molecules in the blend. Fig. 6 shows the breaking elongation of the fibers in dry and wet states. The alteration of breaking elongation showed a tendency similar to that of the tensile strength, and the maximum value of 23.1% (in the dry state) was achieved when the CM-chitosan content was 10 wt%. The wet breaking elongation decreased with an increase of CM-chitosan content. So through controlling the blend condition, fiber with better mechanical property than pure alginate can be achieved.

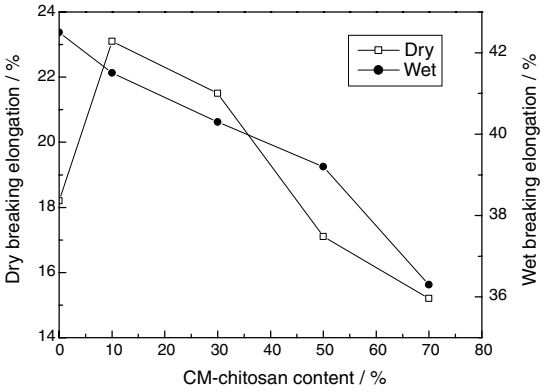

Fig. 6. The effect of CM-chitosan content (wt%) on breaking elongation of blend fibers.

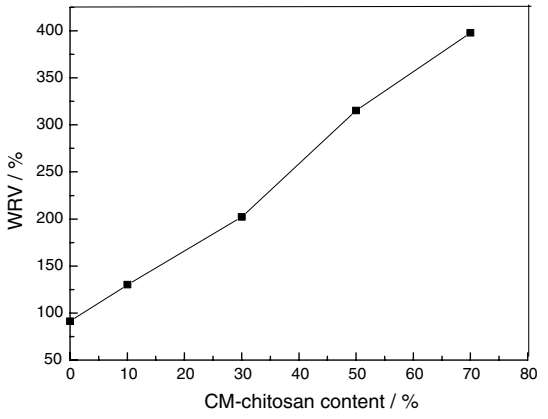

Fig. 7. The effect of CM-chitosan content (wt%) on the WRV of blend fibers.

3.3. Water-retention properties

The water-retention values (WRV) of alginate/CM-chitosan blend fibers increase dramatically as the CM-chitosan content is raised (Fig. 7). The water-retention values of the blend fibers were in the range 130–398%, obviously higher than that of pure alginate fiber, which has the lowest values (91%) (Table 1). The improvement in water-retention is due to the excellent water-retention ability of CM-chitosan. The good hydrophilicity is important for application as a good wound dressing fiber.

The mechanical properties and water-retention properties of fibers treated with $AgNO_3$ or HTCC were not significantly different from those of un-treated fibers (Table 1).

3.4. Antibacterial testing

Un-treated fibers have little antibacterial activity but the fibers treated with silver nitrate or HTCC have good antibacterial activity to *S. aureus* (Table 1). The bacterial reduction rate of calcium alginate fiber treated with HTCC was in the range 85–90%. It is well known that the introduction of silver ions can enhance antibacterial ability of the materials. The calcium/silver alginate fiber with high antibacterial activity was produced by treating calcium alginate fiber with silver nitrate, and its bacterial reduction rate reached above 99.9%, which was superior to those treated with HTCC. In conclusion, the treated fiber exhibited better antibacterial activity than the un-treatment fiber.

4. Conclusions

Alginate and CM-chitosan blend fiber can be obtained by spinning their solution through a viscose-type spinet into a coagulation bath containing aqueous $CaCl_2$. A strong intermolecular interaction between alginate and CM-chitosan molecule occurred in the blend fibers, this being due to good miscibility between alginate and CM-chitosan molecules. The optimal tensile strength and breaking elongation in dry state were obtained when the CM-chitosan contents were 30 and 10 wt%, respectively. The wet tensile strength and breaking elongation decreased with increase of CM-chitosan content. The introduction of CM-chitosan in the blend fiber improved water-retention properties of the blend fiber compared to that of pure alginate fiber. The fibers treated with aqueous solutions of silver nitrate and HTCC, respectively, possessed good antibacterial activity to *S. aureus* and these treatments had not changed the mechanical and water-retention properties of the fibers significantly. This novel alginate and CM-chitosan blend fiber would seem to hold potential for wound dressings.

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