Structure and Properties of Blend Fibers Prepared from Alginate and Konjac Glucomannan

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ABSTRACT: Alginate/konjac glucomannan (KGM) blend fibers, prepared by spinning their mixture solution through a viscose-type spinneret into a coagulating bath containing aqueous $CaCl_2$ and ethanol, were studied for structure and properties with the aid of infrared spectroscopy and scanning electron micrography. The analyses indicated a good miscibility between alginate and KGM because of the strong interaction. The dry tensile strength of the blend fiber increased with increase in KGM content. The wet tensile strength of fibers decreased with increase in KGM content. The optimal breaking elongations in dry and wet state were obtained when the KGM contents were 30 and 10 wt %, respectively. The most obvious change is that the introduction of KGM in the blend fiber can dramatically improve water-retention properties of blend fiber compared with pure alginate fiber. The fibers treated with aqueous solution of silver nitrate have good antibacterial activity to *Staphylococcus aureus*. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3903–3907, 2007

Key words: alginate; konjac glucomannan; blend fibers; miscibility; properties

INTRODUCTION

Alginate is linear copolymer of β-(1,4)-linked D-mannuronic acid and α-(1,4)-linked L-guluronic acid units, which exists widely in many species of brown seaweeds. Alginate fibers can be prepared by extruding solutions of sodium alginate into a bath containing calcium salt solution or acidic solution to produce the corresponding calcium alginate or alginic acid fibers, respectively. Alginate fibers have been extensively used in wound dressing applications because of their excellent biocompatibility, nontoxicity, 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.[1] 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 healing environment, which promotes healing and leads to a 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 proinflammatory signal that may initiate a resolving inflammation characteristic of healing wounds.[3] Therefore, many commercially available wound dressings contain calcium alginate fibers.

Konjac glucomannan (KGM), whose main chain is composed of β-1,4-pyranoside bond-linked mannose and glucose units with a low degree of acetyl groups, is a high molecular water-soluble nature polysaccharide, which is extracted from the tuber of *Amorphophallus konjac* plant.[4] *A. konjac* grows in mountain or hilly areas in subtropical regions mainly in the South East of Asia. It has been used as food and food additives in China and Japan for more than 1000 years. KGM has the ability to lower blood cholesterol and sugar level, help with weight loss, promote intestinal activity and immune function, etc. In recent year, the studies on the applications of KGM and its derivatives have been extended greatly from food and food additives to various fields, such as pharmaceutical, biotechnical, and fine chemical

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industry.[5] In recent year, KGM was reported to be used as wound dressing because of its properties such as high absorbency and wound healing acceleration.[6,7]

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 treatment with an aqueous solution of silver nitrate.

It is well known that blending is an effective and convenient method to improve the performance of polymer materials. In our laboratory, we have successfully prepared a series of blend fibers based on alginate.[9–11] In the present study, novel bicomponent fibers were prepared from alginate and konjac. The structure and properties of the blend fibers were studied through infrared (IR) spectra and scanning electron micrography (SEM). The mechanical properties and water-retention values (WRV) of blend fibers were also measured with regard to the different proportions of the two components. The blend fiber can become potential wound dressing materials.

EXPERIMENTAL

Materials and methods

Sodium alginate was purchased from Shanghai Chemical Reagents Company (Shanghai, China), chemical grade.

KGM was extracted and purified from the tuber of *A. konjac* (supplied by Fangxian Konjac Institute, Hubei, China) according to a published procedure.[9]

All the other reagents used are of analytical grade.

Preparation of blend fibers

KGM was dissolved in distilled water to prepare a 2 wt % solution. Sodium alginate was dissolved in distilled water at room temperature to a concentration of 5 wt % and then mixed with KGM. The mixed solutions 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 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 (stretching ratio is 20%) in distilled water, and then air-dried to afford fibers. According to the KGM contents of 10, 30, 50, and 70 wt %, the blend fibers were labeled as AK10, AK30, AK50, and AK70, respectively. The pure alginate fiber and KGM were coded as AL and KGM, respectively.

Antibacterial treatment of the fibers

The pure alginate fiber and blend fibers (AL, AK10, AK30, AK50, and AK70) were placed in a treatment bath containing silver nitrate (0.01 wt %) for 10 min, rinsed, and dried. The antibacterial fibers were coded as AL_{Ag}, $AK10_{Ag}$, $AK30_{Ag}$, $AK50_{Ag}$, and $AK70_{Ag}$.

Characterization of fibers

IR spectra 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 so as to obey the Lambert–Beer law. The morphological structure of

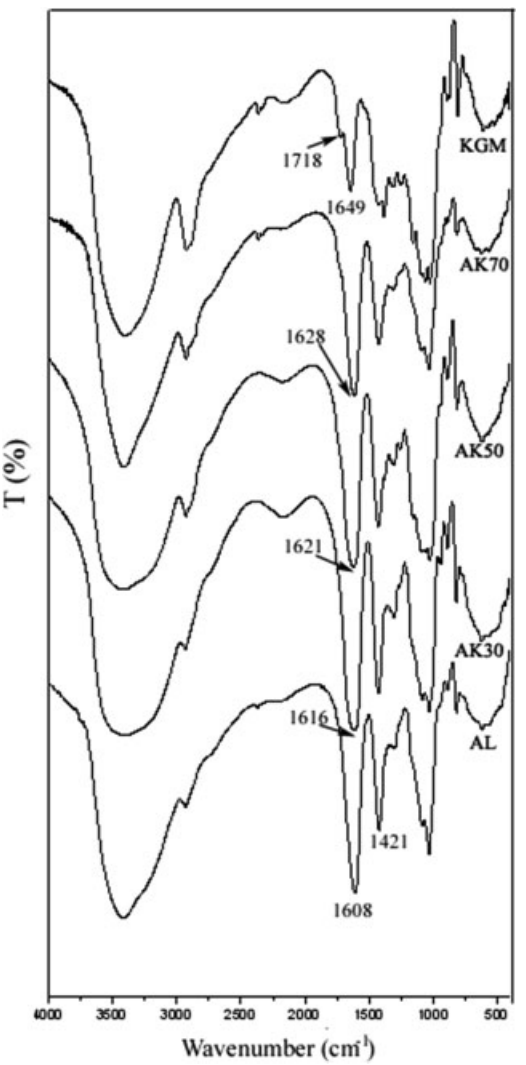

Figure 1 IR spectra of AL, AK30, AK50, AK70, and KGM.

the blend fiber samples was studied with Hitachi SX-650 (Japan) SEM. 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, 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 before mechanical testing. The WRV of fibers were calculated as follows:

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

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

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 terms 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:

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

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

RESULTS AND DISCUSSION

Structure and morphology

The IR spectrum of alginate (Fig. 1) showed absorption bands at 3430 cm^{-1} (OH stretching), 1608 cm^{-1} (COO^- asymmetric stretching), and 1421 cm^{-1} (COO^- symmetric stretching). The carbonyl at 1718 cm^{-1} is assigned to the aceto groups in KGM, and the characteristic absorption bands of mannose in KGM appeared at 876 and 808 cm^{-1}.[12] For the blend fibers, the stretching of carbonyl at 1718 cm^{-1} of KGM disappeared. The absorption band at around 1608 cm^{-1} for the blend fibers, concerned with COO^- asymmetric stretching, shifted to a higher wave number and the absorption band at around 1421 cm^{-1}, concerned with COO^- symmetric stretching, shifted to a lower wave number with the introduction of KGM. Based on this evidence, it can be concluded that a strong interaction exists between alginate and KGM molecules.

The selected fibers were examined by SEM (Fig. 2). The surfaces of AK30 and AK50 showed homogeneous morphology, suggesting high miscibility

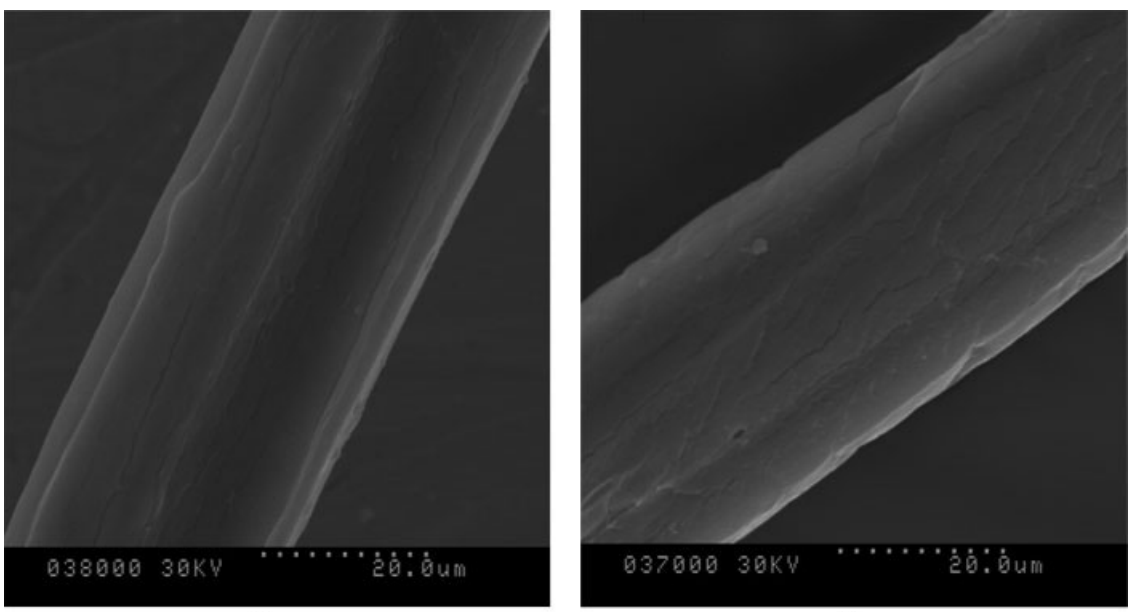

Figure 2 SEM photographs of the blend fibers: (a) surface of AK30, (b) surface of AK50.

TABLE I
The Properties of the Blend Fibers

Fiber	The bacteria reduction rate (BRR)	Tensile strength (dry/wet) (cN/tex)	Breaking elongation (dry/wet) (%)	WRV (%)
AL	0	10.21/2.51	18.2/42.5	91
AK10	0	11.72/2.21	24.4/61.5	182
AK30	0	12.39/1.85	34.5/50.6	650
AK50	0	13.95/0.92	25.4/40.2	700
AK70	0	14.32/0.40	20.4/30.1	1000
AL_{Ag}	>99.99	10.32/2.54	18.5/40.5	89
$AK10_{Ag}$	>99.99	11.43/2.23	23.5/63.5	191
$AK30_{Ag}$	>99.99	12.43/1.74	35.7/51.7	656
$AK50_{Ag}$	>99.99	13.82/0.85	24.8/42.3	703
$AK70_{Ag}$	>99.99	14.40/0.40	21.6/28.9	1008

between alginate and KGM. The fibers displayed striation along the fiber length, and this agreed with the literature.[13]

Mechanical properties of fibers

It is known that the interaction between polymers should influence the mechanical properties of the blend polymer. The effect of KGM content on the tensile strength of fibers in dry and wet states is shown in Table I and Figure 3. The dry tensile strength of the blend fiber increased with increase in KGM content. The maximum value was observed for AK70, achieved 14.32 cN/tex. The wet tensile strength of fibers show reverse alteration tendency compared with the dry tensile strength, decreased with increase in KGM content. The addition of KGM was effective in inducing an improvement in the dry tensile strength of the blend fibers. The wet tensile strength of blend fibers is attributed to calcium alginate content. KGM is a water-soluble macromolecule, and hence wet tensile strength decreased with increase in KGM content. Table I and Figure 4 show the breaking elongation of the fibers in dry and wet states. The maximum value of 34.5% (in the dry state) was achieved when the KGM content was 30 wt %. The wet breaking elongation achieved maximum value (61.5%) when the KGM content was 10 wt %. So through controlling the blend condition, fiber with better mechanical property than pure alginate can be achieved. The mechanical properties and water-retention properties of $AgNO_3$-treated fibers were not significantly different from the untreated fibers (Table I). The latter implies that the silver ion was more like a coating, not penetrating the alginate-based fibers.

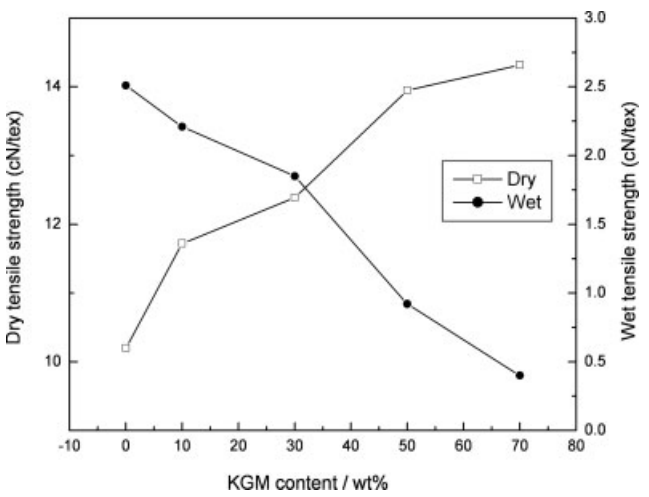

Figure 3 The effect of KGM content (wt %) on tensile strength of the fibers.

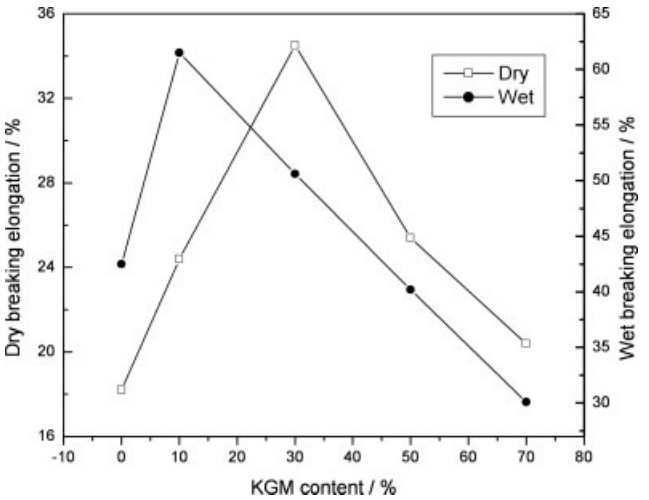

Figure 4 The effect of KGM content (wt %) on breaking elongation of the fibers.

Water-retention properties

The WRV of alginate/KGM blend fibers increase dramatically as the KGM content is raised (Fig. 5). The WRV of the blend fibers were in the range 182–1000%, obviously higher than that of pure alginate fiber, which has the lowest values (91%; Table I). The improvement in water-retention is due to the excellent water-retention ability of KGM. The good hydrophilicity is important for application as a good wound dressing fiber.

Antibacterial testing

The antibacterial properties of the fibers were investigated (Table I) showing that untreated fibers did not have antibacterial activity and the fibers treated with $AgNO_3$ have good antibacterial activity toward *S. aureus*. It is well known that silver ion has good antibacterial properties. The alginate-based fibers

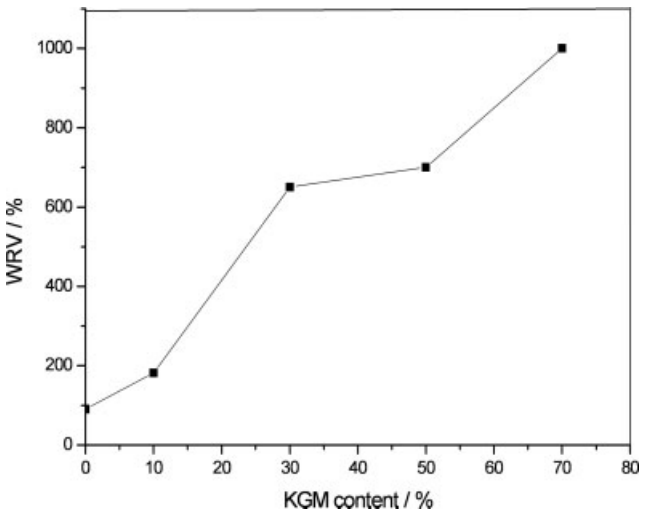

Figure 5 The effect of KGM content (wt %) on the WRV of the fibers.

were immersed in silver nitrate solution, and the calcium alginate fiber is converted into calcium/silver alginate fiber. Thus, the treated fiber has good antibacterial activity compared with the untreated fiber.

CONCLUSIONS

Alginate and KGM blend fiber 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 KGM molecule occurred in the blend fibers. There were good miscibility between alginate and KGM molecule because of the strong intermolecular interaction. The dry tensile strength of the blend fiber increased with increase in KGM content. The wet tensile strength of fibers decreased with increase in KGM content. The optimal breaking elongation in dry and wet state was obtained when the KGM contents were 30 and 10 wt %, respectively. The most obvious change is the introduction of KGM in the blend fiber can dramatically improve water-retention properties of blend fiber compared with pure alginate fiber. The $AgNO_3$-treated fibers have good antibacterial activity toward *S. aureus*. This novel alginate and KGM blend fiber is a kind of promising fiber in the application of wound dressing.

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