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# Preparation and Properties of Chitosan/Konjac Glucomannan Blend Fibers

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Chitosan and konjac glucomannan (KGM) blend fibers were prepared by spinning their solution through a viscose-type spinneret into a coagulating bath containing aqueous sodium hydroxide and ethanol. The structure and properties of the blend fibers were studied with the aids of infrared spectra (IR), scanning electron micrography (SEM) and X-ray diffraction (XRD). The structure analysis indicated that there were strong interaction and good miscibility between the chitosan and KGM molecule which resulted from intermolecular hydrogen bonds. Mechanical properties and water-retention properties were measured. Through controlling blend conditions, blend fibers can obtain better mechanical properties than the pure chitosan fiber. The water-retention values (WRV) of blend fibers increase as the amount of KGM is raised. The fibers treated with alcoholic solution of acetic acid have good antibacterial activity to *Staphylococcus aureus*.

**Keywords:** chitosan; konjac glucomannan; blend fibers; miscibility; mechanical properties; water-retention properties

## 1 Introduction

Chitin, a (1 → 4)-linked N-acetamido-2-deoxy- $\beta$ -D-glucan, is the second most abundant polysaccharide next to cellulose, which is the main structural component of crab and shrimp shells. Chitosan is the fully or partially deacetylated form of chitin. Chitin and chitosan has good biocompatibility, biodegradability, and various biofunctionalities (1, 2). Recent observations have suggested that chitin and chitosan can promote rapid dermal regeneration and accelerate wound healing (3). Chitosan and chitin fibers have been tested as a biocompatible dressing or covering material for accelerating the wound-healing (4, 5). Owing to a high molecular weight, chitosan forms viscous solutions in dilute aqueous acetic acid that can be used to spin fibers. Its fiber forming properties have been investigated by several workers (6).

Konjac glucomannan (KGM), whose main chain is composed of  $\beta$ -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 (7). *Amorphophallus konjac* grows in mountainous 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. Konjac glucomannan has the ability to lower blood cholesterol and sugar level, help with weight loss, promote intestinal activity and immune function etc. In recent years, the studies on the applications of konjac glucomannan and its derivatives have been extended greatly from food and food additives to various fields, such as pharmaceutical, bio-technical and fine chemical industry (8). In recent years, KGM was reported to be used as the wound dressing due to its properties such as high absorbency and accelerates wound healing (9, 10).

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 chitosan and konjac. The structure and properties of the blend fibers were studied through infrared spectra (IR), scanning electron micrography (SEM) and X-ray diffraction (XRD). The mechanical properties and water-retention values 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.

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## 2 Experimental

### 2.1 Materials and Methods

Chitosan was supplied by Yuhuan Ocean Biochemistry Co. Ltd, in Zhejiang Province in China. The degree of deacetylation (DD) determined by elemental analysis was 0.93, and the molecular weight calculated from the GPC method (11) was  $5.7 \times 10^5$ . Standard pullulans for GPC were purchased from Showa Deuko, Tokyo, Japan. Konjac glucomannan was extracted and purified from the tuber of *amorphophallus konjac* (supplied by Fangxian Konjac Institute, Hubei, China) according to a published procedure (12).

All of the other reagents used are of analytical grade.

### 2.2 Preparation of Blend Fibers

A 4 wt% chitosan aqueous solution was obtained by adding the required amount of chitosan with stirring to the known volume of 2 wt% acetic acid aqueous solution. Konjac glucomannan was dissolved in distilled water at room temperature to a concentration of 2 wt% and then mixed with chitosan. 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 an aqueous solution of 10 wt% sodium hydroxide and ethanol to form fibers. The as-spun fibers were washed and stretched (stretching ratio is 20%) in distilled water, then dried. According to the Konjac glucomannan contents of 10, 20, 30, 40 and 50 wt%, the blend fibers were labeled as CK10, CK20, CK30, CK40 and CK50, respectively. The pure chitosan fiber and Konjac glucomannan were coded as CS and KGM, respectively.

### 2.3 Antibacterial Treatment of the Fibers

The pure chitosan fiber and blend fibers (CS, CK10, CK20, CK30, CK40 and CK50) were placed in a treatment bath containing an alcoholic solution of acetic acid (0.05 wt%) for 50 min and dried under vacuum to a constant weight. The antibacterial fibers were coded as ACS, ACK10, ACK20, ACK30, ACK40 and ACK50.

### 2.4 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 morphological structure of the blend fiber samples were studied with a 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) and using a Cu K $\alpha$  target at 40 kV and 50 mA. The diffraction angle ranged from 5° to 40°. The tensile strength ( $\sigma_b$ ) and the breaking elongation ( $\epsilon_b$ ) 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:

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

Where  $W_0$  denotes the original weight (g) of fiber which was dried at 80°C until a constant weight is achieved,  $W_1$  is the weight of the fully swollen fiber that was centrifuged at 4000 rev/min 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 a 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 were 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:

$$BRR = (N_1 - N_2)/N_1 \times 100\%$$

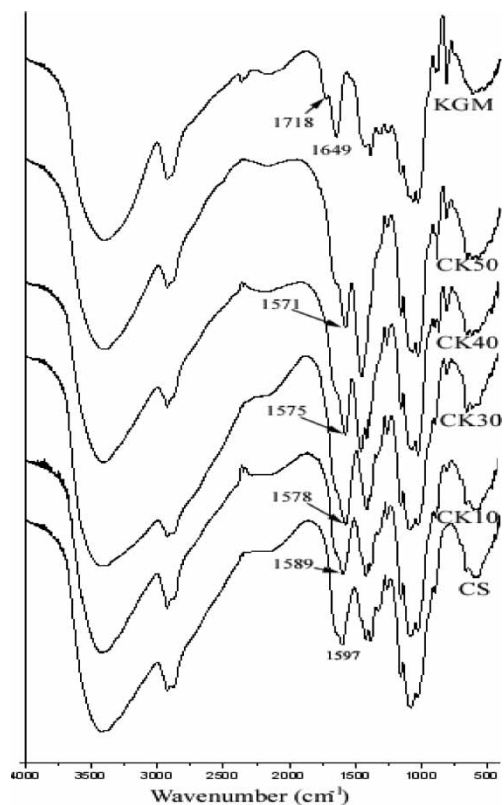
Where  $N_1$  &  $N_2$  are the average number of colonies arising from pre and post incubation cultured samples, requisitely.

## 3 Results and Discussion

### 3.1 Structure and Morphology

The IR spectra of chitosan (CS), KGM and blend fibers are shown in Figure 1. The infrared spectrum of chitosan shows the 1597  $\text{cm}^{-1}$  amino characteristic peak. The absorption band of amide I at 1656  $\text{cm}^{-1}$  was very weak, and this agreed with the high DD (13).

The carbonyl at 1718  $\text{cm}^{-1}$  is assigned to the aceto groups in KGM. The absorption band at 1649  $\text{cm}^{-1}$  assigned to the stretching of intramolecular hydrogen bonds, and the characteristic absorption bands of mannose in KGM appeared at 876  $\text{cm}^{-1}$  and 808  $\text{cm}^{-1}$  (12). For the blend fibers, the stretching of carbonyl at 1718  $\text{cm}^{-1}$  and intramolecular hydrogen bonds at 1649  $\text{cm}^{-1}$  of KGM disappeared. The absorption band at around 1597  $\text{cm}^{-1}$  for the blend fibers, concerned with the amino characteristic peak, shifted to a

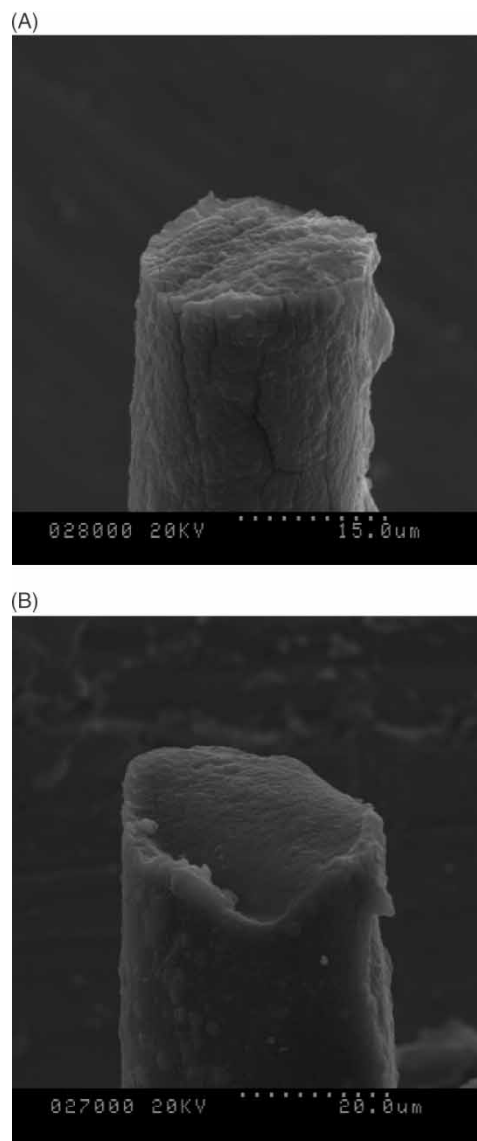


**Fig. 1.** IR spectra of CS, CK10, CK30, CK40, CK50 and KGM.

lower wave number with the introduction of KGM, suggesting that the new hydrogen bonds between chitosan and KGM molecules in the blend fibers occurred. Based upon this evidence, it can be concluded that strong interaction exists between chitosan and KGM molecules.

The sections of the blend fibers were examined by scanning electron microscopy to verify the compatibility between chitosan and KGM molecules (Figure 2). The cross-sections of CK30 and CK50 showed a smooth and homogeneous morphology, suggesting high miscibility and blend homogeneity between chitosan and KGM.

Figure 3 presents the X-ray diffraction pattern of Chitosan, KGM and their blend fibers. The diffraction of Chitosan shows typical peaks around  $10.3^\circ$ ,  $15^\circ$  and  $20^\circ$  (15). The pure KGM shows a non-crystalline state and only has a very broad peak around  $20^\circ$ . If chitosan and KGM have low compatibility, each polymer has its own crystal region in the blend films. So X-ray diffraction patterns are expressed simply as mixed patterns of chitosan and KGM with the same ratio as those for blending. However, the patterns of the blend films showed typical peaks around  $10.3^\circ$  of chitosan disappeared. With the increase of KGM, the diffraction peak corresponding to  $15^\circ$  and  $20^\circ$  of chitosan becomes gradually lowered, and the diffraction angle deviated farther and farther accordingly. It is obvious that the presence of interaction between KGM and chitosan prevents or disturbs chitosan from

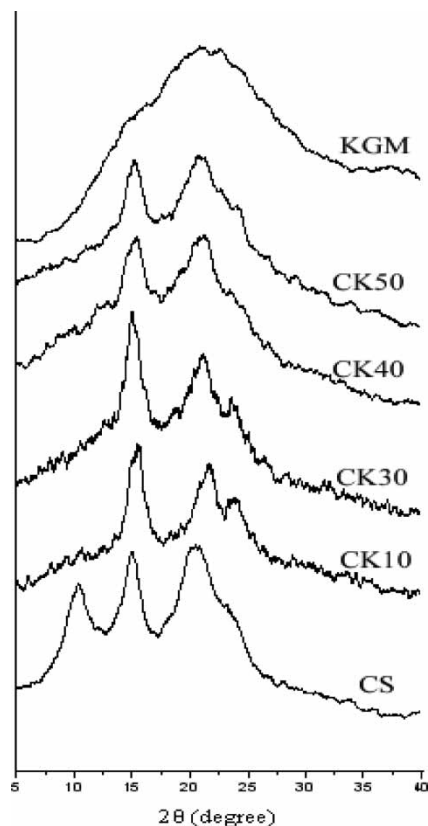


**Fig. 2.** SEM photographs of the blend fibers: Cross-section of CK30 (A) and CK50 (B).

crystallization by comparison with the diffraction pattern of chitosan with that of blend fibers. This supports the conclusion that relative good miscibility exists between chitosan and KGM.

### 3.2 Mechanical Properties of Fibers

The effect of KGM content on the tensile strength of fibers in dry and wet states is shown Table 1. The dry tensile strengths of the CK10, CK20, and CK30 were higher than that of pure chitosan fiber, and the maximum value was observed at CK20 achieved 12.85 cN/tex. The maximum value of wet tensile strength was observed at CK20 achieved 5.38 cN/tex. Table 1 shows the breaking elongation of the fibers in dry and wet states. The alteration



**Fig. 3.** The X-ray diffraction patterns of CS, CK10, CK30, CK40, CK50 and KGM.

of breaking elongation of blend fibers in dry states is very few by comparison with pure chitosan fiber. Breaking elongation of the wet fibers of CK10 and CK20 were higher than that of pure chitosan fiber, with the maximum value observed for CK20 having a 54.5% value. 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 chitosan fiber.

### 3.3 Water-Retention Properties

The water-retention properties of the blend fibers is shown Table 1. The water-retention values (WRV) of chitosan/KGM blend fibers increases with the increasing of KGM content. The WRV of the blend fibers were in the ranges of 162–232%, obviously higher than that of pure chitosan fiber, which has the lowest values (120%). The improvement in water-retention is due to KGM being more hydrophilic than chitosan, which could promise the wide application of chitosan/KGM blend fibers as biomedical dressing.

### 3.4 Antibacterial Testing

The antibacterial properties of the fibers were investigated (Table 2) showing that untreated fibers have little antibacterial activity and the fibers treated with acetic acid have good antibacterial activity toward *Staphylococcus aureus*. The study has demonstrated that chitosan acetate showed high solubility and antibacterial activity against *Staphylococcus aureus* (15). The chitosan acetate fibers were prepared by being treated with an alcoholic solution of acetic acid. It can

**Table 1.** The properties of the blend fibers

Fiber	Chitosan/konjac (wt/wt)	Tensile strength (cN/tex) (Dry/Wet)	Breaking elongation (%) (Dry/Wet)	WRV (%)
CS	100/0	10.89/4.41	23.1/43.5	120
CK10	90/10	11.56/5.18	24.4/50.3	162
CK20	80/20	12.85/5.38	23.3/54.5	175
CK30	70/30	12.25/3.95	22.3/42.4	181
CK40	60/40	10.45/3.56	21.5/42.3	214
CK50	50/50	9.54/3.01	21.3/40.1	232

**Table 2.** The antibacterial properties of the blend fibers

Fiber	Chitosan/konjac (wt/wt)	Bacteria reduction rate (%)	Fiber	Chitosan/konjac (wt/wt)	Bacteria reduction rate (%)
CS	100/0	6.12	ACS	100/0	>99.99
CK10	90/10	5.68	ACK10	90/10	>99.99
CK20	80/20	5.33	ACK20	80/20	>99.99
CK30	70/30	4.33	ACK30	70/30	>99.99
CK40	60/40	3.11	ACK40	60/40	>99.99
CK50	50/50	3.05	ACK50	50/50	>99.99

dissolve in water and the untreated fiber is insoluble. Thus, the treated fiber containing chitosan acetate has good antibacterial activity compared with the untreated fiber. The treated fiber, which interacts with the wound exudates to form a moist gel, can be used for wound dressing. Such gel provides the wound with a moist and axenic healing environment, which promotes healing and leads to better cosmetic repair of the wound.

#### 4 Conclusions

Chitosan and konjac glucomannan (KGM) blend fibers can be obtained by spinning their solution through a viscose-type spinneret into a coagulating bath containing aqueous sodium hydroxide and ethanol. The strong intermolecular interaction between chitosan and KGM molecule occurs in the blend fibers. There is good miscibility between chitosan and KGM molecule, due to the strong intermolecular interaction. The best values of the dry and wet tensile strength were obtained when the KGM content was 20 wt%. The optimal breaking elongation in dry and wet state were obtained when the KGM content were 10 wt% and 20%, respectively. The introduction of KGM in the blend fiber can improve water-retention properties of blend fiber compared to pure chitosan fiber. The treated fibers treated by acetic acid have good antibacterial activity toward *Staphylococcus aureus*. This novel chitosan and KGM blend fiber is promising for wound dressing applications.

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