

# Preparation and Characterization of Alginate/Gelatin Blend Fibers

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Received 30 January 2004; accepted 24 August 2004

DOI 10.1002/app.21610

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Alginate and gelatin blend fibers were prepared by spinning their solution through a viscose-type spinneret into a coagulating bath containing aqueous CaCl<sub>2</sub> and ethanol. The structure and properties of the blend fibers were studied with the aid of infrared spectra, scanning electron micrography, X-ray diffraction, and thermogravimetric analysis. Mechanical properties and water-retention properties were measured. The best values of the tensile strength and breaking elongation of blend fibers were obtained when gelatin content was 30 wt %. The water-retention

values of blend fibers increase as the amount of gelatin is raised. The structural analysis indicated that there was strong interaction and good miscibility between alginate and gelatin molecules resulted from intermolecular hydrogen bonds. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1625–1629, 2005

**Key words:** alginate; gelatin; blend fibers; miscibility; mechanical properties; water-retention properties

## INTRODUCTION

Alginates are linear copolymers of  $\beta$ -(1-4)-linked D-mannuronic acid and  $\alpha$ -(1-4)-linked L-guluronic acid units, which exist widely in many species of brown seaweeds. Alginates are traditionally known in several applications from the food and drink industry to the pharmaceutical industry.<sup>1</sup> Alginate fibers can be prepared by extruding solutions of sodium alginate into a bath of calcium ions. The resultant calcium alginate fibers are then dried to give tough fibers that can be collected on spools for knitted fabrics or directly chopped for use in nonwoven materials. Alginate fibers, typically 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 sodium ions in the exudates. 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.<sup>2</sup> In addition, alginate-containing dressings have been demonstrated to activate macrophages within the chronic wound bed and generate a proinflammatory signal which may initiate a resolving inflammation characteristic of healing wounds.<sup>3</sup> Therefore, many commercially available wound dressings

contain calcium alginate fibers. However, the application of alginate wound dressings is hindered because of the high cost in China.

Gelatin, which is widely found in nature and is the major constituent of skin, bones, and connective tissue, can easily be obtained by a controlled hydrolysis of the fibrous insoluble protein, collagen. The denatured type of collagen, gelatin, has been used in medicine as plasma expander, wound dressing, adhesive, and absorbent pads for surgical use.<sup>4</sup> Recently, gelatin has been demonstrated to exhibit activation of macrophages<sup>5,6</sup> and high hemostatic effect.<sup>7</sup> Consequently, gelatin has been used in a wide variety of wound dressings.<sup>8,9</sup>

It is well known that blending is an effective and convenient method to improve the performance of polymer materials. Gelatin is practical and more economical than alginate. Thus, in the present study, the novel blend fibers were prepared from alginate and gelatin. The structure and properties of the blend fibers were studied through infrared spectra (IR), scanning electron micrography (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The mechanical properties and water-retention values of blend fibers were also measured with regard to the different proportions of the two components.

## EXPERIMENTAL

### Materials

Chemical grade sodium alginate and gelatin were both purchased from Shanghai Chemical Reagents Co.

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(Shanghai, China). All of other reagents used are of analytical grade.

### Preparation of blend fibers

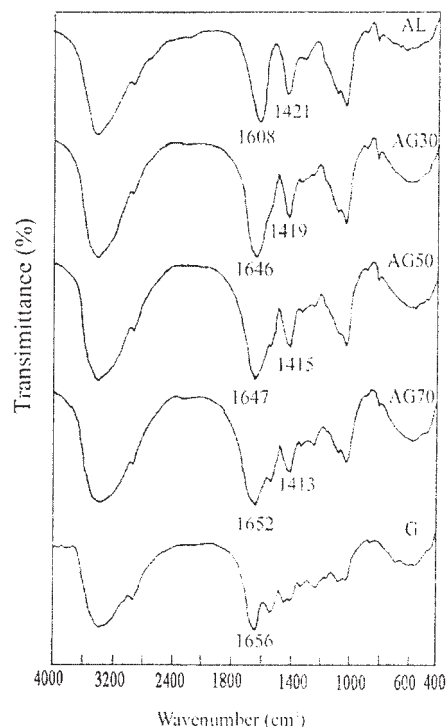
A 12 wt % gelatin aqueous solution was obtained by adding the required amount of gelatin with stirring to the known volume of distilled water at 90°C. Sodium alginate was dissolved in distilled water at room temperature to a concentration of 5 wt % and then mixed with gelatin. The mixed solutions were vigorously stirred at room temperature for 1 h 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 1 h. 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 provide fibers. According to the gelatin contents of 10, 30, 50, and 70 wt %, the blend fibers were labeled as AG10, AG30, AG50, and AG70, respectively. The pure alginate fiber and gelatin were coded as AL and G, respectively.

### Characterization of fibers

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 obey the Lambert–Beer Law. The morphological structure of the blend fiber samples was studied with a Hitachi SX-650 (Japan) scanning electron microscope. XRD patterns of the sample were measured with a Shimadzu Labx-XRD-6000 diffractometer (Japan) and used a CuK $\alpha$  target at 40 kV and 50 mA. The diffraction angle ranged from 5° to 40°. The crystallinities of the sample were calculated by the equation<sup>10</sup>:

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

where  $F_c$  and  $F_a$  are the areas of crystal and noncrystalline regions, respectively. TGA of the samples was performed with a DT-30B thermal analyzer (Shimadzu Co., Japan). The conditions were under a nitrogen atmosphere, a flow capacity of 30 mL/min, a heating range of 20–500°C, and a heating rate of 10°C/min. 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



**Figure 1** IR spectra of AL, AG30, AG50, AG70, and G.

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

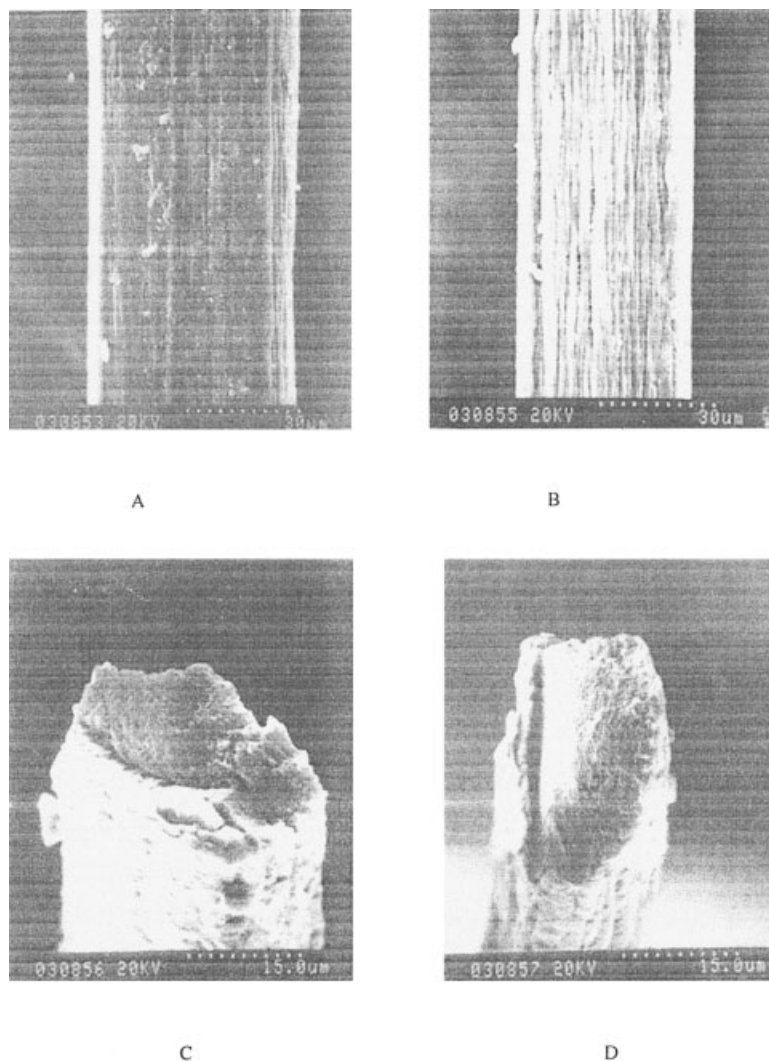
$$\text{WRV} = (W_1 - W_0) / W_0 \times 100\%$$

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

## RESULTS AND DISCUSSION

### IR spectral analysis

The IR spectra of the samples of AL, AG30, AG50, AG70, and G are shown in Figure 1. The IR spectrum of gelatin has the following characteristic absorption bands: 3400  $\text{cm}^{-1}$  (NH stretching), 1656  $\text{cm}^{-1}$  (amide I, CO, and CN stretching), 1544  $\text{cm}^{-1}$ , and 1238  $\text{cm}^{-1}$  (amide II and III, respectively, mainly NH bending and CN stretching).<sup>11</sup> The IR spectrum of alginate showed absorption bands at 3418  $\text{cm}^{-1}$  (OH stretching), 1608  $\text{cm}^{-1}$  ( $\text{COO}^-$  asymmetric stretching), and 1421  $\text{cm}^{-1}$  ( $\text{COO}^-$  symmetric stretching). In the spectra of the blend fibers, the absorption band at around 3408  $\text{cm}^{-1}$  concerned with OH stretching vibration for AL slightly broadened and shifted to a lower wave number with the increase of gelatin, suggesting the formation of an intermolecular hydrogen bond. The strong absorption band at 1608  $\text{cm}^{-1}$  for AL fiber



**Figure 2** SEM photographs of the blend fibers: (A) surface of AG10; (B) surface of AG30; (C) section of AG10; (D) section of AG30.

assigned to the asymmetric stretching vibration of  $\text{COO}^-$  has coupled with the absorption at  $1656\text{ cm}^{-1}$  in gelatin and shifted to a higher wave number. At the same time, the absorption at  $1421\text{ cm}^{-1}$  assigned to the symmetric stretching vibration of  $\text{COO}^-$  has shifted to  $1419$ ,  $1415$ , and  $1413\text{ cm}^{-1}$  in AG30, AG50, and AG70, respectively. Based on this evidence, it can be concluded that a certain degree of interaction between alginate and gelatin molecules is due to the formation of intermolecular hydrogen bands. This interaction resulted in the miscibility of two kinds of macromolecules, as observed by SEM.

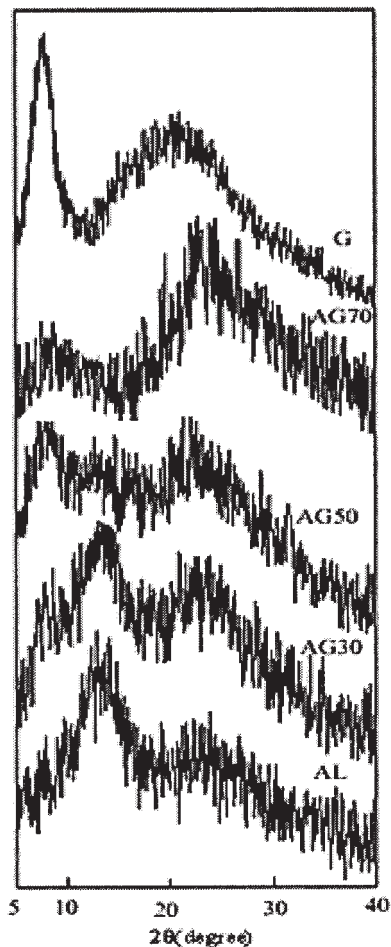
#### SEM observations of fibers

The surfaces and sections of the blend fibers were examined by scanning electron microscopy to verify the compatibility between alginate and gelatin molecules (Fig. 2). The surfaces and sections of AG10 and

AG30 showed a smooth and homogeneous morphology, suggesting high miscibility and blend homogeneity between alginate and gelatin.

#### XRD analysis

Figure 3 presents the X-ray diffraction pattern of alginate, gelatin, and their blend fibers. Two typical peaks in  $2\theta = 7.6^\circ$  and  $20^\circ$  were observed for gelatin. The diffraction of alginate shows typical peaks around  $14^\circ$  and  $23^\circ$ .<sup>12</sup> The diffraction intensities of gelatin at  $7.6^\circ$  decreased drastically in the blend, and the diffraction peak of alginate at  $14^\circ$  rapidly weakened with an increase in the content of gelatin. The crystallinity was calculated and the order was  $G > AG70 > AG50 > AG30 > AG10 > AL$ . It is obvious that the crystallinities of blend fibers decreased with the addition of alginate, which can be explained that intermolecular interaction destroyed



**Figure 3** The X-ray diffraction patterns of AL, AG30, AG50, AG70, and G.

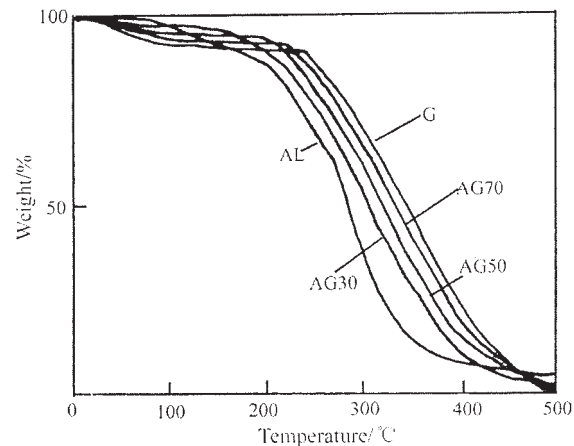
the regularity of gelatin. The results suggest good miscibility for the blend fibers. The results also supported the conclusion drawn from SEM and IR that the good miscibility existed between alginate and gelatin was due to the strong interaction from the intermolecular hydrogen bonds.

#### TG analysis

Figure 4 shows the TGA thermograms of the samples of AL, AG30, AG50, AG70, and G. The starting temperature of the greatest degradation of the blends shifted to higher temperatures with the increase of gelatin content. The thermal stability of the blend fibers is of the following order: G (249°C) > AG70 (233°C) > AG50 (228°C) > AG30 (224°C) > AL (213°C). This order is the same as that of their crystallinities, indicating that their crystalline domains and the intermolecular interaction enhanced the thermal stability of the fibers.<sup>13</sup>

#### Mechanical properties of fibers

The effect of gelatin content on the tensile strength of fibers in dry and wet states is shown in Figure 5 and

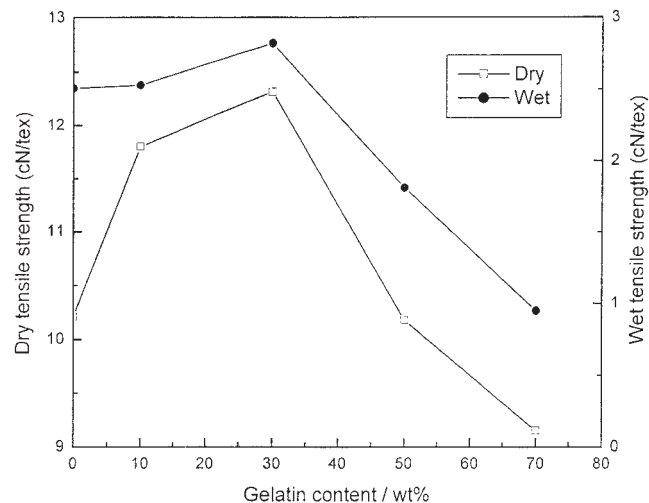


**Figure 4** TGA curves of AL, AG30, AG50, AG70, and G.

Table I. The dry and wet tensile strengths of the AG10 and AG30 were higher than that of pure alginate, and the maximum value observed at 30% gelatin content achieved 12.31 cN/tex in the dry state and 2.82 cN/tex in the wet state, respectively. The increase in tensile strength of this blend fiber can be explained by the presence of some interaction between alginate and gelatin molecules in the blend. 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, and the maximum value of 21.3% (in the dry state) and 70% (in the wet state) was achieved when the gelatin content was 30 wt %. Therefore, through controlling blend condition, blend fiber can obtain a better mechanical property than pure alginate, which is comparatively more expensive.

#### Water-retention properties

The water-retention properties of the blend fibers are plotted in Figure 7 as a function of the weight content



**Figure 5** The effect of gelatin content (wt %) on tensile strength of the fibers.

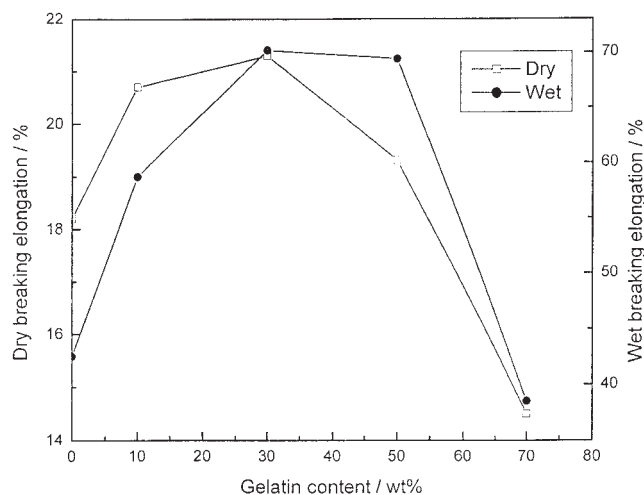


**TABLE I**  
The Properties of the Blend Fibers

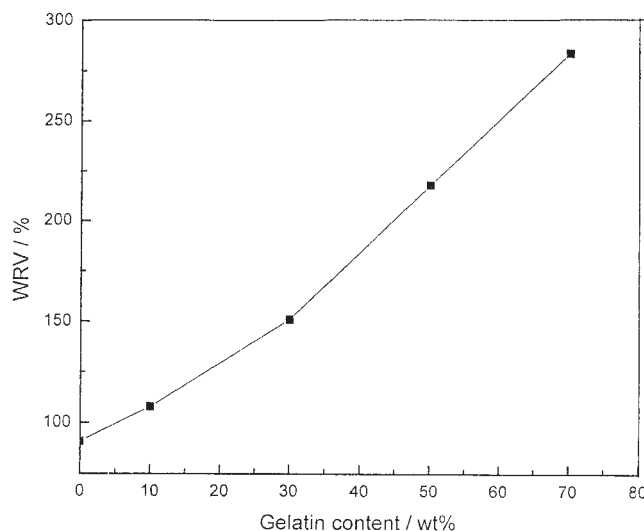
Fiber	Alginate/gelatin (wt/wt)	Tensile strength (cN/tex) (dry/wet)	Breaking elongation (%) (dry/wet)	WRV (%)
AL	100/0	10.21/2.51	18.2/42.5	91
AG10	90/10	11.80/2.53	20.7/58.7	108
AG30	70/30	12.31/2.82	21.3/70.2	151
AG50	50/50	10.18/1.81	19.3/69.4	218
AG70	30/70	9.15/0.95	14.5/38.5	284

of gelatin. Figure 7 shows that the WRV of alginate/gelatin blend fibers increase as the amount of gelatin is raised. The WRV of the blend fibers were in the ranges of 108–284%, obviously higher than that of pure algi-

nate fiber, which has the lowest values (91%) (Table I). Introduction of  $\text{Ca}^{2+}$  decreased alginate's hydrophilicity. The improvement in water retention is due to gelatin being more hydrophilic than calcium alginate.



**Figure 6** The effect of gelatin content (wt %) on breaking elongation of the fibers.



**Figure 7** The effect of gelatin content (wt %) on the WRV.

## CONCLUSIONS

Alginate and gelatin blend fiber can be obtained by spinning their solution through a viscose-type spinneret into a coagulation bath containing aqueous  $\text{CaCl}_2$  and ethanol. The strong intermolecular interaction between the alginate and gelatin molecule occurred in the blend fibers. There was good miscibility between alginate and gelatin molecules. The best values of the tensile strength and breaking elongation were obtained when gelatin content was 30 wt %. The introduction of gelatin in the blend fiber can improve the water-retention properties of blend fiber compared to pure alginate fiber. This novel alginate and gelatin blend fiber is a promising substitute of pure alginate fiber in the application of wound dressing.

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