Preparation of Alginate/Soy Protein Isolate Blend Fibers through a Novel Coagulating Bath

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ABSTRACT: Alginate and soy protein isolate blend fibers were prepared by spinning their solution through a viscose-type spinneret into a novel coagulating bath containing aqueous $CaCl_2$, HCl, and ethanol. The structures and properties of the fibers were studied with the aids of infrared spectra (IR), X-ray diffraction (XRD), and scanning electron micrograph (SEM). Mechanical properties and water-retention properties were measured. And with the sample of AS1 fiber (soy protein isolate weight content was 10%), the effects of the composition of the novel coagulating bath were also studied. The best values of the tensile strength of AS1 were 14.1 cN/tex in the dry state and 3.46 cN/tex in the wet state, respectively. Both the dry state and wet state breaking elongation were also having the best value 20.71% and 56.7% with AS1. Mechanical properties of the AS1 enhanced with the $CaCl_2$ content increased in the coagulating bath. When the HCl content was 1%, the mechanical property of the fiber was best. Ethanol in the coagulating bath increased the wet mechanical properties of the fiber by 41.2% (tensile strength) and 45.1% (breaking elongation) when the ethanol weight content in the coagulating bath was 50%; but it had little effect on the dry mechanical properties. And the water-retention value (*WRV*) of blend fibers decreased as the amount of soy protein isolate was raised. The structure analysis indicated that there were strong interaction and a certain level of miscibility between alginate and soy protein isolate. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 425–431, 2006

Key words: blending; fibers; structure; strength

INTRODUCTION

Sodium alginate is a water-soluble salt of alginic acid, a naturally occurring nontoxic polysaccharide found in all species of brown algae. It was widely used in food and pharmaceutical industries.[1,2] It contains two uronic acids, β-(1–4)-linked D-mannuronic acid (M) and α-(1–4) linked L-guluronic acid (G), and is composed of homo-polymeric blocks M–M or G–G, and blocks with an alternating sequence, the M–G blocks.[3] And sodium alginate has a unique property of crosslinking in the presence of multivalent cations such as calcium ions in aqueous media, which takes mainly at junctions in the G–G sequence rich chain region known as the 'egg box junctions,'[4,5] resulting in the formation of the insoluble calcium alginate. 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 as a calcium salt, interaction 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.[6] 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.[7] As a result, many commercially available wound dressings contain calcium alginate fibers. But the cost of the application of alginate wound dressings is high.

In recent years, soy products such as soy oil, soy protein isolate, soy whole flour, and soy protein concentrated have been considered as an alternative to petroleum polymer because of their abundant resources, low cost, perfect adhesiveness, and good biodegradability.[8,9] And soy protein isolate has been researched as environmental-friendly materials in the fields of adhesives,[10] plastics,[11,12] textile fibers,[13,14] and various binders.[15]

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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 blend fibers from chitosan with poly (vinyl alcohol).[16] We have also produced blend films by alginate,[17,18] chitosan,[19] and soy protein isolate[20] with other natural polymers. The results showed that all those blend fibers and films had better properties than pure ones. So it is an interesting work to blend alginate with soy protein isolate to make bi-component fibers. And coagulating bath also played an important role in making fibers. So we invented a novel coagulating bath and studied the effects of the composition of the coagulating bath on the properties of the blend fibers. In the present experiment, the structure and properties of the blend fibers were studied with the aids of infrared spectra (IR), X-ray diffraction (XRD), and scanning electron micrograph (SEM). The mechanical properties and water-retention values of blend fibers were measured with regard to the different proportions of the two components. The work may contribute materials corresponding with green chemistry and sustainable development strategy.

EXPERIMENTAL

Materials

Sodium alginate was purchased from Shanghai Chemical Reagents Company (Shanghai, China). Soy protein isolate was purchased from DuPont-Yunmeng Protein Technology Co. Ltd. (Yunmeng, China). The weight–average molecular weight (M_w) of soy protein isolate determined by a multi-angle laser light-scattering instrument (MALLS) (DAWN® DSP, Wyatt Technology Co., Santa Barbara, CA) equipped with a He–Ne laser (λ = 632.8 nm) was found to be 2.05 $\times$ 10^5.[21] The moisture content, protein content, and amino acid compositions of soy protein isolate were analyzed, respectively, by thermogravimetric analysis (TGA, TG209, NETZSCH Co., Germany), a Kjeletc1030 self-analyzer (F. Hoffmann-La Roche Co., Basel, Switzerland) according to the semimicro Kjeldahl principle, and high-performance liquid chromatography (HPLC, Waters Co., Milford, MA), and the results are summarized in Table I. Other reagents were all analytical reagents and all commercially available and used as received.

TABLE I
Components of Soy Protein Isolate by TGA, Amino Acid Analysis, and HPLC

Components	Content (%)
Moisture	5.01
Protein	92.32 (dry basis)
Glutamate	18.68
Aspartate	11.38
Leucine	7.39
Arginine	7.05
Lysine	5.77
Isoleucine	5.11
Proline	5.01
Serine	4.73
Phenylalanine	4.50
Valine	4.13
Alanine	4.06
Glycine	3.71
Threonine	3.43
Tyrosine	3.37
Histidine	2.10
Methionine	1.00
Cysteine	0.91

Preparation of blend fibers

Sodium alginate was dissolved in distilled water at room temperature to a concentration of 5 wt %. A 10 wt % soy protein isolate aqueous solution was obtained by adding the required amount of soy protein isolate with stirring to the known volume of 10 wt % NaOH aqueous solution at room temperature. 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 % $CaCl_2$ and 2 wt % HCl aqueous solution with ethanol to form fibers. The volume ratio of $CaCl_2$ and HCl aqueous solution to ethanol was 50/50. The as-spun fibers were washed and stretched (stretching ratio is 20%) in distilled water, then air-dried to afford fibers. According to the soy protein isolate contents of 10, 30, 50, and 70 wt %, the blend fibers were labeled as AS1, AS3, AS5, and AS7, respectively. The pure alginate fiber and soy protein isolate were coded as AL and SPI, respectively. And we also produced different AS1 fibers by changing the composition of the coagulating bath.

Characterization of fibers

Infrared spectra (IR) of the sample were recorded with a Nicolet-170SX FTIR. The test specimens were cut into small pieces for preparation of KBr discs. The samples were made thin enough so to obey the Lambert–Beer Law.

X-ray diffraction (XRD) patterns of the sample were measured with a Shimadzu Lab-XRD-6000X diffractometer (Japan), using a CuKα target at 40 kV and 50 mA. The diffraction angle ranged from 5° to 45°.

The morphological structure of the blend fiber samples was studied with Hitachi *S*-570 (Japan) scanning electron microscopy (SEM).

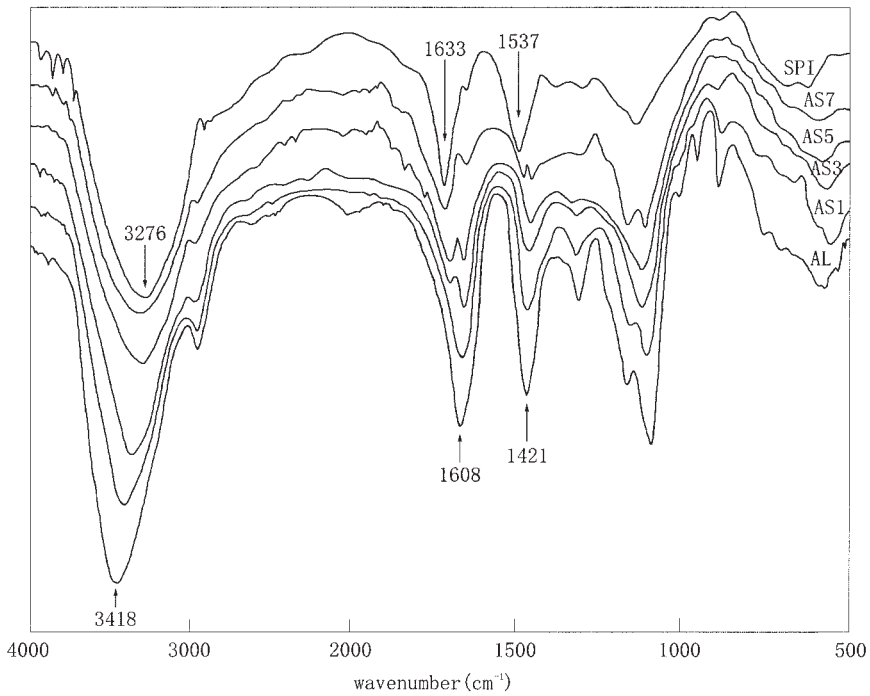

Figure 1 IR spectra of AL, AS1, AS3, AS5, AS7, and SPI.

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. Every experiment was done five times.

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 was achieved and W_1 is the weight of fully swollen fiber that was centrifuged at 4000 rpm/min for 10 min. All the experiments were done in triplicates.

The amount of Ca^{2+} crosslinked on the blend fibers was evaluated by a Xintian WF-5 (China) atomic absorption spectrophotometer at 422.7 nm. Every experiment was done in triplicates.

RESULTS AND DISCUSSION

IR spectral analysis

The IR spectra of the samples of AL, AS1, AS3, AS5, AS7, and SPI were shown in Figure 1. As for the pure sodium alginate, the characteristic absorption band at 3418 cm^{-1} was due to the stretching vibration of O—H group; those at 1608 and 1421 cm^{-1} were due to the asymmetric stretching vibration and symmetric stretching vibration of —COO^- group.[22] For the pure soy protein isolate, the absorption band around 3276 cm^{-1} was concerned with the stretching vibration of *N*—H group, and the characteristic absorption bands at 1633 and 1537 cm^{-1} were attributed to Amide I(C═O) and Amide II(*N*—H), respectively. In the spectra of the blend fibers, the absorption band at around 3418 cm^{-1} concerned with O—H stretching vibration for AL shifted to a lower wave number and became wider with the increase of soy protein isolate. The absorption band at 1608 cm^{-1} for AL fiber assigned to the asymmetric stretching vibration of —COO^- shifted to a higher wave number. At the same time, the absorption at 1421 cm^{-1} assigned to the symmetric stretching vibration of —COO^- also shifted to a higher wave number and faded gradually until its disappearance. Those changes confirmed that there was good compatibility between the alginate and soy protein isolate molecules.

XRD analysis

Figure 2 presented the X-ray diffraction patterns of alginate, soy protein isolate, and their blend fibers. The diffraction of alginate shows typical peaks around 14° and 23°.[23] The typical diffraction peaks of soy protein isolate were around 8.5°, 19.5°, and 24.5°. In the blend fibers, with the increasing content of soy protein isolate, diffraction intensities of alginate at 14° faded gradually until its disappearance, and the dif-

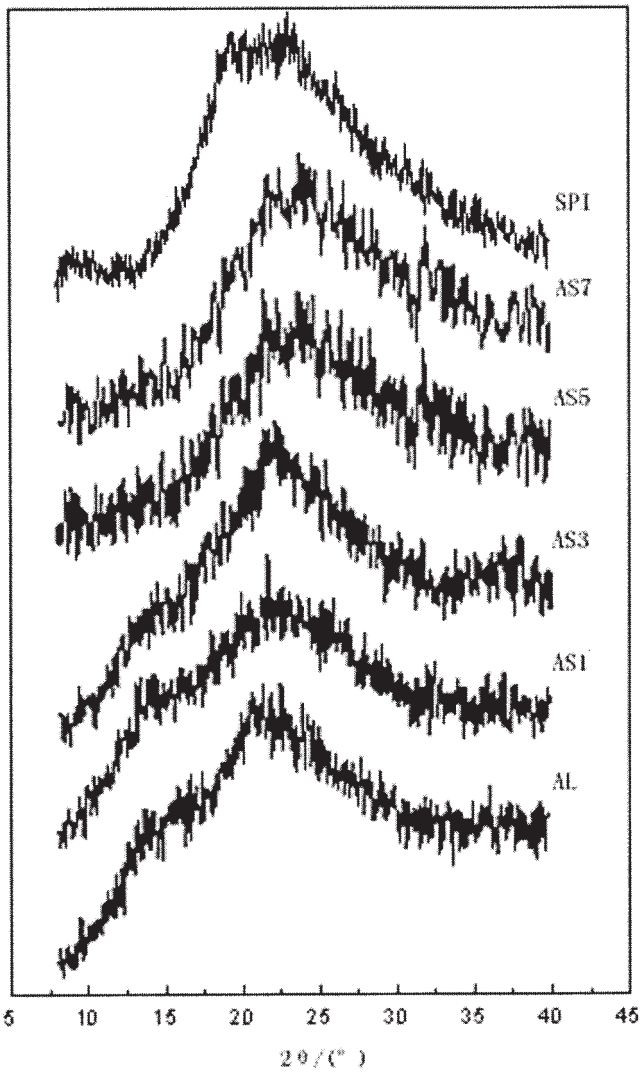

Figure 2 The X-ray diffraction patterns of AL, AS1, AS3, AS5, AS7, and SPI.

fraction peaks of soy protein isolate at 8.5° and 19.5° rapidly enhanced. The changes of diffraction intensities can be explained that intermolecular interaction and Ca^{2+} crosslinking destroyed the regularity of soy protein isolate. The results suggested the good compatibility for the blend fibers. The results can also be supported by the conclusion drawn from following experiments that good compatibility existed between alginate and soy protein isolate.

SEM observations of fibers

The surfaces of the blend fibers were examined by scanning electron microscopy to verify the compatibility between alginate and soy protein isolate molecules (Fig. 3). The surfaces of AS1 and AS3 showed a smooth and homogeneous morphology, suggesting high miscibility and blend homogeneity between alginate and soy protein isolate. Good compatibility and a certain level of miscibility are necessary, because they can change the physical properties of materials.

Atomic absorption spectrum analysis

The amount of Ca^{2+} that was crosslinked on the fibers AL, AS1, AS3, and AS5 were 2.6, 1.2, 0.89, and 0.42 mmol/g, respectively. This change can be explained that the strong intermolecular interactions between alginate and soy protein isolate remarkably decrease the possibilities of Ca^{2+} crosslinking to the carboxyl groups of alginate. So the amount of Ca^{2+} crosslinked on the blend fibers decreased greatly as the amount of soy protein isolate was raised.

Mechanical properties of fibers

Effects of the compositions of the coagulating bath

The effects of the composition of the coagulating bath on the properties of AS1 fiber were shown in Table II. The results indicated that the three different components of the coagulating bath could influence the properties of AS1 fiber to different degree. With the content of $CaCl_2$ increased, the dry properties of the fiber

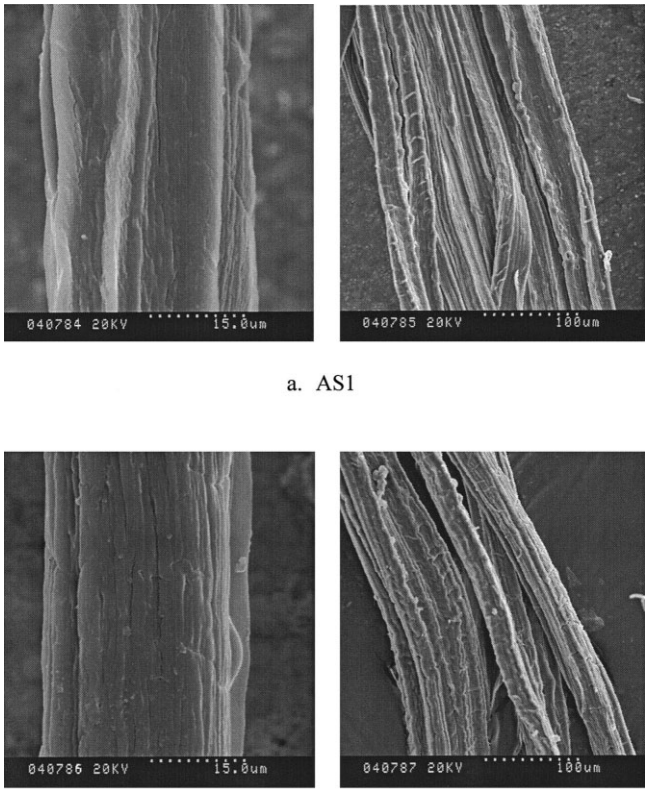

Figure 3 SEM photographs of the blend fibers: (a) AS1 and (b) AS3.

TABLE II
The Effects of the Composition of the Coagulating Bath on the Properties of AS1

Composition of the coagulating bath			Tensile strength (cN/tex)		Breaking elongation (%)	
$CaCl_2$	HCl	Ethanol	Dry	Wet	Dry	Wet
2.5	1.0	0	13.2	2.44	16.8	43.1
5.0	1.0	0	14.1	2.78	20.8	46.9
10.0	1.0	0	14.2	2.66	21.7	46.4
5.0	0.5	0	14.0	2.53	19.3	44.2
5.0	2.0	0	12.5	2.45	14.1	39.1
5.0	1.0	25.0	14.2	3.21	20.7	53.1
5.0	1.0	50.0	14.1	3.46	20.7	56.7

enhanced, but the trend became slow; and the maximum value of wet properties was observed at 5 wt % $CaCl_2$ content. The component of HCl is to coagulate soy protein isolate. When the content of HCl was 1 wt %, the properties of the fiber were the best. The increase of the content of ethanol could improve the wet properties of the fiber remarkably. When compared with the properties of the AS1 fiber in the coagulating bath without ethanol, the tensile strength (wet) and breaking elongation (wet) were increased by 41.2 and 45.1% when the ethanol weight content in the coagulating bath was 50%, respectively; but it had little effect on the dry properties. Maybe the ethanol molecules participate in the coagulation process and enhance the wet properties of the fibers.

Effects of the components of the fibers

The effect of soy protein isolate content on the tensile strength of fibers in dry and wet states was shown in Figure 4. The dry and wet tensile strengths of the AS1 and AS3 were higher than that of pure alginate, and the maximum value was observed at 10 wt % soy protein isolate content achieved 14.1 cN/tex in the dry state and 3.46 cN/tex in the wet state, respectively. The increase in tensile strength of this blend fiber can be explained by the presence of some strong interaction between alginate and soy protein isolate molecules in the blend. Figure 5 showed 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 20.7% (in the dry state) and 56.7% (in the wet state) was achieved when the soy protein isolate content was 10 wt %. The same changing trend confirmed that there were strong interactions between the intermolecular hydrogen bonds and Ca^{2+} crosslinking. So 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 were plotted in Figure 6 as a function of the weight content of soy protein isolate. Figure 6 showed that the

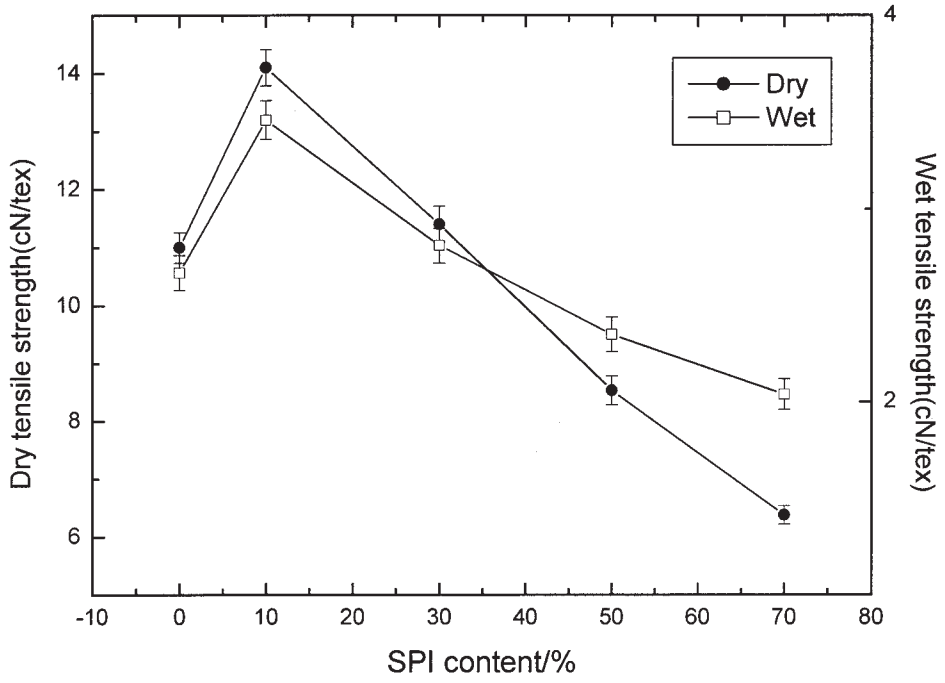

Figure 4 The effect of soy protein isolate content (wt %) on tensile strength of the fibers.

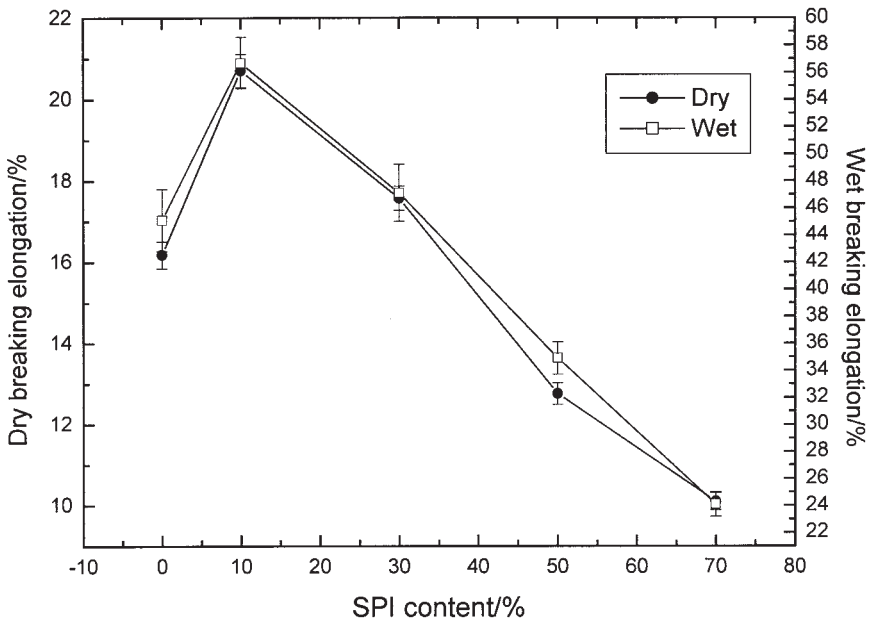

Figure 5 The effect of soy protein isolate content (wt %) on breaking elongation of the fibers.

water-retention values (*WRV*) of alginate/soy protein isolate blend fibers decreased as the amount of soy protein isolate was raised. The water-retention values (*WRV*) of the blend fibers were in the ranges of 61–89%, obviously lower than that of pure alginate fiber, which has the highest values (96%). The decrease in water-retention was due to soy protein isolate being more hydrophobic than calcium alginate.

CONCLUSIONS

Alginate and soy protein isolate blend fiber can be obtained by spinning their solution through a viscose-type spinneret into a coagulation bath containing aqueous $CaCl_2$, HCl, and ethanol. The strong intermolecular interaction between alginate and soy protein isolate molecule and Ca^{2+} crosslinking occurred in the

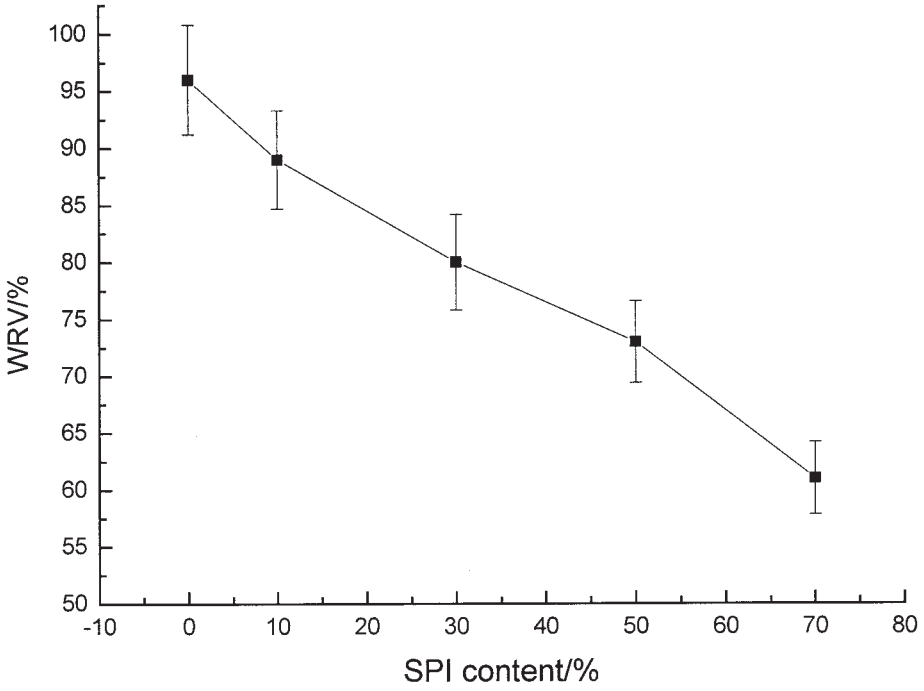

Figure 6 The effects of soy protein isolate content (wt %) on the WRV.

blend fibers. There were good compatibility between alginate and soy protein isolate molecules. The best values of the tensile strength and breaking elongation were obtained when soy protein isolate content was 10 wt %. The composition of the novel coagulating bath also influenced the properties of the fibers. The water-retention value (*WRV*) of blend fibers decreased as the amount of soy protein isolate was raised.

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