

Blend Films from Konjac Glucomannan and Sodium Alginate Solutions and Their Preservative Effect

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Received 28 July 1999; accepted 22 November 1999

ABSTRACT: In order to enhance the mechanical properties of konjac glucomannan film in the dry state and research the application of konjac glucomannan on food preservation domain, blend transparent film was prepared by blending 3 wt % sodium alginate aqueous solution with 4.5 wt % konjac glucomannan aqueous solution and dried at 40°C for 4 h. The structure and properties of the blend films were studied by infrared, wide angle X-ray diffraction, scanning electron microscopy, and differential thermal analysis. Crystallinities of blend films were increased with the increase of sodium alginate. The tensile strength and breaking elongation of the blend films in dry state were obviously higher than those of both sodium alginate and konjac glucomannan films. Tensile strength of the dry blend film achieved 77.8 MP_a when the retention of sodium alginate in the film was 27.9 wt %. The structure analysis indicated that there was a strong interaction between konjac glucomannan and sodium alginate, and this is resulted from the intermolecular hydrogen bonds. Moisture content and degree of water swelling of the blend films were increased due to the introduction of sodium alginate. Results from the film coating preservation experiment to litchi and honey peach showed that this blend film had water-holding ability. The fruit weight loss rate and rot rate both decreased by various values. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 617–626, 2000

Key Words: konjac glucomannan; sodium alginate; blend film; blend; miscibility; hydrogen bonds; preservative film.

INTRODUCTION

Konjac glucomannan, a polysaccharide whose main chain is composed of β -1,4 pyranoside bond linked mannose and glucose,^{1,2} has long been used as a health food in China and Japan. Konjac glucomannan has wide applications in the food industry,^{3,4} in the chemical industry,^{5,6} and in biochemistry.^{7,8} In recent years, exploitation of natural fruit and food preservatives such as chitin⁹ and chitosan¹⁰ have drawn more and more attention. The application of konjac glucomannan

to the food and fruit preservation domain has drawn the interest of many researchers due to its advantages of economy, convenience, and obvious effect on preservation over the conventional food and fruit preservation methods such as temperature and atmosphere condition, radiation, and chemical protection. Extensive studies of food and fruit preservation of konjac glucomannan and its chemically modified derivatives have been reported.^{11–14} In these reports, film-coating technology was mostly adopted. The good tensile strength is indispensable for the application of food preservation film materials. So enhancement of the mechanical property of konjac glucomannan in dry state is necessary for its practical application.

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Journal of Applied Polymer Science, Vol. 77, 617–626 (2000)
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Blending is an effective method to improve the performance of films. Generally, when the two components used to blend are compatible, the blend films can form homogeneous structure and show better physicochemical properties than the individual components. Alginates comprising linear chains of 1,4-linked β -D-mannuronate and α -L-guluronate with widely varying monomer composition of mannuronate to guluronate¹⁵ are widely used in industry, agriculture, medicine and pharmacy, food processing, and construction.¹⁶ In this paper, sodium alginate, a polyelectrolyte having rigid molecular chains¹⁷ and good film-forming ability, was used to blend with konjac glucomannan in order to research the modifying solution to improve the mechanical property of konjac glucomannan film in the dry state. Sodium alginate and konjac glucomannan are both natural polymers, and both have biocompatibility, biodegradability, and hydrophilicity. The innocuousness, biodegradability, and good water solubility are important and interesting for this promising food and fruit preservative film material. The morphological structure, miscibility, mechanical properties, swelling capacity of the blend films were studied by infrared (IR), wide angle X-ray diffraction (WAXD), differential thermal analysis (DTA), scanning electron microscope (SEM), electron tensile test, and swelling test. The relationship between the blends' structure and their physicochemical properties was discussed.

EXPERIMENTAL

Preparation of Blend Films

Konjac glucomannan was extracted and purified from the tuber of *Amorphallus konjac* (supplied by Zhuxi Konjac Institute, Hubei) as follows: Konjac tubers were sliced about 5 mm in thickness then dried under sunlight for a week. The dried sheets were pulverized by a mill. The crude flour was immersed in 70% (v/v) aqueous methanol for 30 min, then dried at 60°C under reduced pressure. Raw konjac flour was extracted with benzene–absolute alcohol (4:1 v/v) and trichloromethane-*n*-butanol (Sevag Method) for 48 h, respectively. The fat and protein extracted flour was dissolved with the mixture of distilled water–30% H₂O₂ (5:1 v/v) and heated at 30°C for 30 min, then stirred vigorously for 2 h. Keeping the mixture at room temperature for 4 h. Then acetone was

Table I The Film Code, Original Blend Ratio of the Solutions of Konjac Glucomannan and Sodium Alginate, and Re_{SA}

Film No.	Blend Ratio (W:W)	$Re_{SA}/\%$
KGM-0	100:0	—
KGM-SA1	90:10	4.9
KGM-SA2	70:30	16.2
KGM-SA3	50:50	27.9
KGM-SA4	30:70	40.9
KGM-SA5	10:90	55.1
SA-0	0:100	65.3

added and stirred. After filtered with a 140 m sieve cloth, the white cotton-like precipitate was squashed and dried at 40°C for 12 h. Water was added to the crude konjac glucomannan obtained to a concentration of 2 wt %. Subsequently, added predetermined amount of 1 g/mL $KAl(SO_4) \cdot 12H_2O$ and centrifuged under 8000 r/min for 30 min, the supernatant was added with adequate isopropanol and stirred, then filtered with a 140 m sieve cloth. After drying the white precipitate at 30°C under nitrogen atmosphere for 12 h, the powdered konjac glucomannan was obtained. Sodium alginate was purchased from Shanghai Chemical Agents Factory.

Konjac glucomannan and sodium alginate were both dissolved in deionized water to a concentration of 4.5 wt % (I) and 3 wt % (II), respectively. A mixture of I and II was stirred energetically and degassed, then was spread over a glass plate. The plate was immersed into a coagulation bath of the mixture of water: waterless alcohol:NaOH of 9:10:1 by weight for 15 min, then rinsed with running water. The transparent films were obtained after dried at 40°C for 4 h. By changing the weight ratio of I to II to 9:1, 7:3, 5:5, 3:7, and 1:9, a series of blend films coded as KGM-SA1, KGM-SA2, KGM-SA3, KGM-SA4, and KGM-SA5 were prepared respectively. The films obtained from pure konjac glucomannan and sodium alginate were coded as KGM-0 and SA-0. The film code, original blend ratio of I and II, and the retention of sodium alginate in the films (Re_{SA}) examined gravimetrically by referring the initial blend ratio of the two solutions with the resultant weight of the dried films are shown in Table I. The thickness of the films were measured to be $40 \pm 5 \mu\text{m}$.

Characterization of Films

The powdered films were blended with potassium bromide and laminated, and their IR spectra were recorded with a Nicolet (U.S.A.) 170SX FT-IR spectrometer. The film samples were coated by gold in 0.1 τ vacuum degree, then their surface morphology was observed on a Hitachi X-650 scanning electron microanalyzer (SEM) and took photos. The X-ray diffraction patterns of the films were recorded with a Rigaku (Japan) Dmax-II X-ray diffractometer and used CuK α target at 40 kV and 20 mA. The diffraction angle was ranged from 5° to 60°. The crystallinities of the films were calculated by¹⁸

$$Xc = Fc/(Fc + Fa) \times 100\%$$

where Fc and Fa are the area of crystal and non-crystalline regions, respectively. The differential thermal analysis of the film samples with about 1 mm length and 1 mm width were performed by a DT-40 thermoanalyzer (Shimadzu Co.) under nitrogen atmosphere with a flow capacity of 30 mL/min from 0 to 500°C at a heating rate of 10°C/min.

The tensile strength and breaking elongation of the films were measured on an electron tensile tester AG-A (Shimadzu Co., Japan) with a tensile rate of 100 mm/min according to the Chinese standard method (GB4456-84). The relatively humidity was 42%. The water content of the films were measured by¹⁹

$$\text{Moisture content} = (w_{r.t.} - w_{110})/w_{r.t.}$$

where w_{rt} and w_{110} are the weight of the films dried at room temperature for 8 h and at 110°C for 1 h, respectively. The degree of swelling of the films were measured by²⁰

$$\text{Degree of swelling} = (w_{wet} - w_{dry})/w_{dry}$$

where w_{dry} and w_{wet} are the weight of dry film and wet film obtained by immersing in deionized water for 3 min, respectively. The films were dried at 110°C for 1 h and balanced in vacuum for 4 h before measurement. The percent light transmittance of the films at the wavelength of 400 and 800 nm was measured using a Shimadzu UV-160A spectroscope.

Film Coating Preservation Experiment

A 10 mL citric acid aqueous solution (0.1 g/mL) was added to the mixture of 4.5 wt % konjac

glucomannan aqueous solution (I) and 3 wt % sodium alginate aqueous solution (II) with the composite ratio of 1:1 by weight. The mixture was degassed for about 2 h after stirring energetically.

Fruits of litchi and honey peach were classified into several groups. Every group contained 10 fruits. They were immersed into the preservative for 2 min, then dried in the air. It took 2 h to let the dry smooth film on the surface of fruit formed at the room temperature (about 31°C). Both the experimental group and control group without immersion and film coating were nakedly preserved at room temperature and at the relatively humidity of 63%. The preserve duration was 7 days. Every day, the change of the surface color of the fruit was observed. The weight loss rate of the litchi and honey peach was calculated by

$$\text{Weight loss} = (W_0 - W)/W_0 \times 100\%$$

where W_0 and W are the original weight and measuring weight of the whole group after preservation, respectively. The fruit rot rate was calculated by

$$\text{Fruit rot rate} = N_r/N \times 100\%$$

where N_r and N are the number of rotten fruits after preservation for a week and that of whole fruits, respectively.

RESULTS AND DISCUSSION

Miscibility

The scanning electron micrographs of the films are shown in Figure 1. The obvious crystalline regions appeared for pure konjac glucomannan (A) and sodium alginate (E) had disappeared for the blend film KGM-SA3 (C), and a intimately and regularly fabric structure could be seen from its morphological photograph, suggesting the high miscibility and blend homogeneity between sodium alginate and konjac glucomannan when the retention of sodium alginate in the film was 27.9%. The disappearance of crystallites exhibited on the photographs for the individual polymer used to blend and the alteration of morphological structure by comparing the photographs of pure film KAM-0 and SA-0 with those of the blend films suggested the occurrence of possible interaction between these two kinds of molecules, and

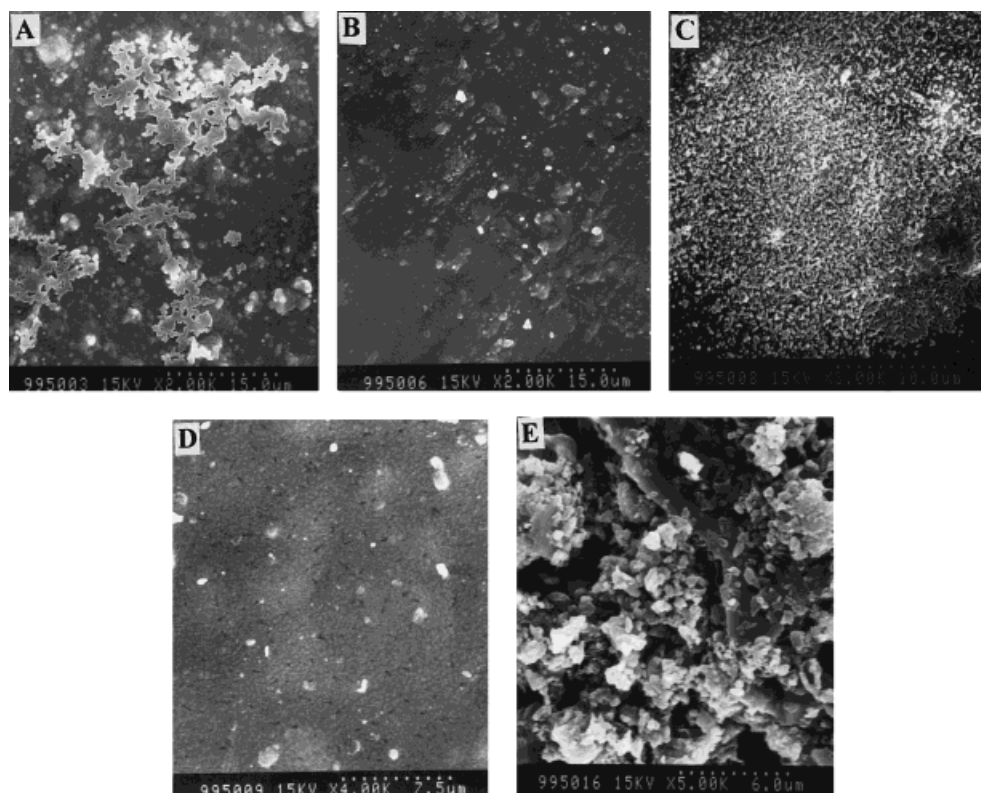


Figure 1 SEM photographs of the films of (A) KGM-0, (B) KGM-SA2, (C) KGM-SA3, (D) KGM-SA4, and (E) SA-0.

this intermolecular interaction broke the individually intermolecular interaction existed in the pure KGM and sodium alginate films.²¹

The optical transmittance of the films at the wavelength of 400 and 800 nm are shown in Figure 2. Generally, transparency of films is an auxiliary criterion to judge the miscibility of blend

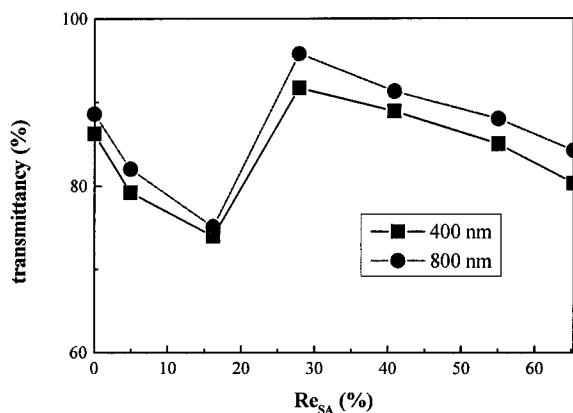


Figure 2 The percent light transmittance of the films at the wavelength of 400 (■) and 800 nm (●) dependence of the content of sodium alginate in the films.

films.²² It obviously can be seen from Figure 2 that the maximum value of transmittance appeared when the retention of sodium alginate in the blend film was 27.9%. It reached 91.7 and 95.8%, corresponding to the wavelength of 400 and 800 nm, suggesting the best miscibility between konjac glucomannan and sodium alginate. In the beginning, the transmittance of the film decreased with the increase of sodium alginate and reached the lowest value when the retention of sodium alginate in the film achieved 16.2 wt %.

The IR spectra of the films at the range of 3800–2600 and 1800–600 cm⁻¹ are shown in Figure 3 and Figure 4. It obviously can be seen from Figure 3 that the absorption band around 3380 cm⁻¹ corresponding to the stretching of —OH narrowed and shifted to gradually high wavelength when the retention of sodium alginate ranged from 0 to 40.9 wt %, indicating intramolecular hydrogen bonded state of pure konjac glucomannan was interrupted. At the same time, the absorption band at 2885 cm⁻¹ assigned to the stretching of methyl group of —COCH₃ for pure konjac glucomannan²³ were weakened gradually

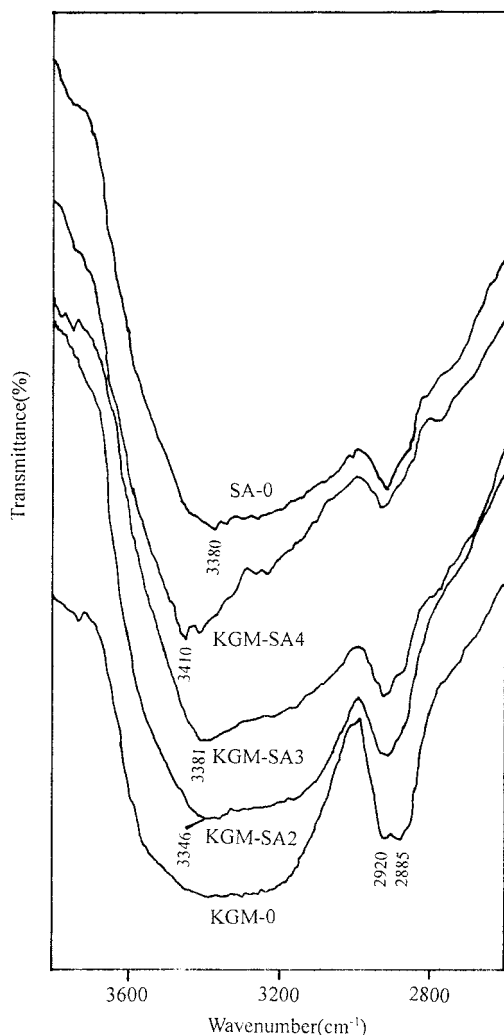


Figure 3 IR spectra of the film samples at the range of $3800\text{--}2600\text{ cm}^{-1}$.

with the increase of sodium alginate, indicating the —COCH_3 group in pure konjac glucomannan was affected by the intermolecular interaction. In other words, it joined in the formation of new hydrogen bonds. For the blend film KGM-SA3, the strong absorption band at 1622 cm^{-1} for SA-0 film assigned to the asymmetric stretching vibration of COO^- ²⁴ has coupled with the absorption band at 1647 cm^{-1} assigned to the stretching of intramolecular hydrogen bonds in konjac glucomannan²⁵ and shifted to 1632 cm^{-1} . Furthermore, the stretching peak of carbonyl group at 1730 cm^{-1} appeared for pure konjac glucomannan, which is assigned to the —COCH_3 groups in pure konjac glucomannan,²⁶ has disappeared for blend films. Based upon the results of FTIR and former sections, it can be concluded that the mis-

cibility between konjac glucomannan and sodium alginate was due to the formation of intermolecular hydrogen bonds. These hydrogen bondings are mainly resulted from the COO^- of carboxyl groups and —OH groups in sodium alginate with the —OH groups and —COCH_3 groups in konjac glucomannan, respectively.

The X-ray diffraction patterns of the films are shown in Figure 5. The crystallinities of the films of KGM-0, KGM-SA2, KGM-SA3, KGM-SA4, and

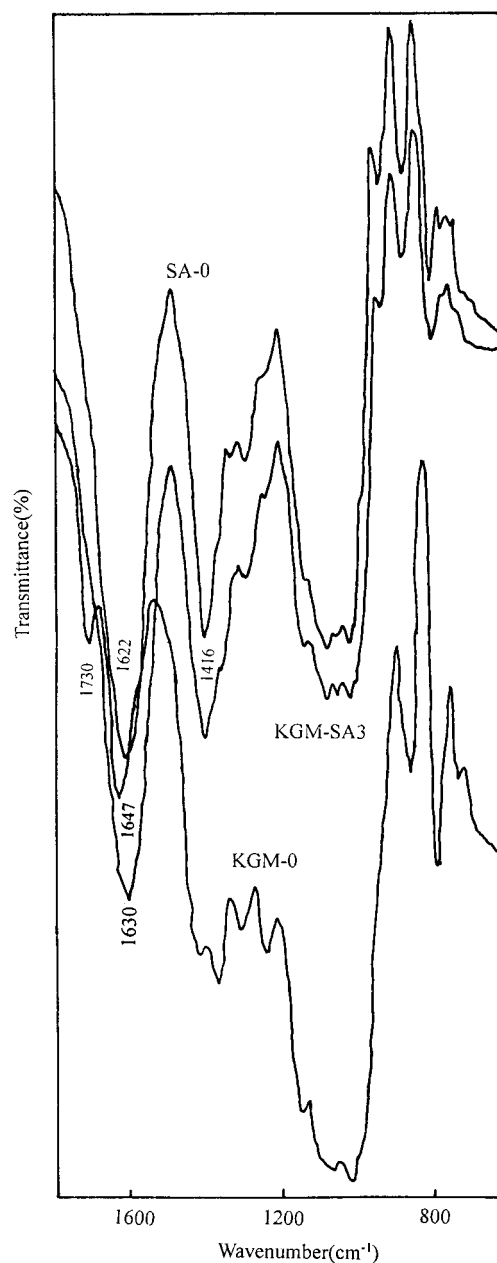


Figure 4 IR spectra of the film samples at the range of $1800\text{--}600\text{ cm}^{-1}$.

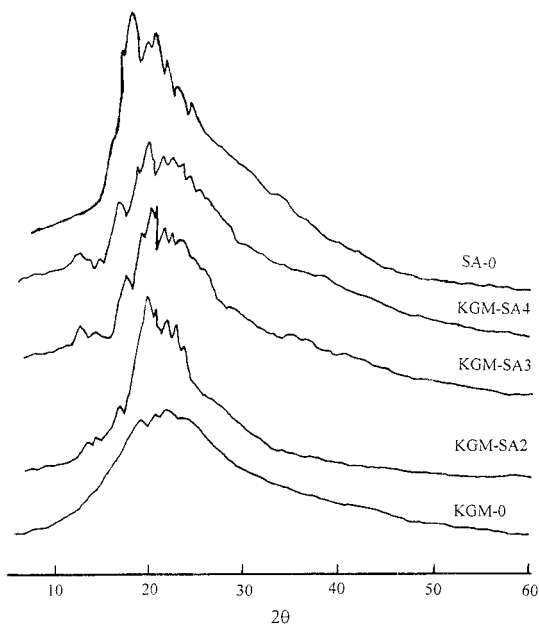


Figure 5 X-ray diffraction patterns of the films.

SA-0 were calculated to be 9.1, 19%, 19, 23, and 31%. It is obvious that the crystallinities of the films increased gradually with the increase of sodium alginate. It can be explained that sodium alginate yields to the interaction coming from konjac glucomannan and could not express its crystallization ability at first, but this resistance weakened with the increase of sodium alginate. At last, the interaction "forced" these two kinds of molecules to coexist in an ordered state; consequently, the good blend miscibility occurred. This result supported the conclusion drawn from SEM and IR that the good miscibility existed between sodium alginate and konjac glucomannan was due to the strong interactions from the intermolecular hydrogen bonds.

Differential Thermal Analysis

The DTA thermograms of the films are shown in Figure 6. The films all show endothermic peaks around 90°C, corresponding to the loss of crystalline water molecules in the films formed during drying progress. In the thermograms of blend films, the endothermic peak around 354°C appeared for pure konjac glucomannan film disappeared; and the temperatures corresponding to the exothermic peaks that assigned to pure sodium alginate film ordered as 256°C (KGM-SA2) > 242°C (KGM-SA3) > 240°C (KGM-SA4) = 240°C (SA-0). The occurrence of single exother-

mic peaks in the thermograms of KGM-SA3 and KGM-SA4 films indicated the blend compatibility between konjac glucomannan and sodium alginate. In contrast, the shoulder endothermic peak corresponding to 238°C appeared in the thermogram of KGM-SA2 film, indicating the bad miscibility between konjac glucomannan and sodium alginate when a small amount of sodium alginate was added.

Mechanical Properties

The tensile strength and breaking elongation dependence of the content of sodium alginate for the films are shown in Figures 7 and 8, respectively. The tensile strengths of the blend films increased with the increase of sodium alginate, and the maximum value that appeared when the retention of sodium alginate was 27.9 wt % achieved 77.8MPa. The alteration of breaking elongation expressed a tendency similar to that of tensile strength, and reached the maximum when the retention of sodium alginate was 27.9 wt %. The conclusion can be draw that the blend of sodium alginate with konjac glucomannan has considerably enhanced the mechanical properties of the blend film in the dry state.

Moisture Content and Water Swelling Property

Degrees of water swelling of the films are shown in Figure 9. With the increase of sodium alginate,

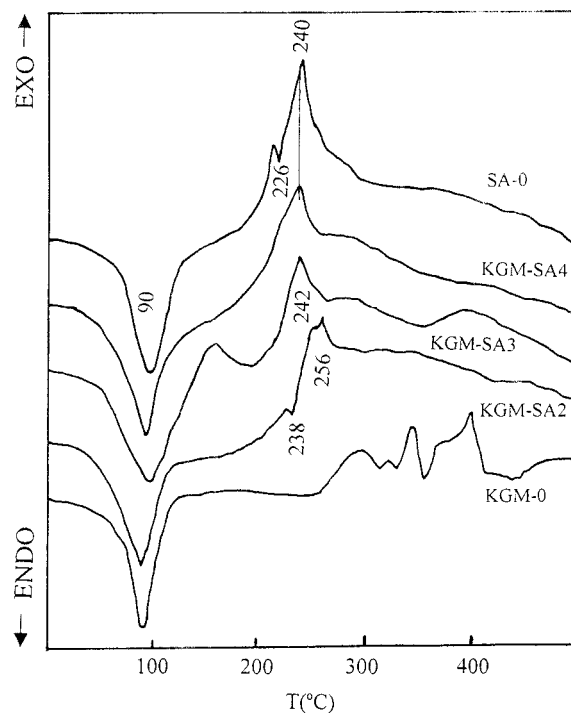


Figure 6 DTA thermograms of the films.

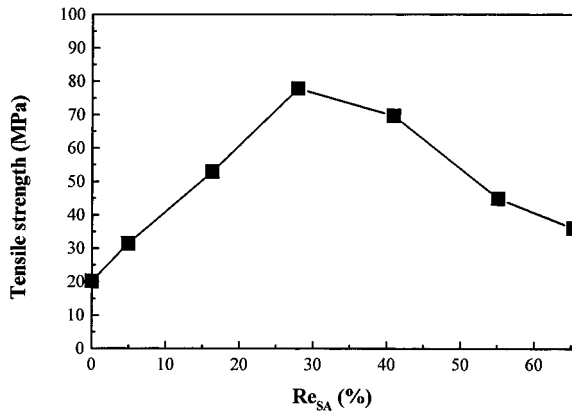


Figure 7 Tensile strength of the films dependence of the content of sodium alginate.

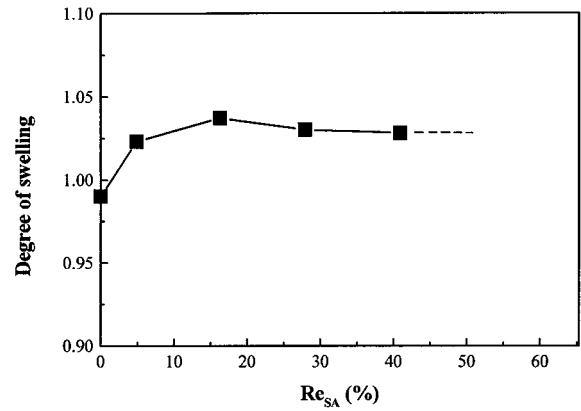


Figure 9 Degree of swelling dependence of the content of sodium alginate for the films.

the degree of water swelling increased gradually, but kept a stable level when the retention of sodium alginate exceeded 16.2 wt %. Regrettably, degrees of water swelling of KGM-SA5 and SA-0 could not be obtained because the film samples were dissolved after immersed in water for 3 min. The higher degree of water swelling indicated that the good water solubility of konjac glucomannan was further enhanced by blending with sodium alginate. Figure 10 shows the moisture content of the films dependence of the content of sodium alginate. Compared to KGM-0, film KGM-SA2, which contains 4.9 wt % sodium alginate, had lower moisture content. When the retention of sodium alginate ranged from 4.9 to 55.1 wt %, the moisture content almost increased linearly. It may be attributed to the gradual increase of crystallinities of the blend films with the increase of sodium alginate, where more and more crystal

water was formed during drying. It is in good agreement with the result of X-ray diffraction analysis.

Film Coating Preservation

Litchi, a kind of expensive fruit abundant in Guangxi province in China, achieved an unprecedented yield this year. However, the particular preserve demand made a large amount of litchi wasted. The fresh red color of the pericarp of litchi may instantly change into brown in less than an hour after taken out from the refrigerator and placed in a slightly dry atmosphere or at a higher temperature. So finding out the solution to delay the brown-altering phenomenon of the fruit's pericarp during preservation is vital to researchers.²⁷ Honey peach, another kind of fruit abundant in Beijing of China, also

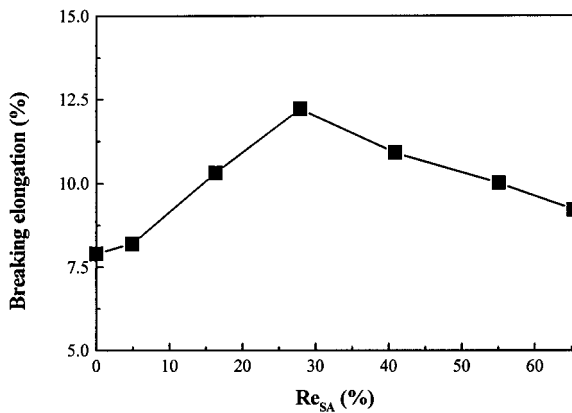


Figure 8 Breaking elongation of the films dependence of the content of sodium alginate.

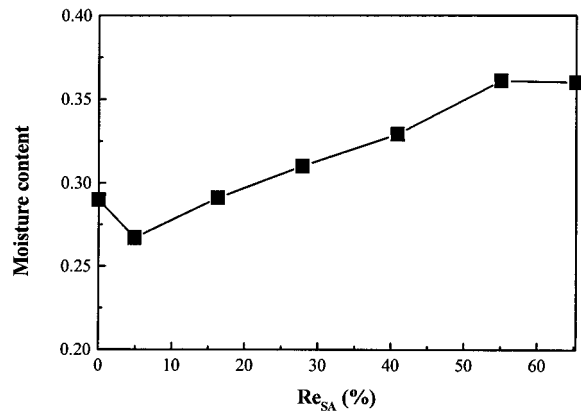


Figure 10 Moisture content dependence of the content of sodium alginate for the films.

Table II Changes of Litchi and Honey Peach Dependence of the Preserve Time

Time (d)	Fruit			
	Litchi		Honey Peach	
	Experimental Group	Control Group	Experimental Group	Control Group
1	No change (pericarp was red)	Color of pericarp became light brown	No change (pericarp was bright red)	Pericarp shrank
2	Red color faded away	Color of pericarp became completely brown	No change	Some brown specks appeared, and pericarp shrank sharply
3	Fresh red color of pericarp lost	Fruit was rigid when pinched and pericarp appeared crack	No change	Areas of brown specks enlarged, and fruit softened badly
4	Color of pericarp became completely brown	Fruit emitted a strong sour smell	Pericarp shrank	Pericarp cracked, and syrup with sour smell flowed out
5	Pericarp cracked, and fruit became rigid	Fruit was mildewed and flowed liquid with bad smell	Shrinkage of pericarp hardened	Large areas of mildew appeared, and fruit rotted away
6	Crack on the surface of pericarp increased	—	Some brown speck appeared	—
7	Fruit emitted liquid with bad smell	—	Dent appeared on the surface of pericarp, and fruit sharply softened	—
Fruit rot rate	47%	90%	28%	100%

faces a problem because of abundant syrup in its mature fruits.

Table II shows the changes of litchi and honey peach during preservation. The red color of litchi of experimental groups was kept for 1 day, and the cracks of pericarp only appeared at the fifth day. Correspondingly, the red color of litchi of the control groups was completely lost within a day, and the cracks of pericarp appeared at the third day. Even worse, fruits of litchi became mildewed and rotted away completely. The fruit rot rate of litchi calculated decreased from 90% for control groups to 47% for film-coating preserved groups. By comparing experimental groups of honey peach with control groups, the time corresponding to the change of pericarp color from light red to brown was decreased; the date corresponding to the appearance of shrinkage was delayed. The

fruit rot rate decreased from 100% for control group to 28% for experimental group. From plots of Figure 11 and 12 describing the weight loss rate dependence of the preserve time for litchi and honey peach, respectively, it is obvious that the weight loss rate against preserve time of these two kinds of fruits both decreased after film-coating preservation. This indicates the good water-holding ability of this blend film. A common tendency was that the increase of weight loss rate sharpened gradually with the increase of preserve time.

The high tensile strength in the dry state of this blend film made it possible for the applications to film-coating or film-packing preservation for foods and fruits. More importantly, this blend film coated onto the fruits can be easily washed away, denoting that the operation of

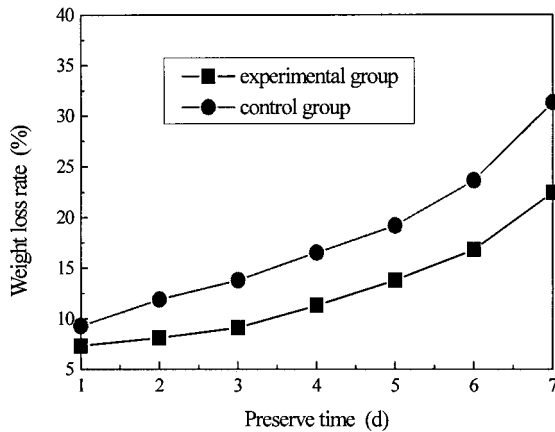


Figure 11 The weight loss rate of litchi dependence of the preserve time.

removing the preservative film was very simple. In fact, konjac glucomannan and sodium alginate are both used as health foods or food additives in many countries. The absolute innocuousness and biodegradability is another attraction for this blend film.

CONCLUSION

A series of transparent blend films were satisfactorily prepared by blending 4.5 wt % konjac glucomannan aqueous solution with 3 wt % sodium alginate water solution according to predetermined ratios and drying at 40°C on glass plates for 4 h. The mechanical properties, moisture content, and water swelling capacity of the blend films were higher than those of konjac glucomannan

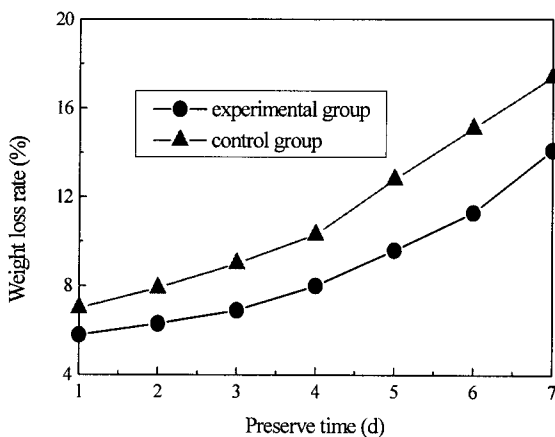


Figure 12 The weight loss rate of honey peach dependence of the preserve time.

nan film. The tensile strength and breaking elongation achieved their maximum values accordingly when the weight retention of sodium alginate in the film was 27.9%. Crystallinity of the blend films increased with the increase of sodium alginate. The good miscibility between sodium alginate and konjac glucomannan was confirmed by the results of SEM, IR, and WAXD. The interaction from the intermolecular hydrogen bonds existing between the COO^- groups of sodium alginate and the hydroxyl groups of konjac glucomannan results in the enhancement of mechanical properties of the blend film. Results of the film-coating preservation showed that the weight loss rate and fruit rot rate of litchi and honey peach both decreased, and the brown-altering of the pericarp was delayed. The high tensile strength in dry state, good water solubility, biodegradability, and water-holding ability of the blend film make it a promising fruit preservative film material.

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