Characterization of Konjac Glucomannan–Quaternized Poly(4-vinyl-*N*-butyl) Pyridine Blend Films and Their Preservation Effect

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ABSTRACT: Novel polymer blends were prepared from a mixture of 2 wt % konjac glucomannan and 4 wt % quaternized poly(4-vinyl-*N*-butyl) pyridine (QPVP) in aqueous solution and dried at room temperature for 72 h. Their structure and properties were studied by infrared, wide-angle X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and differential scanning calorimetry. Thermal stability in the dry state was reduced with increasing content of QPVP. Compared with QPVP film, the tensile strength of the films was improved in the dry state. The maximum value of 12.74% tensile break elongation was reached when the content of QPVP was 30%. Structural analysis indicated that clear phase separation was observed when the content of QPVP was only 50%. Results from the filmcoating preservation experiments with lychee showed that this blend film had water-holding ability. The fruit weight loss rate and rot rate both decreased in various degrees. The potential uses of these novel polymer films could be as preservative films. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1868–1875, 2004

Key words: konjac glucomannan; quaternized poly(4-vinyl-*N*-butyl) pyridine (QPVP); films; polysaccharides; structure

INTRODUCTION

The development of new applications of polysaccharides is currently the focus of extensive studies because of the expected applicability in, for example, industrial, biochemical, and medical fields. 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] Konjac glucomannan can be extruded into films for coating and packing applications. In recent years, exploitation of natural fruit and food preservatives, such as chitin[9] and chitosan,[10] has drawn increasing attention. The application of konjac glucomannan to food and fruit preservation has also drawn interest among many researchers because of its advantages of economy, convenience, and obvious preservative effects over conventional food and fruit preservation methods, such as temperature and atmosphere condition, radiation, and chemical protection. Extensive studies of food and fruit preservation using konjac glucomannan and its chemically modified derivatives have been reported.[11–15] Good tensile strength and ability to attack bacteria are indispensable for the application of food and fruit preservation film materials. Quaternized poly(4-vinyl-*N*-butyl) pyridine (QPVP) is a special functional polymer used in such areas as liquid crystalline, electrolyte polymer, and bioorganic polymer. Vilene Co. Ltd. (Tokyo, Japan)[16] reported that poly(4-vinyl) pyridine quaternized by C_4–C_{18} bromoalkane and $PhCH_2Br$ has the ability to strongly attack bacteria and promote an affinity for microorganisms, and poly(4-vinyl) pyridine quaternized by $PhCH_2Br$ can prevent and inhibit germ infection generated by microorganisms in soil. Osama et al.[17] reported that quaternized poly(4-vinyl-*N*-octyl) pyridine can adsorb 99.9% bacteria (viable cell counts 10^8/mL) in water over a period of 1 h. Blending is an effective method of improving the performance of films. Generally, when the two components used in a blend are compatible, the blend films can form a homogeneous structure and show better physicochemical properties than those of the individual components.

In this article, konjac glucomannan, which has good film-forming and coating ability, was used to blend with QPVP to investigate possible improvements in the mechanical properties of QPVP film in the dry state. For this present article, the morphological structure, miscibility, and mechanical properties of the blend films were studied by infrared (IR), wide-angle

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TABLE I
Blend Components of All Samples and Codes

	Code					
	KGM-0	KGM-1	KGM-2	KGM-3	KGM-4	QPVP
Weight ratio of I to II	100 : 0	90 : 10	70 : 30	50 : 50	30 : 70	0 : 100

X-ray diffraction (WXRD), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and tensile tests. The relationship between structures of the blends and their physicochemical properties will be discussed.

EXPERIMENTAL

Preparation of blend films

Poly(4-vinyl) pyridine (PVP) was prepared by radical polymerization in mass at 60°C for 18 h under a N_2 atmosphere according to the method in the literature[18] using azobisisobutyronitrile (AIBN) (0.5 wt %) as initiator. The resulting product was dissolved in absolute ethanol and precipitated in ether, filtered, and dried under vacuum to give a white product. Its molecular weight ($M_\eta = 3.1 \times 10^4$ g/mol) was determined by a Ubbelohde viscometer (Cannon–Ubbelohde, State College, PA). The quaternization of the polymer was carried out by heating the solution of polymer and *n*-bromobutane in nitromethane at 75–78°C under N_2 for 72 h. The resulting quaternized product was precipitated from ether.

Konjac glucomannan was extracted and purified from the tuber of *Amorphallus konjac* (supplied by Chongqing Konjac Factory, Chongqing, China) as follows: konjac tubers were sliced about 5 mm in thickness then dried under sunlight for 1 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 in a mixture of distilled water–30% H_2O_2 (5:1 v/v) and heated at 30°C for 30 min, stirred vigorously for 2 h, keeping the mixture at room temperature for 4 h, after which acetone was added and stirred. After filtration with a 200 μm sieve cloth, the white cottonlike precipitate was compressed and dried at 40°C for 12 h. Water was added to the obtained crude konjac glucomannan to a concentration of 2 wt %. Subsequently, we added a predetermined amount of 1 g/mL KA1$(SO_4) \cdot 12H_2O$ based on the crude konjac glucomannan and centrifuged under 8000 rpm for 30 min. The supernatant was combined with adequate isopropanol and stirred for precipitation of konjac glucomannan, then filtered with a 200

μm sieve cloth. After drying the white precipitate at 30°C under nitrogen atmosphere for 12 h, the powdered konjac glucomannan was obtained.

Konjac glucomannan was dissolved in deionized water to prepare a concentration of 2 wt % solution (I). QPVP was dissolved in deionized water to a concentration of 4 wt % (II). A mixture of I and II was vigorously stirred and degassed, then was spread over a Teflon plate. The films were obtained after drying at room temperature for 72 h. The blend components of all samples and their codes are listed in Table I. The thickness of the films was measured to be 30 ± 5 μm.

Characterization of films

IR spectra of the films (attenuated total reflection mode) were recorded with a 170SX FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). Film samples of about 30 μm thickness were coated with gold in a 13.3 Pa vacuum, then their surface morphologies were observed on a Hitachi S-570 scanning electron micrograph (Hitachi, Osaka, Japan). The WXRD patterns of the films of 30 μm thickness were recorded with a Shimadzu XRD-6000 (Kyoto, Japan) diffractometer by using a Cu–K_α target at 40 kV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 50 to 4°. The TG and DSC of the film samples with 1 mm length and 1 mm width were performed by a Systsys 16TG/DAT/DSC instrument (France) under a nitrogen atmosphere with a flow capacity of 30 mL/min from 20 to 500°C, at a heating rate of 10°C/min.

The tensile strength (σ_b) and breaking elongation (ε_b) of the films were measured on a versatile tensile tester (CMT-6503, Shengzhen SANS Test Machine Co. Ltd., China) with a tensile rate of 100 mm/min according to the Chinese standard method (GB4456-84). The size of the samples was 70 mm length, 10 mm width. The experimental temperature and relative humidity were 20°C and 47%, respectively.

Film-coating preservation experiment

The film of KGM-2 was chosen for testing because it had the best mechanical properties and miscibility. The mixture of 2 wt % konjac glucomannan aqueous solution and 4 wt % QPVP aqueous solution, with the composite ratio of 70:30 by solid weight, was degassed
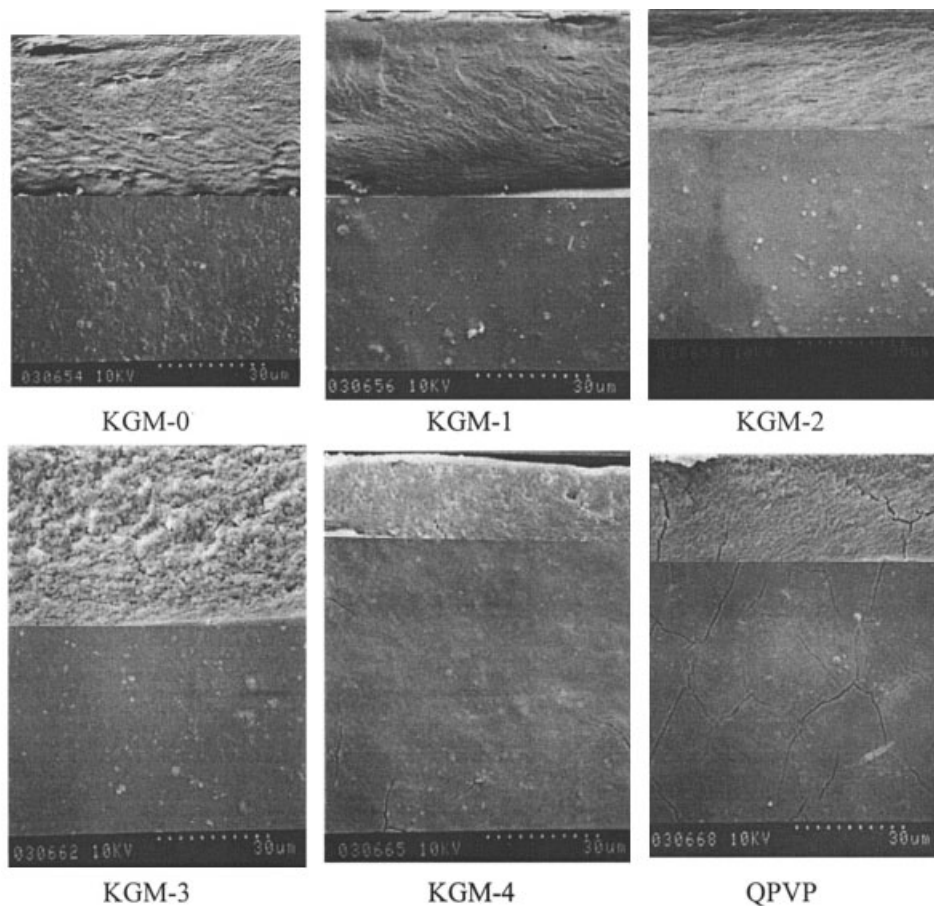
Figure 1 SEM microphotographs of the investigated films.

for about 0.5 h after vigorous stirring. Lychee Fruits were classified into several groups. Every group contained 10 fruits. They were immersed in the preservative for 2 min and then dried in air to allow a dry smooth film to form on the surface of fruit at room temperature (about 32°C) for 2 h. Both the experimental group and the control group were preserved in the open at room temperature at relative humidity of 65%. The duration of preservation was 7 days. Every day, the change of the surface color of the fruit was observed. The weight loss rate of the lychee was calculated by

$$\text{Weight loss} = (W_0 - W)/W_0 \times 100 \qquad (1)$$

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

$$\text{Rot rate of fruit} = \frac{N_r}{N \times 100\%} \qquad (2)$$

where N_r and N are the number of rotten fruits after preservation for 7 days and that of whole fruits, respectively.

RESULTS AND DISCUSSION

Morphological characterization of the films

The scanning electron micrographs of the films are shown in Figure 1. The upper section of every micrograph is its cross section and the bottom section of every micrograph is its surface section. The films of KGM-1, KGM-2, and KGM-4 were transparent and their surfaces showed heterogeneous morphology, although their cross sections were homogeneous, which meant good miscibility between konjac glucomannan and QPVP. With increasing weight of QPVP, the surface of all blend films became increasingly smooth and well distributed. As evident in comparing photographs of the blend films with that of pure KGM-0 film, only the cross section of KGM-3 appeared phase-separated, indicating immiscibility. When the content of QPVP attained 70%, immiscibility was not markedly apparent in the morphology of KGM-4. These facts indicated the good miscibility between konjac glucomannan and QPVP when the content of QPVP was less than 30% or more than 70%. The possible reason is that QPVP dispersed in a continuous phase of konjac glucomannan when the content of QPVP was less than 30% and the konjac glucomannan dis-
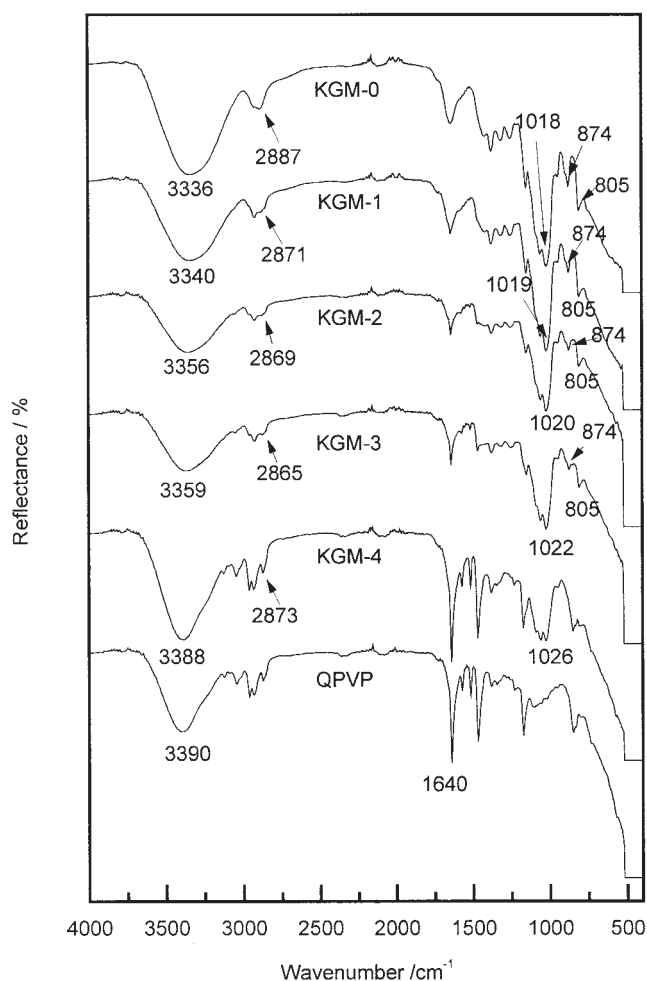
Figure 2 IR spectra of the film samples in the range 4000–400 cm^{-1}.

persed in a continuous phase of QPVP when the content of QPVP was in excess of 70%.

FTIR spectra of the films

Information on the molecular interaction between components can be obtained by spectroscopic vibrational analysis. The IR spectra of these films in the range of 4000–400 cm^{-1} (attenuated total reflection mode) are shown in Figure 2. The characterization peaks of all samples and their origin are listed in Table II. From IR spectra of KGM-0, we know that stretching peaks of –CH$_2$– are at 2918, 2887, 1411, and 1375 cm^{-1} and the absorption band at 1640 cm^{-1} is attributed to intramolecular hydrogen bonds. The peaks at 1061 and 1018 cm^{-1} are assigned to the stretching vibration of C—O—C. The peak at 3336 cm^{-1} is assigned to the stretching vibration of –OH.[19] The molecular structure of QPVP shows peaks at 1640, 1571, and 1516 cm^{-1} that relate to the vibration of NR$_4$, C=N, and C=C (pyridine ring),[20] and the stretching vibration of –CH= (pyridine ring) present at 3124 and 3045 cm^{-1}. The peak at 3390 cm^{-1} is assigned to the stretching vibration of –OH (absorbed water), as shown in curve QPVP in Figure 2.

It is clear in Figure 2 that the stretching vibration of hydroxyl groups in the blend films KGM-1, KGM-2, KGM-3, and KGM-4 appear at 3340, 3356, 3359, and 3388 cm^{-1}, respectively. The absorption band, corresponding to the stretching vibration of –OH in the blend films, shifted gradually to higher wavenumbers when the content of QPVP increased, indicating that the intramolecular hydrogen bonded state of pure konjac glucomannan was interrupted. It may simply be that the shift is attributable to increasing amounts

TABLE II
FTIR Analysis of All Samples and Origins

Code	Characterization peaks (cm^{-1})	Origin
KGM-0	2918, 2887, 1411, 1375	Stretching peaks of –CH$_2$–
	3336	Stretching vibration of –OH
	1018	Stretching vibration of C—O—C
KGM-1	2918, 2871, 1411, 1375	Stretching peaks of –CH$_2$–
	3340	Stretching vibration of –OH
	1019	Stretching vibration of C—O—C
KGM-2	2918, 2867, 1411, 1375	Stretching peaks of –CH$_2$–
	3356	Stretching vibration of –OH
	1020	Stretching vibration of C—O—C
KGM-3	2918, 2887, 1411, 1375	Stretching peaks of –CH$_2$–
	3359	Stretching vibration of –OH
	1022	Stretching vibration of C—O—C
KGM-4	2918, 2865, 1411, 1375	Stretching peaks of –CH$_2$–
	3388	Stretching vibration of –OH
	1026	Stretching vibration of C—O—C
QPVP	3124, 3045	Stretching vibration of –CH=
	3390	Stretching vibration of –OH(H$_2$O)
	1640, 1571, 1516	Vibration of NR$_4$, C=N, C=C

of absorbed water as the content of QPVP is increased.[21] At the same time, under electrostatic interaction, the bond of C—O—C in the blend films KGM-1, KGM-2, KGM-3, and KGM-4, when compared with that of pure konjac glucomannan, shifted increasingly to higher wavenumbers: the peaks of C—O—C in the blend films KGM-1, KGM-2, KGM-3, and KGM-4 appear at 1019, 1020, 1022, and 1026 cm^{-1}, respectively. The stretching vibration of $-CH_2-$ in the blend films, when compared with that of pure konjac glucomannan at 2887 cm^{-1}, was weakened and gradually shifted to lower wavenumbers with increasing QPVP content: the peaks corresponding to the stretching of $-CH_2-$ in the films KGM-0, KGM-1, KGM-2, and KGM-3 appear at 2887, 2871, 2867, and 2865 cm^{-1}, respectively. This effect is a consequence of changes in electronic distribution in the molecular structure of konjac glucomannan resulting from the strong electrostatic interaction. With increasing QPVP content, the characteristic absorption of QPVP at 1640 cm^{-1} in the blend films became stronger and the characteristic absorption bands of mannose in the blend films at 874 and 805 cm^{-1} gradually became weaker, indicating that strong electrostatic interaction exists between these molecules.

Crystallinity of the films

X-ray diffraction patterns of pure and blend films are shown in Figure 3. The pattern of konjac glucomannan shows a broad peak at $2\theta = 21.3°$, and several small and weak peaks appear at 11.02, 24.4, 30.28, and 44.76° (2θ). The pattern of QPVP shows a broad peak and a stronger peak at $2\theta = 21.86$ and 5.06°, respectively. If KGM and QPVP have low compatibility, each polymer would have its own crystal region in the blend films, so X-ray diffraction patterns would be expressed simply as mixed patterns of KGM and QPVP with the same ratio as those for blending. By comparing the patterns of the films KGM-1 and KGM-2 with that of KGM-0, it is obvious that the intensity of the diffraction peak at $2\theta = 21.3°$ of the films KGM-1 and KGM-2 gradually increased with the increase of QPVP up to 30%, the peak at $2\theta = 30.28°$ disappeared, and the peak at $2\theta = 44.7°$ shifted to a lower Bragg angle.

It can be explained that the electrostatic adhesion between KGM and QPVP induced these two kinds of molecules to coexist in an ordered state and, consequently, good blend miscibility occurred. Although the X-ray diffraction of KGM-3 has significantly less noise than that of the other four samples shown, the characteristic peaks of KGM at $2\theta = 11.02, 24.4$, and 30.28° and QPVP $2\theta = 5.06°$ are clearly shown. The pattern of the blend film KGM-3 simply shows a mixed pattern of these two kinds of polymer when the weight of QPVP is 50%. The peak at $2\theta = 44.7°$ shifts weakly to a higher Bragg angle in KGM-4, and the
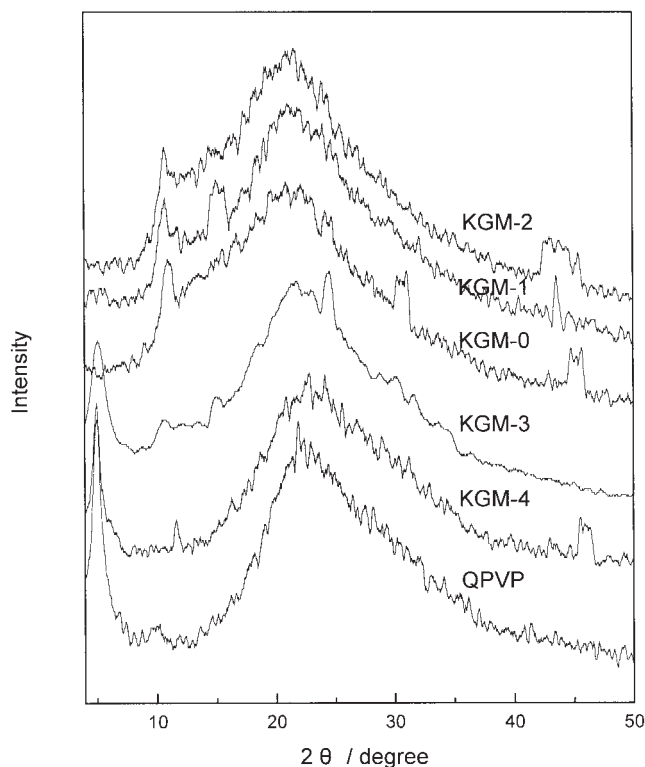

Figure 3 X-ray diffraction patterns of the films.

characteristic peaks of KGM at $2\theta = 11.02, 24.4$, and 30.28° disappeared, which indicates that KGM and QPVP were miscible. This result supports the conclusion, drawn from SEM, that good miscibility existed between KGM and QPVP when the content of QPVP was less than 30% or more than 70%: phase separation appeared when the content of QPVP was 50%.

Thermal stability

The TG curves of the films are shown in Figure 4. A small weight loss of about 12% at 113–120°C was assigned to the release of moisture from the samples. The films of KGM-0, KGM-1, and KGM-2 showed one step of active weight loss with increasing temperature in the temperature range of 220–340°C; the greater weight losses were found at 280, 280, and 273°C, respectively, and the curves of KGM-0 and KGM-1 are identical. The films of KGM-3 and KGM-4 showed three or four steps of weight loss with increasing temperature in the temperature range of 220–340°C; the film of KGM-3 displayed the characteristics of a mixture of KGM and QPVP, the TG curve of KGM-4 was similar to that of TG QPVP, the greatest weight loss of KGM-3 was found between 252 and 317°C, and the greatest weight loss of KGM-4 was found between 256 and 331°C. Most weight loss of all films was attributed to the decomposition of QPVP and KGM.
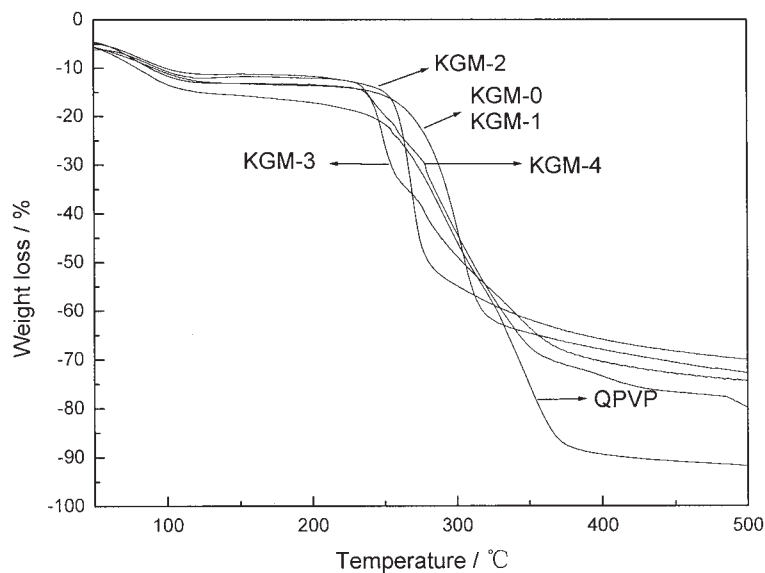
Figure 4 TG thermograms of the films.

The order of thermal stability of the films was KGM-0 $\approx$ KGM-1 > KGM-2 > KGM-3 $\approx$ KGM-4 $\approx$ QPVP.

The DSC curves of the films are displayed in Figure 5. The curves of all the films showed an endothermic peak at 113–120°C, which was attributed to the loss of moisture. The exothermic peak around 280°C of pure KGM films resulted from the thermal degradation of KGM. The two exothermic peaks around 262 and 321°C of QPVP are attributed to the thermal degradation of QPVP. The DSC curves of KGM-0, KGM-1, KGM-2, and KGM-4 show one major exothermic peak: it is probable that these results were caused by the good miscibility. The DSC curve of KGM-3 however, displayed two exothermic peaks, which may be attrib-

utable to the overlapping of exothermic peaks from KGM and QPVP. These results of the TG and DSC analysis are in agreement with results of SEM and X-ray analysis.

Mechanical properties

The study of mechanical properties is very important for determining the performance of a material that is expected to undergo various kinds of stress during use. The tensile strength and breaking elongation dependency on the content of QPVP for these films are shown in Figure 6. The tensile strengths of the blend films decreased linearly with the increase of QPVP: it
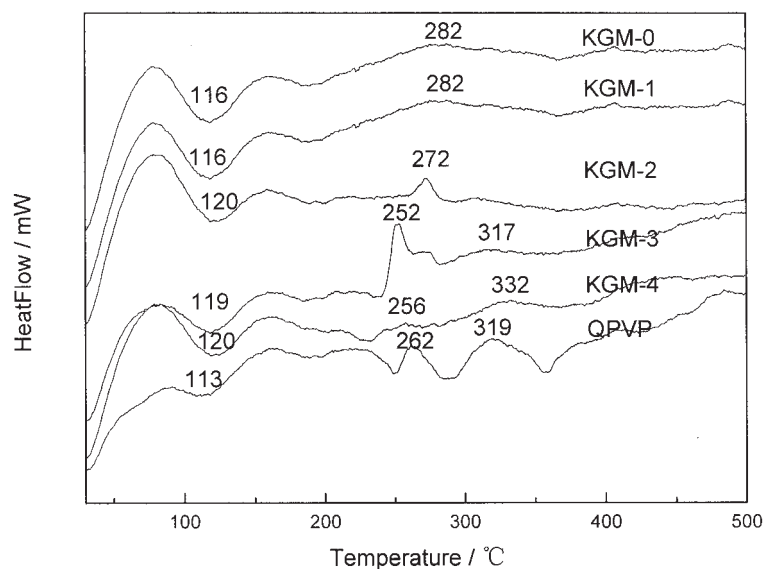

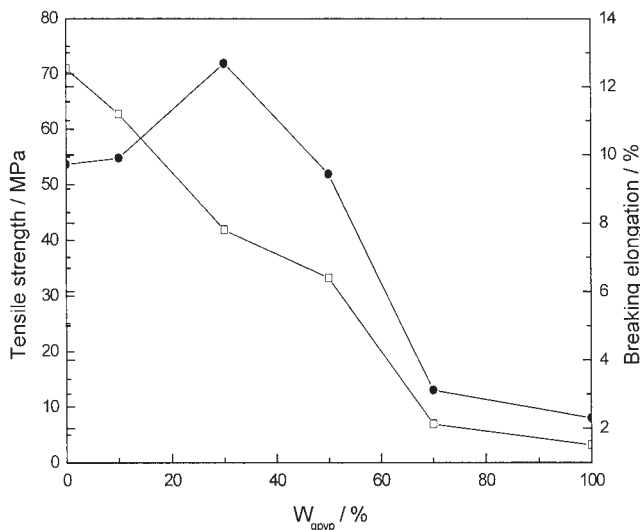**Figure 5** DSC thermograms of the films.

Figure 6 Tensile strength and breaking elongation of the films as a function of the QPVP content: -□-, tensile strength; -●-, breaking elongation.

can be explained that electrostatic interaction with QPVP impaired the hydrogen bond interaction of KGM. With the increase of QPVP, the electrostatic interaction became stronger and phase separation appeared at KGM-3. The film of KGM-4 consisted mainly of QPVP, whose tensile strength was poor, and thus its tensile strength was poorer. The maximum value of 12.74% tensile break elongation was reached when the content of QPVP was 30%: it may be that the electrostatic interaction between KGM and QPVP impaired the partial hydrogen bond interaction of KGM molecules, which facilitated sliding of the KGM molecular chains or the stretch of the KGM molecular chains. Increasing content of QPVP led to more electrostatic interaction, which destroyed the hydrogen bond inter-

action, thus causing phase separation that enabled ready breaking of the films. These mechanical properties agree with the microscopic structure discussed above.

Film coating preservation

Lychee is a subtropical fruit that rots easily during preservation and transport. It is thus necessary to find a preservative to delay the rot and water loss. Lychee fruits were purchased from the market. Based on our findings with SEM, IR, thermal stability, and mechanical properties, KGM-2 film was chosen as the preservative. Table III shows the changes that lychee fruits undergo during preservation. The lychees, in experimental groups and control groups coated with pure KGM, were kept for 1 day. The red color of lychees for groups without coating was completely lost within a day and fruits became mildewed and rotted away completely by the fourth day. The rot rate of lychee for experimental groups, control groups coated with pure KGM, and control groups without coating were 10, 43, and 90%, respectively.

From the plots of Figure 7, which show the weight loss rate dependency on preservation time, it obvious that the weight loss rate against preservation time decreased after film-coating preservation, and the tendency of the weight loss rate of both pure KGM film and blend film showed no difference. This indicates the good water-holding ability of both the blend film and pure KGM film. However, the rot rate of lychee coated with the blend film was less than that of lychee coated by pure KGM. The blend film possibly has an ability to attack bacteria and there is a synergistic effect of KGM and QPVP. The preservation ability of the blend film also was better than that of blend film from KGM and sodium alginate.[15] A common ten-

TABLE III
Physical Changes of Lychee with Various Preservation Times

| Time (days)	Experimental group (blend film)	Control group (pure KGM film)	Control group
1	No change (pericarp was red)	No change (pericarp was red)	Color of pericarp became light brown
2	Red color faded away	Red color faded away	Color of pericarp became completely brown
3	Fresh red color of pericarp lost	Fresh red color of pericarp lost	Fruit was rigid and pinched when pericarp appeared crack
4	Color of pericarp became completely brown	Color of pericarp became completely brown	Fruit emitted a strong sour smell
5	Percicarp cracked, and fruit became rigid	Percicarp cracked, and fruit became rigid	Fruit was mildewed and flowed liquid with bad smell
6	Crack of pericarp increased	Crack of pericarp increased	
7	Fruit emitted liquid with bad smell	Fruit emitted liquid with bad smell	
Rot rate	10%	43%	.90%
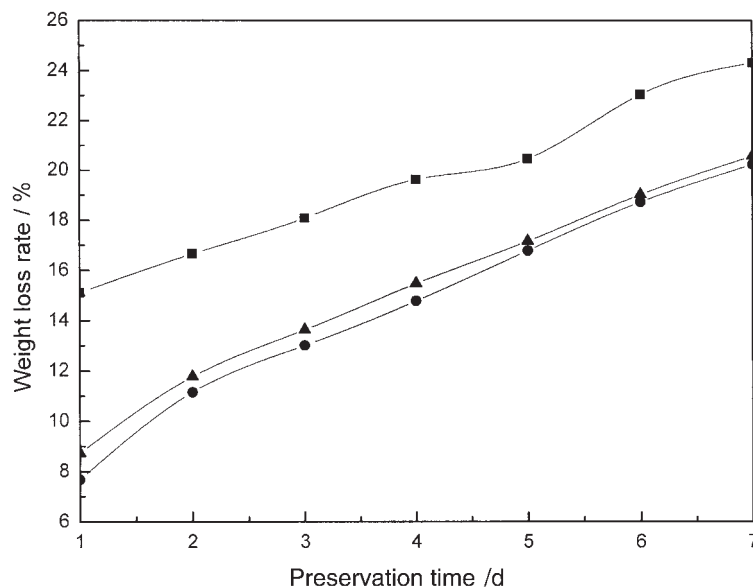
Figure 7 Weight loss rate of lychee dependency on the preservation time: -■-, control group; -▲-, experimental group; -●-, control group (pure KGM film).

dency was that the increase of weight loss rate was gradually sharpened with the increase of preservation time.

Experiments on biological impact of ingestion and bacterial resistant property of the blend should be made in the future. The film should be washed off before eating.

CONCLUSIONS

A series of novel polymer blends were prepared with a mixture of 2 wt % konjac glucomannan and 4 wt % quaternized poly(4-vinyl-*N*-butyl) pyridine (QPVP) in aqueous solution and dried at room temperature for 72 h. There was good miscibility between konjac glucomannan and QPVP when the content of QPVP was less 30% or in excess of 70%, as confirmed by the results of SEM and WXRD. The thermostability and tensile strength of the films in the dry state were reduced with increasing content of QPVP. The maximum value of 12.74% tensile break elongation was reached when the content of QPVP was 30%. Structural analysis indicated that the electrostatic interaction of QPVP and konjac glucomannan impaired the partial hydrogen bond interaction of KGM, which facilitated sliding of the KGM molecular chains or the stretching of the KGM molecular chains. With increasing content of QPVP more electrostatic interaction destroyed the hydrogen bond interaction, which caused phase separation. Experimental results from the films of KGM-2 as a coating preservative with lychee showed that this blend film had water-holding

ability. The fruit weight loss rate and rot rate both decreased. These novel polymer blends could be used as preservative films.

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