

Synthesis and Characterization of Konjac Glucomannan/Poly(Vinyl Alcohol) Interpenetrating Polymer Networks

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ABSTRACT: Novel interpenetrating polymer networks (IPNs) coded as KP were synthesized successfully from poly(vinyl alcohol) (PVA) and konjac glucomannan (KGM) in the presence of glutaraldehyde as a crosslink agent. The transparent IPN films that were 40 μm thick were prepared by means of conventional solvent-casting technique and dried at room temperature for 2 days. The structure and miscibility of the KP films were studied by Fourier transformed infrared spectra, scanning electron microscopy, differential scanning calorimetry, wide-angle X-ray diffraction, and ultraviolet visible spectroscopy (UV-Vis). The results indicated that strong intermolecular interaction caused by crosslink bonding between PVA and KGM occurred in the

IPN films, resulting in wonderful miscibility when the reaction time is 4 h. The tensile strength, elongation at break, and moisture uptake was much higher than that of the pure PVA film, KGM film, and uncrosslinked blend films. In other words, the structure of IPN endowed the films with excellent performance, so the new material has promising applications to food package film and agricultural film because of its biodegradability. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2775–2780, 2004

Key words: konjac glucomannan; poly(vinyl alcohol); interpenetrating polymer networks; biodegradable; crosslinking

INTRODUCTION

Petroleum-based films dominate today's food packaging and agricultural film applications because of their low cost, light weight, high strength, easy processibility, etc. However, most synthetic polymers are not biodegradable. With the rising concerns about environmental issues, particularly the pollutions caused by the nonbiodegradable materials that were widely used in rapid consumer goods, many new biodegradable materials from agricultural natural polymers have been developed.^{1–3}

Interpenetrating polymer networks (IPNs) are a blend of two or more crosslinked polymers that are mutually held together by permanent entanglement.⁴ IPN materials have drawn much attention because of the special properties brought about by the interlocking of polymer chains.⁵ Polyurethane,⁶ acrylic acid ester,⁷ and epoxy resin⁸ are the usual materials for IPNs; however, research on IPN materials from cellulose,⁹ poly(vinyl alcohol) (PVA),^{10,11} etc. also revealed interesting results.

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Konjac glucomannan (KGM), a low-cost polysaccharide consisting of 1,4-linked β -D-mannose and β -D-glucose units in a molar ratio of 1.6 : 1 with a low degree of acetyl groups at the side chain C-6 position and having a molecular weight of 0.67 to 1.9 million on average obtained from the tubers of *Amorphophallus konjac* plants,^{12–14} has been generally used in food, medical, chemical engineering, and other fields because of its unique physical and chemical properties, especially its film-forming ability.¹⁵ In our previous work, we characterized its molecular morphology and chain parameters,¹⁶ gelatin mechanism,¹⁷ and also successfully prepared a composite coating by crosslinking KGM with PVA¹⁸; because of the startling scour resistance (6000 times), the coating has been applied to the paint industry.

Natural polymers often present good biocompatibility, but their mechanical properties are often poor; yet PVA, a water-soluble synthetic biodegradable polymer, is widely used as paper-strengthening, adhesive agent, and painting, and can also be applied to environmentally friendly film materials individually or to blend with natural polymer. However, Xiao et al. reported that the simple blending film of KGM and PVA is immiscible,¹⁹ and we also proved its immiscibility in theory by viscometry.¹⁸ In our latest study, we prepared IPN film by using a crosslinking method by glutaraldehyde as a

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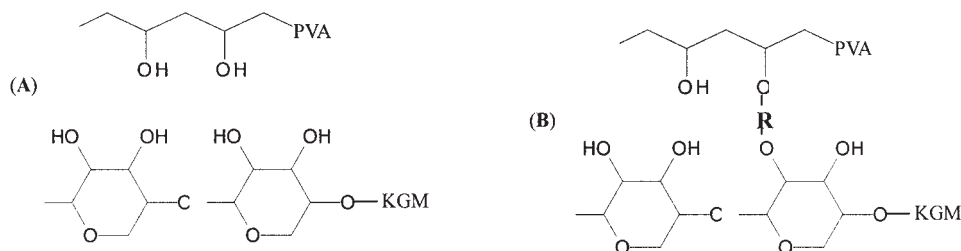


Figure 1 The noncrosslinked (A) and crosslinked (B) structure of KGM and PVA.

crosslink agent based on both of them having enough hydroxyl groups (Fig. 1).

The main purpose of this work was to achieve a deeper insight into the fundamental physical properties of the KGM/PVA IPN films. The morphological structure, thermal stability, and mechanical properties of the IPN films were studied by Fourier transform infrared spectra (FTIR), wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and an electron tensile tester. The relationship between the structure and properties of the IPN films is discussed also.

EXPERIMENTAL

Materials

KGM was extracted and purified from the tuber of *A. konjac* (supplied by Enshi Chuye Konjac Institute, Hubei, China) as follows. Konjac tubers were sliced to about 8 mm in thickness and then dried under heated air at 65°C for about 6 h. The dried sheets were pulverized by a mill. The crude flour was immersed in 50% (v/v) aqueous methanol for 3 h and then dried at 50°C under reduced pressure. Then, the raw konjac flour was extracted with benzene–absolute alcohol (4 : 1 v/v) and trichloromethane–*n*-butanol (Sevag method) five times,²⁰ respectively. The fat- and protein-extracted flour was dissolved with a mixture of distilled water [30% H₂O₂ (5 : 1 v/v)] and heated at 40°C for 20 min; after environmental cooling to room temperature, the hydrosol was centrifuged at 16,000 rpm for 20 min (Himac Centrifuge, Hitachi). Then, acetone was added to the supernatant and stirred. After being filtered with a 120- μ m sieve cloth, the white cottonlike precipitate was squashed and dried by vacuum freeze-dry (Alphal-Z, Germany). Then, the KGM was obtained, and the viscosity–average molecular weight (M_v) of the KGM was determined by viscometry to be 1.01×10^5 according to the Mark–Houwink equation $[\eta] = 6.1 \times 10^{-2} M_w^{0.73}$ at 25°C.¹⁶ The weight-average molecular weight (M_w) of the KGM not treated with H₂O₂ is 1.04×10^6 , determined by using light scattering (LS) [DAWN-DSP multi-angle laser photometer (Wyatt Technology Co., USA)]. We

have also proved that KGM with less molecular weight is in favor of miscibility with PVA (Beijing Organic Chemical Plant, Beijing, China).¹⁸

The PVA was purchased from Beijing Organic Chemical Plant (Beijing, China) and the degree of polymerization (DP) is 1700(100).

Synthesis of KP films

The ratio of [KGM]/[PVA] was pre-given to be 3 : 7 and the weight of crosslink agent glutaraldehyde (Tianjin Fucheng Chemical Agent Plant, Tianjing, China) was 7.8% of the total weight of PVA and KGM via trial test. A three-necked flask was fitted with a stirrer; a thermometer and the third neck were used as a feed port. PVA (70.0 g) was added into the flask until the deionized water (890 mL) in the flask was heated to 50°C and then sequentially heated up to 83°C for about 1.5 h until the PVA dissolved completely. KGM (30.0 g) was plunged into the flask as soon as possible. After about 40 min, the KGM swelled fully and the mixed hydrosol was adjusted to pH 4.5 with 0.1 mol L⁻¹ HCl (Shanghai Chemical Agent Plant, Shanghai, China), and 7.8 g glutaraldehyde was dropped into the flask for 10 min. We controlled the crosslinking reaction at 83°C for different times, which means the reaction time was given as 0, 1, 2, 3, and 4 h, respectively. After neutralizing the reaction system with 1 mol L⁻¹ NaOH (Shanghai Chemical Agent Plant, Shanghai, China) to pH 7, the mixture was degassed and then spread over a glass plate. The transparent films were obtained after drying at room temperature for 2 days. By controlling different reaction times, 0, 1, 2, 3, and 4 h, a series of films coded as KP1, KP2, KP3, KP4, and KP5 were obtained (the reaction time could not be prolonged or else the mixed hydrosol would gelatinize). The pure KGM film and the pure PVA film were coded as KGM and PVA, respectively. The thickness of the films was measured to be about 40 μ m. The films were vacuum dried at room temperature for 3 days and were then used for the measurements.

Characterization of films

The powdered films were blended with potassium bromide and laminated, and their IR spectra were

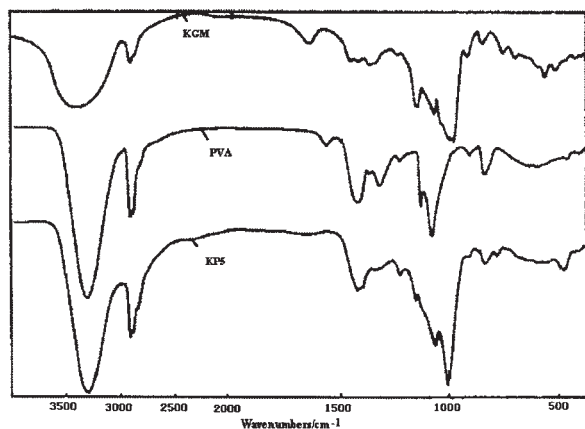


Figure 2 FTIR spectra of the KGM, PVA, and KP5 films.

recorded with a Nicolet (USA) Nexus 470 FTIR spectrometer. Film samples of about 40 μm thickness were coated with gold in 0.1 τ vacuum degree; then, their cross-section morphologies were observed on a Hitachi X-650 SEM. The X-ray diffraction (XRD) patterns of the films were recorded with a Rigaku (Japan) D/max-IIB X-ray diffractometer and used a $\text{CuK}\alpha$ target at 30

kV and 50 mA. The diffraction angle ranged from 60 to 3°. The crystallinities of the films were calculated by²¹

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

where F_c and F_a are the areas of crystal and noncrystalline regions, respectively. The DSC of the film samples with a weight about 20 mg was performed by a DSC 822e/400 (Mettler-Toledo, Switzerland) under a nitrogen atmosphere with a flow capacity of 25 mL/min from 0 to 400°C at a heating rate of 10°C/min. The percentage of light transmittance (T) of the films of about 40 μm thickness in the wavelength range of 300–700 nm was measured by using a Shimadzu UV-160A (Japan) spectroscope. The tensile strength (σ_b) and breaking elongation (ϵ_b) of the films were measured on an electron tensile tester CMT-6503 (Shenzhen Sans Test Machine Co., Ltd., China) with a tensile rate of 100 mm/min according to the Chinese standard method (GB4456-96).²² The moisture uptake of the films was calculated as

$$W = [(W_l - W_0) / W_0] \times 100\%$$

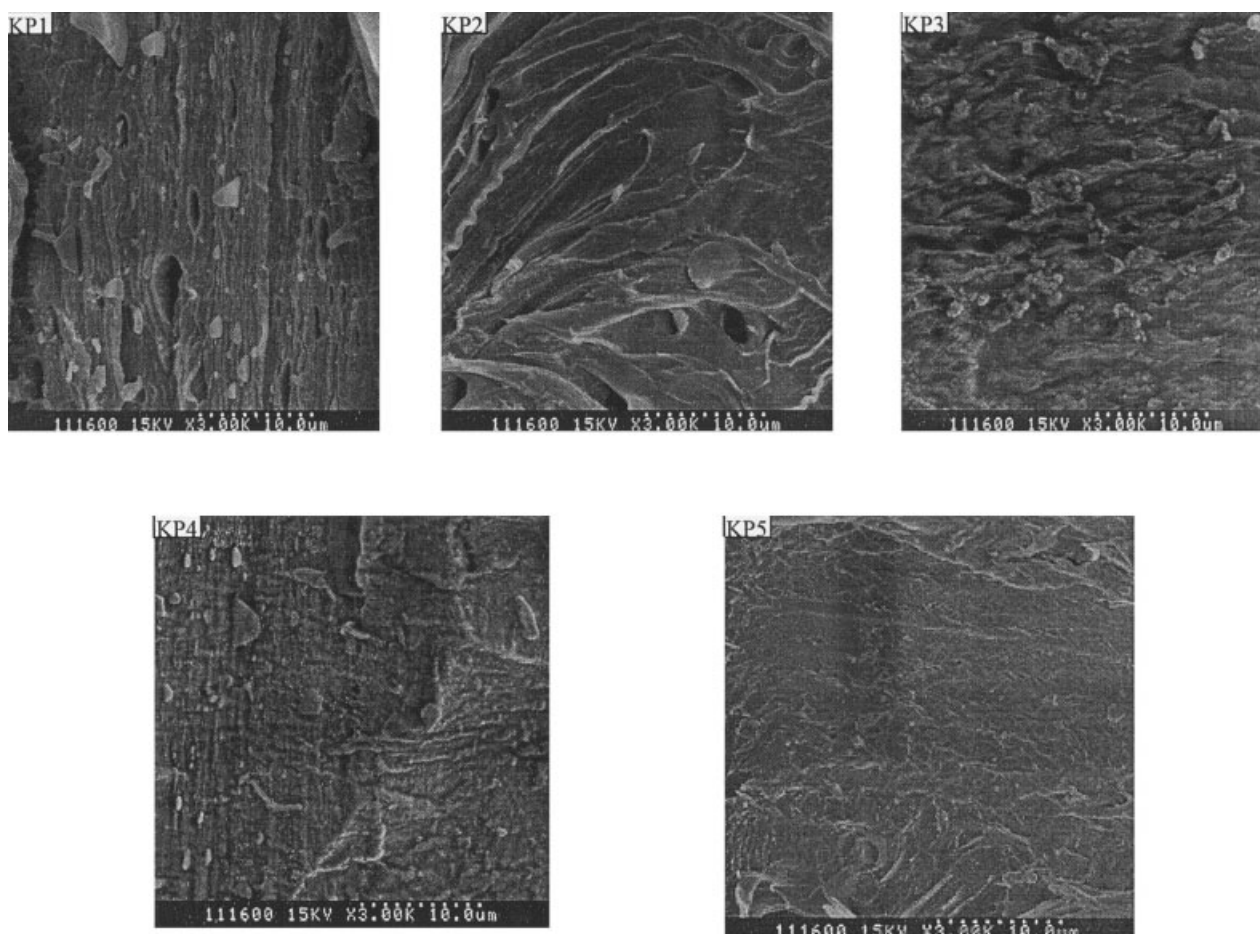


Figure 3 SEM photographs of the cross section for the KP films.

where W is the moisture uptake, and W_1 and W_0 are the weights of the films in soaked and dried states, respectively. The films were dried at 45°C for 3 days before measurement.

RESULTS AND DISCUSSION

Structure and miscibility

The IR spectra of the films of KGM, PVA, and KP5 are shown in Figure 2. The absorption band at 3401 cm^{-1} and the peaks at 2903 cm^{-1} are assigned to the stretching of —OH groups and C—H of methyl in KGM; the characteristic absorption bands of mannose in KGM appeared at 874 and 808 cm^{-1} .¹⁷ The broad peak at 1637 cm^{-1} and the cluster peaks in the range of 1350–1450 cm^{-1} are assigned to stretching of C—O of associate hydroxy group and the deformation vibration of —CH₂ in the —CH₂OH group in KGM, respectively. The absorption band at 3342 cm^{-1} and the peaks at 2941–2908 cm^{-1} are assigned to the stretching of —OH groups and C—H of methyl in PVA. The broad peak at 1571 cm^{-1} and the cluster peaks in the range of 1236–1425 cm^{-1} are assigned to stretching of C—O of associate hydroxy group and the deformation vibration of —CH₂ in the —CH₂OH group in PVA, respectively. Compared with the spectrum of pure KGM and PVA, the following notable changes have taken place in KP5 after crosslinking: (1) The stretching of —OH groups shifts to 3330 cm^{-1} , and the peak shape and width are similar to that of PVA, indicating that the hydrogen bond structure of is also similar to that of PVA; however, due to the process of crosslink reaction and blend, the new hydrogen bond between KGM and PVA occurred and shifted to a lower wave number. (2) The stretching of C—O of associate hydroxy at around 1600 cm^{-1} disappeared, which intended for the density of hydroxy group to decrease sharply coupled with the process of crosslink reaction. In addition, the deformation vibration of —CH₂ also shifted to 1243–1432 cm^{-1} and obviously broadened. (3) Distinct from all of the absorption of both KGM and PVA, three characteristic peaks of acetal occurred at 1166, 1080, and 1024 cm^{-1} , which further indicated that strong intermolecular interaction between PVA and KGM exists in KP5 owing to crosslink bonding.

Although crosslink reaction has occurred in KP, it still is difficult to decide whether the IPNs were formed. Figure 3 showed the SEM photographs of the cross section of the KP1, KP2, KP3, KP4, and KP5 films. When KGM and PVA were a simple blend (KP1, crosslink reaction time was 0), the cross-section morphologies of the film KP1 were an obvious phase separation, just as reported of Xiao's.¹⁹ The phase separation decreased in the company of an increase of the crosslink reaction time (KP2, KP3, KP4). When the reaction time was 4 h (KP5), the cross-section mor-

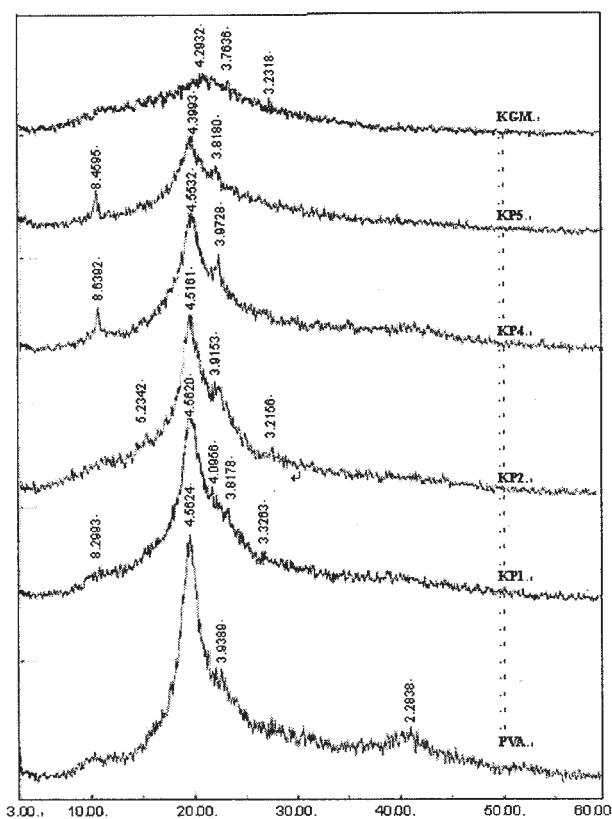


Figure 4 WAXRD diffraction patterns of the KP1, KP2, KP4, KP5, KGM, and PVA films.

phologies of the film KP5 were homogeneous and compact, suggesting a wonderful miscibility and strong intermolecular interaction between PVA and KGM. The crosslink bond was attributed with the forming of IPNs.

XRD is another important method to characterize the miscibility of two or more polymers; generally, when the crystalline component and the noncrystalline component in a composite material have good miscibility, its crystallinity is lower than the individual crystalline component. The WAXRD patterns of the KP1, KP2, KP4, KP5, KGM, and PVA films are shown in Figure 4. A new crystal peak at 2θ values of 22.1° appeared for KP2 when the reaction time was 1 h; in addition, another new crystal peak (10.6°) appeared for KP4 when the reaction time was 3 h. The intensity of both new crystal peaks became stronger and at the same time the crystal peaks at 20.5° of PVA became weaker in the company of increasing the reaction time. The crystallinities also decreased with increasing the reaction time (KP1 > KP2 > KP4 > KP5), and the change in crystallinity was attributed to the strong interaction in KP films. The coexistent appearance of new crystal peak, decrease in crystallinity, and changes in original crystal peaks indicated that interpenetrate reaction between KGM and PVA has occurred, and it would result in the changes of the physical properties of IPNs films observed later.

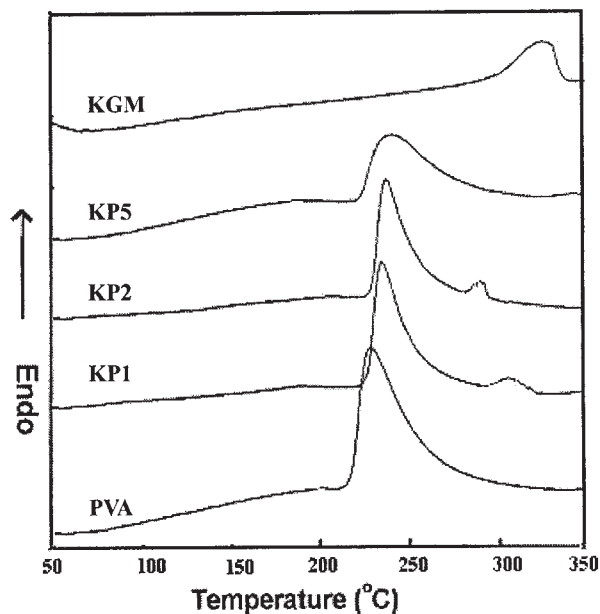


Figure 5 The DSC curves of the KP1, KP2, KP5, KGM, and PVA films.

Figure 5 shows the DSC curves of the KP1, KP2, KP5, KGM, and PVA films. PVA reveals a relatively large and sharp melting endothermic peak at 227°C, while a faintish melting endothermic peak of KGM occurred at around 322°C. On the other hand, broad melting endothermic peaks of PVA and KGM segments, caused by a crosslinking reaction and IPN formation, appeared at around 235 and 308°C in KP1; closing up each other to 239 and 288°C in KP2, the endothermic curve of KP5 segments became broader and the peak only shifted to a higher temperature at around 241°C. In general, the glass-transition temperature (T_g) of a crosslinked polymer is difficult to detect by using the ordinary DSC technique; in this article, we did not give the exact value of T_g , but in view of the changes of shape, number, and location of the

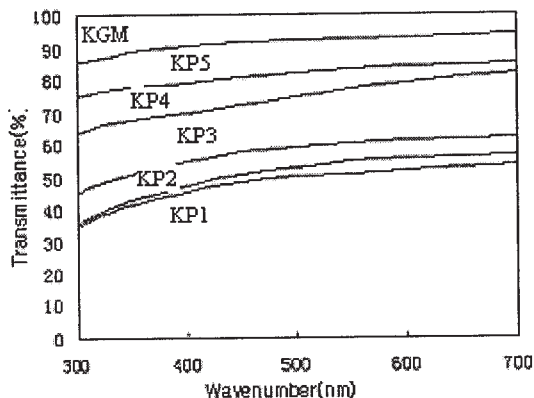


Figure 6 The optical transmittance of KGM and its blend films.

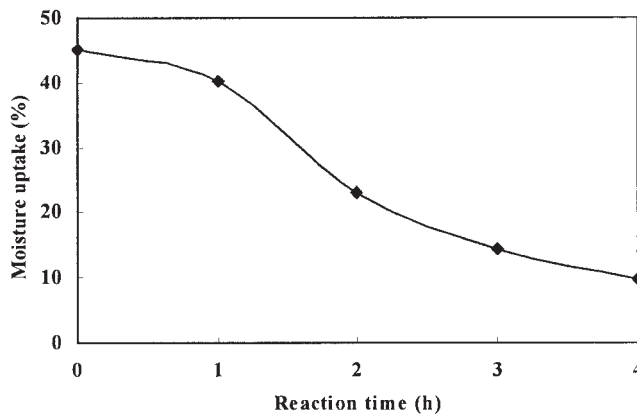


Figure 7 Moisture content of the KP films a function of reaction time.

endothermic peaks in DSC curve, it still has considerable value to give proof of the strong intermolecular interaction and the IPNs. This result supports the conclusion of miscibility between KGM and PVA in the films and was in good agreement with those from SEM, FTIR, and WXR. D.

Generally, transparency of films is an auxiliary criterion to judge the miscibility of two or more polymer-mixed films.²³ The optical transmittancy ($T\%$) dependence of the wavelength (λ) for the KP and KGM films is shown in Figure 6. The best optical transmittancy of KP5 IPN film at ultraviolet-visible wavelengths (UV-Vis; 200–700 nm) was observed among all of the KP films, indicating the best miscibility between KGM and PVA. The optical transmittancy of the KP films increased with the reaction time, indicating the process of interpenetrating reaction.

In view of FTIR, SEM, WAXD, DSC, and UV-Vis analyses of the KP, KGM, and PVA films, it can be concluded that the IPNs were synthesized because of the crosslink bond between KGM and PVA.

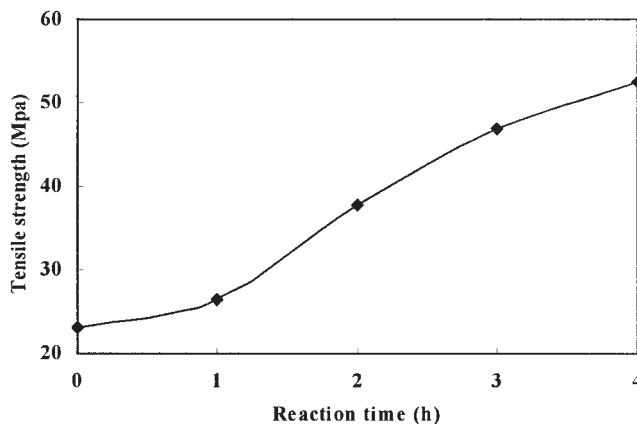


Figure 8 The tensile strength of the KP films as a function of reaction time.

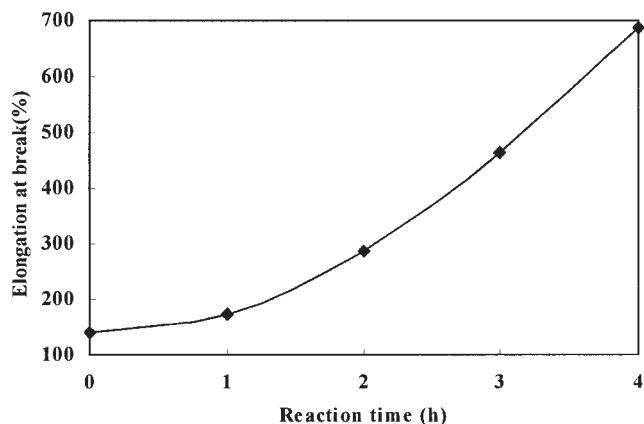


Figure 9 The elongation at break of the KP films as a function of reaction time.

Properties of the IPN films

The moisture content of the KP films as a function of reaction time is shown in Figure 7. The water absorbability of the KP films decreased with the increase of reaction time. Taking aggressive and chemical structures into account, a lot of hydrophilic hydroxy groups on both PVA and KGM molecular chain were blocked up to hydrophobicity and exhibited the homogeneous and compacted morphological structure. As for the effect of the interactions of hydrogen bonds in the KP films, it is worth further study.

The study of mechanical properties is of primary importance for determining the performance of materials, especially that of film materials. The tensile strength and elongation at break of the films were plotted as functions of the reaction time, as shown in Figures 8 and 9, respectively. The crosslink reaction of KGM and PVA was effective in improving the mechanical properties of the KP films. The tensile strength of the KP4 and KP5 was higher than that of pure components films (KGM, 32.3 MPa; PVA, 35.5 MPa) and reached a maximum value at a reaction time of 4 h. However, the simple blend of KGM and PVA (KP1) showed minimal value at even much lower value than the pure films. The remarkable increase in tensile strength of IPN films indicated that intermolecular interactions through crosslink bond occurred in the films and the new IPNs brought about the new property.

In general, IPNs often have excellent elasticity. Figure 9 shows that the elongation at break also increased with the increase of reaction time, which might be attributed to the interpenetrating polymer networks. Maybe the occurrence of hydrogen bonding interactions in the films could be taken into account.

CONCLUSION

A series of KP films from KGM and PVA was prepared by crosslink reaction in conventional solvent-casting technique. With an increase of the reaction time to 4 h, the IPNs were synthesized successfully. FTIR confirmed the formation of crosslink bonds and SEM, WAXD, DSC, and UV-Vis proved the information of the interpenetrating networks between KGM and PVA. As a result of the changes of chemical structures and aggressiveness, the transparent films brought out greatly enhanced mechanical properties and moisture uptake, making it possible to apply the IPN film to food packaging and agricultural film.

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