

Blend Films from Chitosan and Konjac Glucomannan Solutions

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ABSTRACT: Blend films were prepared by blending 7 wt % konjac glucomannan (KGM) aqueous solution with 2 wt % chitosan (CH) in acetate solution and dried at 40°C for 4 h to obtain the transparent films. Their structure and properties were studied by infrared (IR), wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). Crystallinities of the blend films decreased with the increase of konjac glucomannan. The thermostability, tensile strength, and breaking elongation of the blend films in dry state were obviously higher than those of both konjac glucomannan and chitosan films. Tensile strength of the dry blend film achieved 73.0MPa when the weight ratio of chitosan to konjac glucomannan was 7:3. The structure analysis indicated that there is a strong interaction between konjac glucomannan and chitosan resulted from intermolecular hydrogen bonds. The water solubility of the blend films was improved by blending with konjac glucomannan, so they have promising applications to soluble antiseptic coating of pills. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 509–515, 2000

Key words: konjac glucomannan; chitosan; blend film; miscibility; hydrogen bonds

INTRODUCTION

Nowadays, the widespread use of synthetic polymer films has resulted in serious environmental pollution problems. The study and exploitation on polymer film materials from renewable resources has drawn more and more attention in view of their environmental friendliness to the earth. In order to improve the performance of the individual natural polymer films, many blend films, prepared by using a solution blend, such as poly(vinyl alcohol)–chitosan,^{1,2} poly(vinyl alcohol)–silk fibroin,³ cellulose–alginate,⁴ chitosan–cellulose,⁵ and cellulose–konjac glucomannan⁶ have been reported. The thermostability and mechanical prop-

erties of these materials were improved, owing to the strong interaction between the two kinds of macromolecules.

The excellent mechanical properties in dry state, water solubility, body compatibility, and biodegradability are vital to medical materials. Blending is an effective method to improve the performance of films. Generally, when the individual components used to blend are compatible, the blend films can form a homogeneous structure and show better physicochemical properties than the individual components. Konjac glucomannan (KGM) is a polysaccharide, whose main chain is composed of B-1,4 pyranoside, bond-linked mannose, and glucose.^{7,8} It has been long used as health food.⁹ Chitin, whose content is only inferior to that of cellulose in nature, is a natural polymer with a repeating unit of B-1,4 linked 2-acetamino-2-deoxy-B-D-glucose.¹⁰ Chitosan (CH) is the deacetylated product of chitin and has dis-

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tinct functional groups that can be easily modified to give good body compatibility and high biological activity.¹¹ It has been widely used as metal ion adsorption agents for polluted water, food additives, and biomedical materials.¹² However, the water insolubility and brittle property in the dry state of chitosan limited its application to biological and medical areas. This article is aimed at researching on an approach to modify chitosan by blending with konjac glucomannan to improve its mechanical properties in the dry state and water solubility. The morphological structure, miscibility, mechanical properties, and swelling capacity of the blend films were studied by infrared (IR), wide-angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron microscope (SEM), electron tensile test, and swelling test. The relationship between the structure and their physicochemical properties is discussed.

EXPERIMENTAL

Preparation of Blend Films

Konjac glucomannan was extracted and purified from the tuber of *amorphophallus konjac* (supplied by Zhuxi Konjac Institute, Hubei, China) as follows. Konjac tubers were sliced to 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 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 added and stirred. After filtered with 140m 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, a predetermined amount of 1g mL KAl(SO₄)_{0.12}H₂O was added and centrifuged under 8000 r/min for 30 min. The supernatant was added with adequate isopropanol and stirred, then filtered with a 140m sieve cloth. The white precipitate was dried at 30°C under a nitrogen atmosphere for 12 h, and the powdered konjac

glucomannan was obtained. Chitosan was prepared from chitin (purchased from Nanxing Chitin Ltd. Co., Suixi, Guangdong, China) by the method of Mima. et al.¹³ Its degree of deacetylation was measured to be 81% by the method of Nakajima.¹⁴

Chitosan was dissolved in a 2-wt % acetate acid water solution to prepare a concentration of 2 wt % solution (I). Konjac glucomannan was dissolved in deionized water, and the insoluble residue was filtered out to a concentration of 7 wt % (II). A mixture of I and II was stirred energetically and degassed, then was spread over a glass plate. 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 CH-KGM1, CH-KGM2, CH-KGM3, CH-KGM4, and CH-KGM5, were prepared, respectively. The films obtained from pure chitosan and konjac glucomannan were coded as CH-0 and KGM-0.

Characterization of Films

The powdered films were blended with potassium bromide and laminated, and their IR spectra were recorded with a Nicolet (USA) 170SX Fourier transform infrared (FTIR) spectrometer. Film samples of about 100 μm thickness were coated with gold in 0.1τ vacuum degree, then their surface morphologies were observed on a ISI-SX-40 scanning electron micrograph (SEM). The X-ray diffraction (XRD) patterns of the films of about 80 μm thickness were recorded with a Rigaku (Japan) Dmax-II X-ray diffractometer and used a CuKα target at 40 kV and 20mA. The diffraction angle ranged from 45 to 5°. The crystallinities of the films were calculated by the following¹⁵:

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

where F_c and F_a are the areas of crystal and noncrystalline regions, respectively. The TGA and DTA of the film samples with 1 mm length and 1 mm width were performed by a PRT-2 TGA–DTA thermobalance (Beijing Optical Instruments Factory, China) under a nitrogen atmosphere with a flow capacity of 30 mL min from 5 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 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 experi-

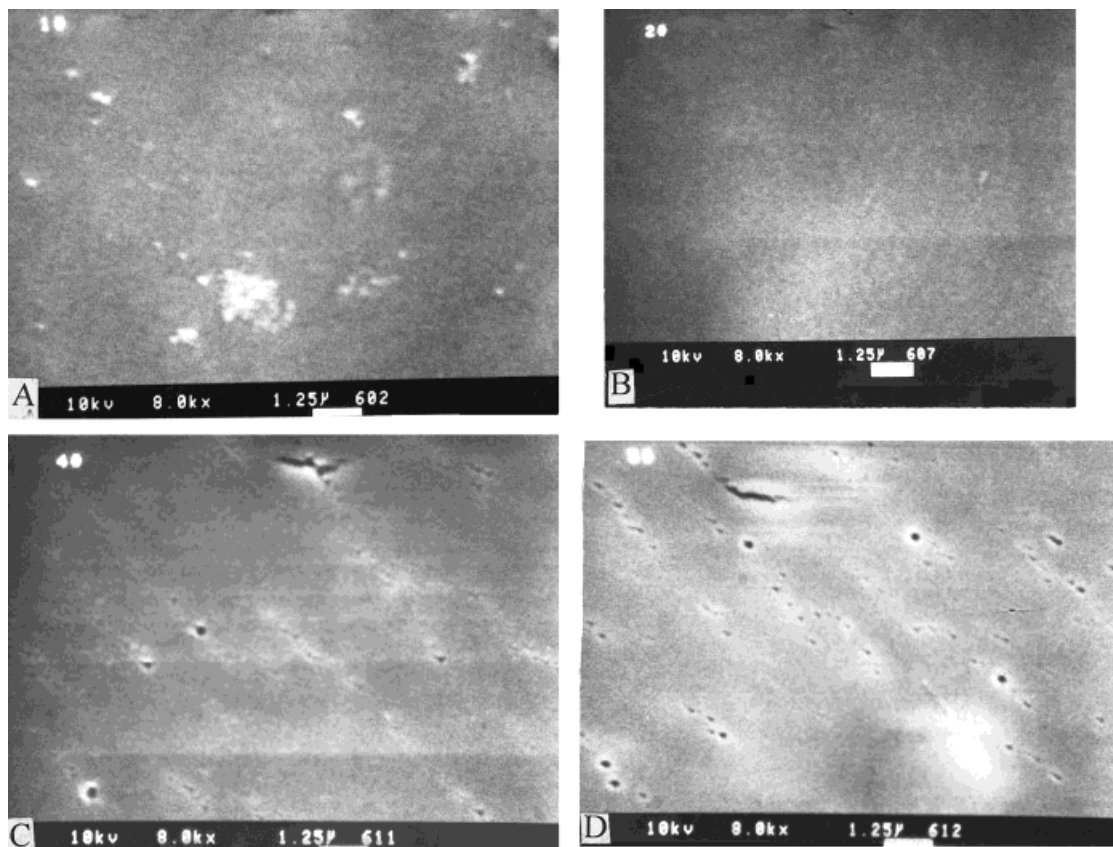


Figure 1 SEM photographs of the films of (A)KGM-0, (B)CH-KGM2, (C)CH-KGM3, and (D)CH-0.

mental temperature and relative humidity were 5°C and 47%, respectively. The degree of swelling (Q_w) of the films were measured by the following²:

$$Q_w = (w_{\text{wet}} - w_{\text{dry}})/w_{\text{dry}}$$

where w_{dry} and w_{wet} are the weight of dry film and wet film obtained by immersing in deionized water for 10 min. The films were dried at 110°C for 2 h before measurement. The percentage of light transmittance (T) of the films in the wavelength range of 200–800 nm was measured using a Shimadzu (Japan) UV-160A spectroscope.

RESULTS AND DISCUSSION

Miscibility

The scanning electron micrographs of the films are shown in Figure 1. The blend film CH-KGM2 showed a smooth and homogeneous surface mor-

phology, suggesting high miscibility and blend homogeneity between chitosan and konjac glucomannan at the composite ratio of chitosan to konjac glucomannan to 7 : 3 by weight. The homogeneous background with stripes was found from the SEM photograph of CH-KGM3, indicating that the miscibility decreased with the increase of konjac glucomannan.

The optical transmittancy ($T\%$) dependence of the wavelength(λ) for the films are shown in Figure 2. Generally, transparency of films is an auxiliary criterion to judge the miscibility of blend films.¹⁶ In Figure 2, the best optical transmittancy of CH-KGM2 at visible wavelengths (300 to 800 nm) was observed, indicating the best miscibility between chitosan and konjac glucomannan. The optical transmittancy of the blend films decreased with the increase of konjac glucomannan, indicating the decrease of miscibility. This is in good agreement with the results from SEM. Interestingly, the transmittancies of the blend films and CH-0 film were

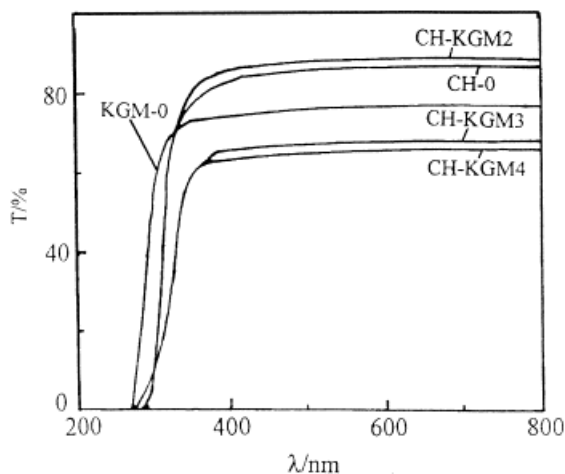


Figure 2 The percentage of light transmittance (T) dependence of the wave number λ for the films.

almost zero at 200–300 nm, showing that they can screen ultraviolet rays.

The IR spectra of the films of KGM-0, CH-0, CH-KGM2, CH-KGM3, and CH-KGM4 are shown in Figure 3. The stretching peaks of C—H of methyl at 2920 and 2885 cm^{-1} and of the carbonyl at 1730 cm^{-1} are assigned to the aceto groups in KGM¹⁷; the characteristic absorption bands of mannose in KGM appeared at 876 and 808 cm^{-1} . The absorption band at 3400 cm^{-1} is assigned to the stretching of N—H groups bonded to —OH in chitosan; the peaks at 1570 and 1256 cm^{-1} are assigned to the characteristic bending absorption band of amino group and the stretching of acrylamide III.¹⁸ For the blend films, the stretching of carbonyl at 1730 cm^{-1} of KGM disappeared; and the stretching of intramolecular hydrogen bonds at 1647 cm^{-1} in KGM coupled and shifted to around 1567 cm^{-1} , suggesting that the new hydrogen bonds between chitosan and konjac glucomannan molecules in the blend films occurred. In the spectra of blend films, the disappearance of the intensive band at 1082 cm^{-1} appears clearly for pure chitosan, which means that an interaction between konjac glucomannan and chitosan has occurred in the blend films.¹⁹ Furthermore, the absorption band around 3400 cm^{-1} broadened and shifted to a lower wave number with the increase of konjac glucomannan, indicating the gradual increase of intermolecular hydrogen bonds between chitosan and konjac glucomannan. Based upon this evidence, it can be concluded that blend miscibility was due to the formation of intermolecular hydrogen bonds between —OH and —NH₂ groups in chitosan and —OH and —COCH₃ groups in konjac glucomannan.²

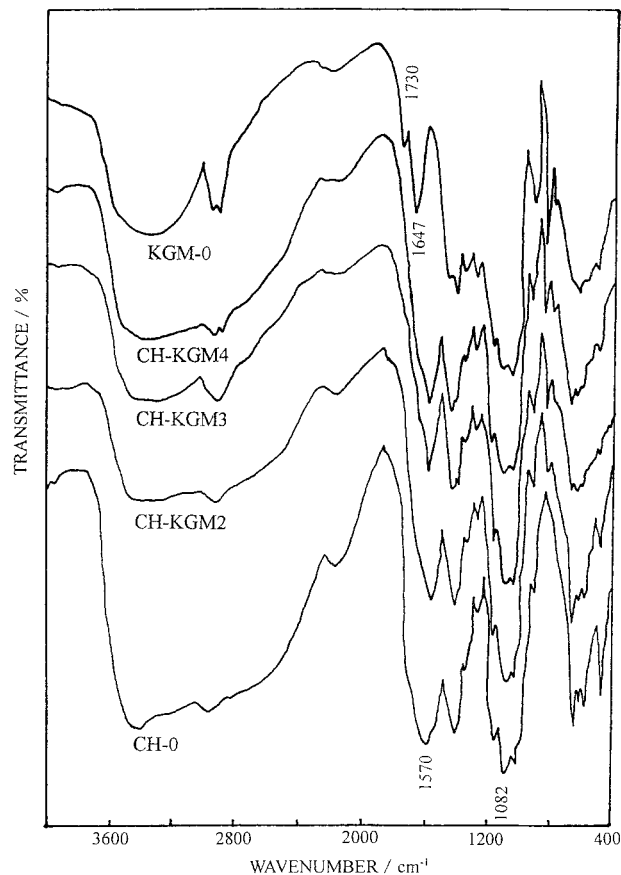


Figure 3 IR spectra of the films.

The XRD patterns of the blend films are shown in Figure 4. The crystallinities of CH-0, CH-KGM2, CH-KGM3, CH-KGM4, and KGM-0 were 44, 30, 16, 11, and 10%, respectively. We can

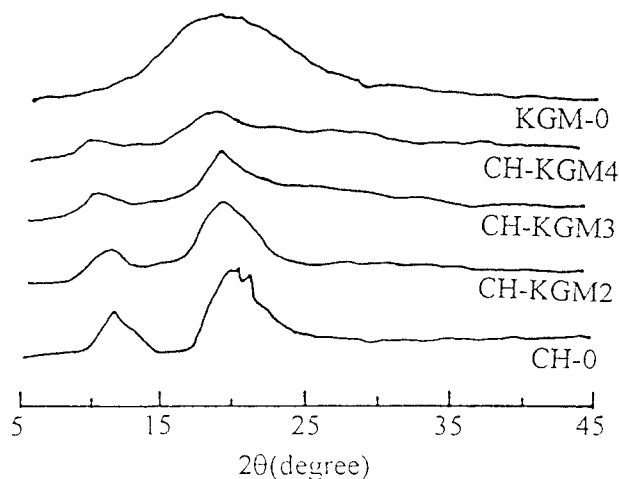


Figure 4 X-ray diffraction patterns of the films.

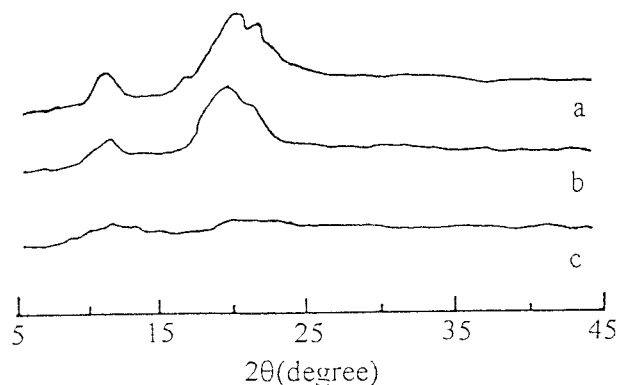


Figure 5 X-ray diffraction patterns of the film CH-KGM2 dried at (a) ambient temperature and (b) 40 and (c) 110°C.

recognize two crystal peaks at around $2\theta = 11.6$ and 20° in the XRD pattern of CH-0. The pure konjac glucomannan film shows a noncrystalline state and only has a very broad peak around $2\theta = 19^\circ$. With the increase of konjac glucomannan, the diffraction peak corresponding to $2\theta = 11.6^\circ$ of CH-0 becomes gradually lowered, and the diffraction angle deviated farther and farther from 11.6° accordingly. The same regularity can be drawn in regard to the second diffraction peak around $2\theta = 20^\circ$. It is obvious that the presence of interaction between konjac glucomannan and chitosan prevents or disturbs chitosan from crystallization by comparison with the diffraction pattern of CH-0 with that of blend films.⁵

The XRD patterns of the blend film CH-KGM2 dried at different temperatures are shown in Figure 5. Unlike the regularity with which the thermal or annealing treatment result in an increase in the crystallinity of cellulose,²⁰ the blend film dried at 110°C shows little crystallization; but the films dried at ambient temperature (about 1–3°C) and 40°C show no sharp discrepancy in crystallinity, which were 34 and 30%, respectively. This supports the conclusion that relative good miscibility exists between chitosan and konjac glucomannan.

Thermal Stability

Figure 6 shows the TGA thermograms of the films of CH-0, CH-KGM2, CH-KGM3, CH-KGM4, and KGM-0. The greatest weight loss points of the films of KGM-0 and CH-0 at 324 and 310°C were attributed to the disintegration of intramolecular interaction and the partial breaking of the molecular structure.²¹ The blend films, however, show

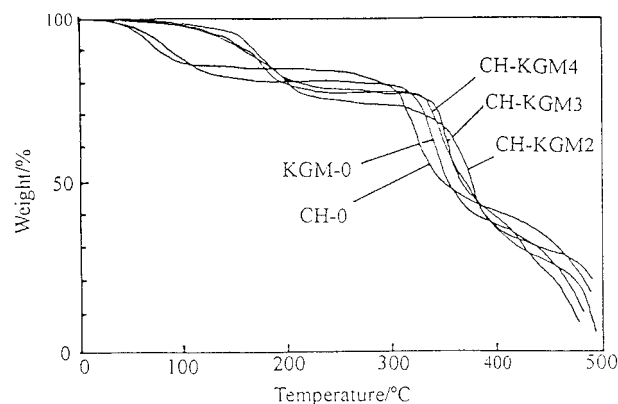


Figure 6 TGA thermograms of the films.

better thermostability than the films of CH-0 and KGM-0 in that the points of maximum weight loss rate corresponded to higher temperatures. The thermostability of the membranes was ordered as: CH-KGM2 (345°C) > CH-KGM3 (336°C) > CH-KGM4 (330°C). It implies that the thermostability of the blend films is enhanced due to the introduction of konjac glucomannan.

The DTA thermograms of the films are shown in Figure 7. The films all show endothermic peaks at the range of 60–90°C, corresponding to the dehydration in the films. All the films show endothermic peaks around 350°C, which resulted from

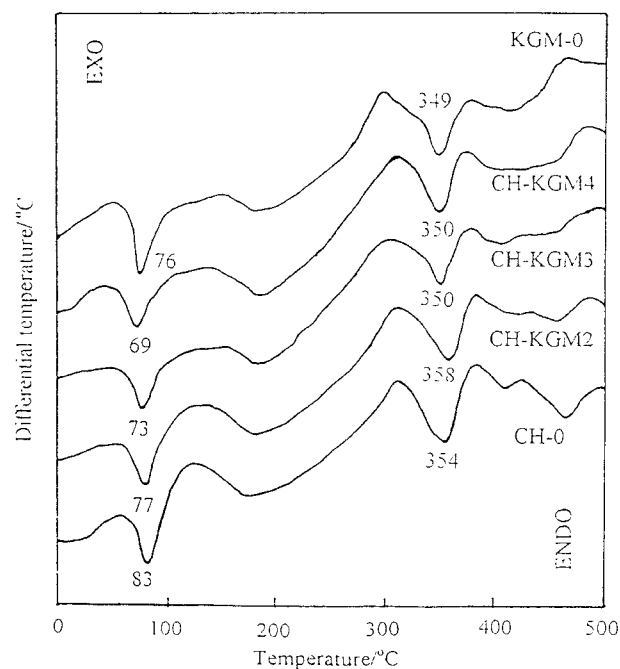


Figure 7 DTA thermograms of the films.

the greatest thermal degradation of the films. With the increase of chitosan, the endothermic peaks at 350°C of the blend film increased gradually. The thermostability of blend film CH-KGM2 was higher than that of the films of chitosan and konjac glucomannan indicated the strong interaction between two kinds of molecules.

Mechanical Properties

The tensile strength (σ_b) and breaking elongation (ε_b) dependence of the content of konjac glucomannan (w_{KGM}) are shown in Figure 8. The tensile strengths of the blend films with w_{KGM} from 10 to 70% were higher than that of both CH-0 and KGM-0, and the maximum value appeared at $w_{\text{KGM}} = 30\%$ achieved 72.5 MPa. The alteration of breaking elongation expressed a tendency similar to that of tensile strength and reached the maximum at $w_{\text{KGM}} = 30\%$. The conclusion that can be drawn is that the blend of chitosan with konjac glucomannan has considerably enhanced the mechanical properties of the blend films in the dry state; and the enhancement of tensile strength may be due to the hydrogen bonding between chitosan and konjac glucomannan, as described in the former section, according to Miya et al.'s interpretation of the PVA–chitosan blend.²²

Water Swelling Property

The degree of swelling (Q_w) of the films are shown in Figure 9. It is obvious that all the blend films have a higher degree of swelling than CH-0. Furthermore, the degree of swelling of the films increased with the increase of konjac glucomannan.

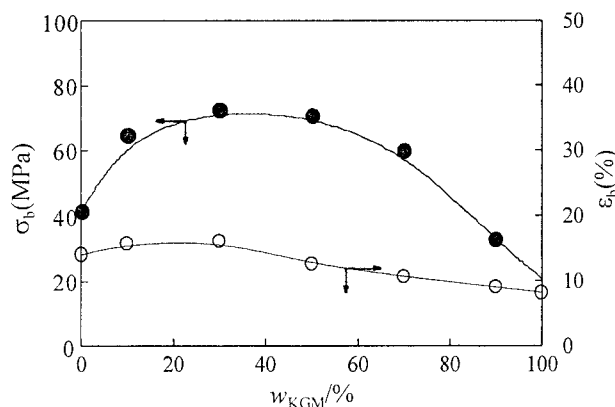


Figure 8 Tensile strength (●) and breaking elongation (○) dependence of the content of konjac glucomannan (w_{KGM}) in the films.

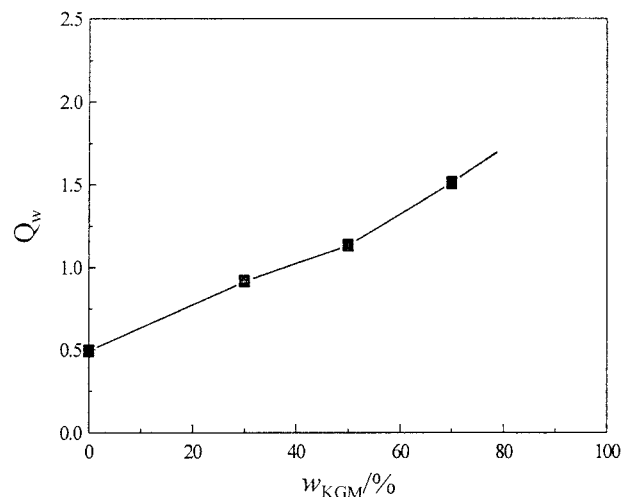


Figure 9 Degree of swelling (Q_w) dependence of the content of konjac glucomannan (w_{KGM}) in the films.

Regrettably, the degree of swelling of the KGM-0 film could not be measured because konjac glucomannan was easily dissolved after immersion in water. The higher degree of swelling of the blend films indicated that the water solubility of chitosan was improved by blending with konjac glucomannan. Therefore, the blend films have promising application to the coating of pills in the control release area, where water solubility is important.

CONCLUSION

A series of transparent blend films were prepared by blending 2-wt % chitosan acetate water solution with 7-wt % konjac glucomannan aqueous solution according to predetermined ratios and drying at 40°C on glass plates for 4 h. The mechanical properties in dry state, thermostability, and water swelling capacity were obviously higher than those of chitosan film. The mechanical properties and thermostability achieved their maximum when the weight ratio of chitosan to konjac glucomannan was 7 : 3. The crystallinity of the blend films decreased with the increase of konjac glucomannan. The good miscibility between chitosan and konjac glucomannan was confirmed by the results of SEM and IR and WAXD. The strong intermolecular hydrogen bonds existing between the amino groups of chitosan and the hydroxyl groups of konjac glucomannan in the blend films result in the enhancement of mechanical properties and thermal stability.

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