

Study on Properties and Aggregation Structures of Deacetylated Konjac Glucomannan/Chitosan Hydrochloride Absorbent Blend Gel Films

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ABSTRACT: A series of novel blend films of deacetylated konjac glucomannan (d-KGM) and Chitosan hydrochloride (CHI·HCl) were prepared successfully by using the solvent-casting technique with different blending ratios of the two polymers. The miscibility and aggregation structure of the blend films were studied by Fourier transform infrared spectroscopy, wide-angle X-ray diffraction and scanning electron microscopy. The results indicated that the blend system of d-KGM and CHI·HCl had a conditional miscibility. A new crystal occurred and hydrogen-bonding interaction was strengthened when the CHI·HCl content in the blend films was 40%. The effects of deacety-

lation degree of KGM, acids (the solvent Chitosan dissolved in), temperature, and the mix ratio on the swelling behavior of the blend films were also studied. The blend film KC3 (CHI·HCl content in the blend films was 30%) had not only the highest equilibrium swelling degree (26 times) but also the highest tensile strength, and it could be regarded as a potential absorbent film material. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1503–1509, 2010

Key words: deacetylated konjac glucomannan; chitosan; water-absorbing ability; miscibility; blend film

INTRODUCTION

Recently, the biodegradable and edible polysaccharides have been gradually and extensively used in the industry of food packaging materials.^{1,2} The application of polysaccharide packaging material in dehumidification and moisture-retarding is attributable to its good water-absorbing ability. However, because of the poor mechanical property, it is restrictively applied in the food packaging, such as packaging films, especially backing diaphragm.

Konjac glucomannan, whose main chain consists of β -1,4 linked mannose and glucose units with a low degree of acetyl groups,^{3–5} is a high molecular weight water soluble nonionic heteropolysaccharide found in tubers of the *Amorphophallus konjac* plant. When konjac flour is dissolved in alkaline coagulant (such as calcium hydroxide, sodium or potassium carbonate), the deacetylation reaction occurs and a thermally stable gel, which is the basis of many oriental traditional foods,^{6–8} can be formed. Alkali gelation is believed to be a consequence of the

formation of associations between acetyl free regions of the backbone.

Chitosan is the most abundant natural polysaccharide containing nitrogen. It is the *N*-deacetylated derivative of chitin, a cationic polysaccharide composed of β -D-glucosamine and *N*-acetyl- β -D-glucosamine residues with 1,4-linkages.^{9,10} Chitosan has desirable biological properties, being biodegradable, biocompatible, nontoxic, bioabsorbable, antibacterial, and having gel-forming ability at low pH.^{11–13} It has been used as artificial skin to accelerate wound and ulcer healing, and as a biocompatible vehicle for sustained release of drug.¹⁴

Several papers reported blend films of Konjac glucomannan (KGM) and other natural or synthetic polymers, such as chitosan,¹⁵ corn starch,¹⁶ and cellulose.^{17,18} Majority of these blend films are water-soluble despite their absorbency. Thus the blend films will dissolve on the food surface when exposed to the cold and fresh food in long term, which leads to the negative influence on sensory quality and utilization. Similar to super absorbent polymer, d-KGM film (the d-KGM powder can be formed through being deacetylated with alkaline ethanol as solvent to a certain degree) is of good water absorbance and insolubility. However, it is natural, nontoxic, and biodegradable.

In this study, the d-KGM was prepared by a novel method and the blend films of d-KGM with CHI·HCl were prepared by using the solvent-casting

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technique. The deacetylation degree of KGM, acids (the solvent Chitosan dissolved in), the temperature of the oven, and the mix ratio effect on the swelling behavior of the blend films was investigated. The aim of this article is to explain the structure, miscibility, and mechanical property of blend films by FTIR, WXR, SEM, and mechanical tests. The blend films of high-absorbent, safe, nontoxic, antibacterial activities were screened out as a potential use for packaging material in food industry, especially chilled meat pallet package.

MATERIALS AND METHODS

Materials

KGM was prepared as our previous work.¹⁹ The viscosity-average molecular weight (Mv) of the konjac glucomannan was determined by viscometry to be 1.3×10^6 according to the Mark-Houwink equation $[\eta] = 5.96 \times 10^{-2} Mv^{0.73}$ at 25°C.

The Chitosan (CHI) was purchased from Zhejiang Jinke Biochemistry Co. The degree of deacetylation was 86.40% and the viscosity-average molecular weight (Mv) was 7.0×10^5 .

Preparation of d-KGM with different degree of deacetylation

Preparation of d-KGM powder was done by dispersing definite quantity KGM powder in 50%(v/v) aqueous alcohol, stirring with water-bathing constant temperature vibrator (WBCTV) at speed 1550 rpm for 30 min at 50°C, adding the desired sodium carbonate (0.1 g/mL) into samples and holding samples with speed 1550 rpm for 24 h at 50°C. And then, it was allowed to cool, precipitated with ethanol, filtered, thoroughly washed with alcohol and dried in a vacuum at 50°C. Additionally, d-KGM with different degree of deacetylation were coded as d1, d2, d3, d4, and d5 used for the subsequent analysis.

Determination of degree of deacetylation (DD)

Five grams of the d-KGM powder and 250 mL of 50% aqueous alcohol were mixed in a 500 mL conical flask to determine the degree of deacetylation in the d-KGM samples. First, the mixed suspension stirred with WBCTV at speed 1550 rpm for 30 min at 30°C, subsequently, cooled down to room temperature. The suspension with 6 mL of 0.4 mol/L KOH solution in the conical flask was sealed and stirred for 48 h to perform the deacetylating reaction. After the reaction, the excess of alkali was back titrated with 0.1 mol/L hydrochloric acid with methyl orange (MO) as an indicator. The titration process for each sample was repeated for three times within

2 h and the repeated results were calculated. The amount of substance of the acetyl in KGM (N_{acetyl}) was obtained by repeating the procedure described above with KGM powder. The degree of deacetylation (%) in the sample was calculated by the following formula

%deacetylation

$$= [N_{\text{acetyl1}} - (V_a - V_b)C_{\text{HCl}} \times 10^{-3}] / N_{\text{acetyl1}}$$

V_a = volume of hydrochloric acid consumed for the blank in liters, V_b = volume of hydrochloric acid consumed for the sample in liters, C_{HCl} = normality of the hydrochloric acid, N_{acetyl1} = the amount of substance of the acetyl in KGM.

Preparation of blend films

After dissolving the purified d-KGM in cold water in water bath at 4°C, stirring with magnetic stirrer until totally soluble to a concentration of 1.25%. CHI was dissolved in a 0.12 mol/L chlorhydric acid to prepare a concentration of 1.25% CHI·HCl. The solution of d-KGM and CHI·HCl with constant mixing ratio 70/30 was stirred for 0.5 h to obtain a clear solution and centrifuged at a speed of 2000 rpm for 15 min at 25°C to remove the air bubbles. Approximately, blend films were obtained when 100 g of this solution was cast onto polystyrene plates and dried in the oven.

The optimization of the condition of the films

The optimal condition for the blend films were obtained through simple factor experiment by changing the DD of the d-KGM, acids (the solvent Chitosan dissolved in) and the temperature of the oven.²⁰ The simple factor experiment conditions are shown in Table I.

Based on the simple factor experiment, according to the method of preparation of blend films mentioned above, a series of blend films were obtained by processing the solution d-KGM and CHI salt with different mixing ratios [100/0, 90/10, 80/20, 70/30, 60/40, and 50/50 d-KGM /CHI salt (w/w)] in the optimal condition and then coded as KC0, KC1, KC2, KC3, KC4, and KC5.

Swelling procedure

The blend films were heated in a polystyrene plate for 10 h at 60°C to balance the moisture content. The weighed masses of dry films (W_0) were dipped in the distilled water at 25°C. At predetermined time intervals, the films were removed from the distilled water and blotted with filter paper to remove excess

TABLE I
The Simple Factor Experiment Conditions of the Films

	d-KGM	Acid	T/°C
1	d1	chlorhydric acid	30
2	d2	acetic acid	40
3	d3	lactic acid	50
4	d4	ascorbic acid	60
5	d5	-	70

distilled water from the films surface; in that case, the masses of the swollen hydrogels (W) were weighed until the hydrogels reached constant weight. The equilibrium swelling degree (Q) can be calculated by the following formula: $Q = (W - W_0) / W_0$.²¹

Measurements of films

Samples were prepared by cutting the film into pieces and grinding the pieces with potassium bromide and laminating. The IR spectra were recorded with a Nicolet Nexus 470 FTIR spectrometer at a resolution of 2 cm^{-1} in the range $400\text{--}4000 \text{ cm}^{-1}$.

The X-ray diffraction (XRD) curves of the films were recorded with a Rigaku (Japan) D/max-RB X-ray diffractometer, and used a Cu $K\alpha$ target at 40 kV and 50 mA. The diffraction angle ranged from 10° to 60° . The crystallinities of the films were calculated by software Jade 5.0.

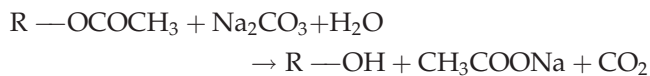
Film samples were fixed onto metallic sample holders and coated with gold under vacuum. The cross-section morphologies were observed with magnifications of $8000\times$ on a Hitachi X-650 SEM.

The optical transparence (T) of films in the wavelength of 480 nm was measured by using a Shimadzu UV-160A (Japan) spectroscopy.

The tensile strength (σ_b) and breaking elongation (ϵ_b) of the films were measured on an electron tensile tester RGT-2 (Shenzhen reger instrument Co., China) with a tensile rate of 250 mm/min according to the Chinese standard method (GB/13022-91).

RESULTS AND DISCUSSION

Deacetylation reaction of konjac glucomannan was carried using sodium carbonate as a modifier. Under such conditions, a saponification reaction between the KGM ($R\text{--}OCOCH_3$) and alkali (i.e., Na_2CO_3) occurred according to the following equation:



The reaction conditions and the results were shown in Figure 1. The results showed that the DD increased as the sodium carbonate content increased linearly in the range 50–80%, which meant the hetero-

ogeneous reaction could be regarded as pseudo first order reaction. The d-KGM film could hardly swell in the water if the DD was greater than 80%, and it could hardly gelatinize if the DD was less than 50%, thus, only the five samples d1(57.58%), d2(59.80%), d3(65.38%), d4(71.64%), and d5(75.02%) were selected for the blend films preparation.

The water-absorbing ability and the optical transparence analysis

The equilibrium swelling degree (Q) and the transparence (T) of simple factor experiment aforementioned on blend films were shown in Figure 2(a,b) and Figure 2(c). The Figure 2(a) showed that at a DD of 59.80% (d2), the Q reached 23, however, at the DD of 75.02%, the Q drops to half of the maximum (11 times). The sharp decrease suggested that a relatively small change of DD was sufficient enough to change the water absorbency enormously. This can be explained as follows: the molecule chain of the d-KGM was exposed gradually with the increased deacetylation degree, which lead to partial crystallization through intermolecular hydrogen-bonding interaction, subsequently, the three-dimensional gel network was formed with the molecule chain of the d-KGM. The crystallization process was strengthened with the increased DD of KGM, whereas the Q of the blend film increased at first but decreased afterward. This is because of the denser three-dimensional gel network which is formed for the much strengthened crystallization. Meanwhile, at the DD of 59.80%, the T value at 480 nm for the blend film reached the maximum (63.93%), which showed that the blend film have a good compatibility.

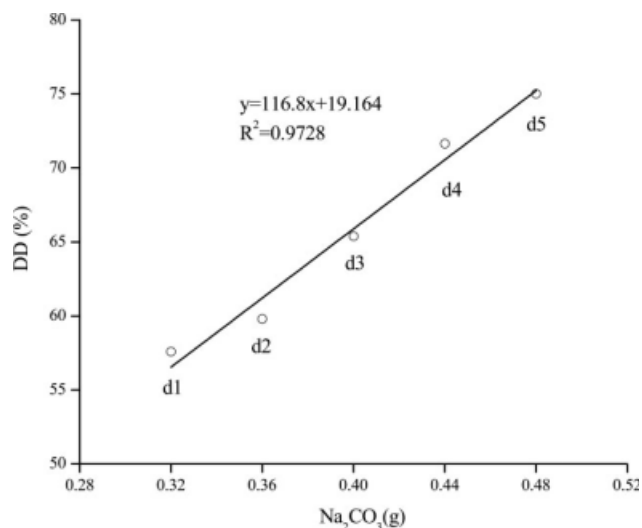


Figure 1 Effect of the sodium carbonate content on the DD of d-KGM (30 g).

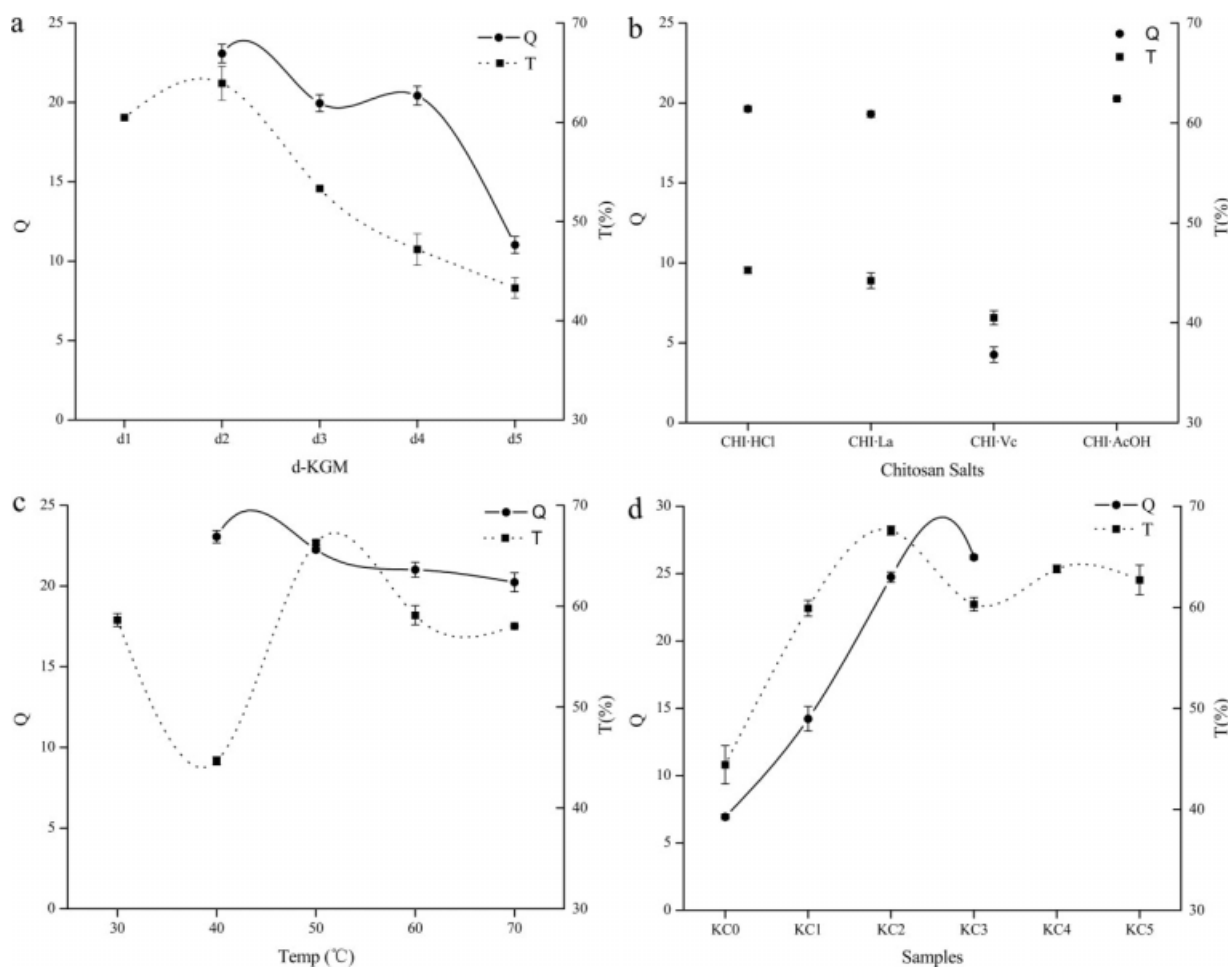


Figure 2 Effect of preparation condition on the equilibrium swelling degree and optical transparency. The a, b, c showed the equilibrium swelling degree (Q) and the optical transparency (T) of the films when changing the kinds of d-KGM, acids, temperatures. The d showed the equilibrium swelling degree (Q) and the transmittance (T) of the films of KC0, KC1, KC2, KC3, KC4, and KC5.

Figure 2(b) showed that the water absorbency varied obviously with different acids which was used to dissolve chitosan. The CHI·HCl was attributable to the water absorbing ability ($Q = 23$), however the CHI·Vc showed an opposite result ($Q = 4$). This can be explained as the dense three-dimensional network because the chemical crosslinking was formed between the d-KGM and the CHI·Vc, which was attributed to the enediol structure of the Vc. At the same time, the value of T of the CHI·HCl (45.27%) was bigger than that of CHI·Vc (40.50%).

The Figure 2(c) showed that the optimal drying temperature was 50°C. The crystallization process and the intermolecular hydrogen-bonding interaction were strengthened as the temperature raised. Thus, the blend films could dissolve in the distilled water when the temperature was lower (less than 30°C). The Q of the blend films increased first, and then decreased when the temperature was higher than 30°C. When the temperature was 50°C, the value of T was the maximum (66.30%).

In the other words, d2 (DD = 59.80%), CHI·HCl should be selected as the blend films composition; meanwhile the temperature should be selected as 50°C.

Prepared under the optimal condition obtained in the simple factor experiment, the effect of the blend films with different blend ratio on the Q and the T was shown in Figure 2(d). The Q of the blend film increased with the increased CHI·HCl in the range of 0–40%. When the Q of KC3 (CHI·HCl content in the blend films was 30%) reached 26, KC4 and KC5 could dissolve in the distilled water. The result indicated that CHI·HCl interfered the crystallization process of the d-KGM. The Q of the blend film increased when the content of CHI·HCl increased.

The a, b, c showed the equilibrium swelling degree (Q) and the optical transparency (T) of the films when changing the kinds of d-KGM, acids, temperatures. The d showed the equilibrium swelling degree (Q) and the transmittance (T) of the films of KC0, KC1, KC2, KC3, KC4, and KC5.

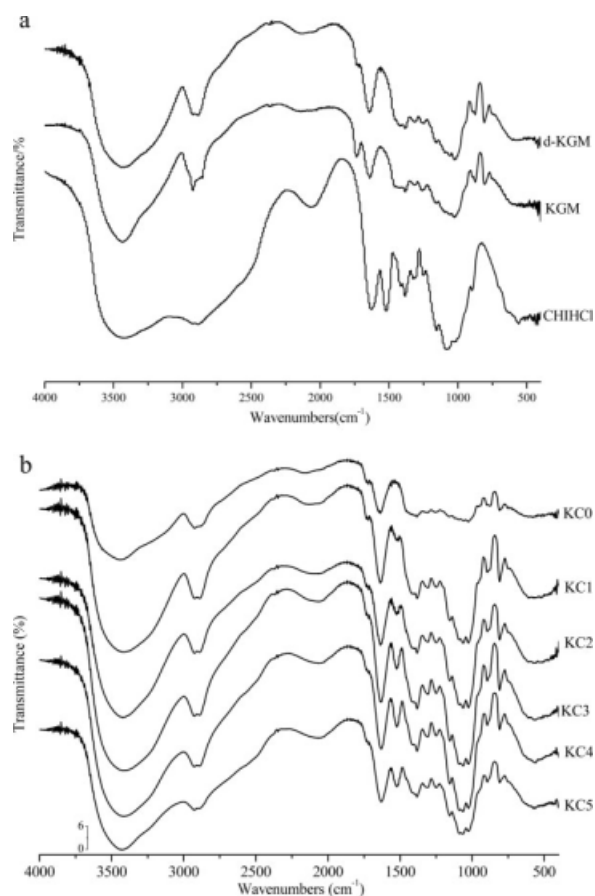


Figure 3 (a) FTIR spectra of the d-KGM, KGM, CHI-HCl; (b) FT-IR spectra of the KC0, KC1, KC2, KC3, KC4, KC5.

Structure characterization

FTIR analysis

FTIR is of importance in the study of the molecular structure. Intermolecular interactions and intramolecular interactions occur when different polymers are compatible, so the FTIR spectrum of the compatible blend polymer is different from that of pure polymer. FTIR spectra of the d-KGM, KGM, CHI-HCl and the blend films were showed in Figure 3. In the IR spectra of the films of KGM, d-KGM, CHI-HCl [Fig. 3(a)], the absorption band at 3427 cm^{-1} and the peaks at 2924 cm^{-1} were assigned to the stretching of $-\text{OH}$ groups and $\text{C}-\text{H}$ of methyl in d-KGM, the characteristic absorption bands of mannose in d-KGM appeared at 886 cm^{-1} and 804 cm^{-1} , the broad peak at 1642 cm^{-1} was assigned to the stretching of $-\text{C}=\text{O}$ of associate hydroxy groups. Significantly, the intensities of the peak at 1720 cm^{-1} that was assigned to the stretching of $-\text{C}=\text{O}$ decreased, which was because of the deacetylation of the KGM.²² The absorption band at 3421 cm^{-1} was assigned to the stretching of $\text{N}-\text{H}$ groups bonded to $-\text{OH}$ in CHI-HCl; the peaks at 1624 cm^{-1} were and the peaks at 1517 cm^{-1} were

assigned to the characteristic bending absorption band of primary amine; the peaks at 1077 cm^{-1} were assigned to the characteristic absorption band of C_6-OH .²³

The Figure 3(b) showed the IR spectra of the films of KC0, KC1, KC2, KC3, KC4, and KC5. Compared with the spectrum of d-KGM and CHI-HCl, the following changes had taken place in the blend films. The absorption band around 3427 cm^{-1} broadened and shifted to a lower wave number with the increase of CHI-HCl, which indicated the gradual increase of intermolecular hydrogen bonds between CHI-HCl and d-KGM, and it shifted to 3418 cm^{-1} in the films of KC4. Meanwhile, the stretching of intramolecular hydrogen bonds at 1637 cm^{-1} in d-KGM coupled and shifted to a lower wave number, suggesting that the new hydrogen bonds between CHI-HCl and d-KGM molecules in the blend films occurred.

WXR analysis

The WXR curves of KC0, KC1, KC2, KC3, KC4, and KC5 films were shown in Figure 4. The crystallinities of KC0, KC1, KC2, KC3, KC4, and KC5 films were 18.03, 17.78, 1.43, 11.82, 10.12, and 2.89, respectively. The pure d-KGM film (KC0) showed a crystal peak at around $2\theta = 11$ and a noncrystalline broad peak around $2\theta = 27$.²⁴ Significantly, adding the CHI-HCl to the d-KGM, the crystal peak became gradually lower, the diffraction angle was nearly at 11 and the noncrystalline phase became wider. When the content of the CHI-HCl was 40%, the noncrystalline state became widest at around $2\theta = 24$. The results indicated that the interaction between d-KGM and CHI-HCl strengthened with the increase of the content of the CHI-HCl, and the intermolecular interaction was the greatest at KC4.

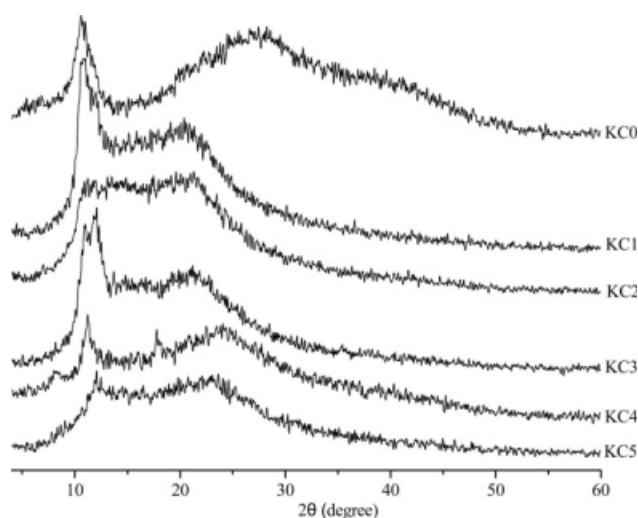


Figure 4 WXR diffraction curves of the KC0, KC1, KC2, KC3, KC4, and KC5 films.

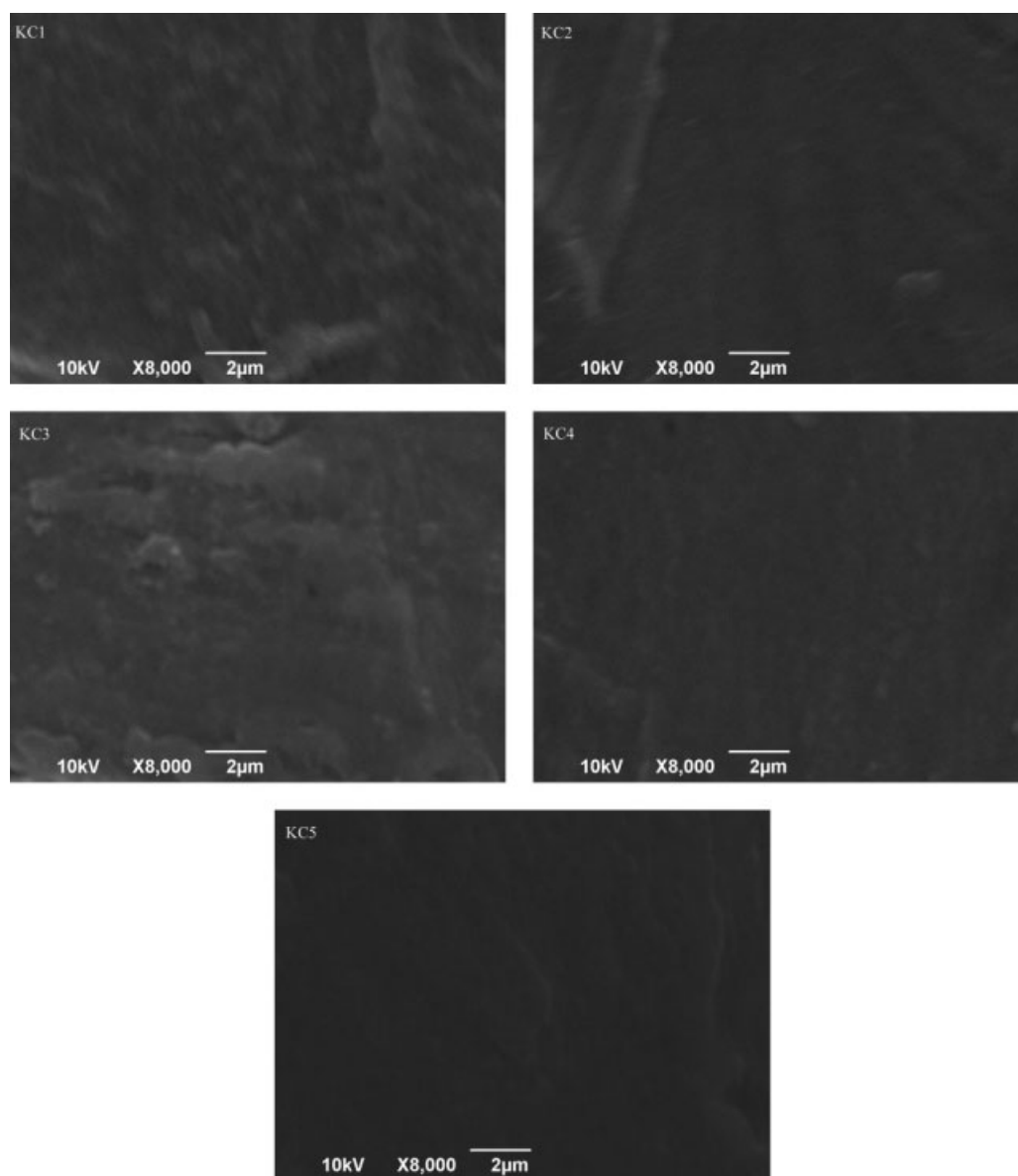


Figure 5 SEM photographs of the cross-section for KC1, KC2, KC3, KC4 and KC5 films.

SEM analysis

SEM is an important method for characterization of the miscibility of two or more polymers. In the SEM photographs of cross-section of the films (Fig. 5), the blend film KC4 showed a smooth and homogeneous surface morphology, suggesting high miscibility and blend homogeneity between the d-KGM and the CHI·HCl at the composite ratio of 6 : 4 by weight. This result supported the conclusion of miscibility between d-KGM and CHI·HCl in the films and was in accordance with those from FTIR and XRD.

Mechanical properties of films

The study of mechanical properties is of primary importance for determining the performance of

materials, especially that of film materials. Figure 6 showed the effect of the composite ratio of the d-KGM and the CHI·HCl on the tensile strength and breaking elongation. The tensile strengths of the blend films increased with the increase of the content of the CHI·HCl. The maximum value of the tensile strengths appeared at KC3 and achieved 162 MPa. The breaking elongation (ϵ_b) of the film was about 5% of average. The considerable enhancement in tensile strength of blend films indicated that intermolecular interaction occurred between the d-KGM and the CHI·HCl.

CONCLUSIONS

A series of transparent blend films were prepared by blending 1.25% w/v aqueous d-KGM

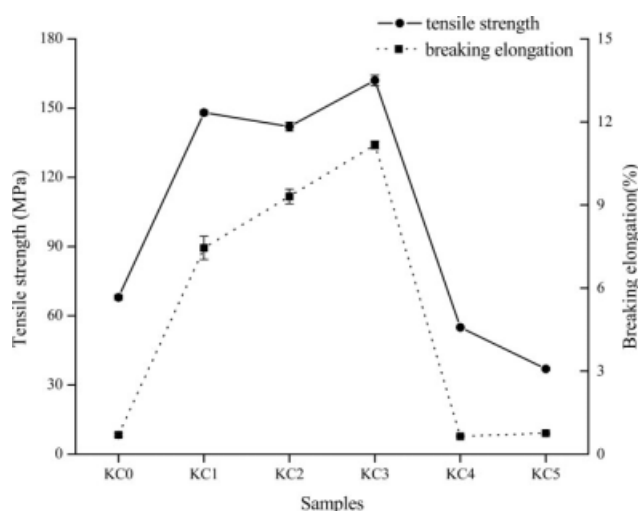


Figure 6 The dependence of tensile strength (σ_b) and breaking elongation (ϵ_b) on the content of KGM.

(DD = 59.80%) with 1.25% w/v CHI-HCl according to predetermined ratios and drying at 50°C on polystyrene plates for 6 h. The analysis by FTIR, WXR, and SEM on the changes of the aggregation structures of the blend films showed that the hydrogen-bonding interaction was strengthened when the CHI-HCl content in the blend films was 40 wt %. However, the results of mechanical and physical properties tests showed that the blend film KC3 had the maximum tensile strength (162 MPa), a higher transparency (60.3%) and greater water solubility (26 times). This was to say, adding the CHI-HCl to the d-KGM, the hydrogen-bonding interaction was strengthened, but the crystallization process of the d-KGM was interfered. The outcomes indicated that the water-absorbing ability of the blend films had the relationship not only with the compatibility of the polymers but also with the crystallization process of the d-KGM. In balance, the blend film would

be of a perfect three-dimensional network and optimal water-absorbing ability.

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