

Improvement of Physical Properties of Crosslinked Alginate and Carboxymethyl Konjac Glucomannan Blend Films

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ABSTRACT: Blend films from carboxymethyl konjac glucomannan and sodium alginate in different ratios were prepared by blending 4 wt % sodium alginate aqueous solution with 2 wt % konjac glucomannan aqueous solution. After crosslinking with 5 wt % calcium chloride aqueous solution, the blend films formed a structure of semi-interpenetrating networks. The structure and physical properties of both uncrosslinked and crosslinked films were characterized by Fourier transformed infrared spectra (FTIR), differential thermal analysis (DTA), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and tensile tests. The results indicated that the mechanical properties and the thermal stability of the films were improved by blending sodium alginate with carboxymethyl konjac glucomannan due to the intermolecular hydrogen bonds between sodium alginate and carboxymethyl konjac glucomannan. The crosslinked blend films with Ca^{2+} , compared with uncrosslinked blend films, exhibited further improved physical properties due to the formation of a semi-IPN structure. Furthermore, the degree of swelling of the crosslinked films was also investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2554–2560, 2002

Key words: crosslinking; carboxymethyl konjac glucomannan; sodium alginate; blend films

INTRODUCTION

Blending, a good method to exploit new polymer materials, has gained wide application in various fields covering food, medicine, textile, and engineering. As a result, various kinds of new materials have appeared and given improvement in material science. Recently, a series of posttreatment methods, such as crosslinking and thermal treatment, have provided much wider application prospects for blend materials. For example, Jin et al. has reported that blend films from poly(vinyl alcohol)/chitosan crosslinked with glutaraldehyde had improved thermal stability and mechanical

properties, and showed a PH-dependent swelling characteristic, which can be applied to controlled-release systems.¹

Konjac glucomannan (KGM), a water-soluble polysaccharide extracted from konjac plants, consists of β -1,4 linked mannose and glucose residues with a low degree of acetyl groups.^{2–4} Due to the high viscosity, stability, and emulsifiability of its aqueous solution, it has promise in food, pharmaceutical, chemical engineering, paper making, and environmental protection aspects.⁵ In our previous work, extensive studies on blend films of konjac glucomannan with such polymers as chitosan, sodium alginate, gelatin, and poly(vinyl alcohol) were reported.^{6–9} By blending, the mechanical properties and thermal stability of the films were improved significantly due to intermolecular interaction through hy-

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drogen bonding formation. In addition, derivatization was also used to improve the physical properties of KGM. It was reported that treating konjac glucomannan with chloroacetic acid, namely, carboxymethyl konjac glucomannan (CKGM), could significantly improve its water solubility and film-forming ability.¹⁰

Sodium alginate (SA) is an abundant polysaccharide, which can be obtained from marine algae. Its main chain contains β -1,4-D-mannuronate and α -1,4-L-guluronate residues and its molar mass distribution is from 50,000 to 200,000.¹¹ Due to its remarkable gelation properties, it has been widely used in food, fabric, and medical fields; for example, SA is of great interest in biomedical applications in hemostatic materials.¹² Moreover, blending SA with other polymers, such as SA/konjac-glucomannan,⁷ SA/cellulose,¹³ and SA/poly(vinyl alcohol),¹⁴ creates a new application field for SA. Owing to its gelation properties in the presence of divalent or trivalent metal ions, a semi-interpenetrating network can be formed after the blend film from SA/polyacrylic is crosslinked with a calcium chloride aqueous solution. The swelling degree of the polymer film can be regulated by the control of the concentration of calcium ion.¹⁵

The aim of this article is to study the structure and properties of the blend films from CKGM/SA and the blend films crosslinked with calcium chloride. The change of structure and properties of the films was measured by IR, DTA, TGA, SEM, and a strength tester. The improvement of the physical properties will be discussed in detail. We predict that this work may contribute basic information to the further application of this kind of crosslinked blend film.

EXPERIMENTAL

Materials

SA was purchased from Shanghai Chemical Agents Factory. Purified KGM was obtained according to our previous work.⁸ CKGM, prepared as 20 g 30 wt % NaOH aqueous solution, was poured into 2 wt % KGM aqueous solution contained in a two-neck flask equipped with mechanical stirrer and dropping funnel. The alkali-konjac glucomannan slurry was stirred at 80°C for 1 h before adding, dropwise, the desired chloroacetic acid aqueous solution. The reaction mixture was then stirred for another 2 h at 80°C, and

then the resulting product was precipitated with acetone, washed with 50 wt % acetone aqueous solution three times, and dried in vacuum to obtain the pure CKGM. Its degree of substitute is 0.74. The other chemical agents were analytically pure.

Preparation of Films

Aqueous solutions of CKGM and SA were prepared separately at room temperature at concentrations of 2 and 4 wt %, respectively. Pure CKGM, pure SA, and a mixture of CKGM and SA, in the desired proportions (10/90, 20/80, 30/70, 40/60, 50/50, CKGM/SA) were cast on glass plates, and the water was allowed to evaporate at room temperature to obtain the films coded as CKGM, SA, CS-1, CS-2, CS-3, CS-4, CS-5, respectively. After being dried, the films were removed from the glass plate and all, except for CKGM, were immersed in 5 wt % calcium chloride aqueous solution for 30 min. After coagulation, the prepared films were washed with deionized water to remove the unreacted calcium chloride. The films undergoing posttreatment were coded as CA, CC-1, CC-2, CC-3, CC-4, CC-5, accordingly. Both the crosslinked and uncrosslinked films were subjected to vacuum drying for 48 h before measurements. The thicknesses of the films were in the range of $40 \pm 5 \mu\text{m}$.

Analyses

Infrared spectra of neat films were obtained using a Nicolet (USA) 170× Fourier transform infrared (FTIR) spectrometer. Thermal properties of samples were measured by a Shimadzu DT-30 thermal analyzer in air atmosphere, at a heating rate of 15°C/min. The decomposition temperatures and weight losses of films were evaluated by considering the intersecting point of the tangents of TGA curves. The cross-sections of the films were examined with a Hitachi-570 scanning electron microscope after gold coating. Mechanical properties of the films were measured by an electronic tensile tester AG-A (Shimadzu Co. Japan) with a tensile rate of 10 mm/min, at a gauge length of 40 mm. The degree of swelling (Q_w) of the crosslinked blend films was measured by the following:

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

where W_{wet} is the weight of wet film obtained by immersing the dried films in deionized water for 1 day, and W_{dry} is the weight of dried film.

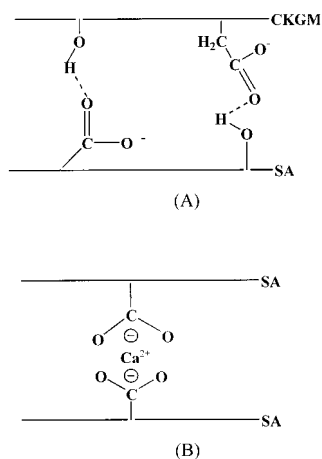


Figure 1 The hydrogen bonds (A) and Ca^{2+} bridge (B) structure.

RESULTS AND DISCUSSION

Structure and Miscibility

The molecular chain of SA contains $-\text{OH}$ and $-\text{COO}^-$ groups that can interact with $-\text{COO}^-$, $-\text{OH}$ in CKGM through hydrogen bonding [Fig. 1(A)]. Crosslinking SA with calcium chloride, SA formed a network through Ca^{2+} bridge [Fig. 1(B)]. CKGM can penetrate into the SA- Ca^{2+} network to form a structure of semi-IPN.

The IR spectra of the films are shown in Figure 2. Compared with the spectrum of KGM in our previous work,⁸ there are changes in the spectrum of CKGM. First of all, a new absorption peak at 1654 cm^{-1} appeared, which belongs to carbonyl group in the unidentate carboxylate, which originated from the intramolecular hydrogen bond formation within CKGM.¹⁵ The intensity of the peak at 1028 cm^{-1} concerned with the stretching vibration of $-\text{O}$ increased. Moreover, the absorption bands around 3400 cm^{-1} shifted to a higher wave number, which is attributed to the introduction of $-\text{CH}_2\text{COO}^-$ into KGM that destroys the original hydrogen bonds involving $-\text{OH}$ within KGM. These changes confirmed that KGM had reacted with chloroacetic acid. In the spectrum of CKGM, the absorption bands, centered at 1604 cm^{-1} , were ascribed to asymmetric stretching vibration of the free carboxylate ion and the peaks at 1421 and 1378 cm^{-1} were concerned with the symmetric stretching vibration of the free carboxylate ion in CKGM.¹⁵ The FTIR spectrum of SA showed strong absorption bands at 3400 cm^{-1} ($\text{O}-\text{H}$ stretching), 1626 cm^{-1} ($-\text{COO}^-$ asymmet-

ric stretching), 1420 cm^{-1} ($-\text{COO}^-$ symmetric stretching).

In the spectra of the blends, with the increase of SA content, the peak at 1654 cm^{-1} disappeared, and the bands at 1604 cm^{-1} shifted to a higher wave number. It can clearly be seen from the spectra that the absorption band centered 3400 cm^{-1} , concerned with stretching of $-\text{OH}$, was broadened and shifted to a lower wave number with the increase of the SA content. All these changes suggested that intermolecular interaction, through the formation of hydrogen bonds between $-\text{COO}^-$, $-\text{OH}$ in SA, and $-\text{COO}^-$, $-\text{OH}$ in CKGM, occurred. However, in the spectrum of the crosslinked blend film CC-1, the absorption band around 3400 cm^{-1} , compared with the uncrosslinked blend film CS-1, obviously nar-

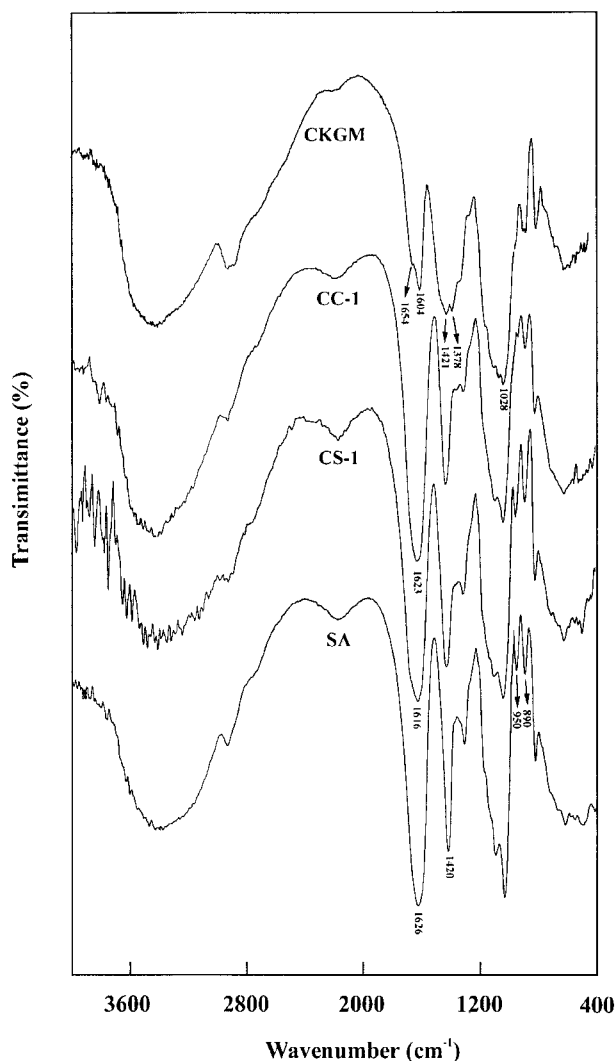


Figure 2 The FTIR spectra of the films.

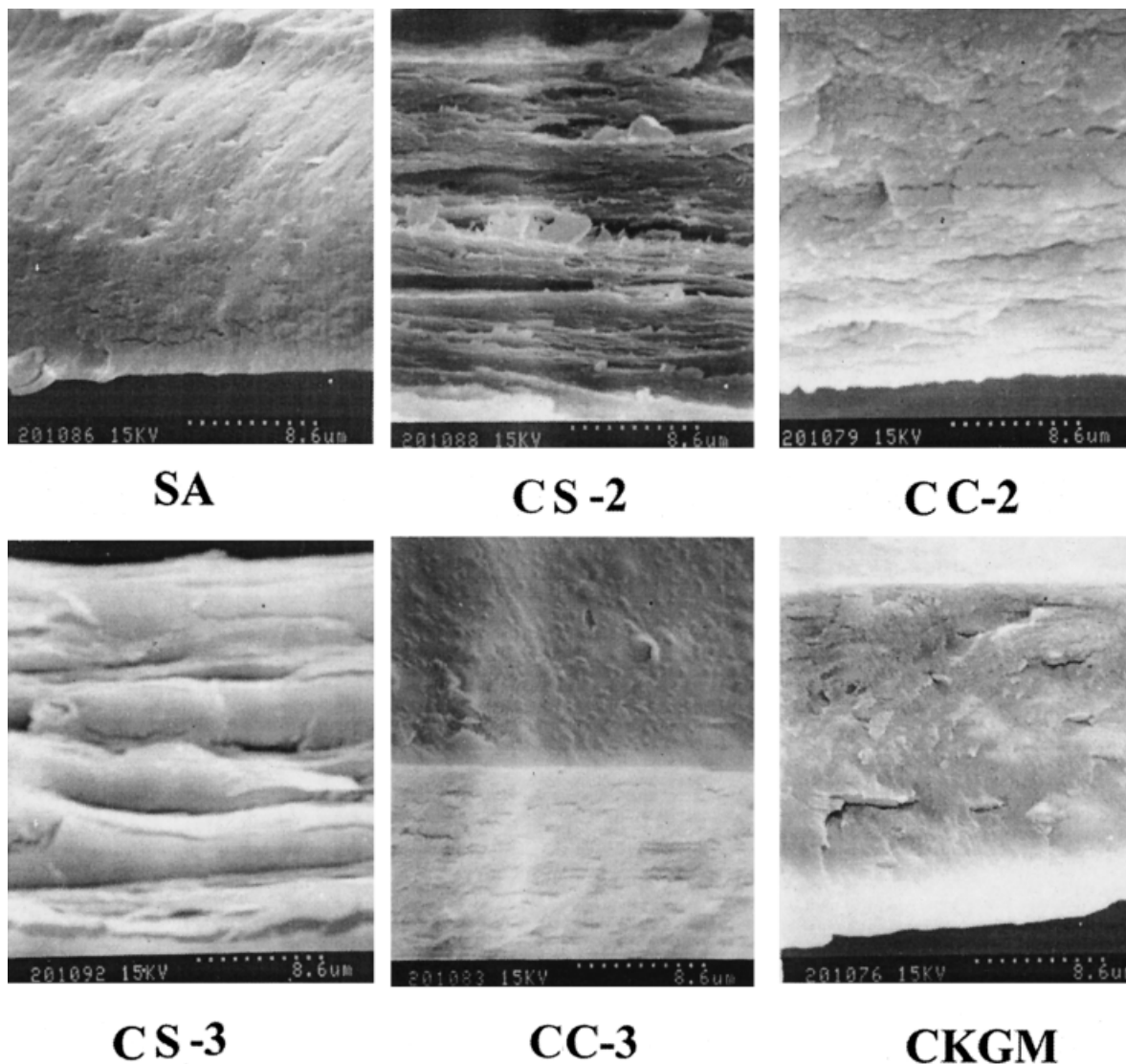


Figure 3 The SEM photographs of the films.

rowed, which can be elucidated by the decrease of the hydrogen bonding interaction between SA and CKGM as SA formed a network with Ca^{2+} .¹³ Furthermore, in the spectrum of CC-1, the absorption bands around 1604 cm^{-1} from CKGM shifted to a much higher wave number than the uncrosslinked blend film, indicating that $-\text{COO}^-$ in the blends was involved in the crosslinking.

The SEM photographs of cross-section of the films are shown in Figure 3. Both pure SA and pure CKGM exhibited dense structures. In the blends, both CS-2 and CS-3 showed less compact layer-like morphological structures, and no phase separation was observed, implying that SA and CKGM were compatible due to hydrogen bonding interaction between them. However, by crosslink-

ing, the cross-section of the blend films changed from rough to smooth. CC-2 and CC-3 showed a dense homogenous structure similar to pure SA and CKGM, indicating that crosslinking with a Ca^{2+} bridge improved the structure inside the blend films by the formation of a structure of semi-interpenetrating networks between SA and CKGM, leading to better component compatibility.^{16,17}

Thermal Stability

Figure 4 shows the DTA thermograms of the films. Pure SA showed an endothermic peak at 98°C that was due to loss of moisture, and two exothermic peaks located at 240 and 450°C that

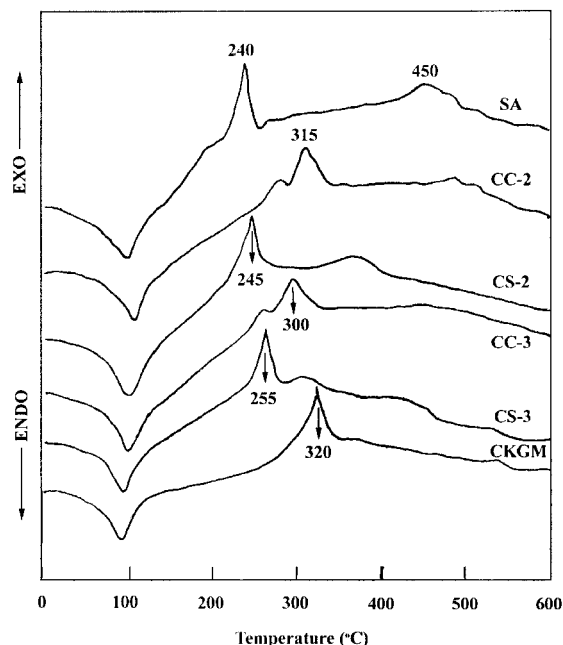


Figure 4 The DTA thermograms of the films.

were attributed to the disintegration of the molecular side chains and main chains, respectively.⁸ Pure CKGM shows exothermic peak at 320°C, attributed to the greater thermal degradation of CKGM. All the blend films shows endothermic peaks around 100°C ascribed to the dehydration in the films, and displayed exothermic peaks in the range of 250–320°C, corresponding to the greater thermal degradation of the films (see results of TGA in Fig. 5). The largest thermal degradation peak shifted to higher temperature, and the peak for SA at 450°C disappeared gradually with the increase of CKGM content, indicating that hydrogen-bonding interaction was established between SA and CKGM. It is interesting to note that, after crosslinking, the blend films CC-2 and CC-3 both showed greater thermal degradation peaks accompanied by a little shoulder peak at a much higher temperature than the uncrosslinked films CS-2 and CS-3, implying that crosslinking can improve the thermal stability through the formation of a structure of the semi-interpenetrating network inside the blend films. Moreover, the thermal stability of CS-2 was improved more than that of CS-3 by crosslinking, which can be explained by the increase of the crosslinking density with the increase of CA content.

The results of TGA are shown in Figure 5. Compared with pure SA, the uncrosslinked blend

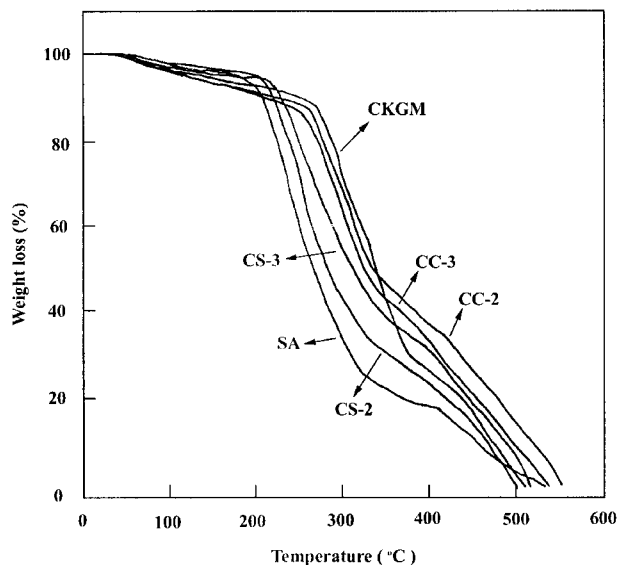


Figure 5 The TGA thermograms of the films.

films CS-2 and CS-3 showed higher beginning disintegration temperature and less weight loss (Table I), resulting from the degradation of the blend films, indicating that the intermolecular interaction through hydrogen bonding between SA and CKGM improved the thermal stability of the films. Moreover, crosslinking further improved the thermal stability of the blend films (see Table I) through the formation of a structure of semi-interpenetrating networks inside the blend films.

Mechanical Properties of the Films

The tensile strength and elongation at break of pure CKGM were 41.8 MPa and 5.9%. Figure 6 shows the dependence of the tensile strength on the CKGM content for the other films. The films without crosslinking had a tensile strength of 40–64 MPa, and the maximum value was observed at 20 wt % CKGM content. This result suggests that the compatibility between SA and

Table I Thermal Stability of the Films

Sample	CKGM	CS-3	CC-3	CS-2	CC-2	SA
Temperature (I)	265	200	250	210	260	195
Temperature (II)	380	335	330	350	325	320
Weight loss (%)	64	62	41	57	38	66

Temperature (I) and (II) represent the starting and ending temperature of greatest thermal degradation.

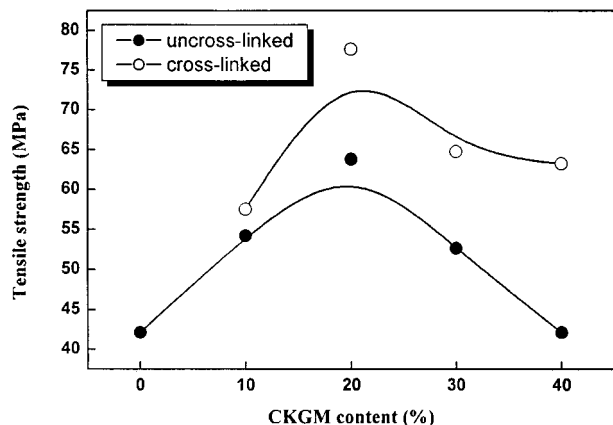


Figure 6 The dependence of tensile strength of the films on the CKGM content.

CKGM, owing to hydrogen bonding interaction, attained its best value when the CKGM content was around 20 wt %. The crosslinked films all showed higher tensile strength than the uncrosslinked films accordingly. The maximum value 77.6 MPa was also observed at 20 wt % CKGM content, indicating that the semi-interpenetrating network structure from CKGM and CA enhanced the mechanical strength of the blend films.

The elongation of the films at break is shown in Figure 7. The resulting curve of the uncrosslinked films exhibits the same trend as the strength curve, and also reached its maximum at $W_{\text{CKGM}} = 20$ wt %. For the crosslinked films, however, the elongation showed quite a different trend from the strength curve. The elongation values of the crosslinked films were all higher than those of

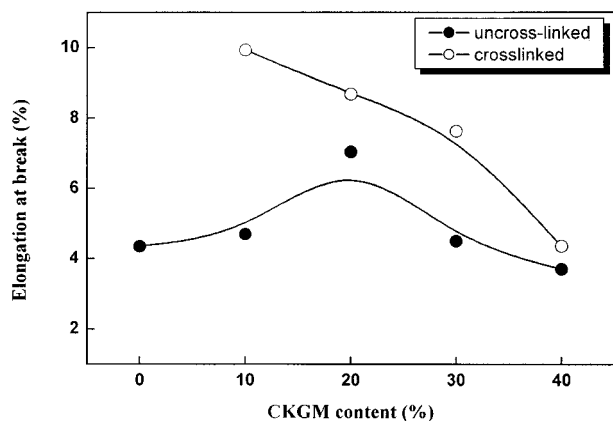


Figure 7 The dependence of elongation at break of the films on the CKGM content.

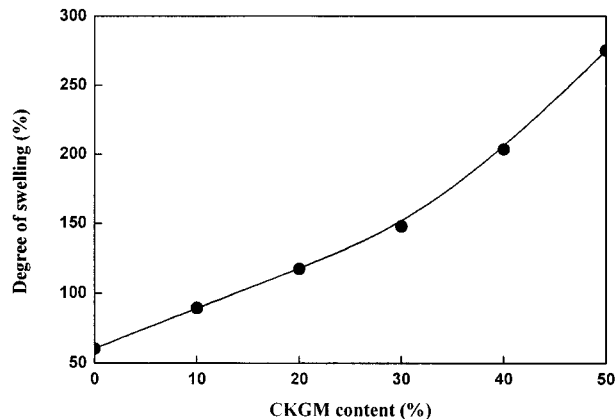


Figure 8 The dependence of water absorption of the crosslinked blend films on the CKGM content.

uncrosslinked films accordingly, indicating that crosslinking had improved the toughness of the films through the formation of the structure of semi-interpenetrating networks. Furthermore, the elongation value decreased dramatically when the CKGM content was over 30 wt %. In the blend films, SA formed networks through Ca^{2+} bridges, resulting in strengthening and toughening of the films. In general, the addition of an appropriate amount of CKGM can effectively form interlocking entangled chains between CKGM and CA networks; however, excessive CKGM prevented SA from forming networks with Ca^{2+} , resulting in decreasing toughness of the films.¹⁸

Swelling Characteristics of Films

Novel changes were observed in the dependence of degree of swelling of the crosslinked films on the CKGM content, as shown in Figure 8. With the increase of CKGM content, the degree of swelling of the crosslinked films increased steadily. In the blends, SA formed a network through Ca^{2+} bridges, which reduced the intermolecular interaction between CKGM and SA.¹³ Thus, free carboxylate ions and hydroxyl groups in the blends increased as the CKGM content increased, resulting in higher accessibility of water to the amorphous region of the blends. On the other hand, the decrease of SA content in the blends led to the decrease of crosslinking density, which also contributed to a higher degree of swelling. This result implies that this kind of crosslinked blend films has considerable water storing ability.

CONCLUSIONS

Polymer films, composed SA and CKGM, were prepared using the solvent casting method, and then crosslinked with calcium chloride. IR confirmed the formation of hydrogen bonds between SA and CKGM, and suggested the occurrence of a semi-interpenetrating network from CKGM, SA, and Ca^{2+} . Mechanical properties and thermal stability of the blend films were significantly improved by crosslinking. It is worth noting that the swelling degree of the crosslinked blend films increased dramatically with the increase of CKGM content, suggesting that the crosslinked films have potential application for water storage materials with good thermal and mechanical properties.

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