

Preparation and Physical Properties of Konjac Glucomannan–Polyacrylamide Blend Films

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ABSTRACT: The blend films of konjac glucomannan (KGM) and polyacrylamide (PAAm) were prepared by using the solvent-casting technique. Transparent blend films were obtained in all blending ratios. The physical properties of the films were investigated by Fourier transform infrared spectroscopy, wide-angle X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and by measurement of mechanical properties. The results indicated the occurrence of intra- and intermolecular interactions of the pure components, as well as the intermolecular interactions between KGM and PAAm through hydrogen bond formation. The thermal stability and mechanical properties of both tensile strength and elongation at break of the films were improved by blending KGM with PAAm. It was worth noting that the blend film had the greatest tensile strength when the KGM content in the blend films was around 30 wt %. Surface morphology of the films observed by SEM was consistent with the above-noted results. Furthermore, the water absorbability of the blend films was also investigated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 882–888, 2001

Key words: konjac glucomannan; polyacrylamide; blend film; hydrogen bond; miscibility

INTRODUCTION

During the past two decades, there has been great scientific and commercial progress in the area of polymer blends. This was driven by the realization that the new molecules are not always required to meet the needs for new materials and that blending can usually be implemented more rapidly and economically than can the development of new chemistry.¹ When strong intermolecular interactions or miscibility phenomena occur between the components, large synergistic effects on both the physical and the mechanical properties can be observed.² Thus, with a miscible polymer blend, a range of price/performance characteristics between the component polymers can

lead to a large number of potentially useful and different products. Many materials with highly functional performance have been prepared in various industries by mixing different polymers.^{3–7}

Konjac glucomannan (KGM), whose main chain consists of β -1,4-linked mannose and glucose units with a low degree of acetyl groups,^{8–10} is a natural water-soluble polysaccharide found in the tubers of the *Amorphophallus konjac* plant. Investigative studies on KGM have successfully led to progress in the pharmaceutical, food, chemical engineering, and fabric industries.¹¹ Because of its unique physical properties, KGM blended with other natural or synthetic polymers has been investigated (e.g., the study by Yue et al.¹² on blends of KGM and pullulan prepared from water-formed transparent films). The mechanical properties and moisture uptake of the blend films increased with the increase of KGM content in the

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blends. Zhang et al.^{13,14} reported the preparation of blend films of KGM and cellulose from cuproammonium solution. The blend films were miscible when the KGM content was in the range of 0 to 30 wt %; moreover, the coagulation condition and content of KGM played important roles in structure and properties of the blend films. Polymer materials based on the blends of KGM with natural, biocompatible polymers (chitosan and sodium alginate) were also designed in our laboratory.^{15,16} The results indicated the occurrence of intermolecular hydrogen bonding between two polymers, resulting in improvement of thermal stability and mechanical strength of the blends.

The success of synthetic polymers, however, relies mainly on their wide range of mechanical properties and transformation processes that allow a variety of different shapes to be easily obtained. Natural polymers often present good biocompatibility, but their mechanical properties are often poor.¹⁷ Polyacrylamide (PAAm), a water-soluble synthetic polymer, is widely used as flocculating, paper-strengthening agents, and also can be applied to enhance the recovery of oil.¹⁸ PAAm can potentially form hydrogen bonds with KGM because of the ability of several primary amide groups on its chain backbone to interact with aceto and hydroxyl groups of KGM. Moreover, PAAm is a polymer of biomedical and pharmaceutical interest, widely studied as a hydrogel for blood-compatible applications.¹⁹ Impelled by the purpose of producing a new polymeric material that possesses both good mechanical properties and biocompatibility, we thus selected PAAm as a candidate to be blended with KGM. The present study focuses on investigation of the physical properties of the blend films prepared by casting the mixed aqueous solution of KGM and PAAm. The structure and physical properties of the films were studied by FTIR, WAXD, TGA, SEM, and strength test. Changes of structure and physical properties of the films are discussed in relation to the blending ratios.

EXPERIMENTAL

Materials and Preparation of the Films

PAAm, purchased from the Chemical Agents Factory (Shanghai), had an average molecular weight (M_w) of 3.0×10^6 . Purified KGM was obtained according to our previous study¹⁵; the viscosity-average molecular weight of KGM was 2.5×10^5

calculated by the Mark–Houwink equation: $[\eta] = 3.8 \times 10^{-2} M^{0.723}$.²⁰ Other chemical agents used were analytically pure and used as received.

Desired quantities of KGM and PAAm were dissolved in water to obtain the solution of 4 wt %, respectively. Pure and two-polymer mixture solutions with different weight ratios (KGM/PAAm: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, and 0/100) were cast on glass plates, and the water was allowed to evaporate at room temperature. Films of both pure composition and the blends were dislodged carefully, and then subjected to further drying under vacuum for 48 h, to obtain the dried films before measurements. The thickness of the films was in the range of $40 \pm 5 \mu\text{m}$.

Measurements

FTIR spectra of the films were measured by a Shimadzu FTIR 8201 spectrometer (Shimadzu, Japan) using KBr pellets. The X-ray diffraction patterns of the films were measured with a Rigaku (Japan) Dmax-II X-ray diffractometer, which used a CuK_α target at 40 kV and 50 mA. The TGA of powdered samples of the films were carried out in an air atmosphere by a Shimadzu DT-30 thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$. The starting decomposition temperature and weight loss values of the samples were evaluated by considering the intersection point of tangents of TGA curves. The dried films were allowed to soak in an atmosphere of 65% relative humidity at 24°C for 6 days, and then subjected to the stress–strain measurements performed by an AG-A electron tensile tester (Shimadzu) in an environment of 65% relative humidity and 24°C using a crosshead speed of 5 mm/min; the specimens used were 10×70 mm (width \times length). The moisture content of the films was calculated with the following equation:

$$W = [(W_1 - W_0)/W_0] \times 100\%$$

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 morphology of film surfaces was examined by a Hitachi SX-650 scanning electron microscope (Hitachi, Japan) after gold coating.

RESULTS AND DISCUSSION

General Properties of the Films

Pure and blend films were transparent and optically clear to the naked eye.

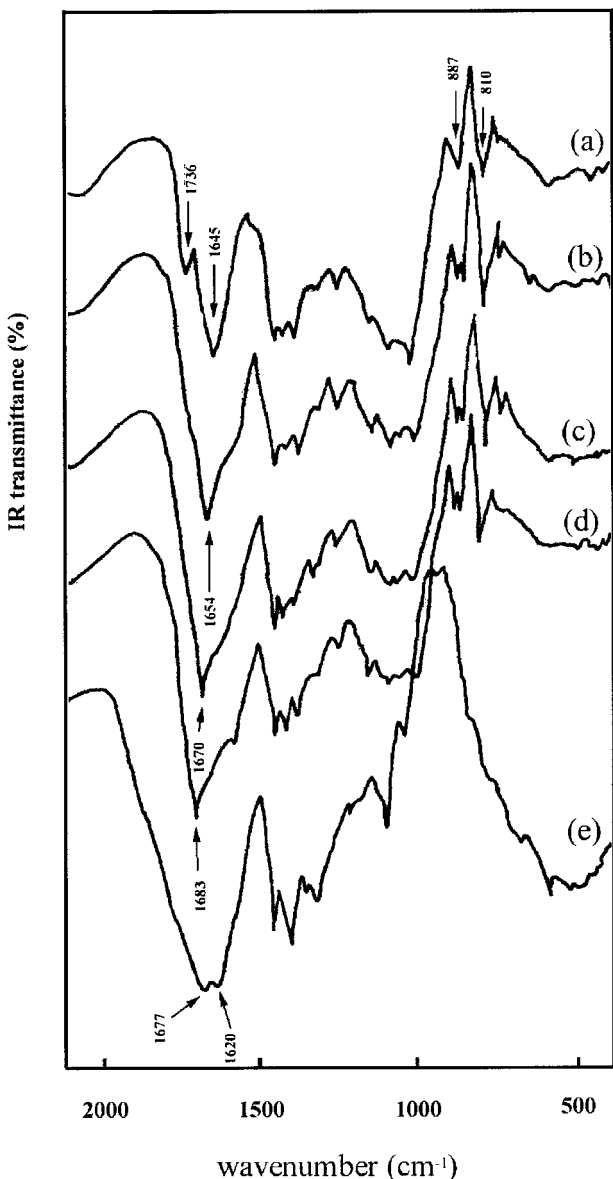


Figure 1 FTIR spectra of KGM (a), PAAm (e), and blend films in the wavenumber range of 2400–400 cm^{-1} . KGM/PAAm composition: (b) 90/10, (c) 80/20, and (d) 70/30.

The FTIR spectra of KGM and PAAm in the wavenumber ranges of 2400–400 cm^{-1} and 4000–2000 cm^{-1} are shown in Figure 1 and Figure 2, respectively. The characteristic absorption bands of mannose in KGM [Fig. 1(a)] appeared at 810 and 887 cm^{-1} .²¹ The stretching vibration peak of C—H of methyl at 2923 cm^{-1} [Fig. 2(a)] and that of the carbonyl at 1736 cm^{-1} were assigned to the aceto groups in KGM.¹⁰ The spectrum of PAAm exhibited strong bands at about 1677 cm^{-1} (CO stretching), 1620 cm^{-1} (NH bend-

ing) [Fig. 1(e)], 3421 and 3197 cm^{-1} (NH stretching), and 2925 and 2856 cm^{-1} (CH bending) [Fig. 2(f)].²²

The spectra of the blends in the wavenumber range of 2400–400 cm^{-1} [Fig. 1(b)–(d)] showed the presence of the absorption bands typical of the pure components, with intensity roughly proportional to the blending ratio. However, some changes occurred: notably, the band at 1736 cm^{-1} assigned to the aceto groups disappeared; and the band at 1645 cm^{-1} , resulting from hydrogen bonding¹⁵ among KGM molecules, shifted to a higher wavenumber with the increase of PAAm content. Therefore, it seemed that the amide

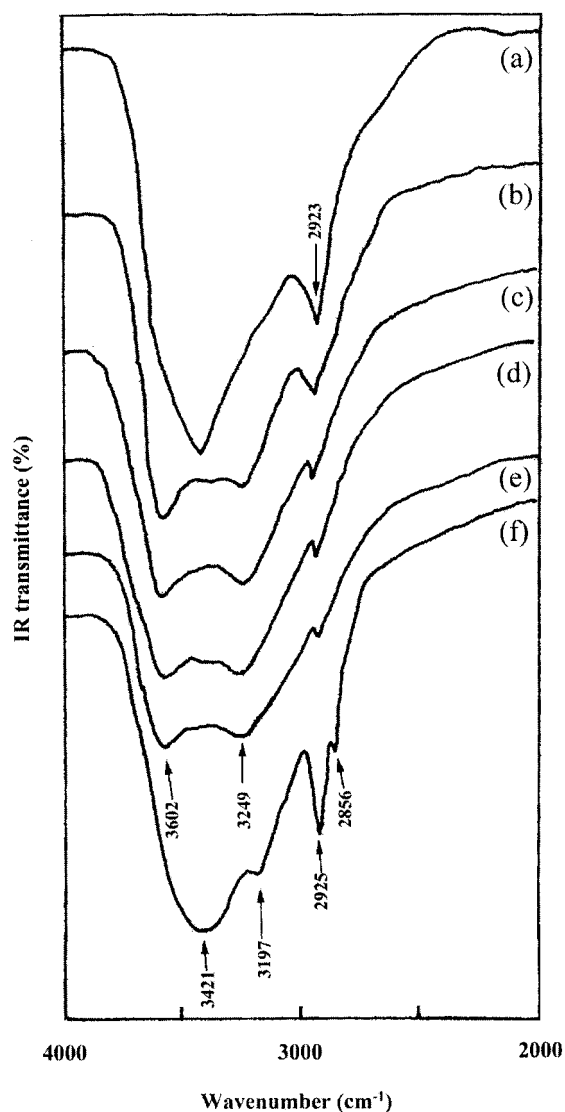


Figure 2 FTIR spectra of KGM (a), PAAm (f), and blend films in the wavenumber range of 2000–4000 cm^{-1} . KGM/PAAm composition: (b) 90/10, (c) 80/20, (d) 70/30, and (e) 60/40.

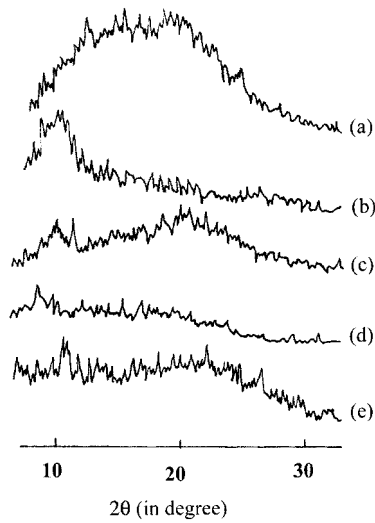


Figure 3 Wide-angle X-ray diffraction patterns of KGM (a), PAAm (e), and blend films. KGM/PAAm composition: (b) 90/10, (c) 70/30, and (d) 50/50.

groups of PAAm should participate in intermolecular hydrogen bonding with $-OH$ and $-COCH_3$ groups of KGM.

To study the hydrogen bond interactions in more detail, difference spectra were calculated by subtracting the spectrum of PAAm from the spectra of the blends. By comparing those spectra with the spectrum of pure KGM, the significant changes of the $-OH$ stretching region for KGM were observed. The major band of KGM centered at about 3400 cm^{-1} , which resulted from the stretching vibration of $-OH$ groups involved in both inter- and intramolecular hydrogen bonds [Fig. 2(a)], broadened and its intensity decreased by blending (the intensity of the decrease was in relation to the blending ratio). Moreover, two new bands appeared at about 3602 and 3249 cm^{-1} [Fig. 2(b)–(e)]. These results implied that part of the hydrogen bonds, in which the OH groups of KGM involved were broken, and the various kinds of hydrogen bonds between KGM and PAAm occurred in different wavenumbers and intensities, resulting from addition of PAAm to KGM, which might account for the band broadening in the $-OH$ stretching region. Similar results can be drawn from the reported blend films of silk

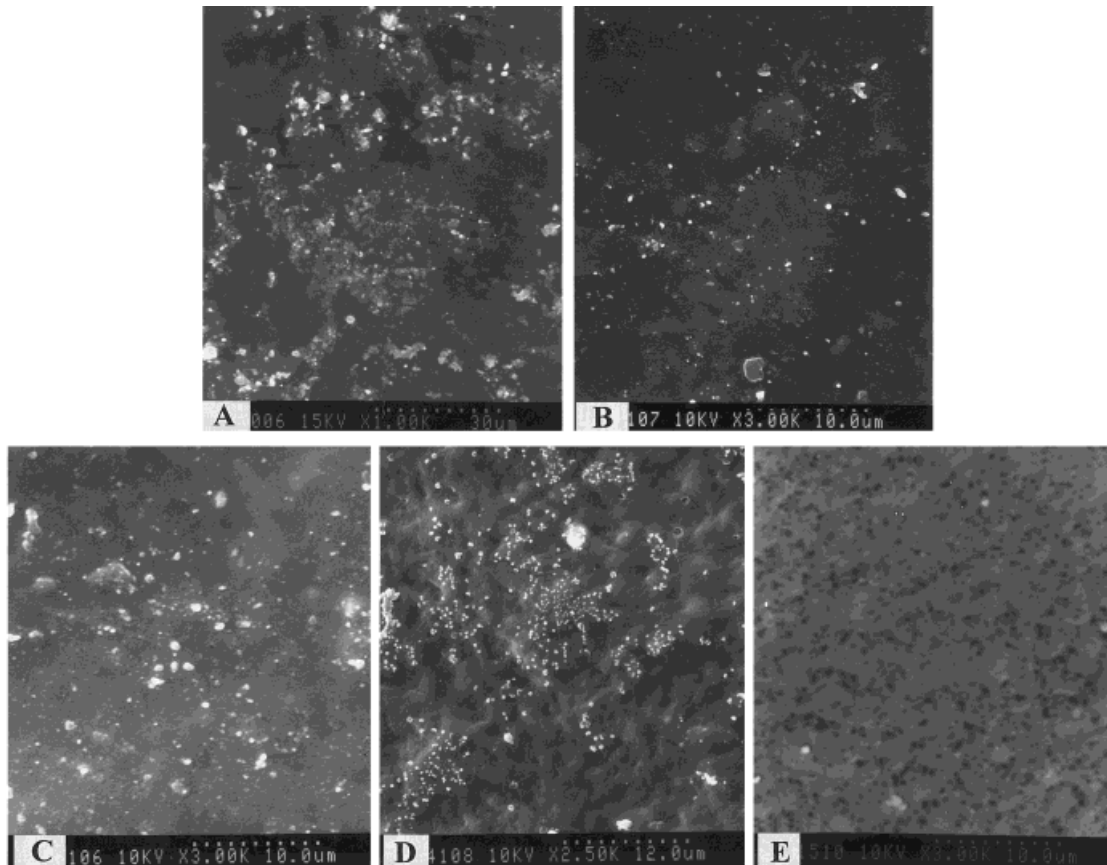


Figure 4 SEM photographs of KGM (a), PAAm (e), and blend films. KGM/PAAm composition: (b) 90/10, (c) 70/30, and (d) 50/50.

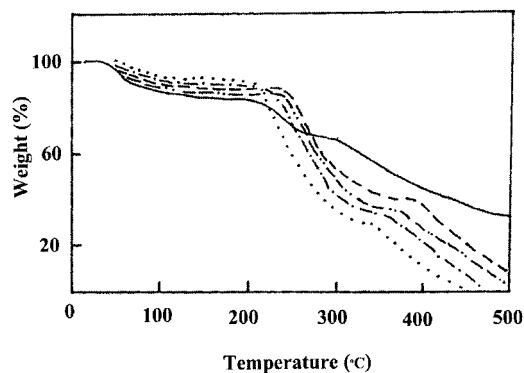


Figure 5 TGA curves of KGM ($\cdot\cdot\cdot$), PAAm (—), and blend films. KGM/PAAm composition: 90/10 (---), 70/30 (— —), and (d) 50/50 (— · —).

fibroin/PAAm.²² In addition, intra- and intermolecular hydrogen bonding interactions among the pure component molecules must be present in the blends because of their ability to hydrogen-bond with themselves. The synergistic effects of the various hydrogen bonds existing in the blends would result in the changes of the physical properties of blends observed later.

The WAXD patterns of the pure and blend films are shown in Figure 3. KGM showed a weak and broad crystalline peak. PAAm did not show any characteristic crystalline peak, indicating PAAm is an amorphous material.¹⁸ If KGM and PAAm have low compatibility, each polymer would have its own crystal region in the blend films, so X-ray diffraction patterns are expressed as simply mixed patterns of KGM and PAAm, with the same ratio as those for blending. However, the weak crystalline peak appeared at $2\theta = 10^\circ$ in the blends when PAAm content was low ($\leq 30\%$). With the increase of PAAm content, the blends showed characteristic amorphous patterns ($\geq 50\%$). These results suggested that intermolecular hydrogen bonding interactions between KGM and PAAm, and intra- and intermolecular hydrogen bonding effects of the pure components must be present in the blends, which destroyed

the original molecular orientation of KGM, resulting in some changes of WAXD patterns of the blends.

The SEM photographs of the pure and blend films are shown in Figure 4. Pure KGM exhibited a morphological structure similar to that reported in the literature.²³ PAAm showed a less compacted amorphous morphology, which was in good agreement with the result from WAXD. The blend films showed smooth surface morphology when the PAAm content was low ($\leq 30\%$) in the blends, indicating the occurrence of good miscibility between KGM and PAAm molecules. As the PAAm content increased ($\geq 50\%$), the morphology of the blend film surfaces changed from being smooth to becoming rough, similar to that of pure PAAm.

The morphological transition of the blends from KGM-like to PAAm-like was consistent with the latter observations concerning the changes in physical properties and mechanical behavior.

Thermal Stability of the Films

The TGA curves of pure and blend films are shown in Figure 5. The KGM showed three steps of weight loss: the initial loss at about 50°C resulted from the loss of water absorbed in the films; the second loss was found at the temperature range of $200\text{--}330^\circ\text{C}$, attributed to disintegrations of the intermolecular side chain²⁴; the third loss, at $330\text{--}450^\circ\text{C}$, was believed to be caused by some type of chemical reactions, such as main-chain disintegrations or rearrangement of some carbon atoms.²⁵ PAAm showed three steps of weight loss located at 50 , 207 , and 308°C : the weight loss at 50°C was attributed to moisture loss; the weight loss at 207°C could be related to thermal processes involving both melting of the PAAm chains and onset of degradation; the weight loss at 308°C was indicative of the occurrence of more extensive thermal degradation processes.²²

TGA curves of all the blends showed the greatest weight loss in the temperature range of $200\text{--}400^\circ\text{C}$, which were attributed to the disintegra-

Table I Thermal Properties of Pure and Blend Films

KGM/PAAm ^a	100/0	90/10	80/20	70/30	0/100
(I) Temperature ($^\circ\text{C}$)	202	218	232	239	207
(II) Temperature ($^\circ\text{C}$)	336	375	382	393	308
Weight loss values (%) in the temperature range of (I) and (II)	73.1	57.4	52.1	49.3	22.4

^a (I) Primary decomposition; (II) secondary decomposition.

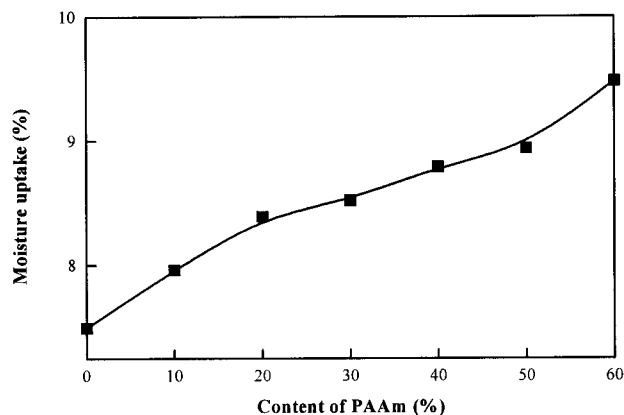


Figure 6 Moisture content of the blend films as a function of blending ratio.

tion of intermolecular and partial breaking of the molecular structure.²⁴ The starting temperature of greatest thermal degradation and the values of the weight loss (Table I) increased in the sequence of 70 : 30 > 80 : 20 > 90 : 10 > PAAM or KGM. This outcome accounted for the higher thermal stability attained by the blends resulting from the synergistic effect of various hydrogen bonding interactions.

Water Absorbability of the Films

The moisture content of the blend films as a function of blending ratio is shown in Figure 6. The water absorbability of the blend films increased with the increase of PAAM content. Taking chemical and aggressive structures into account, PAAM contains a lot of primary amide groups on its chain bone and exhibits the less-compacted morphological structure, which seems to indicate a higher accessibility of water to PAAM. The addition of this amorphous material to KGM, as well as the interactions of hydrogen bonds in the amorphous regions of the blends, might have changed both the structure and the behavior of the original KGM crystalline domain, resulting in the higher water molecule uptake of the blends. The results are similar to those of silk fibroin/cellulose²⁶ and silk fibroin/sodium alginate²⁴ blend films.

Mechanical Properties of the Films

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 blends were plotted as functions of the blending

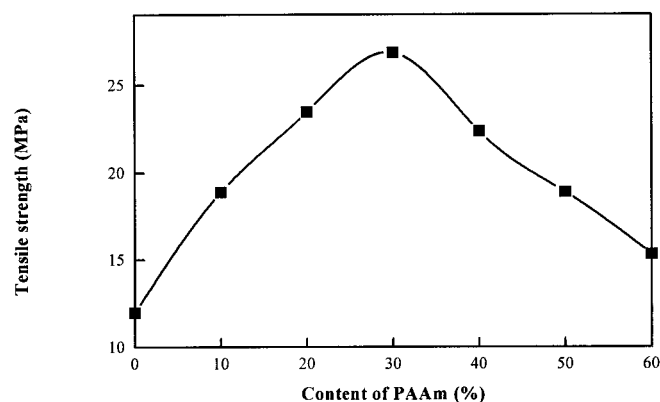


Figure 7 Tensile strength of the blend films as a function of the blending ratio.

ratio, as shown in Figure 7 and Figure 8, respectively.

The addition of PAAM to KGM was effective in improving the mechanical properties of the blend films. The tensile strength of the blends was higher than that of pure components and reached a maximum value at about 30 wt % of PAAM content. The remarkable increase in tensile strength of blend films indicated that all kinds of intra- and intermolecular interactions through hydrogen-bond formation occurred in the films. Figure 8 shows that the elongation at break increased with the increase of PAAM content, which might be attributed to various factors, such as the intrinsic properties of PAAM, the higher hygroscopic of the blends, and the plasticizing effect of the water absorbed in the films. Meanwhile, the occurrence of hydrogen bonding interactions in the blends should be taken into account. PAAM played an important role in improving the mechanical properties of the blends, such as those

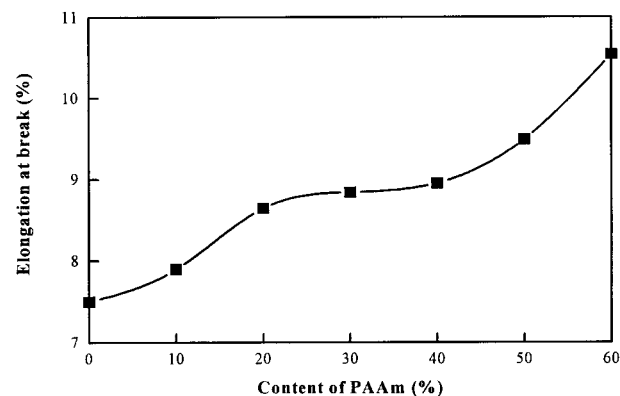


Figure 8 Elongation at break of the blend films as a function of the blending ratio.

reported for the blend films of silk fibroin and PAAm.²²

CONCLUSIONS

Results of this investigation showed that PAAm could be usefully added to KGM for preparation of transparent blend films by using the solvent-casting method. The blend films exhibited some interesting physical properties. It was noteworthy that thermal stability, water absorbability, and mechanical properties of the blends were improved by blending PAAm with KGM. These synergistic effects were attributed to the formation of specific intermolecular interactions between KGM and PAAm. The nature of these interactions was determined by means of FTIR, which showed that the pattern of the -OH stretching region for pure KGM was distributed by addition of PAAm, and new intermolecular hydrogen bonding formed between two kinds of polymer chains. Meanwhile, intra- and intermolecular hydrogen bonding interactions of pure components occurring in the blends were also an important factor.

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