Characterization of Konjac Glucomannan–Gelatin Blend Films

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ABSTRACT: Novel blend films of konjac glucomannan (KGM) with gelatin were prepared by using the solvent-casting technique. Transparent blend films were obtained in all blending ratios of the two polymers. The structure and physical properties of the films were investigated by Fourier transform IR, wide angle X-ray diffraction, thermogravimetric analysis, differential thermal analysis, scanning electron microscopy (SEM), and strength tests. The results indicated that intermolecular interactions between the KGM and gelatin occurred that were caused by hydrogen bonding and the physical properties of the films largely depended on the blending ratio. The crystallinities of the blend films decreased with the increase of the KGM. The thermal stability and mechanical properties (tensile strength and elongation at break) of the films were improved by blending KGM with gelatin. It is worth noting that the blend films had a good tensile strength of 38 MPa when the KGM content in the blend films was around 30 wt %. The surface morphology of the blend films observed by SEM displayed a certain level of miscibility. Furthermore, the water absorbability of the blend films was also measured and discussed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1596–1602, 2001

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

INTRODUCTION

Nowadays, there is rising concern about environmental issues, particularly those related to effective management of postconsumer waste. This ecological awareness has led to development of new biodegradable materials, which can be valid alternatives in specific situations when recycling or incineration is difficult or not economically feasible.[1] Consequently, natural polymers and biodegradable polymers have become attractive as suitable materials for environmental conservation. Many highly functional materials have been developed in various industries by mixing different polymers.[2]

Konjac glucomannan (KGM), whose main chain consists of β-1,4 linked mannose and glucose units with a low degree of acetyl groups,[3–5] is a water-soluble polysaccharide of the tubes from the *Amorphophallus konjac* plant. The research work on KGM was successful in fields such as pharmaceuticals, food, and chemical engineering. Several articles reported blend films of KGM and other natural or synthetic polymers, such as pullulan,[6] cellulose,[7,8] and hydroxypropylcellulose.[9] The blend of KGM with pullulan prepared from water formed transparent films. The mechanical properties and moisture uptake of the blend films increased with the increase of the KGM content in the blend. Zhang et al.[7,8] reported the preparation of blend films of KGM with cellulose from cuproammonium solution. The blend films were miscible when the KGM content was in the range

of 0–30 wt %. The coagulation condition and content of the KGM play an important role in the structure and properties of the blend films. In our previous works,[10] blend films of KGM and chitosan were prepared and characterized by Fourier transform IR (FTIR), wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and other analytical methods. The results indicated that intermolecular hydrogen bonding occurred between the two polymers, resulting in the improvement of the thermal stability and mechanical strength.

Gelatin is a well-characterized protein fragment obtained by partial degradation of water-insoluble collagen fiber.[11] Because of its nontoxicity and good living body compatibility, gelatin has been widely used in the biomaterials,[12–14] food,[15] and cosmetic[16] fields. However, it is difficult to form a gelatin film and film is brittle, limiting its further applications. To introduce superior properties into the gelatin, a simple method is to blend a polymer of gelatin and KGM by mixing the two polymers in an aqueous solution. Thus, gelatin can be expected to act as a material to supply essentially superior properties and KGM is expected to act as a material to support better forming ability and higher extensible mechanical properties to the gelatin. In this study, blend films of KGM with gelatin were prepared by using the solvent-casting technique. The physical properties and morphology of the blend films were studied by FTIR, WAXD, DTA, TGA, SEM, and strength tests. The effects of the blending ratios of the blend films on the properties were studied in detail. These results might be helpful in finding further applications in biomedical, pharmaceutical, and other fields for the blend materials from natural polymers with enhanced functional performance.

EXPERIMENTAL

Materials

The gelatin was purchased from Chemical Agents Factory of Shanghai, and the weight-average molecular weight (M_W) was determined to be 5.0 $\times 10^4$ with gel permeation chromatography, and protein (bovine serum albumin M_W = 68,000; r-globulin M_W = 55,000 and 25,000; egg-white protein M_W = 43,300; ribonuclease M_W = 3700; cytochrome M_W = 11,700) was used as a standard.

Purified KGM was obtained according to our previous work.[10] The viscosity-average molecular weight of KGM was 2.5×10^5 as calculated by the Mark–Houwink equation: $[\eta] = 3.8 \times 10^{-2} M^{0.723}$.[17] The other chemical agents were analytically pure.

Preparation of Films

Desired quantities of gelatin were dissolved in hot water at 100°C and then cooled down at room temperature to obtain a 3 wt % solution (I). KGM was dissolved in water to obtain a solution of 3 wt % (II). Pure KGM, pure gelatin, and a mixture of I and II with different KGM/gelatin weight ratios (70/0, 60/10, 50/20, 40/30, 30/40, 20/50, 10/60, and 0/70) were cast on a Teflon gasket, and then the water was evaporated at room temperature to obtain transparent films. The pure films and blends were dislodged carefully and then subjected to vacuum drying for 48 h to obtain the dried films before measurement. The thickness of the film was 80 ± 5 μm. The films with the different ratios mentioned above were coded as KGM, KG-1, KG-2, KG-3, KG-4, KG-5, KG-6, and GE, respectively.

Measurements

The FTIR spectra of the films were measured by a Nicolet 170SX FTIR spectrometer with KBr pellets. The X-ray diffraction patterns of the films were found with a Rigaku (Japan) Dmax-II X-ray diffractometer with a CuKα target at 40 kV and 50 mA and a diffraction angle of 40–4°. The crystallinities (X_c) of the films were calculated by[18]

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

where F_c and F_a are the areas of the crystal and noncrystal regions, respectively. The TGA and DTA of powered samples of the films were performed on a PRT-2 TGA-DTA thermobalance (Beijing Optical Instruments Factory) under a nitrogen atmosphere with a flow capacity of 30 mL/min. The stress–strain measurements were performed on an AG-A electron tensile tester (Shimadzu Co.) at 24°C and 60% relative humidity using a crosshead speed of 5 mm/min; the specimens (80 ± 5-μm thickness and 4-mm width) were 30 mm long. The morphology of the film surfaces was examined by using a Hitachi SX-650 scanning electron microscope after gold coating.

The weight of the dried samples (W_0) was measured directly. Then they were dipped in distilled water to attain a constant final weight (W_1) and set in an atmosphere of 24°C and 60% relative humidity for 2 days to obtain the final weight (W_2). The degree of swelling (Q_W) and moisture uptake (W_m) were calculated with the following equations:

$$Q_W = (W_1 - W_0)/W_0$$

$$W_m = (W_2 - W_0)/W_0 \times 100\%$$

RESULTS AND DISCUSSION

General Properties of Films

Pure and blend films were transparent and optically clear to the naked eye. The KGM film was easily dissolved in the distilled water.

FTIR is of importance in the study of the molecular structure. The width and intensity of the spectrum bands, as well as the position of the peaks, are all sensitive to environment changes and to the conformations of macromolecules on the molecular level. Intermolecular interactions occur when different polymers are compatible, so the FTIR spectrum of the blend is different from those of pure polymers, which is advantageous to the study of the extent of polymer compatibility. Figure 1 shows the IR spectra for the films of KGM, the blends, and gelatin in the wavelength range of 4000–400 cm^{-1}. The characteristic absorption bands of the mannose in the KGM appeared at 810 and 880 cm^{-1}.[19] The stretching peaks of the C—H of methyl at 2894 and 2921 cm^{-1} and of the carbonyl at 1736 cm^{-1} are assigned to the aceto groups in KGM.[20] As is well known, the absorption bands of amides I–V are conformationally sensitive bands for polypeptides and protein.[21] The FTIR spectrum of gelatin showed strong absorption bands at 3200–3500 (NH stretching), 1667 (amide I, CO, and CN stretching), 1549 and 1239 (amides II and III, respectively, mainly NH bending and CN stretching), and 650 cm^{-1} (amide V, CN torsion, and NH bending).

As far as the position and intensity of the various bands of the blend films are concerned, the major bands centered at 3200–3500 cm^{-1} showed significant changes, which broadened and shifted to a higher wave number. Moreover, their intensity was decreased by blending and the extent of
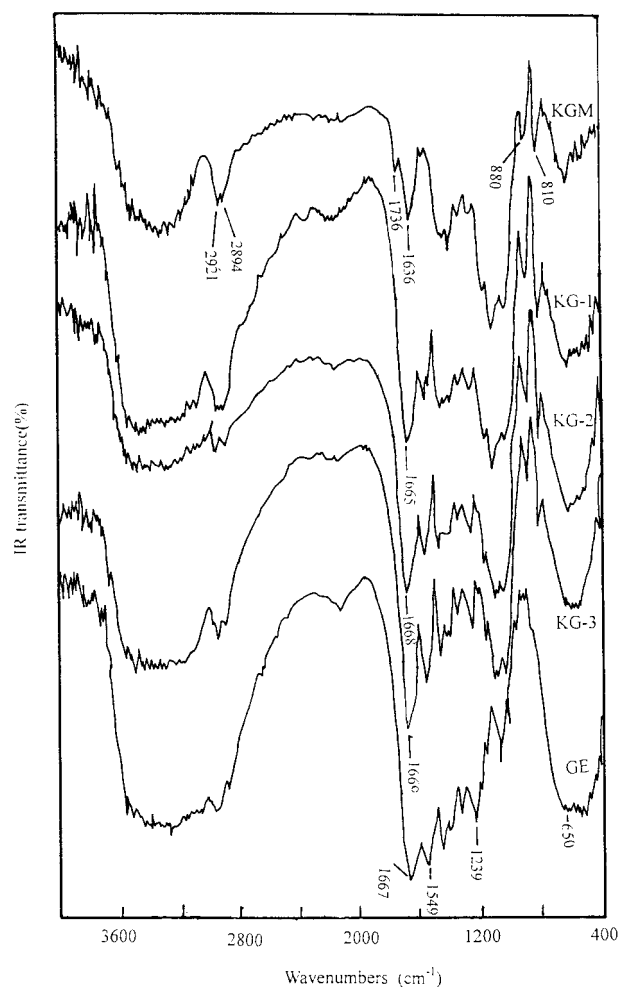

Figure 1   FTIR spectra of pure and blend films.

the decreases was related to the blending ratio. The peak at 1736 cm^{-1} for KGM disappeared in the spectra of the blend and the peak at 1636 cm^{-1} shifted to around 1669 cm^{-1} with the increase of gelatin. These significant changes mentioned above indicated the presence of interactions between the KGM and gelatin molecular chains through hydrogen bond formation.

Crystallinities of Films

X-ray diffraction patterns of pure and blend films are showed in Figure 2. Two typical peaks in 2θ = 7.6° and 18° were observed for gelatin as reported.[22] If KGM and gelatin have low compatibility, each polymer has its own crystal region in the blend films. So X-ray diffraction patterns are expressed as simply mixed patterns of KGM and gelatin with the same ratio as those for blending. However, the patterns of the blend films showed
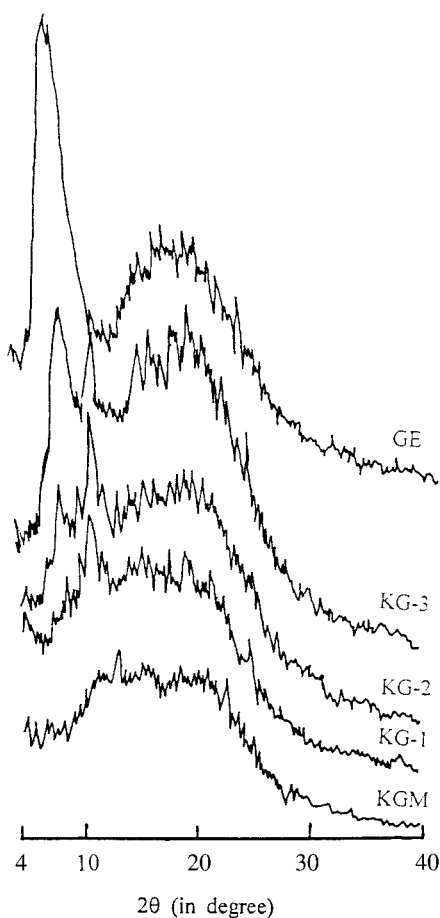
Figure 2   WAXD of pure and blend films.

the peak intensity at around $2\theta = 18°$ decreased and the diffraction peak at $2\theta = 7.6°$ disappeared gradually with the increase of KGM content. A new peak at around $2\theta = 10°$ appeared in the blend films. The crystallinity was calculated and the order was GE > KG-3 > KG-2 > KG-1 > KGM. The changes of the diffraction patterns indicated that an intermolecular hydrogen bonding interaction occurred between the two polymers and destroyed the original crystalline domains of gelatin and KGM, resulting in a new crystalline domain at 10°.

Thermal Properties of Films

The thermal behavior of the pure and blend films was investigated by means of DTA measurements (Fig. 3). The DTA curve of the pure KGM film showed the endothermic peak at about 66°C was due to loss of moisture. An exothermic peak appearing at about 266°C was attributed to the greatest thermal degradation of KGM. The DTA

curve of gelatin showed exothermic peaks at about 320 and 420°C, which were attributed to the disintegration of the intermolecular side chains and main chains, respectively.

Overlapping of the characteristic thermal transition of KGM and gelatin seemed to be the main feature emerging from the above DTA results. However, some changes appearing in the DTA curves of the blend films may suggest that hydrogen bonding interaction was established between the KGM and gelatin. It is worth noting that all films showed exothermic peaks at about 260–320°C, which resulted from the greatest thermal degradation of the films (see TGA results). With the increase of the gelatin content in the blend, the greatest thermal degradation peak shifted to a higher temperature. The two exothermic peaks for gelatin above 400°C turned into one peak in the blend films.

The results of the TG measurements of pure and blend films are shown in Figure 4. The starting temperature of the greatest degradation of the blends shifted to higher temperature with the increase of gelatin content. The thermal stability of the blend films was in the following order: GE (245°C) > KG-3 (235°C) > KG-2 (230°C) > KG-1 (210°C) > KGM (203°C). This order is the same as that of their crystallinities, indicating that their crystalline domains and hydrogen bonding interaction enhanced the thermal stability of the films.[23]
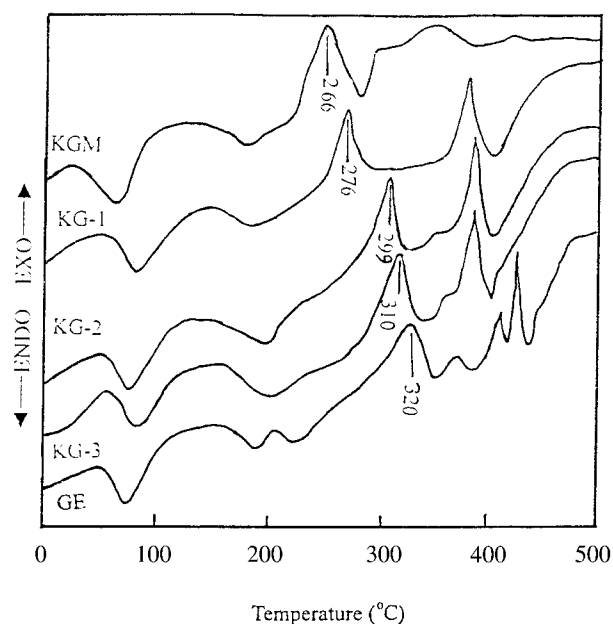

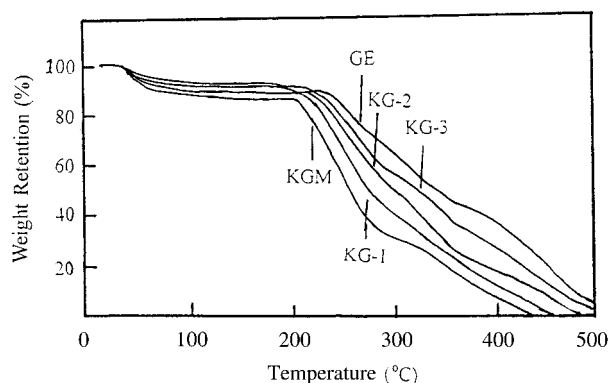**Figure 3**   DTA curves of pure and blend films.

Figure 4 TGA curves of pure and blend films.

Mechanical Properties of Films

Because polymer materials, such as films, may be subjected to various kinds of stress during use, the determination of the mechanical properties involves not only scientific but also technological and practical aspects.[24]

The dependence of the tensile strength on the KGM content for the blend films is shown in Figure 5. The tensile strength of the blend films was higher than films of KGM and gelatin and reached a maximum point at about 30 wt % KGM content, achieving 38 MPa. The remarkable increase in the tensile strength of the blend films indicated the presence of intermolecular interactions between KGM and gelatin molecules in the films.

The dependence of the elongation at break on the KGM content for the blend films is shown in Figure 6. The elongation at break of the blend films increased with the increase of the KGM.
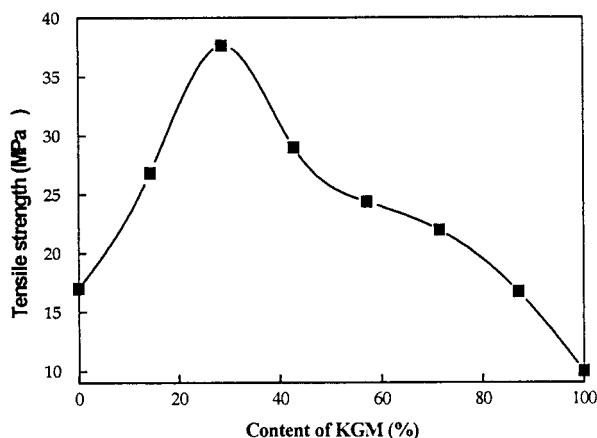

Figure 5 The dependence of the tensile strength on the KGM content for the blend films.
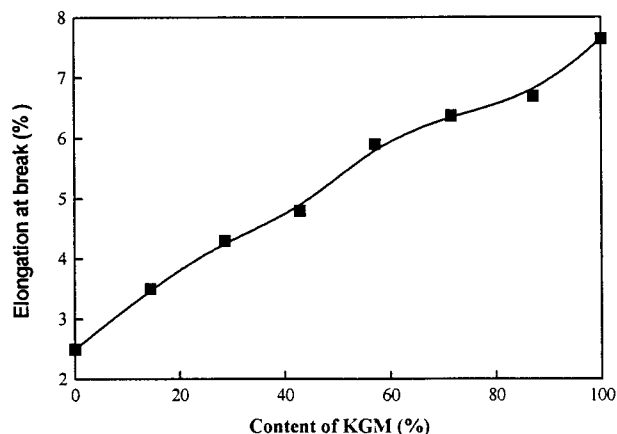

Figure 6 The dependence of the elongation at break on the KGM content for the blend films.

This result might be attributed to such factors as the hydrogen bonding interaction between the two polymers, the plasticizing effect of water absorbed in the films, and so forth. Meanwhile, the increase of crystalline domains suppressing the slipping behavior of polymer molecular chains should be taken into account. KGM play a key role in improving the mechanical properties of gelatin films. Similar conclusion have been drawn from results of silk fibroin films blended with alginate and cellulose.[23,24]

Morphological Characteristics of Films

The surface morphology of pure and blend films by SEM are shown in Figure 7. The pure KGM film exhibits a better uniform microstructure, which leads to the formation of film with densely packed KGM chains. The pure gelatin film showed a typically crystalline structure. As the KGM increased, the morphology of the blend film surfaces changed from being smooth to becoming microphase separated, implying that the miscibility between the two kinds of polymers changed from good to a certain level of miscibility, which may have led to the decrease of crystallinity.[25] Good miscibility and a certain level of miscibility are necessary, because they can change the physical properties of the materials.

Water Absorbability of Films

Generally, the chemical structure and aggregate structure can both affect the water absorbability of gelatin. Taking the chemical structure into account, blending gelatin with KGM can increase the water absorbability of the blend films because
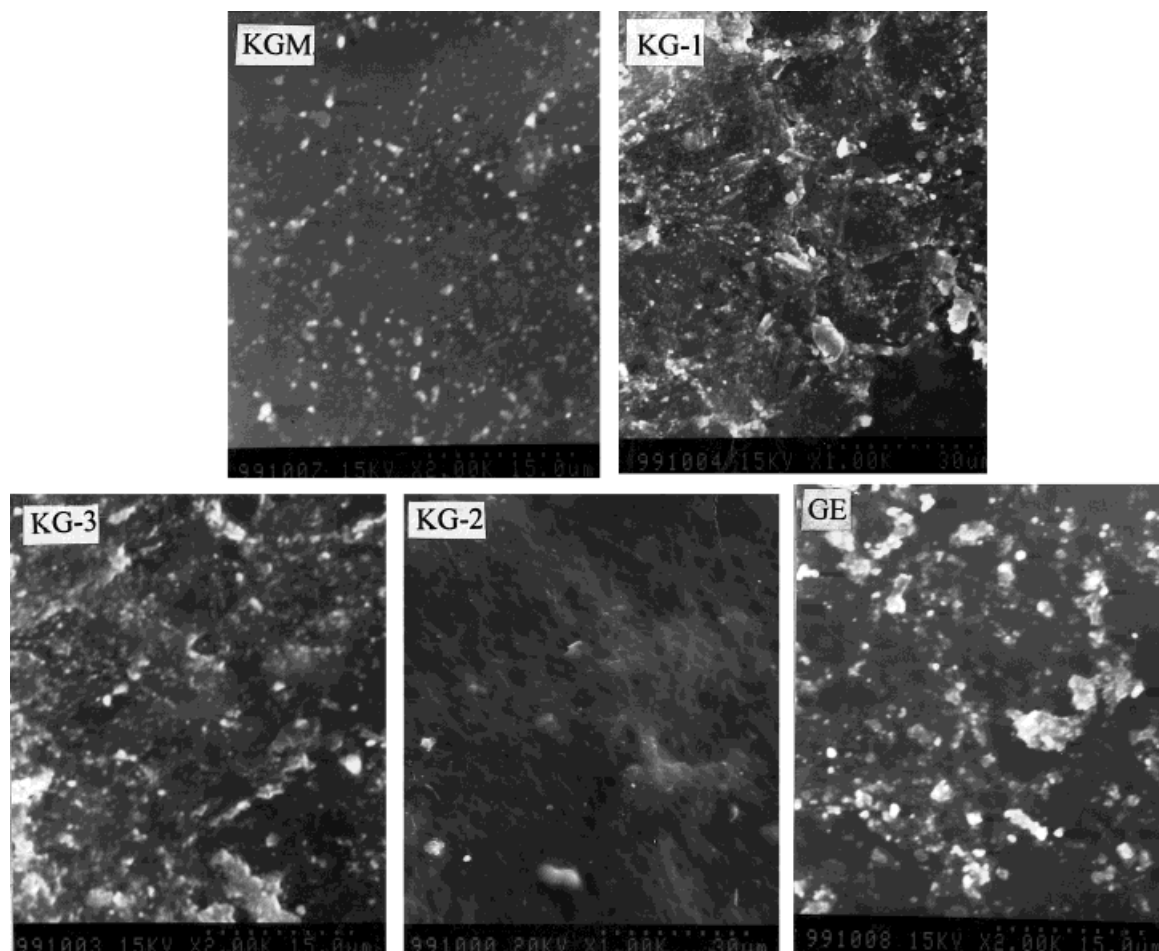
Figure 7   SEM photographs of pure and blends films.

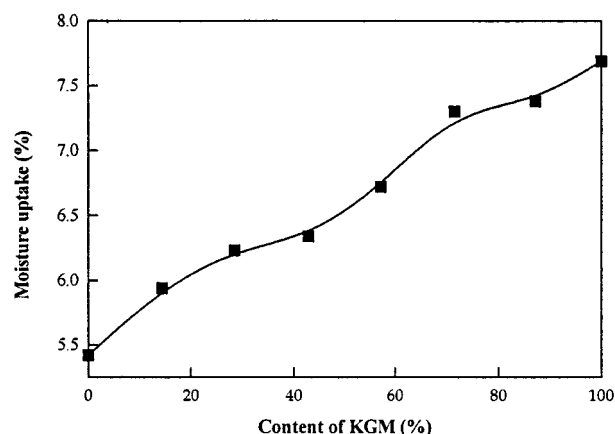KGM contains a lot of hydrophilic hydroxyl groups. Figure 8 shows the dependence of the moisture uptake on the KGM content for the blend films. As expected, the addition of KGM to the gelatin resulted in higher moisture uptake. This result seems to explain the behavior of improving the elongation at break of the blend materials as resulting from the plasticizing effect of water absorbed in the films. The dependence of the degree of swelling on the KGM content for the blend films is shown in Figure 9. Regretfully, the degree of swelling of the pure KGM film could not be obtained because of its water solubility. A tendency similar to the behavior of the moisture uptake is expressed in Figure 9: the degree of swelling of the blend films increased with the increase of the KGM content.

Figure 8   The dependence of the moisture uptake on the KGM content for the blend films.

CONCLUSIONS

The results reported confirm that KGM was satisfactorily added to gelatin for preparation of
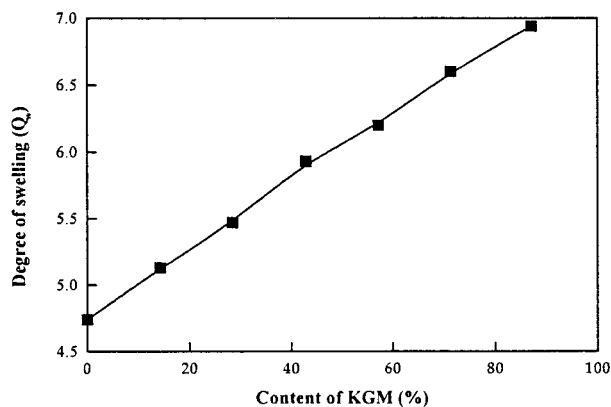
Figure 9   The dependence of the degree of swelling on the KGM content for the blend films.

transparent blend films by using the solvent-casting method. The physical properties of the blend films depended on the blending ratio. The results from IR and WAXD indicated the presence of interactions between the KGM and gelatin in the films. The crystallinities of the blend films decreased with the increase of KGM content. The thermal properties, water absorbability, and mechanical properties of the blend films were improved. It is noteworthy that blending KGM with gelatin permitted the preparation of films with excellent mechanical behavior when the KGM content in the blend film was about 30 wt %. The KGM plays an important role in the enhancement of the tensile strength and elongation at break of the blend films. This result was probably due to the interactions that should mainly depend on the ability of KGM and gelatin to establish intermolecular hydrogen bonds.

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