Study on Physical Properties of Blend Films from Gelatin and Polyacrylamide Solutions

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ABSTRACT: Blend films of gelatin and polyacrylamide (PAAm) were prepared by casting the mixed aqueous solutions of both samples in different ratios. All blend films obtained are optically clear to the naked eye. The structure and physical properties of the films were studied by FT-infrared (FTIR), wide-angle X-ray diffraction (WAXD), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The experimental results show that the blend films exhibit the higher thermal stability and improved mechanical properties of both tensile strength and elongation at break in dry states, which suggests the occurrence of interaction detected by FTIR between gelatin, PAAm, and water molecules in the films. The morphological transition of the blend films from gelatin-like to PAAm-like was observed by SEM. Furthermore, moisture content and water swelling property of the blend films were also investigated, which was consistent with the results from SEM. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 949–955, 2002

Key words: gelatin; polyacrylamide; blend films; physical properties; hydrogen bonds

INTRODUCTION

With polymer blends exhibiting two-phase behavior, definite advantages can be derived if mechanical compatibility can be achieved. With miscible polymer mixtures, mechanical compatibility is assured, and a property compromise between the constituents is therefore achieved.[1] In the recent two decades, polymer blends as a class of materials encompass many different products resulting form the combination of two or more components.[2] Their potential applications in different fields are now becoming more and more obviously.

Polymer blending materials are widely used in the biomedical field. However, blend materials from either synthetic or natural polymers alone are not always able to meet all the complex demands of biomaterials. The success of synthetic polymers as biomaterials relies on their wide range of mechanical properties, transformation processes that allow a variety of different shapes to be easily obtained, and low production cost. Biological polymers present good biocompatibility, but their mechanical properties are often poor, the necessity of preserving biological properties complicates their processability, and their production or recovery costs are very high.[3] Keeping these factors in view, biologically polymeric materials on blends of synthetic and natural polymers had been well reported in recent years, such as poly(vinyl alcohol) (PVA)/silk fibroin,[4–6] PVA/chitosan,[7,8] and PVA/gelatin.[9]

Gelatin is a degraded form of collagen that is a connective tissue protein present in most of the vertebrates.[10] Because of its properties of nontoxic, nonirritant, and good living body compati-

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bility, gelatin has been widely used in many fields of food, pharmacology, and cosmetic applications.[11]

Usually, the formation of specific intermolecular interactions through hydrogen bond formation between two or more polymers is responsible for the observed mixing behaviors and properties of the blends.[12,13] The selection and use of polymers can potentially form hydrogen bonds when two polymers mixed, as well as study the properties of the blend films are of importance to find further applications of the resulting materials for biomedical and pharmaceutical devices. Polyacrylamide (PAAm) is a water-soluble polymer with several primary amide groups on its chain backbones,[14] which can form hydrogen bonds well with gelatin, so PAAm as a suitable candidate blended with gelatin is therefore selected. Moreover, PAAm is a polymer of biomedical and pharmaceutical interest widely studied as hydrogel for blood compatible applications.[15]

In this article, blend films of gelatin and PAAm were prepared by the casting solution method. The physical properties and morphology of the blend films were studied by means of FTIR, WAXD, TDA, TGA, SEM, tensile measurements, and water absorbability. The physical properties and morphology will be detailed discussed in relation to the blending ratios. The results reported in this article might be help in finding further application of those blending materials having enhanced functional performance in biomedical and pharmaceutical fields.

EXPERIMENTAL

Materials

Gelatin was purchased from Chemical Agents Factory of Shanghai, the average molecular weight (M_w) was determined to be 5.0×10^4 with gel permeation chromatography, and the protein was used for calibration. PAAm was purchased from the Chemical Agent Supplier of Shanghai, whose average molecular weight (M_w) was 3.0×10^6. Other chemical agents used were of analytical grade.

Preparation of the Films

Gelatin and PAAm were dissolved in water to obtain the solution of 3%, respectively. The pure and mixture of both polymer aqueous solutions with different weight ratios (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100, gelatin/PAAm) were cast on a Teflon gasket and allowed the water to evaporate at room temperature. The films of pure and the blend were dislodged carefully, and then subjected to further drying under vacuum for 2 days. The dried films of different ratio above were coded as Gel, GP-1, GP-2, GP-3, GP-4, GP-5, and PAAm, respectively. The films thickness ranged 80 ± 5 μm.

Measurements

FTIR spectra of the films were recorded on a Nicolet (U.S.A) 170SX FTIR spectrometer and used as KBr pellets. The X-ray diffraction patterns of the films about 80 μm thickness with a Rigaku (Japan) Dmax-II X-diffractometer operated at 40 kV and 50 mA using CuK_α radiation. The diffraction angle was ranged 40–5° and crystallinity (X_c) of the films was calculated by[16]

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

where F_c and F_a is the area of crystal and noncrystal regions, respectively. The TGA and DTA of powered samples of the films were performed in room atmosphere by a Shimadzu DT-30 thermal analyzer, the temperature was raised to 500°C at heating rate of 10°C/min. The stress–strain measurements were performed by an AG-A electron tensile tester (Shimadzu Co.) at the environment of 10°C and 60% relative humidity using a crosshead speed of 5 mm/min, the specimens (80 ± 5 μm thickness and 10 mm width) used were 70 mm long. The morphology of film surfaces was examined by a Hitachi SX-650 scanning electron microscopy (Japan) after gold coating. The dried films were set in the room temperature for 2 days, and dipped into distilled water to attain a constant soaked final weight. Moisture regain and degree of swelling were calculated with following equation:

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

$$Q_w = (W_2 - W_0)/W_0$$

where W is moisture regain and Q_w is degree of swelling, W_0, W_1, W_2 are weight of dried films, set in the room temperature and soaked state, respectively.

RESULTS AND DISCUSSION

FTIR Spectra of the Films

FTIR is of importance to study the molecular structure. The width and intensity of spectral

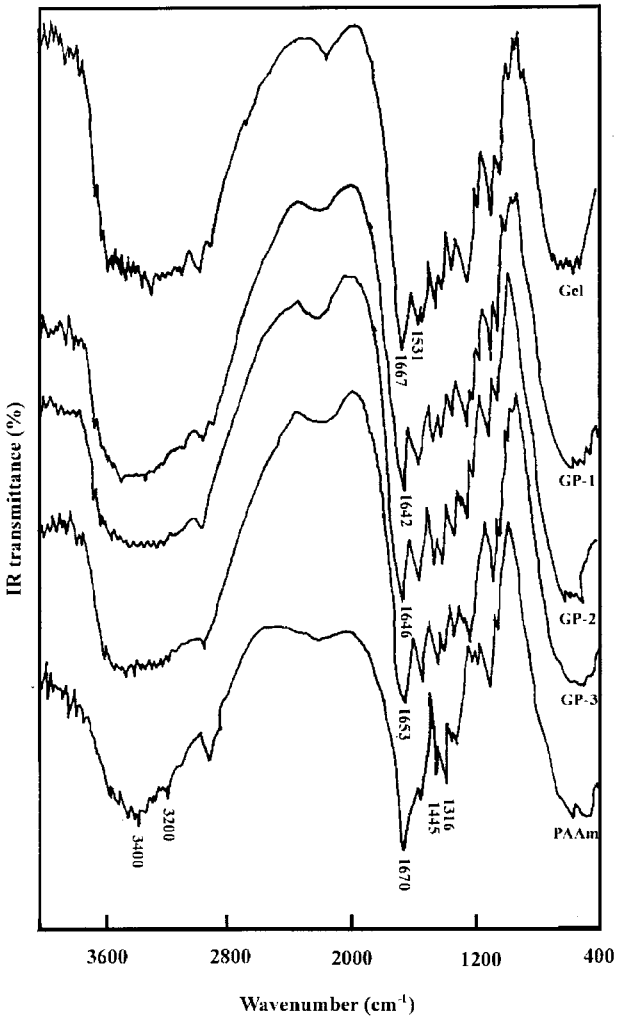

Figure 1 The FTIR spectra of pure and blend films.

bands as well as position of peaks are all sensitive to environmental changes and to conformations of macromolecule on molecular level. Intermolecular interactions occur when two polymers are compatible. So the FTIR spectra of the blends are different from those of the pure polymer, which is advantageous to study the extent of compatibility of the blend polymers. Figure 1 shows the infrared spectra for the films of gelatin, the blends and PAAm in the wave number range of 4000–400 cm^{-1}. The IR spectrum of gelatin shows strong absorption bands at 3300 cm^{-1} (NH stretching), the peaks at 1667 cm^{-1}, 1531 cm^{-1} attributed to carbonyl stretching and amino groups, respectively.[17,18] The IR spectrum of PAAm exhibits strong bands at 3400 and 3200 cm^{-1}, which are assigned to stretching vibration of N—H and 1670 cm^{-1} (C═O stretching).[14,19] The bands at 2932 cm^{-1} (CH stretching) and 1500–1300 cm^{-1} (various CH bending) were also detected.[14]

The spectra of the blends are characterized by the presence of the absorption bands typical of the pure components, with the intensity roughly proportional to the blending ratio. However, the NH stretching band centered at 3300 cm^{-1} for gelatin boarded, and its intensity decreased by blending. Incorporation of PAAm leads to a small modification in the spectrum of gelatin, i.e., shifting of both carbonyl (1667 cm^{-1}) and amino bands (1531 cm^{-1}). These changes of mentioned above imply that the occurrence of hydrogen bonds between gelatin and PAAm molecules.

Crystallinity of the Films

X-ray diffraction patterns of pure and the blend films are showed in Figure 2. The pattern of gelatin shows two typical peaks in $2\theta = 7.6°$ and 18°, which is consistent with the reported result.[11] The pattern of PAAm, as showed in Figure 2, has very weak board shape, indicating PAAm is an amorphous material.[19] If gelatin and PAAm have low compatibility, each polymer would have its own crystal region in the blends, so X- ray diffraction patterns are expressed as simply mixed patterns of gelatin and PAAm with the same ratio as those for blending, although no peaks other than those for gelatin and PAAm themselves were detected in the patterns of the blend films. However, the intensity of diffraction peak at $2\theta = 7.6°$ for gelatin decreased, and the intensity of the peak at $2\theta = 18°$ increased compared with gelatin resulted from addition PAAm to gelatin. The crystallinity of Gel, GP-1, GP-2, and GP-3 was 69, 59.6, 64.2, and 51.8%, respectively. The change of crystallinity of the blends, according to Lee et al.'s analysis[20] of the PVA/chitosan blend system, means the occurrence of intermolecular hydrogen bonding between two components, and this interaction prevents the gelatin from "crystallization" by comparison of diffraction pattern for pure gelatin with that for the blends.

Thermal Stability

Figure 3 shows the DTA curves of gelatin, the blends, and PAAm. The pure gelatin film shows an endothermic peak at 68°C attributed to the loss of moisture, the endothermic peak at 211°C marks the transition from the glass to rubber state (T_g).[9,21,22] The curve of pure PAAm film is characterized at about 240°C, which is attributed

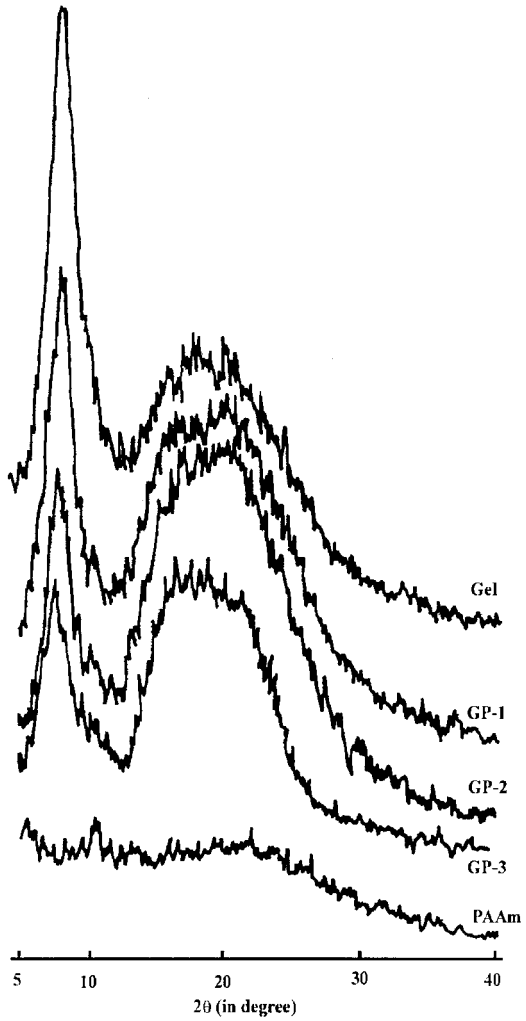

Figure 2 The wide-angle X-diffraction patterns of pure and blend films.

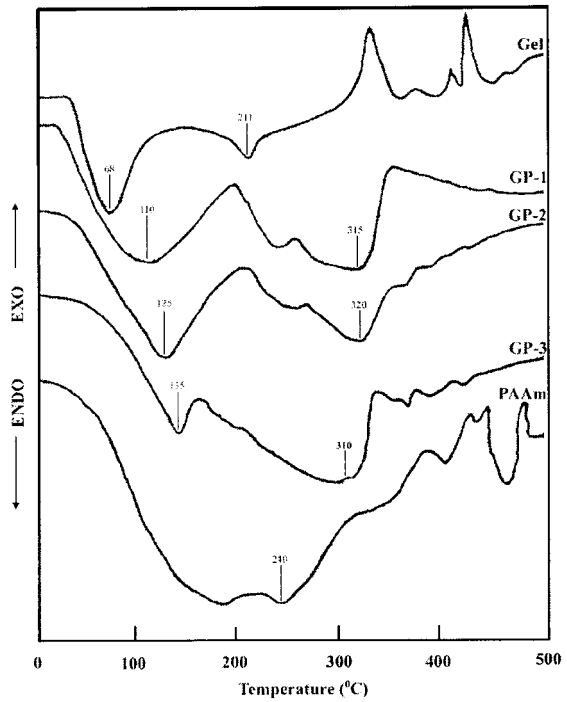

Figure 3 The DTA curves of pure and blend films.

to various thermal induced transitions, such as melting of PAAm chains and beginning of thermal degradation[14] (also see the TGA result).

The curves of the blend films shows the new exothermic peaks appeared in the temperature range of 150–200°C and the characteristic peaks above 300°C for pure gelatin and PAAm disappeared. All blend films showed endothermic peaks at around 325°C, which resulted from the greatest degradation of the films (see TGA result). Significant changes of DTA curves of the blend films suggest that strong interaction established between gelatin and PAAm molecules.

TGA results of pure and blend films are shown in Figure 4. The curve of pure gelatin shows two zones of weight loss. The first weight loss at approximately 60 –70°C was due to the loss of water; the second weight loss started at about 240°C, showing that taking place of different extent thermal degradation of the gelatin. PAAm shows three steps of weight loss located at 100, 200, and 340°C.[14] The former is attributed to moisture loss; weight loss at 200°C can be related to thermal processes involving both melting of the PAAm chains and onset of degradation. The third

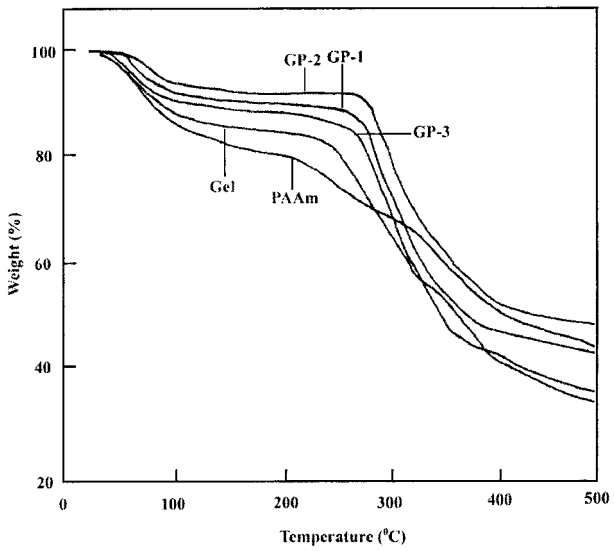

Figure 4 The TGA curves of pure and blend films.

drop at 340°C is indicative of the occurrence of more extensive thermal degradation processes.

TGA curves of all blend films show the greatest weight loss in the temperature range of 250–400°C, which are believed due to the disintegration of intermolecular and partial breaking of the molecular structure.[23] As shown in Figure 4, it is understood the blend films show better thermal stability than pure components. The greatest degradation temperature increased in the sequence of GP-2 (284°C) > GP-1 (279°C) > GP-3 (275°C), which is the same as that of their crystallinity, implying thermal stability of the films was improved by their crystalline domains and hydrogen bonding interactions.[24]

Mechanical Properties of the Films

Because polymer materials, such as films, may be subjected to various kinds of stress during being used. The study of mechanical properties is of primary importance for determining the performance of materials. The tensile strength and elongation at break of pure and blend films were plotted as a function of the blending ratio are showed in Figures 5 and 6, respectively.

Blending PAAm with gelatin is effective in improving the mechanical properties of the blend films. The maximum value of tensile strength appeared when PAAm content in the blend films was 20 wt %. The trend of the tensile strength curve is in good agreement with the results from WAXD and DTA, indicating hydrogen bond is advantageous to the improving of mechanical properties. The elongation at break increased with the

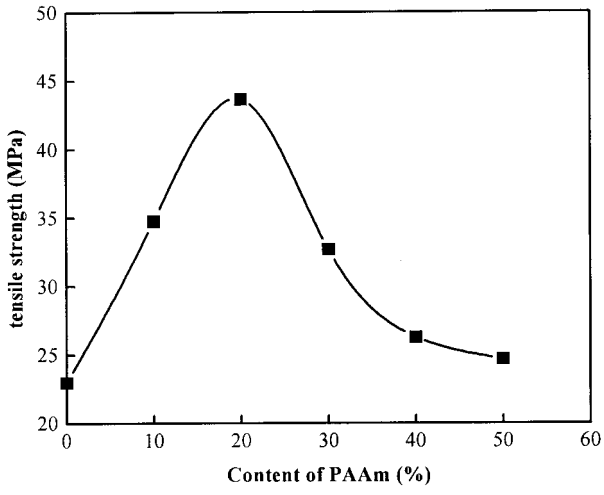

Figure 5 The tensile strength of the blend films as a function of the blending ratio.

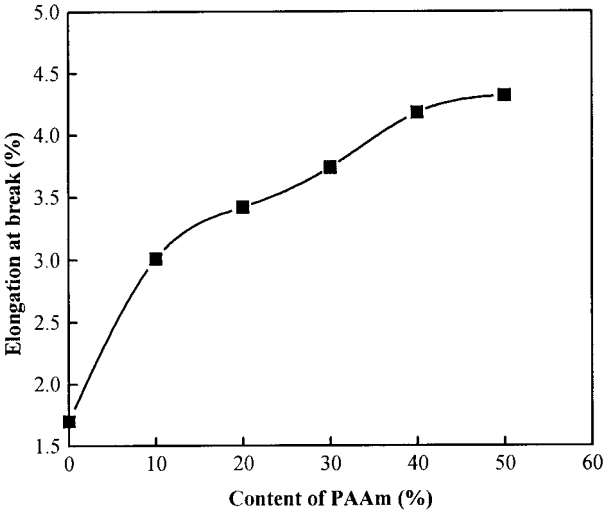

Figure 6 The elongation at break of the blend films as a function of the blending ratio.

increase of PAAm content, which may be due to the factors of the higher hygroscopicity of the blend, the plasticizing effect of the water absorbed, and the intermolecular hydrogen bond between the gelatin and PAAm.[25]

Morphological Characteristics of the Films

The surfaces exposure to the air of pure and blend films were examined by SEM, and the morphology is showed in Figure 7. With the content of PAAm increase in the blends, the morphological structure of the blends change from dense to loose, resulting in the appearance of microporous in the blends and assuming the morphological structure of PAAm.

The morphological transition from gelatin-like to PAAm-like is induced by the addition of PAAm to gelatin. These results are consistent with the above and latter-reported observation concerning the changes in physical properties. Especially, the less compacted morphological structure exhibited by the blends with higher PAAm content is in good agreement with the moisture absorption behavior.

Moisture Content and Water Swelling Property

Figure 8 shows dependence of the equilibrium moisture content on the content of PAAm. At first, the moisture absorbability of the blend films was increased sharply when 10 wt % PAAm was added to gelatin. This may be attributed to higher hygroscopicity of the material blended. However, the equilibrium moisture content of the blend

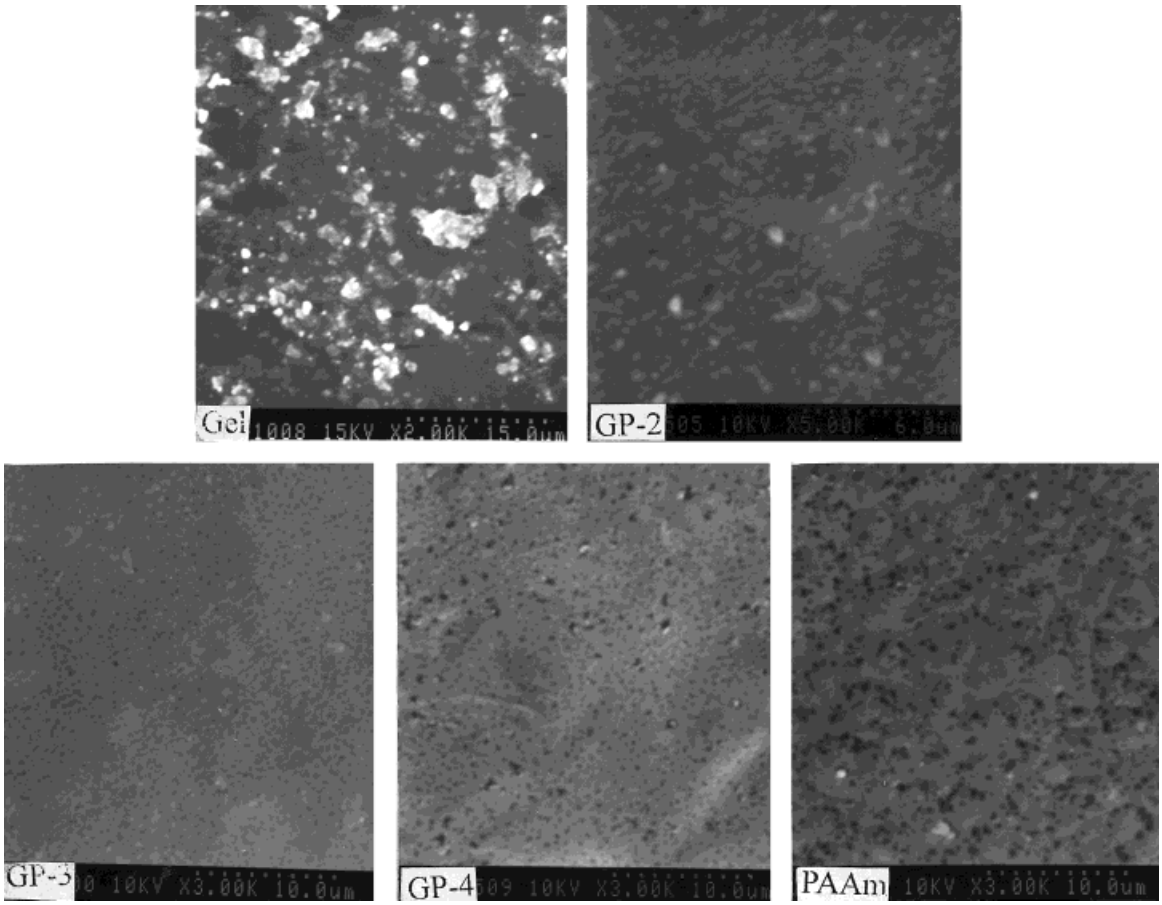

Figure 7 SEM photographs of pure and blend films.

films with the PAAm content in the range of 10–30 wt % was almost unchanged due to the higher crystallinity of films, which partly prevented a combination among water, hydrophilic amino acid residues, and amide groups.[24] The decreased crystallinity of the blend films with higher PAAm content resulted in forming microporous polymeric materials, which is advantageous to the higher moisture absorbability of blend films.

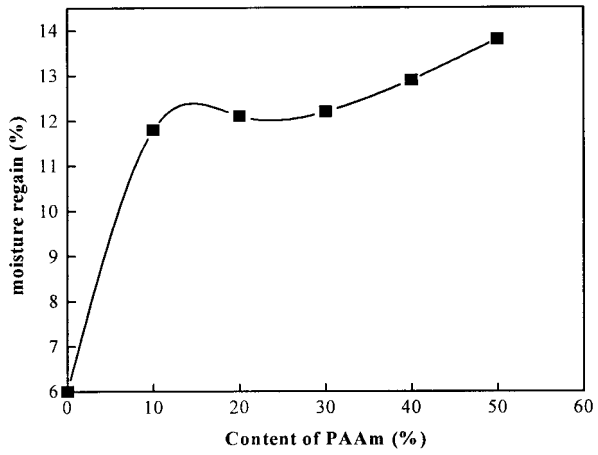

Figure 8 Moisture content of the blend films as a function of the blending ratio.

Generally, both chemical and aggregate structure can affect the water absorbability of the materials.[26] PAAm is a high hydrophilic material because of its chemical and aggregate structure. The blends of PAAm and gelatin can form microporous and less compact morphological structures. Taking those factors in view, blending PAAm with gelatin should improve the water absorbability of the films. As showed in Figure 9, the improved water absorbability of the films resulted in the equilibrium degree of swelling increase with the increase of PAAm content.

CONCLUSIONS

The results reported in this study show that PAAm could be usefully added to gelatin for prep-

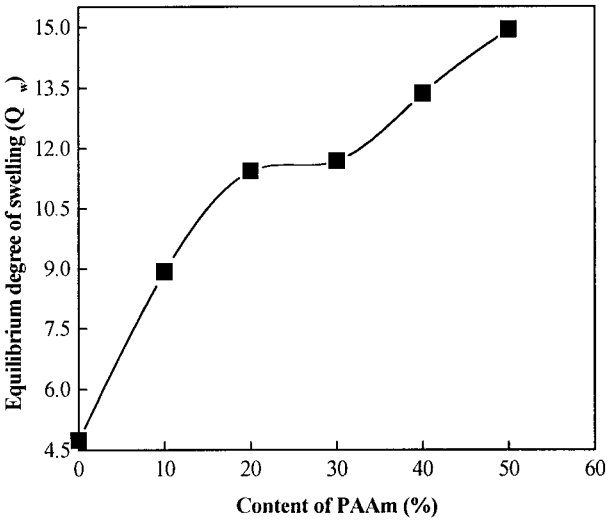

Figure 9 Equilibrium degree of swelling of the blend films as a function of the blending ratio.

aration of transparently blend films by using the casting method. The resulting blend films exhibited the higher thermal stability and improved mechanical properties compared with the pure constituent. It is noteworthy that the blend film with 20 wt % PAAm content showed the most increased thermal stability, improved mechanical properties, and best miscibility among the blend films with different weight ratios. These properties were attributed to formation of interaction between two kinds of molecules. The interaction should mainly depend on the ability of both gelatin and PAAm to establish interchain hydrogen bond detected by FTIR. Meanwhile, the water absorbability of the films was significantly improved by blending.

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