Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Xiao, Chaobo , Weng, Lihui , Lu, Yongshang and Zhang, Lina(2001) 'BLEND FILMS FROM CHITOSAN AND POLYACRYLAMIDE SOLUTIONS', Journal of Macromolecular Science, Part A, 38: 8, 761 — 771
To link to this Article: DOI: 10.1081/MA-100104446
URL: http://dx.doi.org/10.1081/MA-100104446

J. MACROMOL. SCI.—PURE APPL. CHEM., A38(8), 761–771 (2001)

BLEND FILMS FROM CHITOSAN AND POLYACRYLAMIDE SOLUTIONS

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ABSTRACT

In this article, blend films were prepared by blending 2 wt% chitosan acetate solution with 2 wt% polyacrylamide (PAAm) aqueous solution. The structure and physical properties of the resulting blend films were analysized by FT-infrared spectra (FT-IR), wide angle X-ray diffraction (WAXD), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), and by tensile tester. The results showed the occurrence of intermolecular interactions between chitosan and polyacrylamide through hydrogen bond formation. The thermal stability, and mechanical properties were improved by blending chitosan with polyacrylamide. It was worth noting that the blend film exhibited the greatest tensile strength 68 MPa and highest thermal stability when the polyacrylamide content in the blends was around 20 wt%. The results from SEM were consistent with the results above. Meanwhile, the water absorbability of the blend films was also discussed.

Key Words: Chitosan; Polyacrylamide; Blend films; Hydrogen bonds; Miscibility.

INTRODUCTION

With the development of biomedical and biotechnological science, the demands on new polymeric materials from natural polymers are increasing rapidly. Blending, an effective way to create new materials, has drawn more and more attention. This is because blending can usually be implemented more rapidly

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and economically than other methods [1]. Mechanical compatibility of the miscible polymer mixtures is assured and a property compromise between the constituents is therefore achieved [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.

In the past decades, both blends of natural-natural polymers and blends of synthetic-synthetic polymers have been widely studied, resulting in large quantities of new materials used in the biomedical field. Natural polymers present good biocompatibility, but their mechanical properties are often poor; synthetic polymers always have good mechanical properties, but their biocompatibility is usually satisfactory. Nowadays, in many fields, especially in biomedical and biotechnological fields, good mechanical properties and good biocompatibility are always both needed. So, only blends of natural-natural polymer or blends of synthetic-synthetic polymer cannot meet the needs of the modern material science. The blends of synthetic and natural polymers have been well reported in recent years, such as silk fibroin/polyacrylamide [3], poly (vinyl alcohol) (PVA)/silk fibroin [4, 5], PVA/chitosan [6, 7]. Their potential applications in many fields are now becoming more and more evident.

Chitosan, a natural polymer, has been extensively studied in the field of biomaterials. It is the deacetylated product of chitin, which consists of a repeating unit of β-1,4 linked 2-acetamino-2-deoxy-β-D-glucose [8]. It has distinct functional groups that can be easily modified to give good compatibility and high biological activity [9]. So it has been widely used as metal ion absorption agents for polluted water, food additives, and biomedical materials. However, its mechanical properties in dry state and water solubility are weak. Blending, such as chitosan/konjac glucomannan [8], chitosan/cellulose [10], chitosan/silk fibroin [11], and carboxymethlated chitosan/alginate [12] has been researched. Due to the occurrence of the strong hydrogen bonds between two components, the physical properties of the blends have been improved significantly.

Polyacrylamide (PAAm), a synthetic polymer, is widely used as flocculating, paper strengthening agents, and can also be applied to enhance the recovery of the oil [13]. Moreover, PAAm is a water-soluble polymer of biomedical and pharmaceutical interest widely studied as hydrogel for blood compatible material [14]. PAAm can interact with some other functional groups, such as –COOH, $-NH_2$, and –C=O groups due to its backbone chain having several primary amido groups. With the purpose of producing new polymeric materials that possess both good mechanical properties and biocompatibility, PAAm as a candidate blended with chitosan was therefore selected. The present study focuses on the preparation and characterization of the blend films from chitosan and PAAm. The blend films were prepared by casting method. The structure and physical properties of the blends were studied by FT-IR, WAXD, TGA, SEM, and strength test. Effects of the blending ratios on the structure and physical properties of the blend films were discussed. The results reported in this study may be contributed to the basic information for developing natural-synthetic polymer blending materials with highly functional performance.

EXPERIMENTAL

Materials and Preparation of Films

Chitosan (CH), whose molecular weight is about 20,000-40,000 and degree of deacetylation is about 80-95%, was prepared from chitin (purchased from Nanxing Chitin Ltd. Co. Suixi, Guangdong, China) by the method of Mima *et al.* [15]. It was dissolved in 2 wt% acetate aqueous solution to prepare the polymer concentration of 2 wt% solution. Polyacrylamide (PAAm) was purchased from the Chemical Reagents Co., Shanghai, China. Its solution was prepared by dissolving PAAm in distilled water to obtain the concentration of 2 wt%. Pure and two polymer mixture solutions with different weight ratios (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, and 0/100 for CH/PAAm) were cast on glass plates and allowed the water to evaporate at the room temperature to obtain the films coded as CH, CP-1, CP-2, CP-3, CP-4, CP-5, and PAAm, respectively. The films of pure and blends were dislodged carefully, and then subjected to further drying under vacuum for 48 hours to obtain the dried films before measurements. The thickness of the films ranged 30 ± 5 μm.

Measurements

Infrared spectra were measured by a Nicolet 170X Fourier transform infrared (FTIR) spectrometer. Wide-angle X-ray diffraction (WXRD) patterns were recorded with a Rigaku D/max-II X-ray diffractrometer (Japan) using CuKα target at 40kV and 50mA. The diffraction angle was ranged from 5° to 45°. Mechanical properties of the films were measured by an electron tensile tester AG-A (Shimazu Co., Japan) with a tensile rate of 10 mm/min, at a gauge length of 40 mm. 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 air surfaces and cross-sections of the films were examined with a Hitachi-570 scanning electron microscope after gold coating. To test water absorbability, dried films were allowed to soak in air with 75% relative humidity at 24°C for 2 days to achieve water absorption equilibrium. The water content of films was calculated by

$$W = (\mathrm{W}_1\text{-}\mathrm{W}_0) / \mathrm{W}_0 \times 100\%$$

where W is water content, W_1 and W_0 are weight (g) of the films in soaked and dried states, respectively.

RESULTS AND DISCUSSION

Miscibility

As far as IR spectra is concerned, if two polymers are compatible, there should be considerable differences between the IR spectrum of the blend and coaddition of the spectra of two components. These differences would be derived from chemical interactions, resulting in band shifts, intensity changes and broadening. The FT-IR spectra of the films with different composition are showed in Figure 1. For the pure chitosan, the strong absorption bands centered at 3300 cm^{-1}

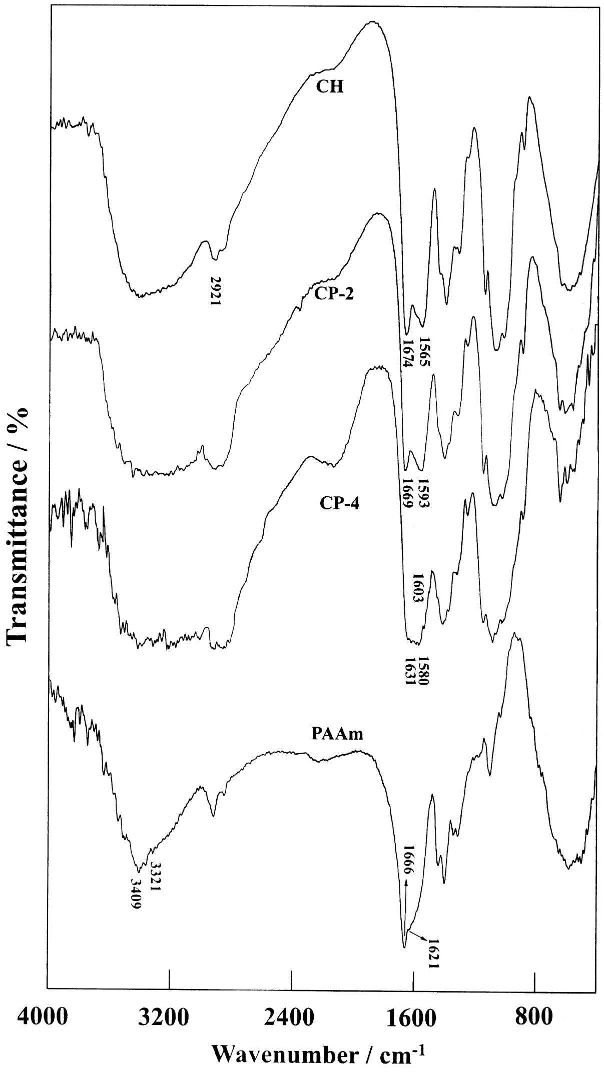

Figure 1. The FT-IR spectra of the films.

are concerned with the stretching vibration of N-H and O-H [16]. And the peaks at 2921 cm^{-1}, 1674 cm^{-1} and 1565 cm^{-1} can be assigned to the C-H stretching, the C=O stretching and N-H bending, respectively. The IR spectrum of the PAAm is dominated by bands at about 3409 and 3321 cm^{-1} (N-H stretching), 2923 cm^{-1}(C-H stretching), 1666cm^{-1}(C=O stretching) and 1621 cm^{-1} (N-H bending), which is in good agreement with the literature data [3, 13]. The IR spectra of blend films CP-2 and CP-4 showed above absorption bands typical of the pure components with the intensity roughly proportional to the blending ratios. However, the absorption bands at 1674 and 1565 cm^{-1} in pure CH showed significant changes in the spectra of the blends. With the increase of PAAm content, the bands at 1674 cm^{-1}of the blends shifted to lower wavenumbers, but the bands at 1565 cm^{-1} shifted to higher wavenumbers, and in the spectrum of CP-4, the absorption bands around 1600 cm^{-1} are split into several sharp peaks, which are attributed to the formation of hydrogen bonds between amido groups in CH and amido groups in PAAm. In addition, the absorption bands of CH around 3300 cm^{-1}, assigned to the stretching vibration of N-H and O-H, were broadened. Meanwhile, their intensity decreased due to introduce of PAAm to CH, and the extent of decrease is related to the blending ratio, implying that part of the hydrogen bonds in CH was broken by the addition of PAAm, and new hydrogen bonds formed between $–NH_2$, -OH groups in CH and $–NH_2$ groups in PAAm.

Figure 2 shows the X-ray diffraction of the pure and blend films. The pure chitosan films showed two characteristic crystalline peaks at $2\theta = 10^o$ and 20.1^o [10]. PAAm did not show any characteristic crystalline peaks, indicating that PAAm is an amorphous material [13]. However, CP-2 showed a new peak at $2\theta = 13.9^o$, in addition to those two original crystalline peaks of pure CH. In the

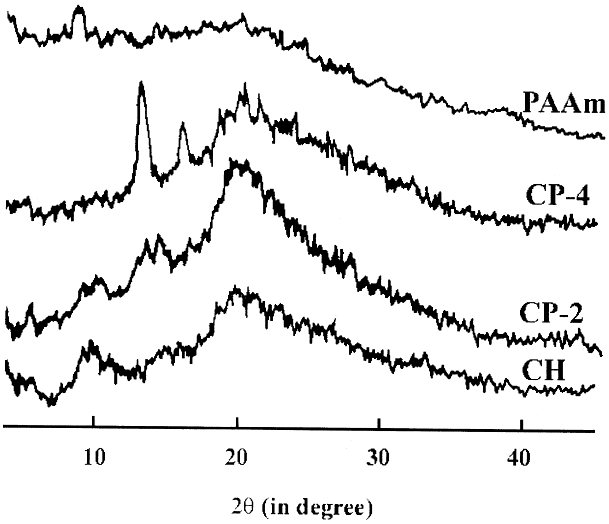

Figure 2. The WAXD patterns of the pure and blend films.

WAXD diffraction Pattern of CP-4, the original peak at 2θ =10° disappeared and new crystalline peaks at 2θ =13.3° and 16° were observed. The results indicated that the formation of intermolecular hydrogen bonding between $-NH_2$, $-NHCOCH_3$, -OH groups in CH and $–CONH_2$ groups in PAAm reduced the degree of molecular orientation in the original crystalline domains of CH, which led to the disappear of original crystalline peaks of CH. Meanwhile, the interaction from hydrogen bonds increased the molecular orientation to higher levels in the new molecular orientation domains, resulting in the occurrence of new crystalline peaks [17].

The scanning electron photographs of the films were showed in Figure 3. The bottom part of the each photo was the surface exposure to air of the films, and the top part was the cross-section of the films. The pure CH film showed a smooth surface structure, which is in good agreement with the literature [8]. The PAAm film has a loose surface morphology though its surface was rough. The blend CP-2 demonstrated the smoothest air surface morphology, indicating the occurrence of good compatibility between CH and PAAm. For the cross-section of the films, both pure CH and PAAm showed microporous homogenous structures. However, the layer–like structure was observed in the photographs of the blend films, and the morphological structure of the cross-section of CP-2 was relatively smoother than that of the other blends, indicating that good compatibility between CH and PAAm was obtained due to hydrogen bonding interaction when the PAAm content in the blends was 20 wt%.

Thermal Stability of the Films

The TGA curves of pure and blend films were showed in Figure 4. The pure CH showed three steps of weight loss. The initial loss at about 100°C was due to a loss of moisture. The second weight loss was observed at the temperature range of 200-350°C, which was attributed to the starting degradation of molecular structure [7]. The third loss, taking place at 400-550°C, was believed to be caused by some type of chemical reactions, such as main chain disintegration or rearrangement of some carbon atoms [17]. Pure PAAm exhibited weight loss at about 100°C, 200°C and 267°C. The weak drop of the TGA curve at 200°C could be concerned with thermal process involving both melting of the PAAm chains and starting of degradation. The thermal degradation, taking place at a maximum rate at 267°C, was due to the occurrence of more extensive thermal degradation processes [3].

The TGA curves of all blends showed greatest weight loss at the temperature range of 240-450°C, which was related to the breaking of the molecular structure, such as the breakdown of side groups of main chain, and disintegration of main chain [3, 17]. The starting and ending temperature of greatest thermal degradation and the values of the greatest weight loss (Table 1) increased in the sequence of PAAm < CH < CP-4 < CP-2. This result indicated that higher thermal stability

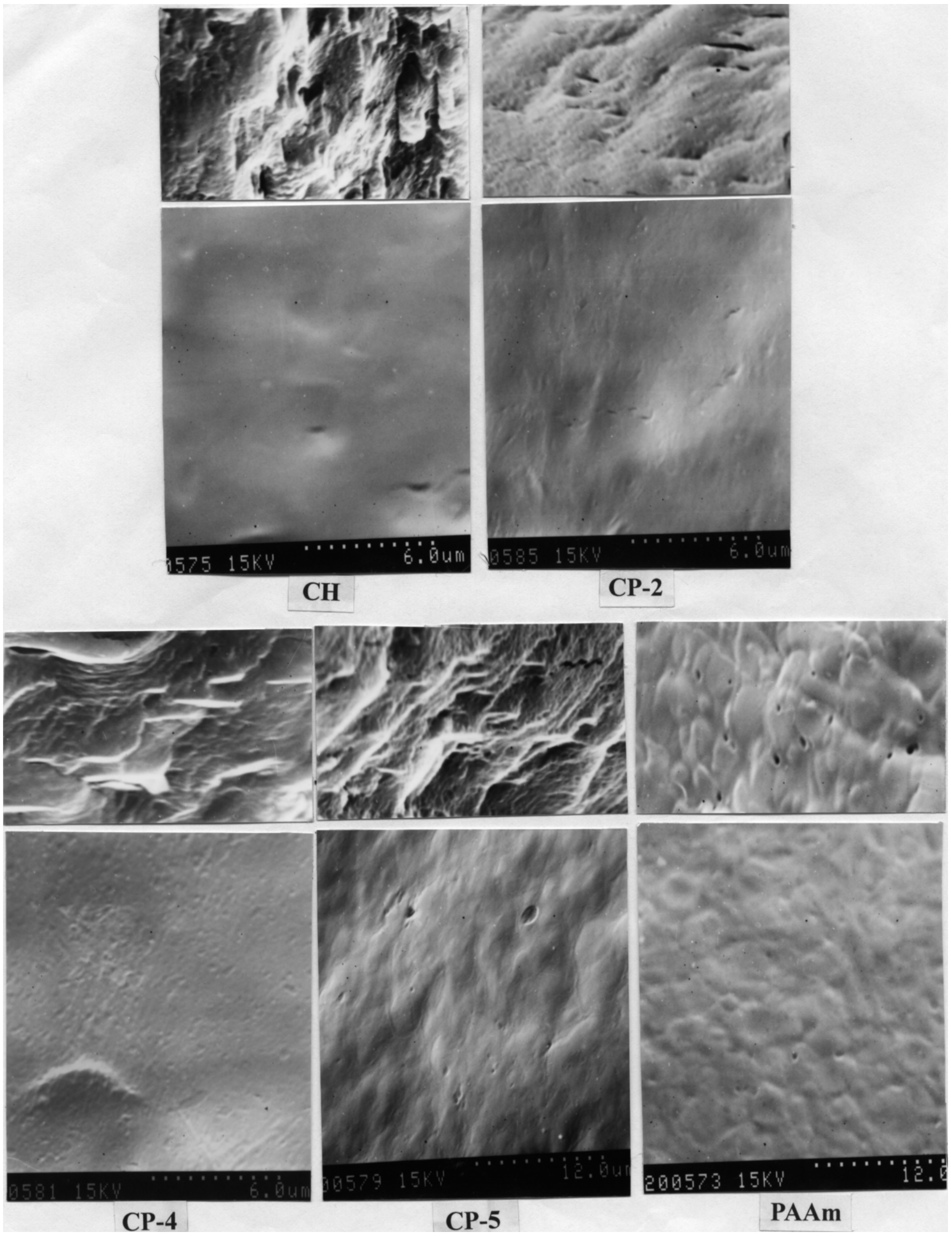

Figure 3. The SEM photographs of the pure and blend films (top and bottom parts represent cross-section and surfaces of the films, respectively)

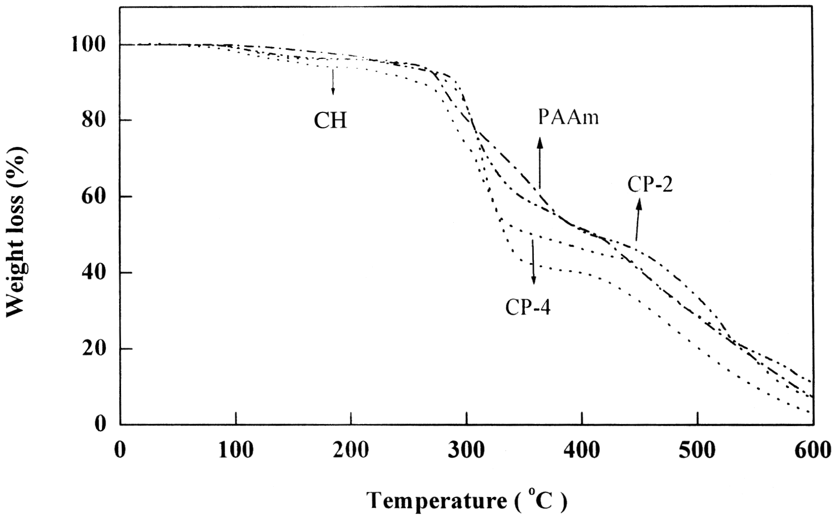

Figure 4. The TGA curves of the pure and blend films.

attained by the blends resulted from the synergistic effect of various hydrogen bonding interactions.

Water Absorption of the Films

The water absorption of the films was plotted as a function of PAAm content shown in Figure 5. Apparently, the blend films showed the higher water absorbability than pure CH. In the whole process, the absorption of the films was invariably improved with the increasing content of PAAm, which can mainly be attributed to the hydroscopicity of PAAm. Moreover, taking the morphological structure into account, the films by blending exhibited a less compact morphological structure than the pure components shown in the SEM photographs, which seemed to indicate a higher accessibility of water to the amorphous regions of the blends [17].

Table 1. The Thermal Properties of the Blend Films

Samples	CH	CP-2	CP-4	PAAm
(I) Temperature (°C)	274	292	286	267
(II) Temperature (°C)	420	450	445	410
Weight loss (%) between I and II	50	37	45	48

(I) Starting temperature of greatest decomposition.
(II) Ending temperature of greatest decomposition.

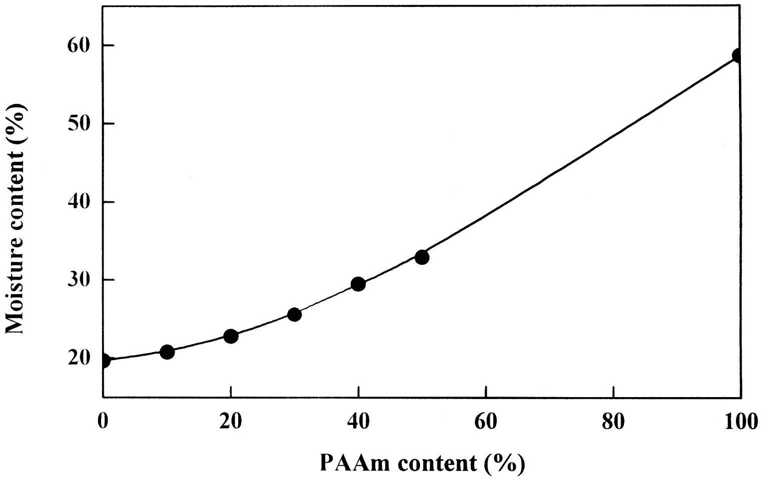

Figure 5. The water absorbability of the films as a function of PAAm content.

Mechanical Properties of the Films

The determination of the mechanical properties is vital to the new materials expected to be subjected to various kinds of stress during use, especially to the film materials [3]. The mechanical properties of the films as a function of the PAAm content were shown in Figure 6. The tensile strength and elongation at break of the CH film were measured to be 39MPa and 13%, respectively. The addition of the PAAm to CH was effective in inducing an improvement of the mechanical properties of the blends. The tensile strength increased with the

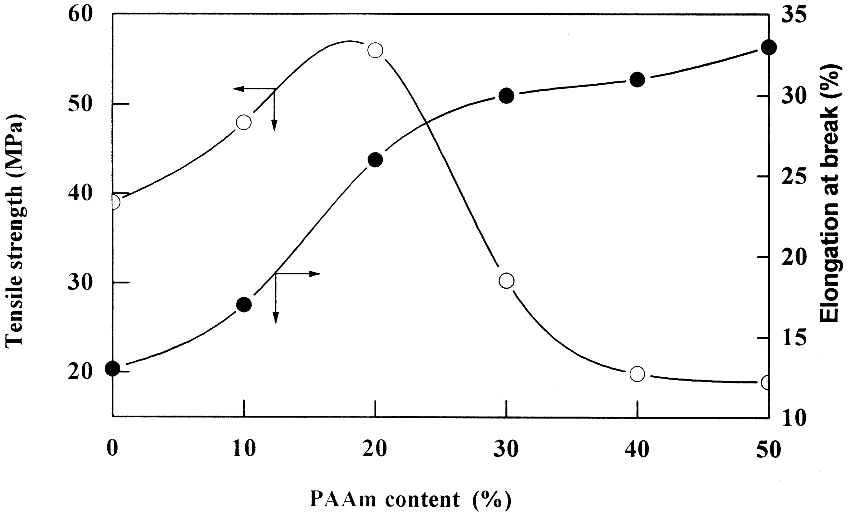

Figure 6. The mechanical properties of the films as a function of the PAAm content.

increase of PAAm when PAAm content in the blends was in the range of 10-25 wt%, to a maximum (68Mpa). This can be explained that CP-2 has a more packed structure than other blends as exhibited in the SEM photographs, and the occurrence of new crystalline shown in WXRD, resulted from the intermolecular interactions caused by hydrogen bonds between CH and PAAm. However, the breaking elongation of the blends increased with increasing PAAm content in the whole process. This effect can be explained from the higher hydroscopicity of the blends, the plasticizing effect of the water absorbed in the films, and the occurrence of hydrogen bonding interactions between CH and PAAm [17, 18].

CONCLUSION

Chitosan-polyacrylamide (CH-PAAm) blend films were prepared by conventional casting method from a mixture solution. The compatibility between CH and PAAm was elucidated by IR, SEM, and WXRD. IR spectra showed the hydrogen bonding interactions between $-NH_{2,}$ $-NHCOCH_3$, -OH groups in CH and $-CONH_2$ groups in PAAm. A SEM study of the blend films exhibited no phase separation in any of the blends. WXRD patterns showed an occurrence of new crystalline peaks in the blends resulting from hydrogen bonds between two components. The water absorbability of the films increased with the increasing of the PAAm content. The higher thermal stability and better mechanical properties were achieved when the blend film contained 20 wt% PAAm content, indicating the best miscibility obtained by blend film CP-2. The blending chitosan with 20 wt% polyacrylamide provide a novel way for chitosan application as a film biomaterial having good physical properties.

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Received November 1, 2000
Revision received February 28, 2001