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PREPARATION AND PHYSICAL PROPERTIES OF BLEND FILMS FROM SODIUM ALGINATE AND POLYACRYLAMIDE SOLUTIONS

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NOTE

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Key Words: Sodium Alginate, Polyacrylamide, Blend Films, Physical Properties, Hydrogen Bonds

ABSTRACT

Blend films of sodium alginate and polyacrylamide (PAAm) were prepared by mixing the aqueous solution of both samples at a different ratio. All blend films obtained are optically clear to the naked eye. The structure and physical properties of the films were studied by FT-infrared (FT-IR), wide angle X-ray diffraction (WAXD), differential thermal analysis (DTA), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and tensile strength test. The results showed that the occurrence of interactions between $-\text{COO}^-$, $-\text{OH}$ groups of sodium alginate and $-\text{CONH}_2$ groups of PAAm in the blends through hydrogen formation. The blend films exhibited the higher thermal stability and improved mechanical properties in dry states. These properties had the maximum value around 20 wt% PAAm content in the blend film. The morphological transition of the blend films from sodium alginate-like to PAAm-like was observed by scanning electron microscopy.

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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, the polymer blends, as a class of materials, encompass many different products resulting from the combination of two or more components [2]. Their potential applications in different fields are now becoming more and more obvious.

The polymer blended materials are widely used in the biomedical field. However, the blend materials from either synthetic or natural polymers alone are not always able to meet all the complex demands of the 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 at a 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 those factors in mind, biologically polymeric materials based on the blends of synthetic and natural polymers have been well reported, such as poly (vinyl alcohol) (PVA)/silk fibroin [4-6], PVA/ chitosan [7, 8], PVA/sodium alginate [9].

Alginates, a naturally occurring polysaccharide obtained from marine brown algae, comprising linear chain of 1,4-linked β -D-mannonic acid and α -L-gulonic acid with widely varying monomer composition of mannonic acid to gulonic acid [10]. Sodium alginate, a polyelectrolyte having rigid molecular chain [11], and good film forming ability, has been extensively exploited and studied in detail on biomedical applications of sodium alginate as a drug carrier [12 -15] and haemostatic materials [16].

Usually, the formation of specific intermolecular interactions through hydrogen bonds formation between two or more polymers is responsible for the observed mixing behaviors and properties of the blends [17, 18]. The selection and use of polymers can potentially form hydrogen bonds when two polymers mixed, as well as the study of the blends properties, are of importance to find further applications of the resulting blend materials for biomedical and pharmaceutical devices. Polyacrylamide (PAAm) is a water-soluble polymer with several primary amide groups on its chain backbones [19], the hydrogen bonding should occur by the interacting of $-\text{CONH}_2$ groups of PAAm with $-\text{COO}^-$, $-\text{OH}$ groups of sodium alginate. So, PAAm as a suitable candidate blended with sodium alginate

was therefore selected. Moreover, PAAm is a polymer of biomedical and pharmaceutical interest widely studied as hydrogel for blood compatible applications [20].

In this paper, blend films of sodium alginate and PAAm were prepared by the casting solution method. The physical properties and morphology of the blend films were studied by means of FT-IR, WAXD, TDA, TGA, SEM, and tensile measurements. The physical properties and morphology will be discussed in detail in relation to the blending ratios. The results reported in this paper might be of help in finding further applications of those blending materials with enhanced functional performance in biomedical and pharmaceutical fields.

EXPERIMENTAL

Materials

Sodium alginate was purchased from the Chemical Agents Factory of Shanghai. PAAm was purchased from Chemical Agent Supplier of Shanghai, whose average molecular weight (M_w) was 3.0×10^6 . Other chemical agents used were analytically pure.

Preparation of the Films

The desired quantities of sodium alginate and PAAm were dissolved in water to obtain the solutions of 4 wt%, respectively. The pure and mixture solutions of sodium alginate and PAAm with different weight ratios (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100, Sodium alginate/PAAm) were cast on a Teflon gasket and allowed the water to evaporate at the room temperature. The films of pure and blends were dislodged carefully, and then subjected to further drying under vacuum for 2 days. The dried films of thickness ranging $80 \pm 5 \mu\text{m}$ were obtained. The films of different ratio above were coded as SA, SAP-1, SAP-2, SAP-3, SAP-4, SAP-5, and PAAm, respectively.

Measurements

FT-IR spectra of the films were recorded on a Nicolet (USA) 170SX FT-IR spectrometer and KBr pellets were used. The X-ray diffraction patterns of the films with a Rigaku (Japan) Dmax – II X –diffractometer operated at 40 kV and 50 mA using CuK_α radiation. The diffraction angle was ranged $40\sim 5^\circ$ and crystallinities (X_c) of the films were calculated by [21]:

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

where F_c and F_a are the area of crystal and noncrystal regions, respectively. The TGA and DTA of powered samples of the films were performed in a room atmosphere by a Shimadzu DT-30 thermal analyzer, and the temperature was raised to 500°C at heating rate of 10°C/min. The stress-strain measurements were performed by a AG-A electron tensile tester (Shimadzu Co.) in 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.

RESULTS AND DISCUSSION

FTIR Spectra of the Films

FT-IR is of importance to the study of the molecular structures. The width and intensity of spectral bands, as well as the position of peaks are all sensitive to environmental changes and to conformations of the macromolecule on a molecular level. Intermolecular interactions occur when different polymers are compatible. So, the FT-IR spectra of the blends are different from those of the pure polymers, which is advantageous to the study of compatibility between two polymers. Figure 1 shows the infrared spectra for the films of sodium alginate, the blends and PAAm in the wavelength range of 4000–400 cm⁻¹. The characteristic peak of sodium alginate appeared at 819 cm⁻¹ [22]. The band of 1633 cm⁻¹ was assigned to the asymmetrical stretching vibration of -COO⁻ groups. The IR spectrum of PAAm exhibiting bands at 3400 cm⁻¹ and 3200 cm⁻¹ which were assigned to a stretching vibration of N-H, 1670 cm⁻¹ (C=O stretching) and 1622 cm⁻¹ (NH bending) [19, 23]. The bands at 2932 cm⁻¹ (CH stretching) and 1500 cm⁻¹–1300 cm⁻¹ (various CH bending) were also detected [19]. The spectra of the blend films are characterized by the presence of the absorption bands typical of the pure component, with the intensity roughly proportional to the blending ratios. The characteristic peak of sodium alginate appeared at 819 cm⁻¹ was observed in all the spectra of the blends. However, with the increase of the PAAm content in the blend films, the absorption peaks at 1633 cm⁻¹ assigned to the asymmetrical stretching vibration of -COO⁻ groups coupled with the peaks at 1670 cm⁻¹, 1622 cm⁻¹ of PAAm and shifted to 1617 cm⁻¹, suggested that the new hydrogen bonds formed between -COO⁻ groups of sodium alginate and -CONH₂ groups of

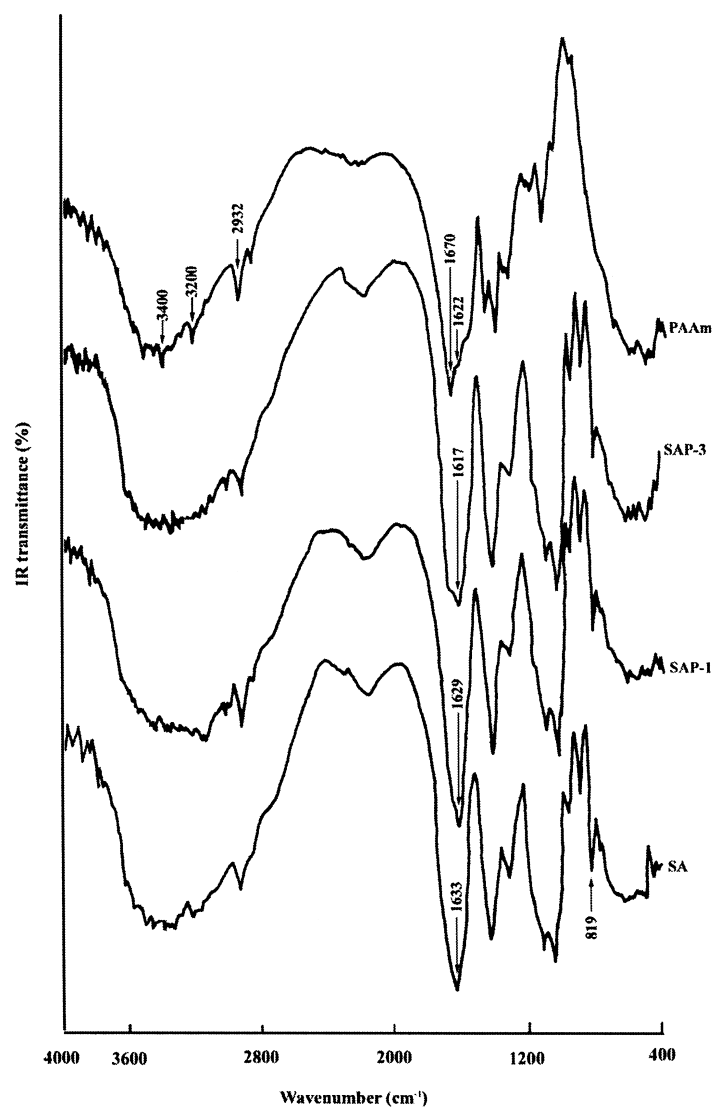


Figure 1. The FT-IR spectra of the pure and blend films.

PAAm. Furthermore, the bands of PAAm centered at about 3400 cm⁻¹ and 3200 cm⁻¹, which were the stretching vibration of -NH₂ groups involved in both inter- and intramolecular hydrogen bonds, broadened and coupled with -OH band of sodium alginate at 3400 cm⁻¹, induced by the addition of sodium alginate to PAAm, implying that the occurrence of hydrogen bonds between -OH groups of sodium alginate and -NH₂ groups of PAAm molecules.

Crystallinity of the Films

X-ray diffraction patterns of pure and the blend films are shown in Figure 2. The pattern of sodium alginate shows a broad peak at $2\theta = 12^\circ$. The pattern of PAAm, has very weak, unoriented shape indicating PAAm is an amorphous material [23]. If sodium alginate 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 sodium alginate and PAAm with the same ratio as those for blending. However, when the PAAm content in the blends was low, the patterns of the blend films show that the intensity of diffraction peak at $2\theta = 12^\circ$ decreased and the intensity of diffraction at $2\theta = 22^\circ$ increased, especially that of SAP-2, as compared with the pure components. As the PAAm content increased in the blends, the blend of SAP-3 shows an unoriented crystalline peak. The crystallinities of the blend films was calculated and the increased order was SA > SAP-2 > SAP-1 > SAP-3. This means intermolecu-

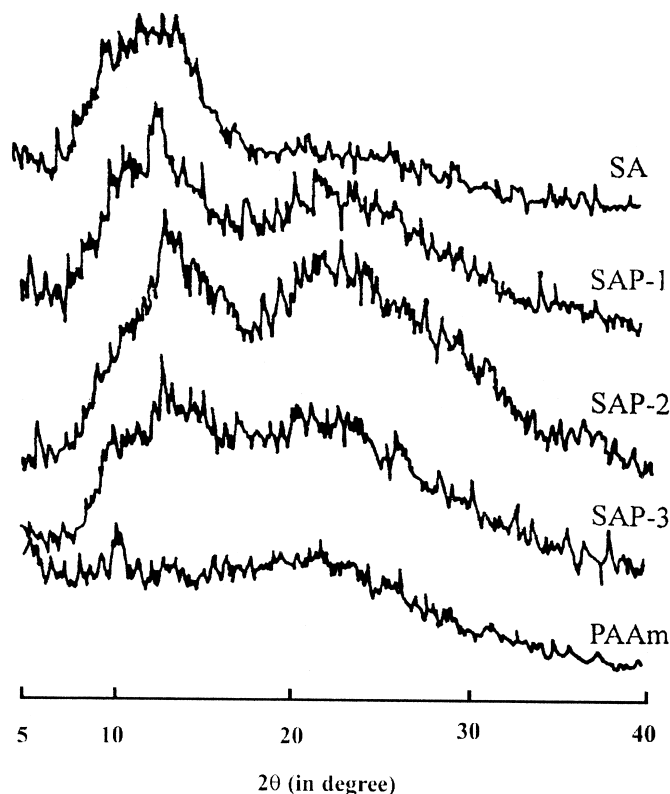


Figure 2. The wide angle X-diffraction patterns of the pure and blend films.

lar hydrogen bonds between sodium alginate and PAAm were introduced, which destroyed the original molecular structure of sodium alginate, resulting in the changes of diffraction patterns.

Thermal Stability

Figure 3 shows the DTA curves of sodium alginate, the blends, and PAAm. The pure sodium alginate film shows an endothermic peak at 95°C attributed to the loss of water absorbed in the films, the exothermic peak at 244°C means the taking place of thermal degradation of intermolecular side chain. The curve of pure PAAm film was characterized at about 240°C, which attributed to various thermal induced transitions, such as melting of PAAm chains and beginning of thermal degradation [19] [see TGA result].

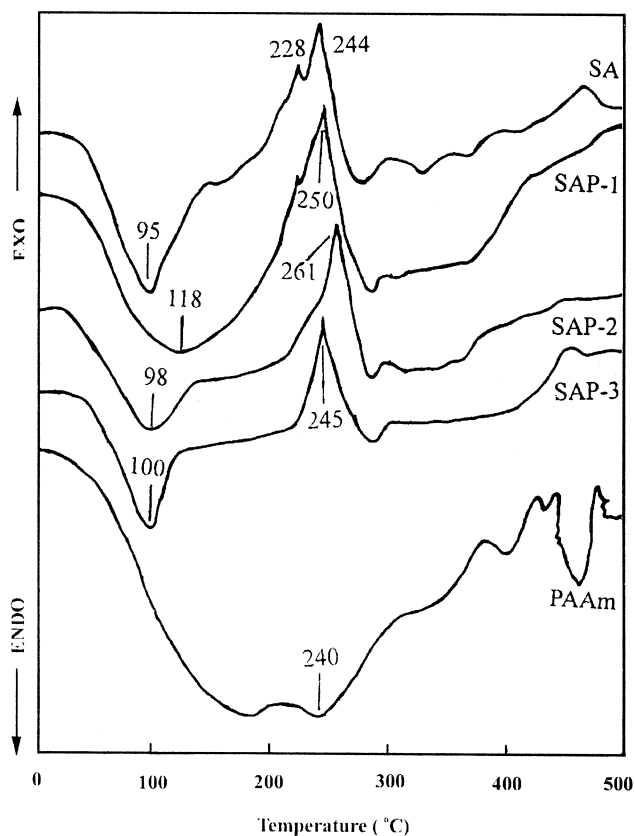


Figure 3. The DTA curves of the pure and blend films.

The curves of the blend films show that the characteristic peaks, at about 228°C for sodium alginate, disappeared gradually. All blend films show exothermic peaks in the temperature range of around 240-260°C, which resulted from the greatest thermal degradation of the blends [see TGA result]. The greatest thermal degradation peak shifted to the higher temperature, resulting from the addition of PAAm to sodium alginate. Significant changes of DTA curves of the blend films suggest that a strong interaction established between sodium alginate and PAAm molecules.

TGA results of the pure and blend films are shown in Figure 4. The curve of pure sodium alginate shows two zones of weight loss. The first weight loss at approximately 60-120°C was due to the loss of water, the second weight loss started at about 220°C, implying that the occurrence of different extent thermal degradation of sodium alginate. PAAm shows weight loss located at 60-100°C, 200°C, and 300°C [19], the former was attributed to moisture loss, weight loss at 200°C could be related to a thermal processes involving both melting of the PAAm chains and onset of degradation, the third drop at 300°C was indicative of the occurrence of more extensive thermal degradation processes.

TGA curves of all blend films show greatest weight loss in the temperature range of 220-270°C, which were believed to be the disintegration of inter-

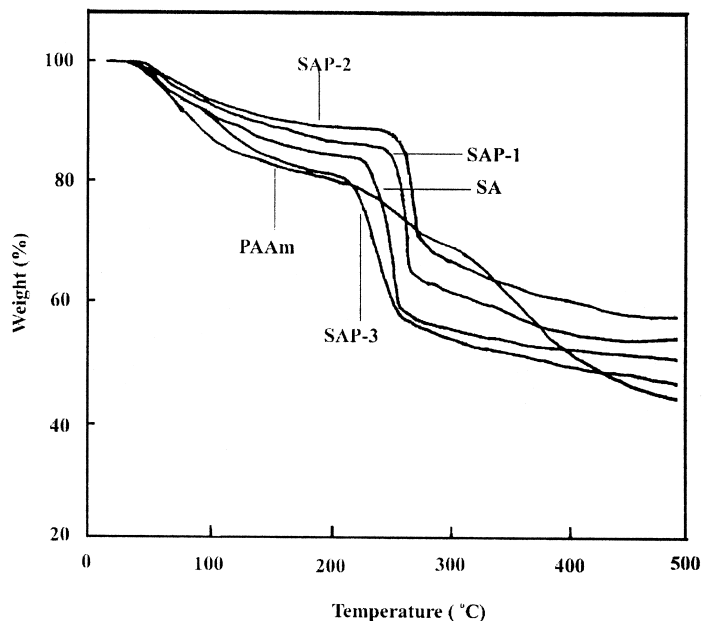


Figure 4. The TGA curves of the pure and blend films.

molecular and partial breaking of the molecular structure. As shown in Figure 4, it is understood that the blend films show better thermal stability than pure components. The starting temperature of the greatest thermal degradation increased in the sequence of SAP-2 (255°C) > SAP-1 (249°C) > SAP-3 (217°C), which is the same as that of their crystallinity, implying thermal stability of the blend films were improved by their crystalline domains and hydrogen bonding interactions [26].

Mechanical Properties of the Films

Because polymer materials, such as films, may be subjected to various kinds of stress 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 the pure and blend films were plotted as a function of the blending ratio shown in Figures 5 and 6, respectively.

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

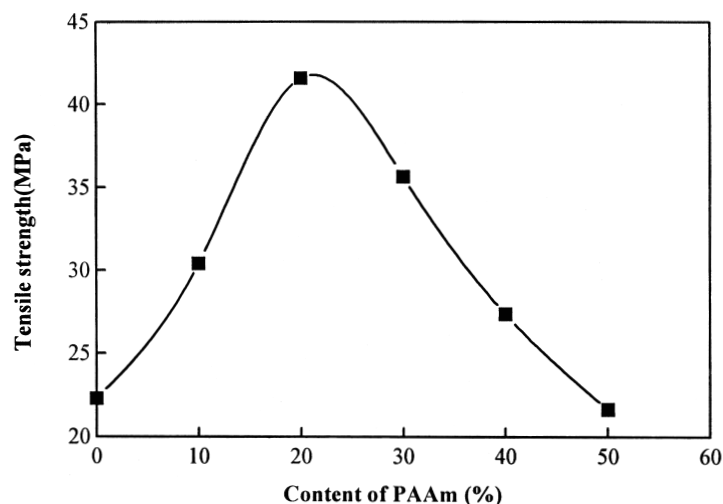


Figure 5. The tensile strength of the blend films as a function of the blending ratio.

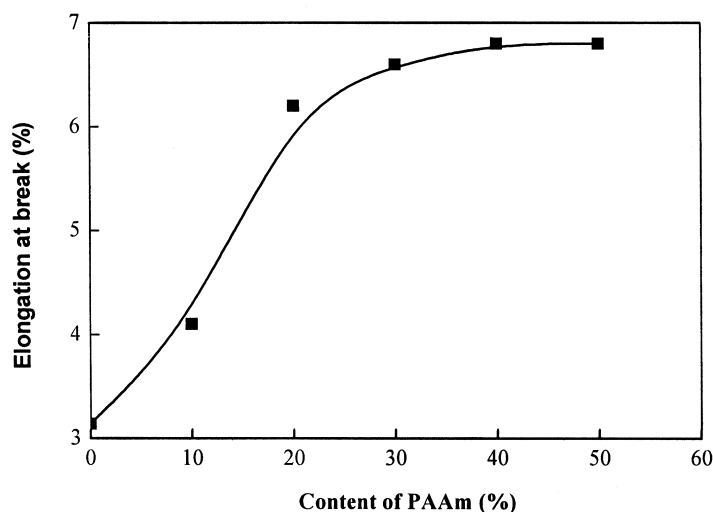


Figure 6. The elongation at break of the blend films as a function of the blending ratio.

increased with an increase of PAAm content. This may be due to the higher hygroscopicity of the blend, plasticizing effect of the water absorbed, and the intermolecular hydrogen bond between sodium alginate and PAAm, such as those reported for the blend films of silk fibroin/sodium alginate [26] and silk fibroin/cellulose [27].

Morphological Characteristics of the Films

Film surfaces exposed to the air were observed by using SEM, and the morphology of the pure and blends was shown in Figure 7. The pure sodium alginate film shows crystalline structure. The SEM photography of PAAm exhibits a less compacted amorphous surface morphology. This is in good agreement with the results from WAXD. The typically molecular orientation for sodium alginate exhibited on the photography disappeared in the blend films. It worth noting the significant changes of morphological structure induced by the addition of even a small amount (10 wt%) of PAAm. The reason for this might be that the addition of a prevalently amorphous material, as well as interaction between sodium alginate and PAAm in the amorphous regions of the blends. This might have changed both the structure and behavior of the sodium alginate molecular domains [27]. As the PAAm increases, the presence of microporous immersed in a homogeneous matrix was observed in the blend films of SAP-1, SAP-3, and SAP-4,

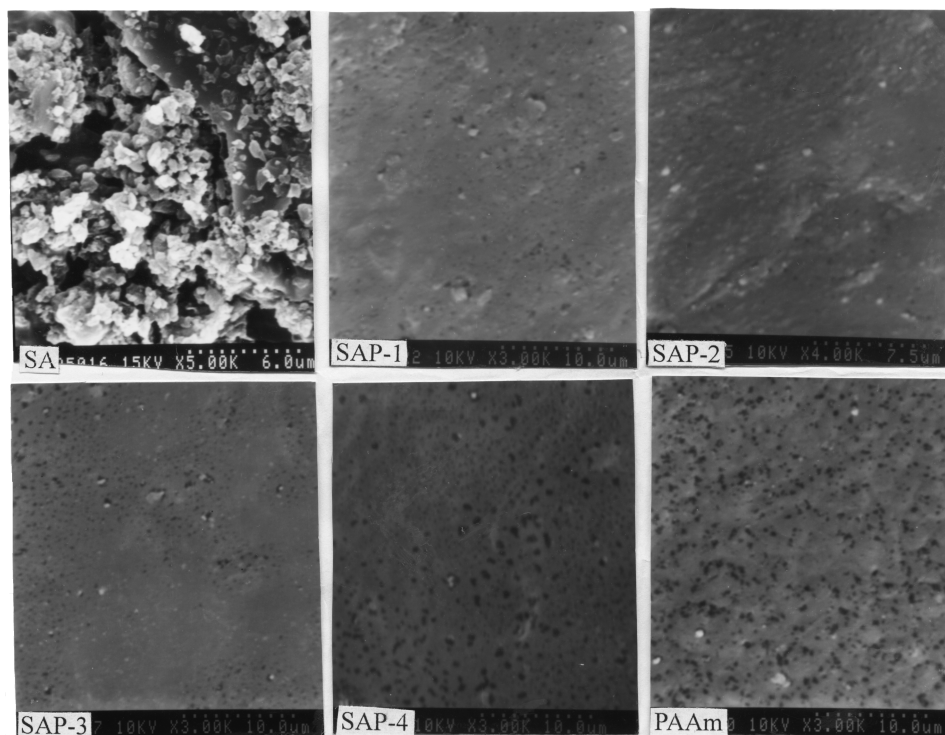


Figure 7. The SEM photographs of the pure and blend films.

resulting in the transition of morphology from sodium alginate-like to PAAm-like.

CONCLUSION

The results reported in this study show that PAAm could be a useful addition to sodium alginate for preparation of transparently blend films by using the casting method. The physical properties of the resulting blend films largely depend on the blending ratios. The blend films exhibited the higher thermal stability and improved mechanical properties compared with the pure constituents. It is noteworthy that the blend film with 20 wt% PAAm content showed the most increased thermal stability, and improved mechanical properties among the blend films with different weight ratios. These properties were attributed to the formation of interaction between two kinds of molecules, the interaction should depend mainly on the ability of both $-\text{COO}^-$, $-\text{OH}$ groups of sodium alginate and

-CONH₂ groups of PAAm to establish a interchain hydrogen bond, which was detected by FT-IR. Meanwhile, the morphological change of the blend films from sodium alginate-like to PAAm-like was observed from SEM, and was consistent with the WAXD result.

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