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BLEND FILMS FROM SODIUM ALGINATE AND GELATIN SOLUTIONS

Chaobo Xiao[a]; Hongjuan Liu[a]; Yongshang Lu[a]; Lina Zhang[a]
[a] Department of Chemistry, Wuhan University, Wuhan, China

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NOTE

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Chaobo Xiao,* Hongjuan Liu, Yongshang Lu, and Lina Zhang

Department of Chemistry, Wuhan University, Wuhan 430072, China

ABSTRACT

Blend films were prepared by blending 4 wt% sodium alginate and 5 wt% gelatin aqueous solutions and dried at room temperature for 2 days to obtain the transparent films. Their structures and properties were studied by infrared (IR) spectra, wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). Significant changes in the shape and intensity of IR spectra absorption frequencies characteristic of either gelatin or sodium alginate were detected by IR analysis. The crystallinities of the blend films decreased with the increase of sodium alginate content. The thermal stability, mechanical properties of tensile strength, and breaking elongation of the blend films were improved by blending sodium alginate with gelatin. It is worth noting that the breaking elongation reached 16.6% when the weight ratio of sodium alginate to gelatin was 1:1, much higher than that of two components. The structure analysis indicated that there is strong interaction between sodium alginate and gelatin molecules resulted from intermolecular hydrogen bonds and ionic interactions. The water absorbability of the blend films was improved due to the introduction of sodium alginate.

Key Words: Sodium alginate; Gelatin; Blend; Blend film; Hydrogen bonds; Miscibility.

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*Corresponding author.

INTRODUCTION

Nowadays, the widespread use of synthetic polymer films has resulted in serious environmental pollution problems. The study and exploitation on polymer film materials from renewable resources have drawn more and more attention in view of their environmental friendliness to the earth. To improve the performance of the individual natural polymer films, many blend films, prepared by using a solution blend, such as poly(vinyl alcohol)-chitosan (1, 2), cellulose-alginate (3), sodium alginate-silk fibroin (4), gelatin-konjac glucomannan (5), have been reported. The thermostability and mechanical properties of these materials were improved, due to the interaction between the two kinds of molecules.

The excellent mechanical properties, water solubility, body compatibility, and biodegradability are vital to medical materials. Blending is an effective method to improve the performance of films. Generally, when the two components used to blend are compatible, the blend films can form homogeneous structure and show better performance than the individual components. Sodium alginate comprising linear chains of 1,4-linked β-D-mannuronate and -L-guluronate with widely varying monomer composition of mannuronate to guluronate (6) are widely used in industry, agriculture, medicine and pharmacy, food processing industry, and construction (7). It possesses good film-forming ability. In our previous work (8), blend films of konjac glucomannan and sodium alginate were prepared and characterized by Fourier transform infrared (FT-IR), wide-angle x-ray diffraction (WAXD), scanning electron microscopy (SEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and other analytical methods. The results indicated the existence of intermolecular hydrogen bonds between two macromolecules. Gelatin is a well-characterized protein fragment obtained by partial degradation of water insoluble collagen fiber (9). Because of its nontoxicity and good living body compatibility, gelatin has been widely used in biomaterials (10–12), food (13), and cosmetic fields. However, the gelatin film is difficult to form and its brittleness limits its further applications.

Sodium alginate and gelatin are both natural polymers, and both have biocompatibility, biodegradability, and hydrophilicity. It is considered that the sodium alginate and gelatin blends prepared using both of these two potentially important functional polymers could contribute to produce new functional polymers with good performance, which can be used in various domains. The miscibility, thermal stability, mechanical properties of the blend films were studied by infrared (IR) spectra, WAXD, SEM, TGA, and electron tensile tester.

EXPERMENTAL

Materials

Sodium alginate and gelatin both were purchased from Shanghai Chemical Agents Factory. The average molecular weight (M_w) of gelatin was determined to be 5.0×10^4 with gel permeation chromatography (GPC).

Preparation of the Films

Sodium alginate was dissolved in distilled water at room temperature to a concentration of 4 wt%. Gelatin was dissolved in deionized water at 90°C to a concentration of 5 wt%. Chosen volumes of sodium alginate solution were added into the required amount of gelatin solution. The resulting solutions were stirred energetically and degassed, then were spread over glass plates. Blend films with different weight ratio were obtained after drying at room temperature for 2 days. By changing the percent content of sodium alginate (10, 30, 50, 70, and 90%), a series of blend films were coded as GS-1, GS-2, GS-3, GS-4, and, GS-5, respectively. The films obtained from pure sodium alginate and gelatin was coded as SA and GE. The thickness of film samples was measured to be 80 ± 5µm. The film samples were kept under vacuum until used.

Characterization of Films

IR spectra of the pure and blend films were measured with a Shimadzu FTIR 8000 (Japan) spectrometer and used as KBr pellets.

WAXDs of the films were performed with a Rigaku Dmax-II X-ray diffractrometer and using a CuKα target at 40 KV and 50 MA. The diffraction angle ranged from 5^o to 50^o. The crystallinities of the films were calculated by (14):

$$Xc = Fc /(Fa + Fc) \times 100\%$$

where Fc and Fa is the area of crystalline and noncrystalline regions, respectively.

The tensile strength and breaking elongation of the films were measured on an electron tensile tester CMT6503 (China) with a tensile rate of 10 mm/min at a gauge length of 40 mm. The temperature and relative humidity were 22°C and 41.5%, respectively.

The DTA and TGA of the film samples with 1-mm width and 1-mm length were performed in a PRT-2 TGA-DTA thermobalance (Beijing Optical Instruments Factory, China) under a nitrogen atmosphere with a flow capacity of 30 mL/min from 0 to 500°C at a heating of 10°C/min.

The surface morphology of the film surfaces was examined with a Hitachi SX-650 scanning electron microscopy (Japan) after being coated with gold under a vacuum degree of 0.1τ.

The weight of completely dried samples (W_0) was measured directly, and then dipped into the distilled water for 5 min, attained weight (W_t). The degree of swelling was calculated with the following equation:

$$\text{Degree of swelling} = (W_t - W_0)/W_0$$

RESULTS AND DISCUSSION

General Properties of the Films

Pure and blend films were all transparent and optical clear to the naked eyes. Film of sodium alginate was easily dissolved in distilled water.

The IR spectra of the films of GE, GS-2, GS-3, GS-4, and SA are shown in Figure 1. The characteristic absorption bands of sodium alginate appeared at 819 cm^{-1}. The IR spectrum of gelatin showed absorption bands at 3400 cm^{-1} (NH stretching), 1654 cm^{-1} (amide I, CO, and CN stretching), 1539 cm^{-1}, 1264 cm^{-1} (amide II and III, respectively, mainly NH bending and CN stretching), and 650 cm^{-1} (amide V, CN torsion and NH bending). It can be obviously seen that the absorption band around 3400 cm^{-1} corresponding to the stretching of –NH group show significant changes, which broadened, shifted to lower wave number, and its intensity decreased when the content of sodium alginate ranged from 0 to 70 wt%, indicating the intramolecular hydrogen bonded state of pure components were interrupted. As it is well known, the absorption bands of amide I-V are conformationally sensitive bands for polypeptides and protein (15). For the blend films, the strong absorption band at 1633 cm^{-1} for SA film assigned to the asymmetric stretching vibration of COO^- has coupled with the absorption at 1654 cm^{-1} in gelatin and shifted to 1652 cm^{-1} and 1650 cm^{-1} in GS-3 and GS-2, respectively. At the same time, the absorption at 1422 cm^{-1} assigned to the symmetric stretching vibration of COO^{-1} has shifted to 1413 cm^{-1} and 1409 cm^{-1} in GS-4 and GS-3, respectively. Based upon this evidence, it can be concluded that a certain degree of interaction between sodium alginate and gelatin molecules due to the formation of intermolecular hydrogen bonds existed. This interaction and possible ionic interactions resulted in the miscibility of two kinds of macromolecules, as observed by SEM (see Fig. 7).

Crystallinities of the Films

X-ray diffraction patterns of pure and blend films are showed in Figure 2. Two typical peaks in $2\theta = 7.6^o$ and 18^o were observed for gelatin as reported (16). Sodium alginate has a broad diffraction peak around 14^o. The crystallinity was calculated and the order was GE>GS-2>GS-3>GS-4>SA. It is obvious that the crystallinities of the blend films decreased with the adding of sodium alginate, which can be explained that the intermolecular interaction destroyed the regularity of gelatin. From these results, it was found that the two polymers were mixed together in a certain range and affected each other in the crystallization during the film formation. By blending of gelatin with sodium alginate, the close packing of the flexible gelatin molecules for the formation of the crystallinities was hindered by sodium alginate molecules, and blend films with less crystallinities were formed.

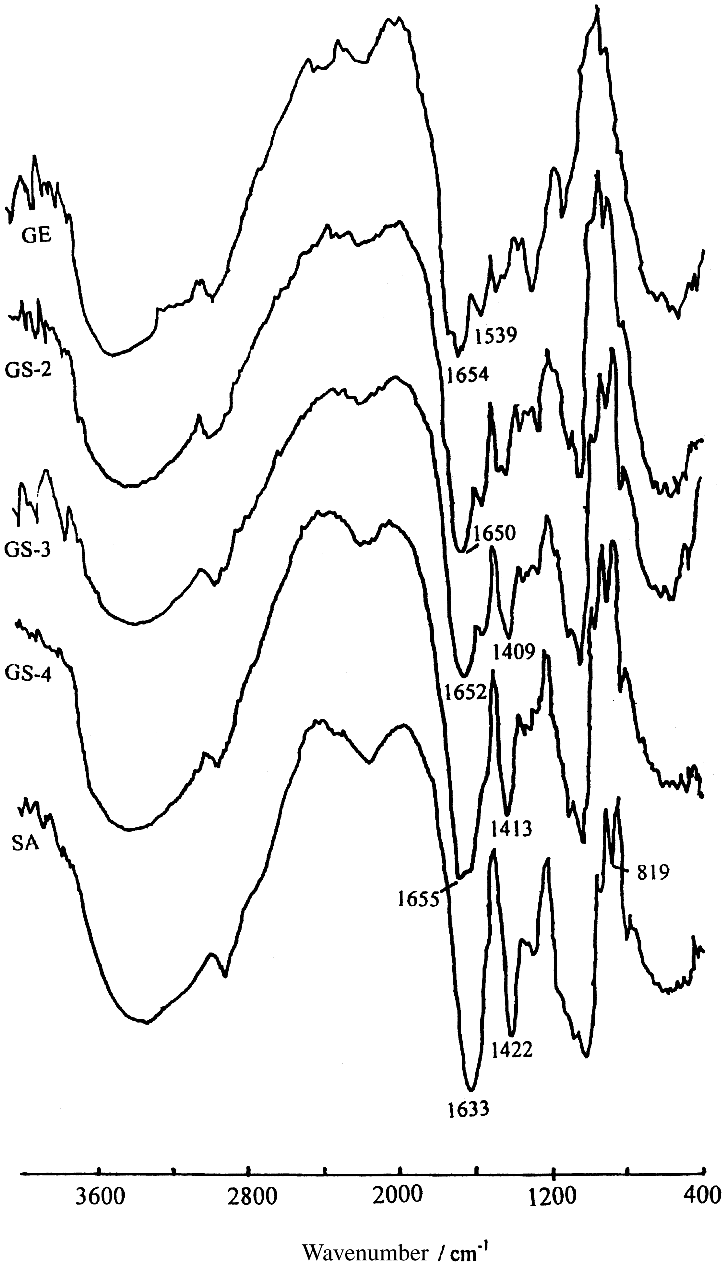

Figure 1. IR spectra of pure and blend films.

Thermal Properties of the Films

The DTA curves of the films are shown in Figure 3. The films all showed endothermic peaks at 60 to 90°C, corresponding to the loss of crystalline water

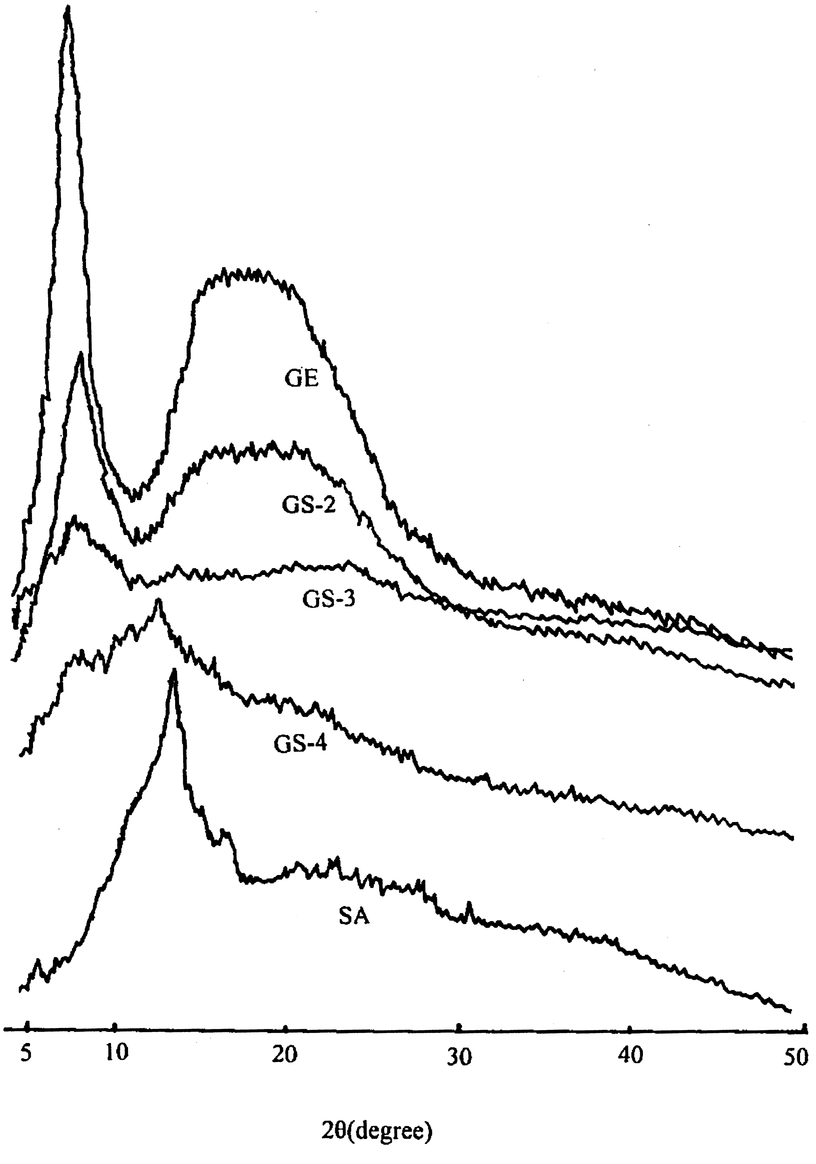

Figure 2. X-ray diffraction patterns of pure and blend films.

molecules in the films formed during drying progress. An exothermic peak appeared at 220°C attributed to the great thermal degradation of sodium alginate (see TGA results). The DTA curve of gelatin show exothermic peaks at about 296°C, 413°C attributed to the disintegration of the intermolecular side chains and main chain, respectively.

In the thermograms of blend films, we can see the greatest exothermic peak appeared at 222°C, 231°C, and 247°C in film GS-3, GS-2 and GS-1, respectively.

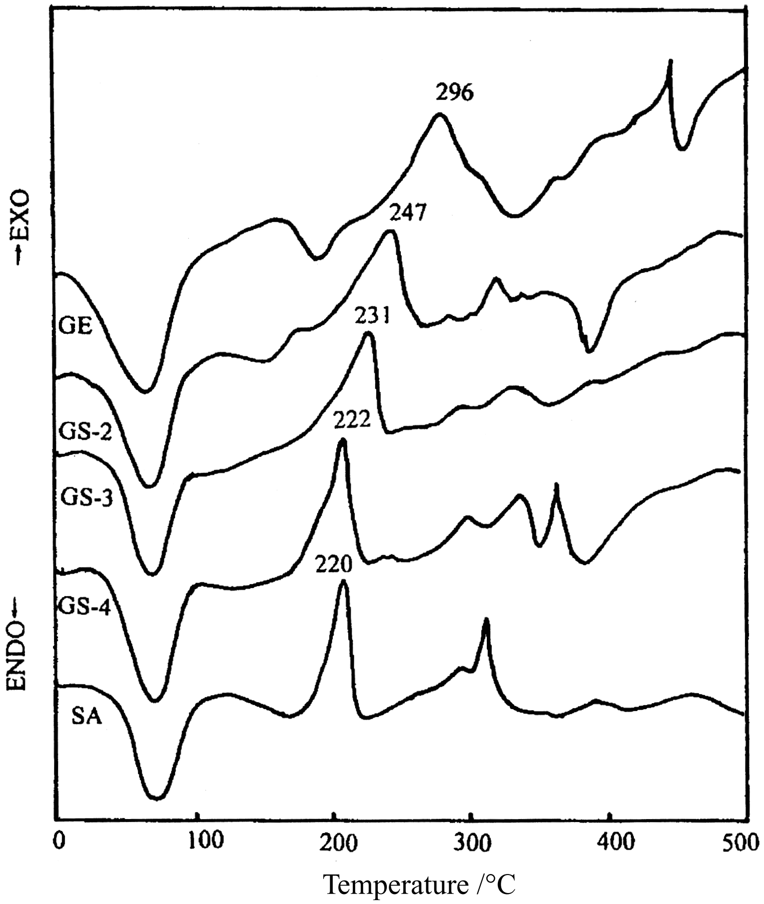

Figure 3. DTA thermograms of pure and blend films.

That is to say, the thermal degradation of SA shifted to higher temperatures with the adding of gelatin compared to sodium alginate. We considered the reason mainly to be that the intermolecular hydrogen bonds of sodium alginate were destroyed, new hydrogen bonds between sodium alginate and gelatin molecules were established, and its bonds energy is higher than that of intermolecular hydrogen bonds of sodium alginate, expect some possible contributions of ionic interaction between sodium alginate and gelatin.

Figure 4 shows the TGA thermograms of the films of SA, GE, GS-2, GS-3, and GS-4. The greatest weight loss of the film SA and GE took place around 220°C and 300°C, respectively. From the TGA curves, we can see the decomposition temperature and weight-retention properties increases in the sequence of GE >GS-2 >GS-3 >GS-4 >SA. It is clear that the more gelatin the films contain, the higher decomposition temperature and weight-retention are. The order is the same as that of crystallinities.

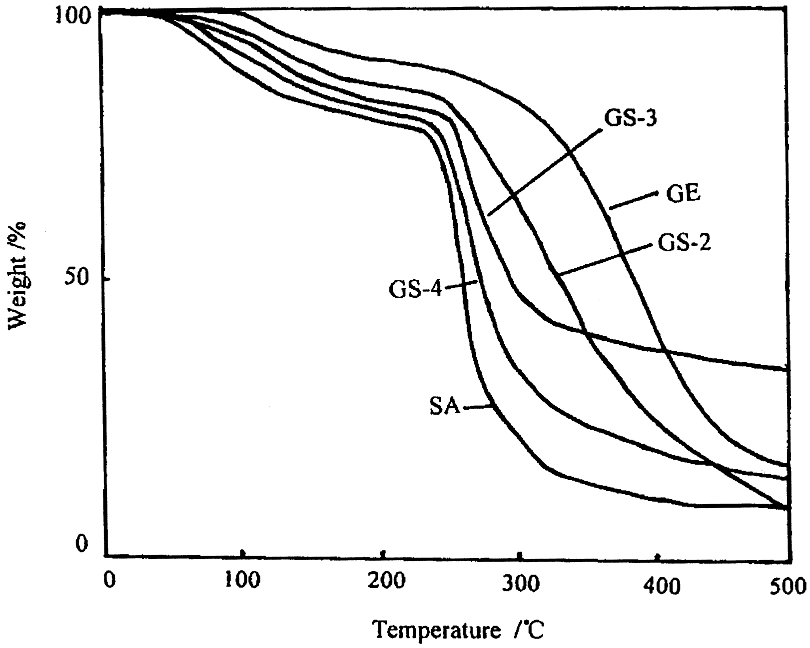

Figure 4. TGA thermograms of pure and blend films.

Mechanical Properties of Blend Films

The tensile strength and breaking elongation dependence on the content of sodium alginate for the films are shown in Figures 5 and 6, respectively. The addition of gelatin to sodium alginate is effective in inducing significant changes in the mechanical properties of the resulting blend films. The behavior of tensile strength seems to vary according to the gelatin content, because this parameter increases with the amount of gelatin. Breaking elongation of the blend films increases with the gelatin content, and the maximum value that appeared at 50 wt% gelatin content achieved 16.6%, much higher than that of two components. This result might be attributed to various factors, such as the higher hygroscopicity of the blends, the plasticizing effect of the additional water molecules absorbed, the ionic interaction between sodium alginate and gelatin, etc. However, the possibility that adjacent sodium alginate and gelatin chains might interact with each other should be taken into account, to explain the sharp increase of breaking elongation.

Morphological Characteristic of the Films

Air surfaces of the pure and blend films were examined by SEM and shown in Figure 7. The uniform microstructure appeared for pure gelatin and sodium alginate had disappeared for the blend film GS-3, and a smooth and homogeneous

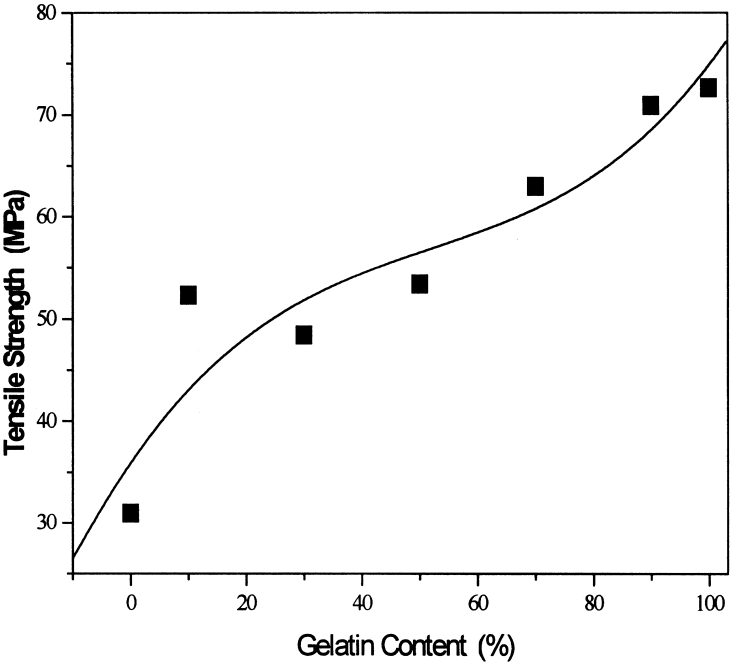

Figure 5. The dependence of tensile strength on the content of gelatin for the films.

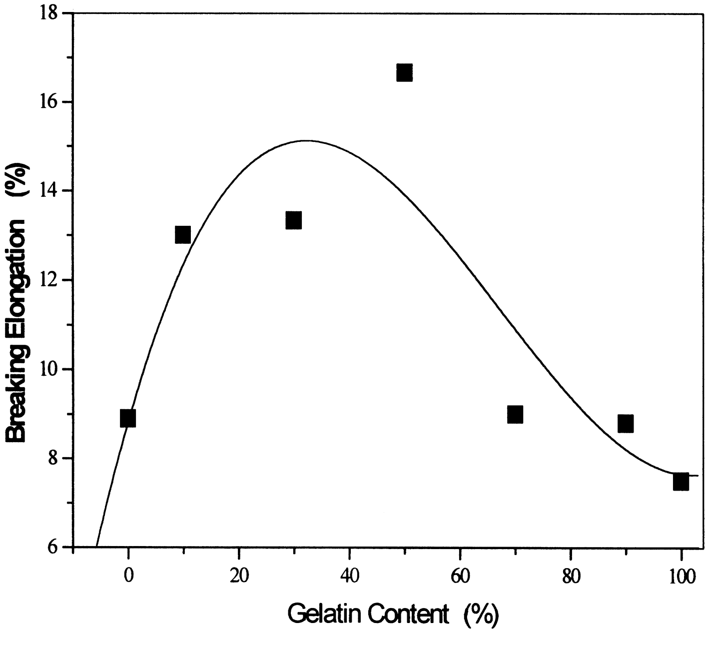

Figure 6. The dependence of breaking elongation on the content of gelatin for the films.

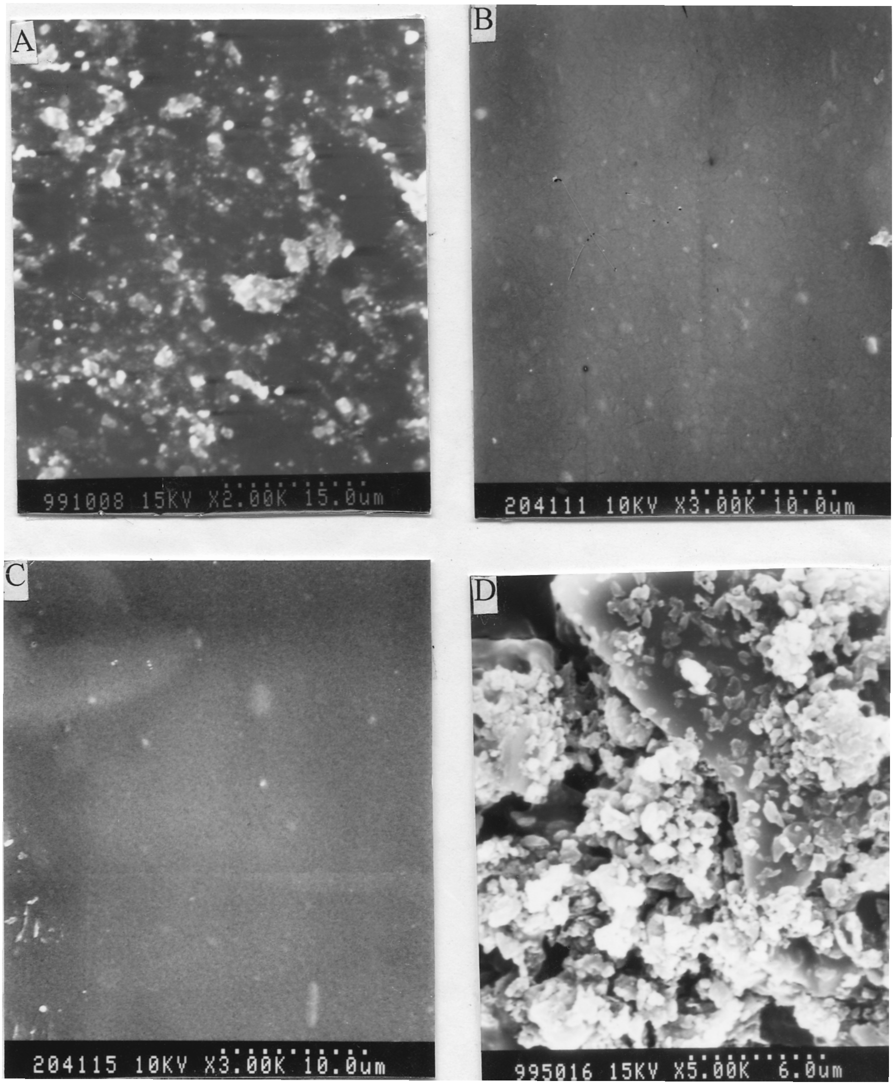

Figure 7. SEM photographs of the films. (A) GE, (B) GS-2, (C) GS-3, (D) SA.

surface morphology, suggesting the high miscibility and blend homogeneity between sodium alginate and gelatin when the sodium alginate content is 50 wt%. The disappearance of crystallinities exhibited on the photographs for the individual polymers and the alteration of morphological structure of the blend films suggested the occurrence of interaction between these two kinds of molecules, and this intermolecular interaction broke the individually intermolecular interaction existed in pure sodium alginate and gelatin films, which coincided with the IR analysis.

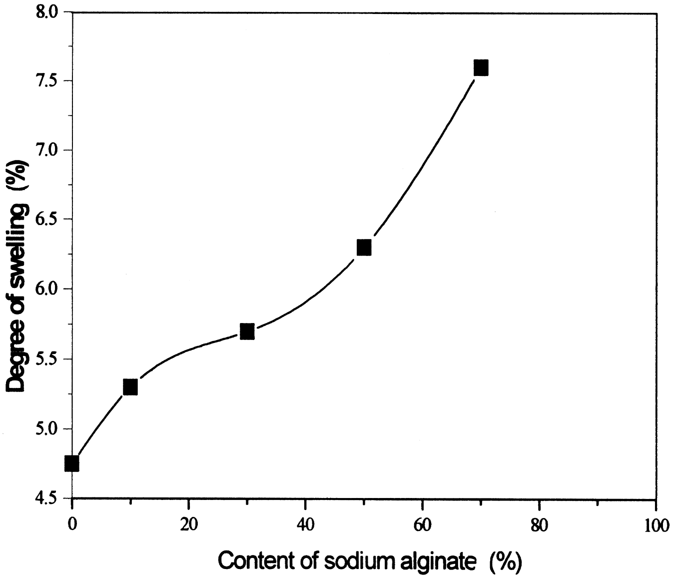

Figure 8. The dependence of degree of swelling on the content of sodium alginate for the films.

Swelling Properties of the Films

The degree of the swelling of the pure SA film could not be obtained because of its strong water solubility. Generally, both chemical structure and aggregate structure can affect the water solubility of gelatin. Taking chemical structure into account, blend gelatin with sodium alginate resulting from many hydrophilic groups can get blend films with good swelling properties. Figure 8 shows the degree of swelling curves of the films. The curve of swelling properties confirms the truth of the view above. The degree of swelling of the blend films were increased with the increase of sodium alginate content.

CONCLUSION

A series of transparent blend films were prepared by blending 4 wt% sodium alginate with 5 wt% gelatin aqueous solutions and dried at room temperature on glass plates for 2 days. Significant changes in shape and intensity of IR spectra absorption frequencies characteristic of either gelatin or sodium alginate have attributed to the presence of interaction between gelatin and sodium alginate molecules resulted from the establish of intermolecular hydrogen bonds. The crystallinities of the blend films decreased with the increased of sodium alginate content. The mechanical properties and thermal stability were improved by blending sodium alginate with gelatin. It is worth noting that the breaking elongation reached 16.6% when sodium alginate content is 50 wt%, much higher than that of the sodium alginate and gelatin. The good miscibility of sodium alginate and gelatin was confirmed by the results of SEM. From these phenomena, we can conclude that it is the strong intermolecular hydrogen bonds and ionic interaction in the blend films that resulted in the enhancements of mechanical properties and thermal stability.

REFERENCES

1. Uragami, T.; Yoshda, F.M. Studies of Synthesis and Permeabilities of Special Polymer Membrane. LI. Active Transport of Halogen Ions through Chitosan Membrane. J. Appl. Polym. Sci. **1983**, *28*, 1361.
2. Kim, J.H.; Kim, J.Y.; Lee, Y.M.; Kim, K.Y. Properties and Swelling Characteristics of Crosslinked Poly(vinyl alcohol)/Chitosan Blend Membrane. J. Appl. Polym. Sci. **1992**, *45*, 1711.
3. Zhang, L.; Zhou, D.; Wang, H ; Cheng, S..Ion Exchange Blended by Cellulose Cuoxam with Alginate. J. Membrane Sci. **1997**, *124*, 195.
4. Liang, C.; Hirabayashi, K. Improvement of Physical Properties of Fibroin Membrane with Sodium Alginate. J. Appl. Polym. Sci. **1992**, *45*, 1937.
5. Xiao, C; Lu, Y.; Gao, S.; Zhang, L. Characterization of Konjac Glucomannan-Gelatin Blend Films. J. Appl. Polym. Sci. (in press).
6. Moe, S.T.; Draget, K.I.; Skjäk-Bræk, G.; Smidsr, O. $^{\phi}$D, Alginate. Food Sci. Technol. **1995**, *67*, 245.
7. Lan, N.P.; Cuong, N.D. Alginate from Alginate and the Use of Alkaline Alginate as Impression Materials. Journ. Mac. Sci., Pure & Applied Chemistry **1996**, *A33* (12), 2026.
8. Xiao, C.; Gao, S.; Zhang, L. Blend Films from Konjac Glucomannan and Sodium Alginate and Their Preservative Effect. J. Appl. Polym. Sci. **2000**, 77, 617.
9. A. Veis, in *The Macromolecular Chemistry of Gelatin*, Vol. 5; Horecker, B.; Kaplan, N.O.; Scherage, H.A., Eds.; Academic Press: New York, 1964.
10. Chatterji, P.; Kaur, H. Interpenetrating Hydrogel Network: 3. Properties of the Gelatin-Sodium Carboxymethyl Cellulose System. Polymer **1992***, 33*, 2388.
11. Rathna, G.; Mohan Rao, D.; Chatterji, P. Hydrogels of Gelatin-Sodium Carboxymethyl Cellulose: Synthesis and Swelling Kinetics. Journ. Mac. Sci., Pure & Applied Chemistry. **1996**, *A33* (9), 1199.
12. Rathna, G.; Mohan Rao, D.; Chatterji, P. Water- Induced Plasticization of Solution Crosslinked Hydrogel Network: Energetics and Mechanism. Macromolecules. **1994**, *27* (26), 7920.
13. Wang, W. Food and Fermentation Industry (China). **1997**, *23* (4), 81.
14. Rabek, J.F. Experimental Methods in Polymer Chemistry Applications of Wide-Angle X-ray Diffraction (WAXD) to the Study of the Structure of Polymers, Wiley Interscience: Chichester, 1980; 505.
15. Krimm, S. Bandekar, Vibration Analysis of Peptides, Polypeptides, and Proteins. Int. J. Pept. Protein Res. **1985**, *26* (4), 407.
16. Yu, J.; Du, Y.; Zheng, H. Blend Films of Gelatin and Chitosan. J. Wuhan Univ. (Nat. Sci. Ed.). **1999***, 45*, 440.

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