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Compatibility and Properties of Biodegradable Blend Films with Gelatin and Poly(vinyl alcohol)

GAO Xiping[1,2], TANG Keyong[1*], LIU Jie[1], ZHENG Xuejing[1], ZHANG Yuqing[2]

(1. College of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China; 2. School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Luoyang 471023, China)

Abstract: The blend films with gelatin and poly(vinyl alcohol) (PVA) were prepared by a solution casting method. The compatibility between gelatin and PVA in the blend films was investigated. The transmittance, Fourier-transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), thermogravimetry analysis (TG), and differential scanning calorimetry (DSC) were employed to characterize the resultant blend films. According to optic result, the opacity of the blend film at the ratio of 20/80 (w/w, Gel to PVA) was the lowest, indicating the best compatibility between Gel and PVA at the ratio. The results of IR, XRD, DSC, and TG revealed an intensive interaction and good compatibility between them in the blend film at the ratio. The mechanical properties and solubility showed that PVA content in the blend films obviously affected the elongation at break and solubility. The mechanical properties and water resistance of gelatin film may be improved by the introduction of PVA.

Key words: gelatin; poly(vinyl alcohol); blend films; compatibility; properties

1 Introduction

Nowadays, white pollution is one of the most important environmental problems. It is caused by a large amount of nondegradable polymers such as polyethylene, polypropylene, polystyrene, *etc*. used by people. To reduce white pollution, natural polymers and biodegradable polymers are being paid more and more attention in academic world because they are good in biodegradation and regeneration.

Gelatin is a kind of natural polymer that may be easily obtained by a controlled hydrolysis of the fibrous insoluble collagen, which is a protein widely found in nature and is the major constituent of skin, bones and connective tissues[1-3]. Because of its excellent biodegradability, biocompatibility and good film-forming[4-6], it is widely used in many fields such as food, health care, cosmetic, packaging, medical industry and so on[7-10]. However, pure gelatin film is usually breakable and easily soluble in water. The mechanical properties are poor[11,12]. So the possible applications as a packaging material used in food, medicine, and biomedicine fields are significantly limited. Therefore, cross-linking or blending with other components are needed to improve the properties of pure gelatin film.

Blending is an effective and convenient method to improve the performance of polymer materials. Many such natural polymers as chitosan[13,14], starch[15,16], sodium alginate[17], protein[18], and such synthetic polymers as poly(vinyl alcohol) (PVA)[19,20], poly (L-lactic acid) (PLA)[21,22], and polyacrylamide(PAM)23] have been studied to be blended with gelatin. PVA, nontoxic and non-irritative, is soluble in water, though it is not easily soluble in cold water. It is good in biodegradability and biocompatibility and has excellent film-forming ability, chemical resistance and mechanical properties[24-26]. The physical properties and water resistance of pure gelatin film may be greatly improved when PVA is introduced in gelatin. The compatibility between the molecules of gelatin and PVA should be taken into consideration if we are going to prepare blend films with gelatin and PVA.

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GAO Xiping(高喜平):E-mail:gxping0818@163.com

*Corresponding author: TANG Keyong(汤克勇): Ph D; Prof.; E-mail: kytang@zzu.edu.cn

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In the present study, the Gel/PVA blend films with different ratios of Gel to PVA were prepared by a solution blending method, and the compatibility between gelatin and PVA was studied. Transmittance, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry analysis (TG), and differential scanning calorimetry (DSC) were employed to characterize the structure of the blend films. The mechanical properties and solubility of the Gel/PVA blend films with different ratios were also investigated.

2 Experimental

2.1 Materials

Gelatin (type B, from bovine bone, analytical grade) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd, Tianjin, China. Poly(vinyl alcohol) (PVA) was from Anhui Wanwei High-tech Materials Industry Co., Ltd., Anhui, China.

2.2 Preparation of blend films

The Gel/PVA blend films were produced by mixing the solution A (gelatin solution) and solution B (PVA solution). To prepare solution A, 10% (W/W), the gelatin was hydrated at room temperature for 30 min, and then dissolved in 55 ℃ water for about 30 min to be completely dissolved. For solution B, 10% (*w/w*), PVA was homogenized in distilled water and then, dissolved at 90 ℃ for 30 min. Solution A and solution B were mixed at 40 ℃ for 30 min to yield the film forming solutions with different ratios of gelatin to PVA. The ratios of gelatin to PVA were 0/100, 20/80, 30/70, 40/60, 50/50, 60/40, 80/20, and 100/0, respectively. The resultant film-forming solutions were cast on polypropylene plates (15×15 cm) and dried at room temperature to yield the different blend films for subsequent study.

2.3 Characterization of the films

2.3.1 Opacity

The absorbency of each film was recorded on an UV-Vis spectrophotometer (7200 Unico, China). The blend films were sampled into rectangle pieces and placed in the test cell of the spectrophotometer. Air was used as the reference. The areas under the absorption curves from 400 to 800 nm were recorded, and the opacity of the blend films was calculated according to the following equation:

$$\text{Opacity}(T)=A_{500}\times 500/L \qquad (1)$$

where A_{500} is the absorption at 500 nm and L is the blend film thickness (um). All the samples were measured three times and the averages were reported.

2.3.2 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of the blend films were recorded using Nicolet iS10(Thermo Scientific, USA) infrared spectroscopy instrument in the range of 4 000-675 cm^{-1} with the resolution of 4 cm^{-1} .

2.3.3 X-ray diffraction (XRD)

The structure of the Gel/PVA blend films was characterized by XRD. All XRD data were collected using a D8 Advance X-ray diffraction instrument (BRUKER Ltd. Germany) in the 2θ range of 2°-40°.

2.3.4 Differential scanning calorimetry (DSC)

The samples of blend films were analyzed by DSC (Diamond DSC, PE Ltd, USA) to determine the glass transition temperatures. The samples were placed in hermetically sealed aluminum pans and heated at 10 oC/min in N_2. An empty pan was used as the reference.

2.3.5 Thermogravimetric analysis (TG)

The thermogravimetric analysis of the blend films was carried out on a NETZSCH TG209 (NETZSCH Ltd, Germany) thermogravimetric analyzer. Non-isothermal experiments were performed in the range from room temperature to 600 ℃ with the heating rate of 10 ℃/min in N_2.

2.3.6 Mechanical properties

Tensile strength (TS) and elongation at break (EB) of the blend films were determined on a microcomputer-controlled electronic testing machine (TY8000, Tianyuan Testing Machine Co. Ltd., Jiangsu, China). All the samples were air-conditioned at 25 ℃ and RH= 55%-65% for 24 hours before being stretched. The dumbbell samples of 25 mm in length and 4mm in width were used, and the stretching speed was 50 mm/min.

2.3.7 Solubility

The blend films were cut into the piece of 1.0×1.0 cm and put in an oven at 105 ℃ to be dried for 2 hours. The samples were then weighed, noted as w_1. After being immersed in 10 mL de-ionized water at room temperature for 24 h, the samples were picked out to be dried at 80 ℃ for 1 hour and re-dried at 105 ℃ for 2 hours. The samples were weighed again, noted as w_2. The solubility of the samples was calculated as

$$\text{Solubility}(\%)=100\times(w_1-w_2)/w_1 \qquad (2)$$

where, w_1 and w_2 are the weights of the samples before and after solubility tests. Three times were done and the averages were reported.

3 Results and discussion

3.1 Opacity

In order to know the compatibility between the molecules of gelatin and PVA, the opacity of the samples was studied. The opacity is contrary to transmittance. The lower the opacity of blend films, the higher is the transmittance of the blend films. A low opacity indicates a good compatibility between gelatin and PVA in the blend films.

The opacity of the blend films at different Gel/PVA ratios is shown in Table 1. Pure gelatin film is lightly yellow and pure PVA film is colorless. The opacity of pure gelatin film is the highest and that of pure PVA film is the lowest. The opacity of the Gel/PVA blend films decreased gradually with increasing PVA content in the blend films. It was obviously observed that the surface of the blend film with the Gel/PVA ratio of 20/80 was transparent and smoother than those with the other ratios, such as 40/60, 50/50, and 60/40. The opacity of the blend film with the Gel/PVA ratio of 20/80 was lower than that of any other blend film. This was probably because of the stronger interaction in the blend film with the Gel/PVA of 20/80. Stronger interaction brought about a better compatibility between them.

Table 1 Opacity and absorption of the blend films with different gelatin /PVA ratios

Gel/PVA(*w*/*w*)	*T*
100/0	1.093
80/20	0.826
60/40	0.722
50/50	0.941
40/60	0.695
30/70	0.656
20/80	0.461
0/100	0.423

At the same time, the opacity of the blend film with the Gel/PVA ratio of 50/50 was higher than that of any other Gel/PVA blend film. This was because the Gel/PVA blend film at the ratio took on two apparent phase separation. This result was caused by weak interaction and bad compatibility between gelatin and PVA in the blend film with the Gel/PVA ratio of 50/50.

3.2 FTIR spectroscopy

FTIR is usually used to study the molecular structure of a matter. In order to know the interaction between molecules of Gel and PVA, FTIR was used to study the effects of hydrogen bonding on gelatin and PVA in terms of molecular and supramolecular structure. Intermolecular interaction occurs when different polymers are compatible. So the FTIR spectrum of the blends is different from those of pure polymers, which is advantageous to the study of the extent of polymer compatibility.

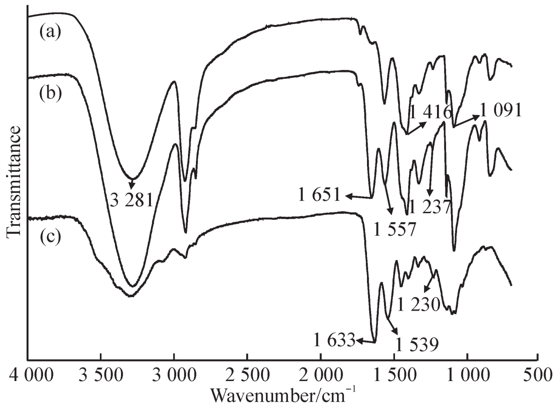

Fig.1 FTIR spectra of PVA, gelatin and Gel/PVA blend film: (a) PVA film; (b) Gel/PVA film at ratio of 20/80; (c) gelatin film

Fig.1 shows the FTIR spectra of pure gelatin film, pure PVA film, and the Gel/PVA blend film with the gelatin/PVA ratio of 20/80. In the infrared spectrum of pure PVA film, the peak at 3 281 cm^{-1} was attributed to the stretching vibration of -OH group, the one at 1 461 cm^{-1} was due to bending vibration of CH-OH, and that at 1 091 cm^{-1} was associated with the stretching of C-O. In the infrared spectrum of gelatin, the absorption band at 1 633 cm^{-1} was related to the stretching of C=O (amide I), the peak at 1 539 cm^{-1} was the stretching of N-H and C-N (amide II), the one at 1 230 cm^{-1} should be the stretching of N-H and C-N (amide III). In the infrared spectrum of Gel/PVA blend film, the changes in absorption band of amide I, amide II, and amide III of gelatin were obviously observed. The absorption band (amide I) changed from 1 633 cm^{-1} to 1 651 cm^{-1} and the absorption band (amide II) varied from 1539 cm^{-1} to 1 557 cm^{-1} and the absorption band(amide III) changed from 1 230 cm^{-1} to 1 237 cm^{-1}. These results suggested that interactions such as hydrogen bonding and intermolecular forces occurred between gelatin and PVA, resulting in a good compatibility between them.

3.3 X-ray diffraction analysis

The X-ray diffraction patterns of gelatin, PVA, and Gel/PVA blend films are shown in Fig.2. From Fig.2, we know that there are two obvious crystalline peaks at 2θ= 8.7°and 19.8° in the diffractogram of PVA film because of its close molecular packing and regular crystallization. For that of gelatin, only a typical crystalline peak at 2θ = 8.8° appeared, indicating that gelatin was a low crystalline polymer. In the X-ray diffraction patterns of Gel/PVA blend films (Fig.2), the diffraction peak of PVA at 19.8° decreased and a new diffraction peak at 29.3° appeared. So there may be a strong interaction between the molecules of Gel and PVA to destroy the original close packing of PVA molecules and a new crystallite formed. At the same time, a new diffraction peak at 9.7° occurred when the weight ratio of Gel to PVA was 20/80, 40/60, and 60/40. It should be noted that for the blend film at the ratio of 20/80, the intensity of the diffraction peak at 9.7° was the strongest in all the samples. This was probably because of the strong interaction between molecules of Gel and PVA at the ratio, which may improve the compatibility between Gel and PVA in the blend film. These results were consistent with those of the opacity mentioned above.

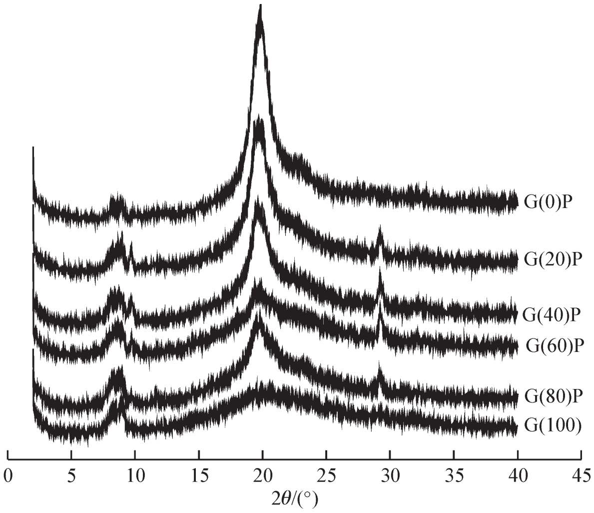

Fig.2 XRD patterns of Gel, PVA, and Gel/PVA blend films
Abbreviations are: G-Gel, P-PVA

3.4 Differential scanning calorimetry

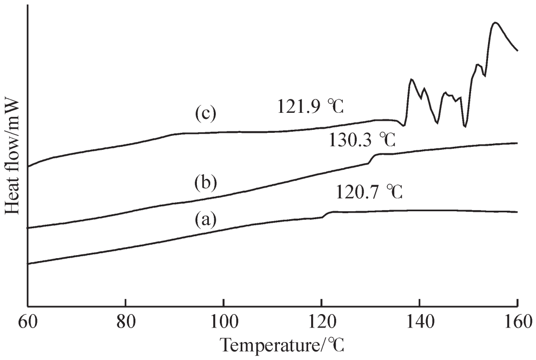

Fig.3 DSC curves of Gel film, PVA film and, Gel/PVA blend film: (a) PVA film; (b) Gel/PVA film at ratio of 20/80; (c) gelatin film

The DSC curves of pure gelatin film, pure PVA film, and blend film at the Gel/PVA ratio of 20/80 are shown in Fig.3. From Fig.3, it can be seen that the glass transition temperature(T_g) of pure gelatin film was 121.9 ℃ and that of pure PVA film was 120.7 ℃. The glass transition temperature of the blend film at the Gel/PVA ratio of 20/80 was 130.3 ℃. So the glass transition temperature of the blend film with the Gel/PVA mass ratio of 20/80 was higher than those of both gelatin and PVA. This was probably because of the intense interaction between the molecules of gelatin and PVA in the blend film to increase the glass transition temperature. A good compatibility between the two components in the blend film at the Gel/PVA ratio of 20/80 was proved again.

3.5 Thermogravimetric analysis

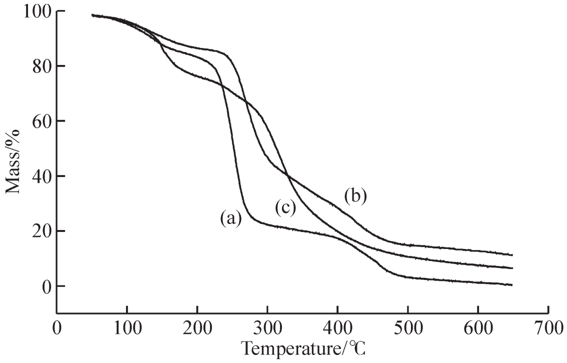

Fig.4 TG curves of PVA, gelatin, and Gel/PVA blend films: (a) PVA film; (b) Gel/PVA film at the ratio of 20/80; (c) gelatin film

The TG curves of pure gelatin film, pure PVA film, and Gel/PVA blend film at the Gel/PVA ratio of 20/80 are shown in Fig.4. Three weight loss stages appeared in the TG curves of PVA film. The first weight loss at 50-150 ℃ was due to the vaporization water absorbed in the sample. The second weight loss at 220-280 ℃ was attributed to the thermal degradation of PVA molecule chain. The third one took place at higher temperature of 400-450 ℃ and owed to the by-product generated PVA during the TG thermal degradation process. Two significant weight losses appeared in the TG curve of gelatin film. The first one at 50-150 ℃ was also due to the evaporation of water absorbed in the sample, and the other one at 200-350 ℃ should be the thermal degradation of gelatin molecule chains.

There are two obvious weight losses in the TG curve of the blend film at the Gel/PVA ratio of 20/80 as shown in Fig.4. The first weight loss at 50-150 ℃ was the vaporization of the water absorbed in the sample, while the other one at 240-460 ℃ was attributable to the thermal degradation of the blend film molecule chains. Compared with the TG curve of pure PVA film with three obvious weight losses, one weight loss stage disappeared in the TG curve of the Gel/PVA blend film. The second degradation temperature of the Gel/PVA blend film was higher than that of pure PVA film. For example, the degradation temperature of the Gel/PVA blend film was at 251, 291 and 326 ℃ when the mass percent was 80%, 50% and 40%, respectively. And the degradation temperature of the pure PVA film was at 220,251 and 257 ℃ when the mass percent of the pure PVA film was 80%, 50% and 40%, respectively. It should be because of the intense interaction between the molecules of gelatin and PVA, which resulted in a good compatibility between the two components to improve the thermal stability of the Gel/PVA blend film.

3.6 Mechanical properties

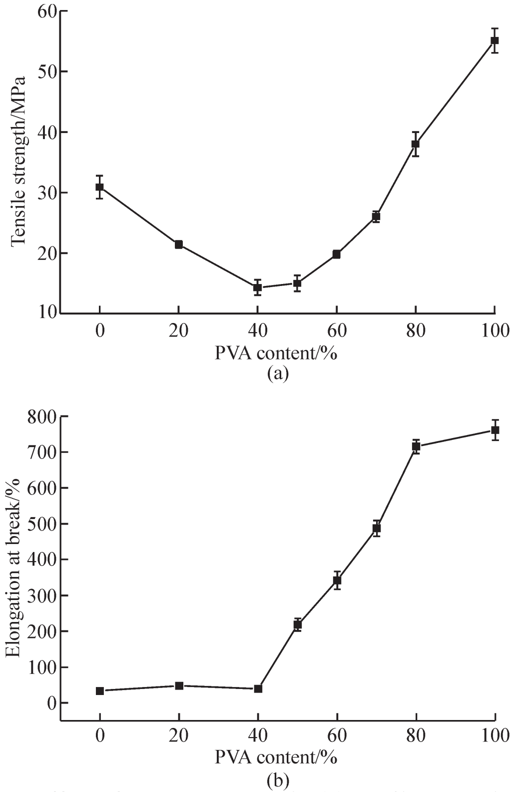

Fig.5 Effect of PVA content on the (a) tensile strength and (b) elongation at break of the Gel/PVA blend films

The effects of PVA content in the Gel/PVA blend films on the tensile strength (TS) and elongation at break (EB) of the blend films are showed in Fig.5. The tensile strength of both pure gelatin and PVA films is high. PVA film is flexible with good mechanical properties. The mechanical properties of the Gel/PVA blend films greatly depended on the PVA content in them. In Fig.5(a), with increasing PVA content, the tensile strength of the blend films decreased firstly and then increased. And, it was found that the tensile strength of the blend film at the Gel/PVA ratio of 20/80 increased to 37.98MPa, compared to 30.91MPa of the pure gelatin film. At the same time, the lowest tensile strength appeared at the Gel/PVA ratio of 60/40. Although there was interaction between the molecules of gelatin and PVA, the interaction was not enough to provide a good compatibility between them. The compatibility between them at the Gel/PVA ratio of 60/40, 50/50, and 40/60 was worse than that at the Gel/PVA ratio of 80/20, 30/70, and 20/80.

Fig.5(b) indicated that the elongation at break of the blend films increased gradually with increasing PVA content. The elongation at break of the blend film at the Gel/PVA ratio of 20/80 increased to 715.38%, compared to 33.5% of the pure gelatin film, the elongation at break was increased more times. PVA was flexile and the molecule chains had good movement ability. In the present study, phase separation was observed at the Gel/PVA ratio of 40/60, 50/50, and 60/40. No phase separation was found at the Gel/PVA ratios of 80/20, 30/70, and 20/80, indicating a good compatibility between the molecules of gelatin and PVA at the ratios. This should be attributed to the interaction between the two components, i.e., hydrogen bonds or electrostatic interaction.

3.7 Solubility

Table 2 Solubility of the blend films with different gelatin /PVA ratios

Gel/PVA ratio	Solubility
100/0	Completely dissolved
80/20	Completely dissolved
60/40	Basically dissolved
50/50	43.3%
40/60	30.8%
30/70	10.2%
20/80	4.3%
0/100	1.6%

The solubility of the Gel/PVA blend films with different Gel/PVA ratios is shown in Table 2. Pure gelatin film was soluble in water. It would be completely dissolved in water after 24 h. The Gel/PVA blend films at the Gel/PVA ratios of 80/20, and 60/40 were completely dissolved on the whole for 24 h. The solubility of the other blend films decreased with increasing PVA content in the Gel/PVA blend films. The solubility of the blend film at the Gel/PVA ratio of 20/80 was the lowest in all the Gel/PVA blend samples. There may be two reasons. Firstly, PVA was not easily soluble in cold water. Secondly, the good compatibility between gelatin and PVA at the Gel/PVA ratio of 20/80 might provide a strong interaction. So the crystallization of the Gel/PVA blend film was changed and the solubility in water was decreased as a result.

4 Conclusions

The Gel/PVA blend films with different Gel/PVA ratios were prepared by solution casting method. The mechanical properties and solubility of the Gel/PVA blend films were studied. The elongation at break and water resistance of the blend films increased gradually with increasing PVA content. These results indicated that the addition of PVA could improve the mechanical properties of the pure gelatin film and change the water resistance of pure gelatin film.

Transmittance, FTIR, XRD, DSC and TG were employed to characterize the structure and properties of the Gel/PVA blend films. The results of transmittance, FTIR, DSC indicated a good compatibility between the molecules of gelatin and PVA at the Gel/PVA ratio of 20/80.This might be because of the intense interaction between gelatin and PVA at the Gel/PVA ratio of 20/80. At the same time, XRD study showed crystalline peaks changed apparently in the Gel/PVA blend films, and this result further affirmed that there existed intense interaction between gelatin molecules and PVA molecules.

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