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Study on preparation and properties of PEG blend film

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PEG (Polyethylene glycol) of biodegradable polymer materials were used to prepare (1 wt%, 3 wt%, 5 wt% and 7 wt%) PEG films. Polyvinyl alcohol (PVA) was added to the PEG solution and mixed films with different mass fraction ratios of PEG/PVA (2:0.66, 2:2 and 2:6) were produced. Sericin (SS) was added to the PEG/PVA mixed solution to make PEG/PVA/SS mixed films with different mass fraction ratios (2:1:2, 1:5:2, 1:5:1, 2:5:1 and 1:1:1). The scanning electron microscope, film thickness measurement, tensile test and the swelling degree and dissolution loss rate test were used to analyze the mixed film. The research results showed that under the experimental conditions the PEG blend film had good film forming properties. The thickness of the blend film increased with the increase of solute mass fraction. The break strength of the PEG/PVA blend film increased with the increase of PVA mass fraction. The break strength, break stretch and break elongation of the PEG/PVA/SS blend film were all good and increased with the increase of PVA content. The results of swelling degree and dissolution loss rate showed that both PEG/PVA and PEG/PVA/SS blend films had good water-holding properties. The dissolution loss rate of blended films was less than 50% besides PEG/PVA (2:2) and PEG/PVA/SS (1:1:1) blend film.

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Keywords: Silk sericin, Polyethylene glycol, Mixed film, Polyvinyl alcohol

1. Introduction

Polyethylene glycol (PEG) is a kind of thermoplastic polymer material with good crystallinity and water solubility [1-4]. Due to its advantages of no toxicity and good biocompatibility, it has been well developed in biomedical field [5-7]. Polyvinyl alcohol (PVA) containing a large number of hydrophilic hydroxyl groups has good water solubility, thermal stability and film formation, etc [8-12]. The production process of PVA which is widely used in the field of biomaterials is mature [13-16]. Silk sericin (SS) as a pure natural material has important value in the ingredients of cosmetics, but the film prepared from pure SS has defects in mechanical properties [17-18]. During silk processing, a large amount of SS is discarded into the waste liquid, which wastes the biological resources [19-22]. Therefore, the protection of the environment and the harmonious development of natural resources make the recycling and utilization of SS very important [23-24]. On the other hand, the recycling of SS will also reduce the pollution load in the waste water and contribute to the construction of an environment-friendly society [25]. In this study, PEG, PVA and SS were used as raw materials to provide theoretical basis for the development of good biodegradable materials.

2. Materials and methods

2.1. Experimental materials and equipment

Materials: PEG (molecular weight 10000, Macklin); SS: Favorsun Pharmaceutical Co., Ltd (Shanghai); PVA (1797: alcoholysis degree 96.0-98.0%, Aladdin).

Experimental equipment: culture dish (radius 6 cm), blue cap bottle (100 ml), UX620H electronic balance (Guangzhou Kexiao Scientific Instrument Co., Ltd.); DF-101S constant

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temperature heating magnetic stirrer (Beijing Kaiya Instrument Co., Ltd.); Field Emission Scanning Electron Microscope Sigma 500 (Carl Zeiss, Germany); HD026N electronic fabric strength meter; YG141LA digital fabric thickness meter (Laizhou Electronic Instrument Co., Ltd.).

2.2. Preparation of film

2.2.1. Preparation of PEG film

The different weights of PEG (1 g, 3 g, 5 g and 7 g) were weighed with an electronic balance and put into the blue cap bottle, then the different weights of deionized water (99 g, 97 g, 95 g and 93 g) were added, respectively. The different mass fraction of PEG solution were prepared at 85 ℃ for 4 h in the constant temperature heating magnetic stirrer with water bath, then they were taken it out and cooled to room temperature. They were poured into the different petri dish with a radius of 6 cm and formed film by air dry.

2.2.2. Preparation of PEG/PVA mixed film

3 parts of 2 g PEG were weighed and PVA (0.66 g, 2 g and 6 g) were weighed, respectively. Then they were put into the blue cap bottle and the deionized water (97.4 g, 96 g and 92 g) was added, respectively. The mixed PEG/PVA with different mass ratio were swollen at room temperature for 30 min and the swelled PEG/PVA mixed solution were put into the constant temperature heating magnetic stirrer with water bath at 95 ℃ for 4 h. The film forming process was the same as 2.2.1.

2.2.3. Preparation of PVA/PEG/SS mixed film

PEG (2 g, 1 g, 1 g, 2 g and 1 g), PVA (1 g, 5 g, 5 g, 5 g and 1 g) and H_2O (95 g, 92 g, 93 g, 92 g and 97 g) were weighed. The PVA/PEG mixed solution prepared was the same as 2.2.2. SS (2 g, 2 g, 1 g, 1 g and 1 g) were weighed and added into the above PVA/PEG solution. They were heated with water bath at 60 ℃ for 2 h. The film forming process is the same as 2.2.1.

2.3. Scanning electron microscope

The surface of the film material was observed by scanning electron microscopy (SEM) at room temperature with magnification of 5000 times.

2.4. Thickness measurement of mixed film

The thickness was measured with thickness gauge, and the thickness range was 0.01 ~ 10 mm with the accuracy of 0.01 mm. The thickness was measured 10 times and the average value was taken.

2.5. Tensile test of mixed film

The mixed film was cut into the rectangle of 10 mm×70 mm and the experimental parameters were set according to GB13022. The tensile rate was at the constant speed of 50 mm/min, and each sample was tested 3 times to calculate the average value.

2.6. Swelling test of mixed film

0.9 wt% salt solution was prepared, 2 cm×2 cm square blend film sample was cut and fully dried. M1 was weighed with the electronic balance and put into the water bath salt solution at 37 ℃ to swell. The sample was taken out at regular intervals and wiped dry the surface solution of the sample to reach the swelling balance. M2 was weighed when the sample mass which reached the swelling balance no longer changed. The sample was dried and M3 was weighed. The calculation formulas of swelling degree (SR) and dissolution loss rate (DR) are as follows:

$$SR = \frac{M2 - M1}{M1} \times 100\% \qquad \text{(Formula 1)}$$

$$DR = \frac{M1 - M3}{M1} \times 100\% \qquad \text{(Formula 2)}$$

3. Results and analysis

3.1. Electron micrograph of film

3.1.1. Electron micrograph of PEG film

Fig. 1 is the electron micrograph of PEG film. Fig. 1a shows that the surface of 1 wt% PEG film is flat, smooth and translucent. The thickness of film is relatively thin. Fig. 1b shows that the surface of 3 wt% PEG film is smooth and slightly white compared with Fig. 1a. The 5 wt% PEG film with good film-forming property has smooth touch and flat surface (Fig. 1c). During the air-drying process, the surface of the film has obvious cracks, but there is no fracture. There is slight curl in the natural state after the film was formed. The color of the film with long V-shaped cracks and thick feel (Fig. 1d) is whiter than that in Fig. 1c. At the macro level, the PEG film is smooth. At the micro level, the surface of the film is corrugated. The 7 wt% PEG film has bumps and cracks. It can be seen from the above that 3 wt% PEG has the best film-forming properties.

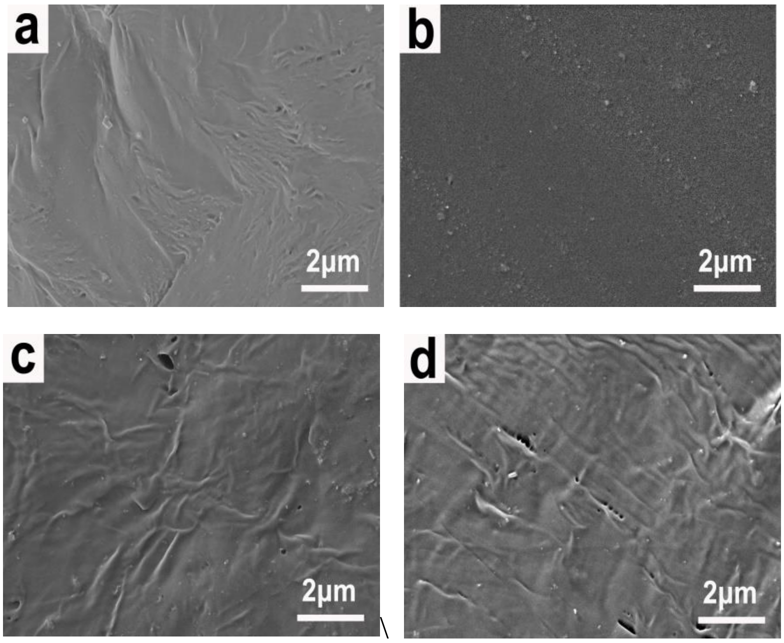

Fig. 1. Electron micrographs of PEG film a 1 wt%, b 3 wt%, c 5 wt%, d 7 wt%.

3.1.2. Electron micrograph of PEG/PVA film

Fig. 2 is the electron microscophs of PEG/PVA blend film. PEG/PVA (2:0.66) blend film (Fig. 2a) is white and transparent, which has cracks and large bulge. The film-forming effect is good. Fig. 2b shows that the surface of PEG/PVA (2:2) blend film is smooth, thin and transparent. Under the electron microscope, the PEG/PVA (2:6) blend film (Fig. 2c) has small debris-like particles, local air bubbles on the surface and lumpy protrusions in the middle. The PEG/PVA blend film is white block in macroscopical view, and small block in microcosmic view. In conclusion, the PEG/PVA (2:2) blend film has the best film-forming property.

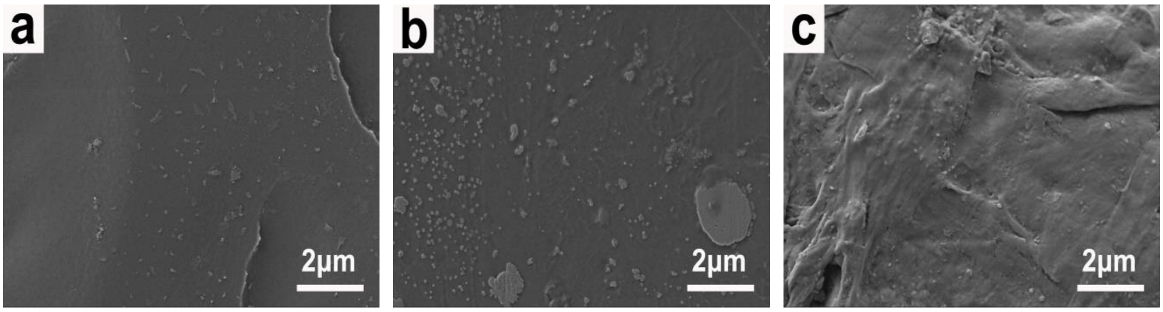

Fig. 2. Electron micrographs of PEG/PVA blend film a 2:0.66, b 2:2, c 2:6.

3.1.3. Electron micrograph of PEG/PVA/SS film

The positive side of PEG/PVA/SS (2:1:2) film (Fig. 3a) has small particles and the reverse side is smooth and flat. The whole film is transparent with a little light yellow and the shape of the mixed film is good. The surface of PEG/PVA/SS (1:5:2) film (Fig. 3b) with soft texture and light yellow is smooth and flat. The shape of the mixed film is good. The surface of PEG/PVA/SS (1:5:1) blend film (Fig. 3c) with local accumulation of small particles is convex and lumpy. The surface with light yellow color and hard handle is partially smooth and flat. The surface of the PEG/PVA/SS (2:5:1) (Fig. 3d) film is transparent, smooth and flat. The surface of the film has bubbles and there are many micropores under the microscopic view. The surface of PEG/PVA/SS (1:1:1) film (Fig. 3e) is flat, yellow and brittle. The membrane is easy to break when taken from the culture dish.

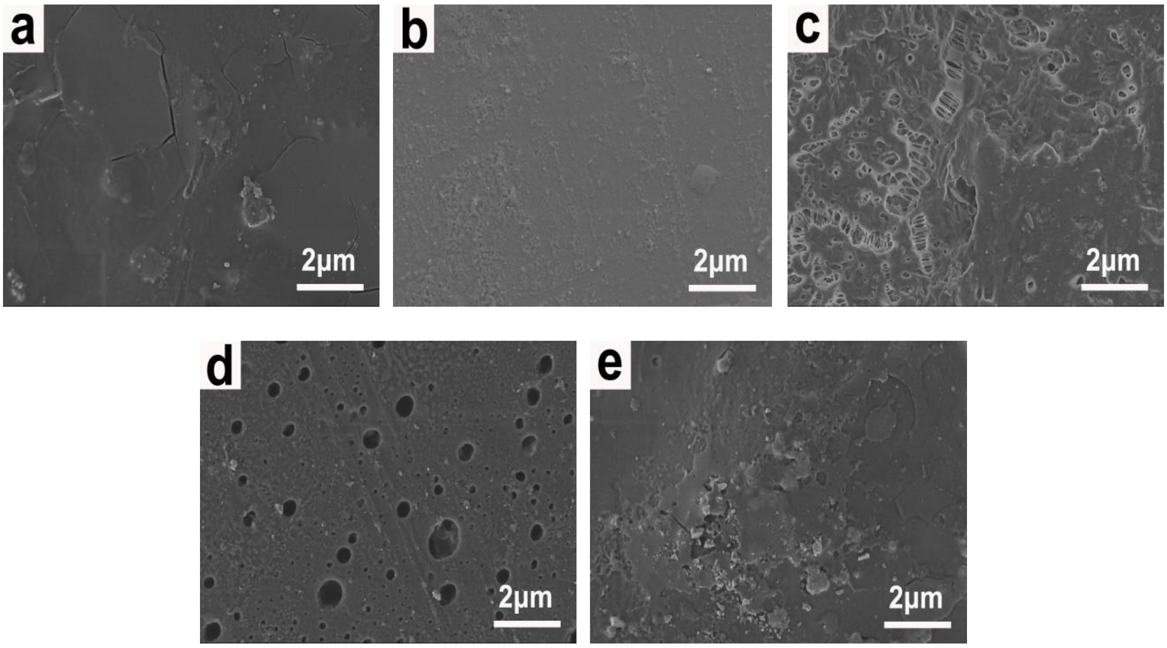

Fig. 3. Electron micrographs of PEG/PVA/SS blend film a 2:1:2, b 1:5:2, c 1:5:1, d 2:5:1, e 1:1:1.

3.2. Thickness of PEG mixed film

According to table 1, the thickness of the PEG film increases with the increase of PEG mass fraction. The thickness of the PEG/PVA blend film also increases with the increase of PEG mass. As can be seen from Table 2, the thickness of PEG/PVA/SS (2:1:2) and PEG/PVA/SS (1:1:1) films increase with the increase of PEG and SS, while the concentration of PVA has remained unchanged. Compared with PEG/PVA/SS (1:5:1) and PEG/PVA/SS (1:5:2), the thickness of the mixed film increases with the mass of SS increases. The thickness of the mixed film will increase with the increase of PVA, PEG or SS.

Table 1. Thickness of PEG and PEG/PVA mixed film Unit/mm.

Mass fraction and ratio	1 wt%	3 wt%	5 wt%	7 wt%	2:0.66	2:2	2:6
Average thickness	0.10	0.18	0.38	0.40	0.19	0.30	0.38

Table 2. Thickness of PEG/PVA/SS mixed film Unit/mm.

Mass ratio	2:1:2	1:5:2	1:5:1	2:5:1	1:1:1
Average thickness	0.32	0.49	0.39	0.62	0.25

3.3. Mechanical properties of PEG and mixed film

It can be seen from table 3 that the break strength, break stretch and break elongation of 1 wt%, 3 wt% and 5 wt% PEG film increase with the increase of PEG mass fraction. The break strength and work of fracture of PEG/PVA blend films with different mass ratios increase with the increase of PVA mass, but the break stretch and break elongation of PEG/PVA (2:2) blend film are the largest and that of PEG/PVA (2:0.66) blend film is the smallest. The reason may be that the ether bond of PEG forms a new covalent bond with the H bond of PVA.

Table 3. Mechanical properties of PEG and PEG/PVA films.

Mass fraction or ratio	1 wt%	3 wt%	5 wt%	2:0.66	2:2	2:6
Break strength/N	7.67	8.33	38.83	13.33	35.67	75.00
Break stretch/mm	6.50	8.28	14.94	14.28	45.57	21.13
Break elongation/%	4.01	16.56	29.89	28.56	91.14	42.27
Work of fracture/J	0.46	0.34	0.44	0.15	1.24	1.35

Table 4. Mechanical properties of PEG/PVA/SS films.

Ratio	2:1:2	1:5:2	1:5:1	2:5:1	1:1:1
Break strength/N	49.67	128.00	191.67	125.83	116.17
Break stretch/mm	57.45	138.51	143.32	136.56	90.85
Break elongation/%	114.90	277.01	286.64	273.13	181.71
Work of fracture/J	2.72	12.45	19.33	3.59	9.22

Under the experimental conditions, as PVA content remains the same, the break stretch, break elongation, break strength and work of fracture decrease with the increase of PEG and SS content according to the comparison of PEG/PVA/SS (2:1:2) and PEG/PVA/SS (1:1:1) in Table 4.

Compared with PEG/PVA/SS (1:5:2) and PEG/PVA/SS (1:5:1), the break strength, break stretch, break elongation and work of fracture increase with the decrease of SS. Compared with PEG/PVA/SS (1:5:1) and PEG/PVA/SS (2:5:1), the break strength, break stretch, break elongation and work of fracture decrease with the increase of PEG. Compared with PEG/PVA/SS (1:5:1) and PEG/PVA/SS (1:1:1), the break strength, break stretch, break elongation and work of fracture increase with the increase of PVA. The change of PVA content has a great influence on the tensile properties of PVA/PEG/SS mixed films. New bonds may be formed between the ether bond of PEG, the H bond of PVA and SS.

3.4. Swelling test of PEG mixed film

Pure PEG film and PEG/PVA (2:0.66) mixed film are easy to be dissolved according to table 5. The higher the content of PVA in the PEG/PVA (2:6) and PEG/PVA (2:2) mixed films, the greater the swelling degree and the smaller the dissolution loss rate. Compared with PEG/PVA/SS (2:1:2) and PEG/PVA/SS (1:1:1), the content of PVA has remained unchanged, the content of PEG and SS increase, the swelling degree increase and the dissolution loss rate decrease. Compared with PEG/PVA/SS (1:5:2) and PVA/PEG/SS (1:5:1), the swelling degree and the dissolution loss rate decrease with the increase of SS content. Compared with PEG/PVA/SS (1:5:1) and PEG/PVA/SS (2:5:1), the swelling degree decrease and the dissolution loss rate increase slightly with the increase of PEG content. Compared with PEG/PVA/SS (1:5:1) and PEG/PVA/SS (1:1:1), the swelling degree increase and the dissolution loss rate decrease with the increase of PVA content.

Table 5. Swelling degree and dissolution loss rate of PEG mixed film.
Unit/M_1(g), M_2(g), M_3(g), swelling degree (%), dissolution loss rate (%)

PEG mixed film	M_1	M_2	M_3	swelling degree	dissolution loss rate
PEG/PVA（2:2）	0.07	0.22	0.016	214	77
PEG/PVA（2:6）	0.18	0.704	0.135	291	25
PEG/PVA/SS（2:1:2）	0.164	0.511	0.092	212	44
PEG/PVA/SS（1:5:2）	0.218	0.751	0.153	244	30
PEG/PVA/SS（1:5:1）	0.11	0.395	0.07	259	36
PEG/PVA/SS（2:5:1）	0.142	0.327	0.088	130	38
PEG/PVA/SS（1:1:1）	0.151	0.386	0.066	156	56

Note: PEG and PEG/PVA (2:0.66) dissolved in the deionized water.

4. Conclusion

This study successfully prepared PEG films with mass fractions of (1 wt%, 3 wt%, 5 wt% and 7 wt%), PEG/PVA (2:0.66, 2:2 and 2:6) films, and PEG/PVA /SS (2:1:2, 1:5:2, 1:5:1, 2:5:1 and 1:1:1) films, in which PEG (3 wt%), PEG/PVA (2:2) and PEG/PVA/SS (1:5:2) have the best film-forming properties. The thickness of the blend film increased with the increase of solute mass. Under the experimental conditions, the higher the mass fraction of PEG, the greater the break strength and break elongation of the film.

The strength of PEG/PVA blend film increased with the increase of PVA mass, while the break stretch of PEG/PVA (2:2) was the largest. In PEG/PVA/SS blend film, the break strength, break stretch and break elongation increased with the increase of PVA content. The more PVA content in PEG/PVA blend film, the greater the swelling degree and the smaller the dissolution loss rate. The water holding capacity of PEG/PVA/SS blend film was all good, and the dissolution loss rate of the films was less than 50% except PEG/PVA/SS (1:1:1).

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