XXXI IULTCS Congress
Valencia (Spain) - September 27th-30th 2011

Paper A15

Mechanical Properties and Hydrophilicity of Gelatin and Poly (3-hydroxybutyrate-co-3-hydroxy-valerate) Blend Films

Ya Li, Lan Jiang, Kaiqi Shi, Jiali Lu, Jingkuan Duan, Shuangxi Shao*
Institute of Materials Engineering, Ningbo University of Technology, Ningbo, China.
Phone: +086-574-87080148, e-mail:nbssx@126.com

Abstract: PHBV and gelatin blend films were prepared and characterized. For the incompatibility of gelatin and PHBV tensile strength of the blend films decreased to the minimum value at the content of gelatin 67% and then increased with gelatin content, the elongation rate at break was lowered with the increase of gelatin composition. Water affinity of the blend films was raised with the addition of gelatin.

Key words: gelatin; PHBV; blend film; biodegradable

1. Introduction

Biodegradable materials have received considerable attention for the growing interest about environmental impact of discarded plastics and resources conservation in recent years[1,2]. In particular products from natural sources, such as starch, gelatin, cellulose or other natural polymers has been widely studied owing to their biological origin, biodegradability, biocompatibility, and commercial availability at relatively low cost, especially in the preparation of synthetic/polymer blends[1,3-8].

Poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is one of bacterially derived polyesters. These polymers have recently attracted considerable attention by scientists from academic and industry mainly because they are biodegradable thermoplastics and elastomers that can be processed through conventional extrusion and moulding process[1,9]. The drawbacks of PHBV are the high cost compared to that of petroleum-based commodities plastics. To reduce the cost or improve the performance properties of PHBV, studies on the modification of PHBV through copolymerization and blending with other polymers has been made in the area of industrial production, medicine and surgical[10-15].

Gelatin can be widely found in nature and is the major constituent of skin, bones and connective tissue, it can be obtained by a controlled hydrolysis of fibrous insoluble protein and collagen[8,16,17]. It is widely used in various applications as manufacturing of pharmaceutical products, X-ray and photographic films development and food processing et al.[18]. Gelatin is characterized by having a high content of the amino acid glycine (33 mol%) and the presence of the amino acid hydroxyproline (10 mol%) and hydroxylysine (0.5 mol%). The properties of gelatin as a typical rigid-chain high molecular weight compound are in many respects similar to those of rigid-chain synthetic polymers, but it is different from the common biopolymers for the presence of both acidic and basic functional groups in the gelatin macromolecules[19]. Gelatin can form a large variety of supermolecular structures

from the simplest globular structure to a well developed fibrillar structure with various intermediate states, the supermolecular structures should be reflected in the physico-mechanical properties of the gelatin materials.

Aimed for the preparation and evaluation of natural biopolymers in the application as biodegradable materials, PHBV/gelatin blend films were developed. Attempts were made to characterize the mechanical strength, the hydrophilicity and morphology of blend films.

2. Experimental

2.1 Materials

Poly-(3-hydroxybutyrate-*co*-valerate) (PHBV) with a 12 mol % of HV was supplied by Ningbo Tianan Biologic Material Co., Ltd. The number-average molecular weight (M_n) and the molecular weight distribution index (M_w/M_n) was measured to be 182 000 g/mol and 1.52, respectively. PHBV was purified before application, the samples were dissolved in chloroform and then precipitated with methyl alcohol. Gelatin was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2 Preparation of Blending Films

PHBV and gelatin was dissolved separately in 2,2,2-trifluoro ethanol (TFE), at a concentration of 5% (w / v) and stirred for complete dissolution. The final composition of the PHBV/gelatin blends were 100/0, 90/10, 80/20, 67/33, 50/50, 33/67, and 0/100, the mixture was poured onto a polytetrafluoroethylene mould. After the evaporation of the solvent, films with a thickness of approximately 0.04 mm were obtained. Mechanical properties, hydrophilicity and morphology of the samples were tested.

2.3 Tensile Tests

For tension testing, 0.03-mm thick samples cut in a rectangular format of 10×100mm were used. A tension analysis was carried out, at a rate of 5 mm/min, a tensile testing system from Instron Corp. was used.

2.4 Contact Angel Measurements

Contact angels were measured at room temperature using a Dataphysics OCA20 Contact Angel system. The drop volume was about 6 μL, and dropped onto the films for five different positions of the same sample.

2.5 SEM analysis

Morphology of the films was evaluated by Hitachi S-4800 scanning electron microscopy (SEM) with an accelerating voltage of 5 kev, the samples were coated with a thin layer of gold before observation.

3. Results and Discussion

3.1 Mechanical properties of blend films

The tensile strength and elongation rate at break of the blend films were plotted as a function of the gelatin content as shown in Figure 1 and Figure 2 respectively. As can be seen from Figure 1, the tensile strength of PHBV film was found to be about 15MPa, while the strength of gelatin film was about 45 MPa. With the increase of gelatin content, the tensile strength decreased to 4.7 MPa at the content of gelatin of 67%, and then it increased with the increase of gelatin content. The results indicate that although the gelatin film has a good tensile strength, the tensile strength of the blend films was not enhanced as expected by blending with gelatin comparing with that of PHBV film. It has been evidenced by FTIR that the blend films were simply physical blending of PHBV and gelatin, no chemical bond formed between the two contents. And for the incompatible of PHBV and gelatin, PHBV and gelatin separated in the blending system, which leads to the low tensile strength.

As known from Figure 2, the elongation at break of PHBV film was 4.0% while that of gelatin film was 1.3%. The elongation at break of the blend films was found to decrease with the increase of gelatin content up to 75% to 0.5% and then it increased when the content of gelatin is greater than 75%. The decrease of the elongation rate at break can be ascribed to the brittleness of gelatin, when the thermoplastic PHBV was blended with gelatin the elastic property of the film increased comparing with pure gelatin films.

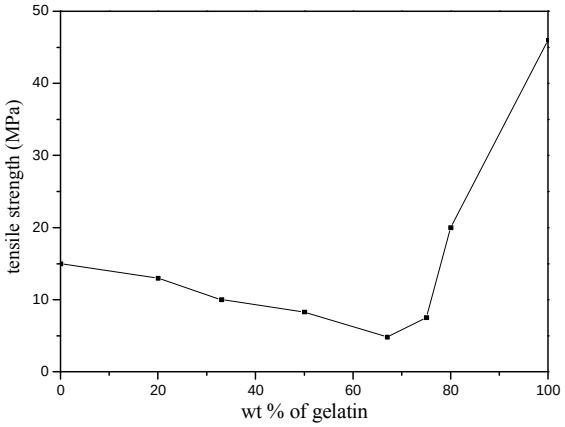

Figure 1 The dependence of tensile strength on gelatin content for the blend films

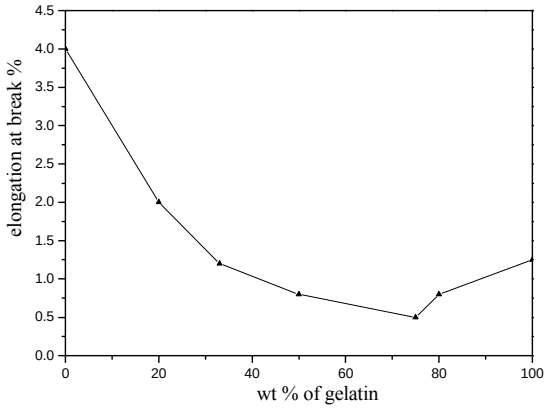

Figure 2 The dependence of % elongation at break on gelatin for the blend films

3.2 Contact angel of blend films

Gelatin can swell in water and dissolve in hot water, it has been reported that the average amount of bound water in helical gelatin was 0.37 g/g gelatin[19] while PHBV is water resistant. Photographs of the films when water drops on the surface were shown in Figure 3, when adding a droplet of water, it was quickly spread on the gelatin film surface which giving a low contact angel of 40° (Figure 3f), even a hole formed on the surface 90s later, this can be ascribed to the rich hydrophilic groups in gelatin structure such as $–NH_2$, –OH, –CONH and –COOH et al. PHBV films show an hydrophobic property with a high contact angel of 108° (Figure 3a). For the hydrophilicity of gelatin, a significant decrease of contact angel with water was observed with the increase of gelatin content in the blend films, as shown in Figure 4.

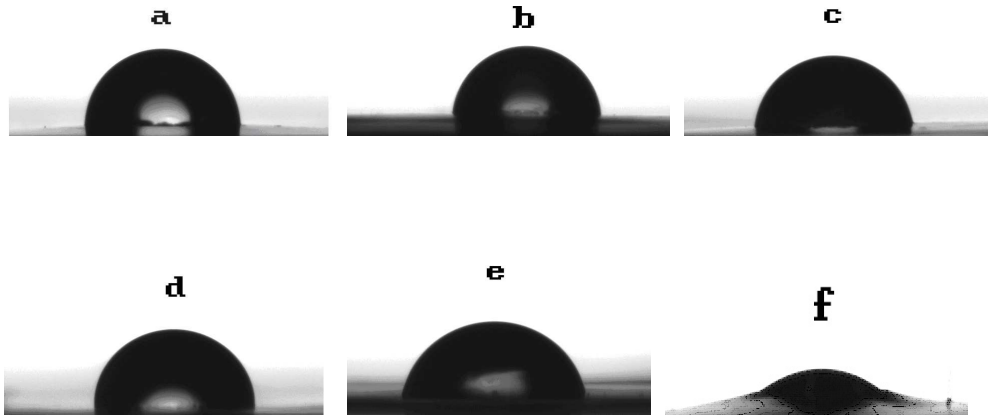

Figure 3 Photographs of water drops on the surface of the films: (a) PHBV, (b) wt gelatin 25%, (c) wt gelatin 33%, (d) wt gelatin 50%, (e) wt gelatin 80%

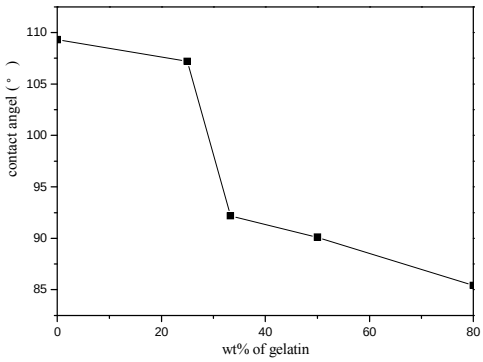

Figure 4 The dependence of contact angel of blend films based on wt % gelatin

3.3 Morphology of blend films

The morphological features of the films detected by the electron micrographs were shown in Figure 5. The surface of PHBV film and the fractured surface of gelatin film shows a dense morphology (Figure 5a and 5e). The morphology of the blend films was porous and the porosity increases with the gelatin composition ranging from 20% to 50% (Figure 5b to 5d). The porous morphology may be responsible for the low tensile strength of the blend films. Although it is not possible to observe the phase separation of PHBV and gelatin in this test, we have proved their

miscibility by POM and DSC, which will be discussed in another manuscript.

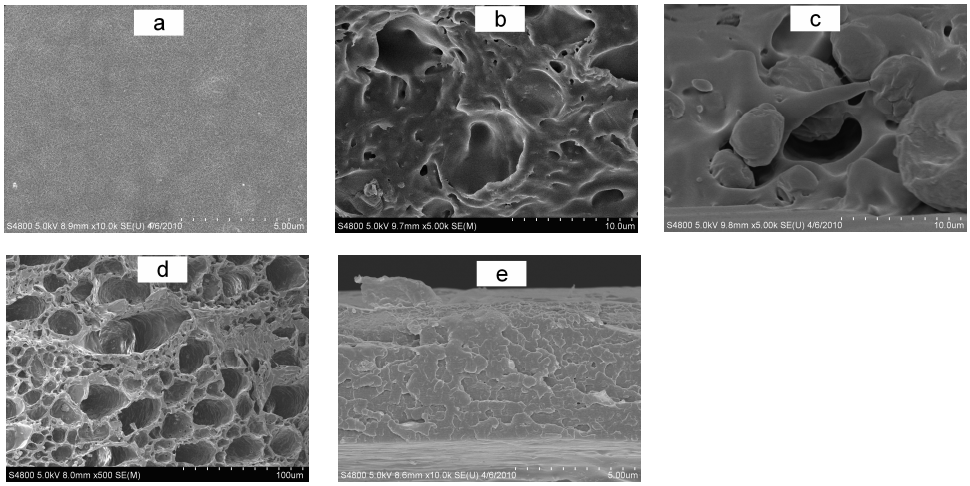

Figure 5 SEM micrograph of fractured surface of PHBV/gelatin films: (a) 100% PHBV, (b) 20% gelatin, (c) 33% gelatin, (d) 50% gelatin, (e) 100% gelatin.

4. Conclusions

The tensile strength and the elongation rate at break of the blend films decreased with the addition of gelatin. Contact angle of the blend films decreased with the increase of gelatin content which implied the increase of hydrophilicity. The pure PHBV and gelatin has a dense structure while the morphology of the blending films is porous as can be seen from the SEM images. The application properties was not improved as expected through simple blending of gelatin and PHBV, further study about the modification reaction of the two components is needed.

Acknowledgment:

This work was supported by the Technological Project of Zhejiang Universities D2007008 and the Natural Science Foundation of Ningbo City (2009A610050).

References:

1. Avella, M.; Errico, M. E., Journal of Applied Polymer Science 77, 232, 2000.
2. Qiu, Z. B.; Yang, W. T.; Ikehara, T.; Nishi, T., Polymer 46, 11814, 2005.
3. Gross, R. A.; Kalra, B., Science 297, 803, 2002.
4. Chiellini, E.; Cinelli, P.; Corti, A.; Kenawy, E., Polymer Degradation and Stability 73, 549, 2001.
5. de Carvalho, R. A.; Grosso, C. R. F., Food Hydrocolloids 18, 717, 2004.
6. M. Pérez-Mateosa, P. M. a. M. C. G.-G., Food Hydrocolloids 23, 53, 2007.
7. Mendieta-Taboada, O.; Sobral, P. J. D.; Carvalho, R. A.; Habitante, A. M. B. Q., Food Hydrocolloids 22, 1485, 2008.
8. Pawde, S. M.; Deshmukh, K., Journal of Applied Polymer Science 109, 3431, 2008.
9. Chiellini, E., **Biorelated polymers:**Sustainable Polymer Science and Technology; Kluwer Academic Plenum Publishers: New York, 2001.
10. Avella, M.; Martuscelli, E.; Raimo, M., Journal of Materials Science 35, 523, 2000.

11. Chen, G. X.; Hao, G. J.; Guo, T. Y.; Song, M. D.; Zhang, B. H., Journal of Materials Science Letters 21, 1587, 2002.
12. Fei, B.; Chen, C.; Wu, H.; Peng, S. W.; Wang, X. Y.; Dong, L. S., Polymer International 53, 903, 2004.
13. Ferreira, B. M. P.; Zavaglia, C. A. C.; Duek, E. A. R., Journal of Applied Polymer Science 86, 2898, 2002.
14. Meng, W.; Kim, S. Y.; Yuan, J.; Kim, J. C.; Kwon, O. H.; Kawazoe, N.; Chen, G. P.; Ito, Y.; Kang, I. K., Journal of Biomaterials Science-Polymer Edition 18, 81, 2007.
15. Liu, H. L.; Dong, L. M.; Wang, C.; Zan, Q. F.; Tian, J. M., Rare Metal Materials and Engineering 36, 40, 2007.
16. Zhang, Y. Z.; Ouyang, H. W.; Lim, C. T.; Ramakrishna, S.; Huang, Z. M., Journal of Biomedical Materials Research Part B-Applied Biomaterials 72B, 156, 2005.
17. Fan, L. H.; Du, Y. M.; Huang, R. H.; Wang, Q.; Wang, X. H.; Zhang, L. N., Journal of Applied Polymer Science 96, 1625, 2005.
18. Yannas, I. V., Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics C 7, 49, 1972.
19. Kozlov, P. V.; Burdygina, G. I., Polymer 24, 651, 1983.