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Modification of hydrophilic poly(vinyl alcohol) film via blending with hydrophobic poly(butyl acrylate-*co*-methyl methacrylate)

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Abstract A series of poly(vinyl alcohol)/poly(butyl acrylate-*co*-methyl methacrylate) [PVA/P(BA-*co*-MMA)] blend films with different P(BA-*co*-MMA) content were prepared by the solution casting method. Surface morphologies of the PVA/P(BA-*co*-MMA) blend films were studied by scanning electron microscopy and atomic force microscopy. Thermal, mechanical, and chemical properties of PVA/P(BA-*co*-MMA) blend films were investigated by differential scanning calorimeter, thermogravimetric analysis, tensile tests, and surface contact angle tests. It was revealed that the introduction of P(BA-*co*-MMA) could affect the properties of the PVA films. The results also showed that, when P(BA-*co*-MMA) mole content is 3 %, the tensile strength and the surface contact angle of the polymer blend film are 20.4 MPa and 43.5°, respectively, suggesting that the polymer blend film holds both a better mechanical property and a better chemical property.

Keywords Morphology · Properties · Modification · PVA/P(BA-*co*-MMA) blend · Film

Introduction

In recent years, polymer blending has been a widely used method for modifying the physicochemical properties of polymer materials [1–4]. An important property of the polymer blend is the miscibility of its ingredients, as it could affect the mechanical properties, the morphology, the permeability, and the degradation [1, 5]. So far, much research regarding the miscibility in multi-component polymer systems has been reported. Among them, the polymer blends between the biopolymers and the

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synthetic polymers are very significant as they could be used as biomedical and biodegradable materials [6–8].

Based on its easy preparation, nontoxic, noncarcinogenic, biodegradable and bioadhesive characteristics, excellent chemical resistance, and physical properties, poly(vinyl alcohol) (PVA), an excellent biomaterial, has attracted much interest for its potential applications [1, 9, 10]. PVA is capable of simulating natural tissues, and is used as contact lenses, the lining of artificial organs, artificial skin (e.g., film), drug delivery, etc. [11–14]. Although PVA holds better mechanical properties in the dry state, its high hydrophilicity could limit its applications [15]. Compared with the PVA homopolymer, some of the polymer blends of PVA present better properties [1].

As noted, PVA chains have a similar melting temperature and decomposition temperature caused by lots of hydrogen bonds [7], indicating that PVA material is not easy to process. The synthetic P(BA-*co*-MMA) (mole ratio of BA to MMA is 3:1) is a flexible and hydrophobic copolymer, and it is expected that the introduction of P(BA-*co*-MMA) into PVA could modify the properties of PVA film. To the best of our knowledge, however, no experimental work has so far been reported on the studies of the properties of PVA/P(BA-*co*-MMA) blend films. In the present work, a series of PVA/P(BA-*co*-MMA) blend films with different P(BA-*co*-MMA) content were prepared by the solution casting method. The morphologies of the polymer blend films were investigated by SEM and AFM techniques. Thermal, mechanical, and chemical properties of the polymer blend films were studied by DSC, TGA, tensile tests, and surface contact angle tests. It was found that the introduction of P(BA-*co*-MMA) into PVA could modify the properties of PVA films.

Experimental

Materials

Poly(vinyl alcohol) ($M_w = 90{,}000$, degree of hydrolysis 99 mol%) was purchased from Shanghai Jianglai Biological Technology (China), and used without further purification. Poly(butyl acrylate-*co*-methyl methacrylate) ($M_w = 30{,}000$, mole ratio of BA to MMA is 3:1) was purchased from Shandong Shituo Chemical (China). Dimethyl sulfoxide (DMSO) and other solvents were of analytical grade and used without further purification.

Preparation of PVA/P(BA-*co*-MMA) blend film

The PVA was dissolved in DMSO solvent to obtain 30 wt% clear polymer solution, while P(BA-*co*-MMA) was dissolved in DMSO solvent to obtain 5 wt% clear polymer solution. According to the various mole ratio of PVA to P(BA-*co*-MMA), the clear polymer blend solutions were obtained. The polymer blend films were prepared as follows: first, the clean glass plates were put in the oven at the temperature of 40 °C, then the polymer blend solutions were put onto the clean glass plates within 5 min and kept at 40 °C for 2 h; second, the temperature of the oven was adjusted to 60 °C, and the polymer blend films were kept for 72 h. By testing the properties of the polymer blend films, the optimum ratio of PVA to P(BA-*co*-MMA) could be obtained. Also, it is revealed that, when P(BA-*co*-MMA) mole content in polymer blend is over 7 %, the polymer blend cannot form continuous film. Scheme 1 presents the proposed structure of PVA/P(BA-*co*-MMA) blend showing the H-bonding interaction between PVA and P(BA-*co*-MMA).

Characterizations

SEM measurements

SEM investigations were carried out using a scanning electron microscope (Sirin 200; FEI, Holland). Gold was sprayed on the polymer blend films in a vacuum. The acceleration voltage was 10 kV.

AFM measurements

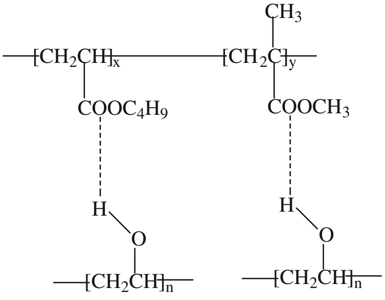
The surface microstructure of the polymer blend film was characterized on a NanoScope IIIA MultiMode AFM instrument (Digital Instruments, USA) in air at ambient conditions using tapping mode probes with constant amplitude (200 mV). A rotated tapping mode etched silicone probe with a resonance frequency of 250 kHz was used. The height images were recorded at the resonance frequency of the cantilever with a scan rate of 1 Hz [16].

DSC measurements

DSC measurements were made on a DSC Q100 (TA, USA) differential scanning calorimeter; the temperature was calibrated with indium in a nitrogen atmosphere. Samples of c. 7 mg were weighed very accurately. The temperature was controlled within the range of 0–300 °C, and the heating rate was 10 °C/min.

TG measurements

Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 4490 C TG–DTA analyzer (Netzsch, Germany) at a heating rate of 10 °C/min under



Scheme 1 Proposed structure of PVA/P(BA-*co*-MMA) blend showing the H-bonding interaction between PVA and P(BA-*co*-MMA)

nitrogen atmosphere over the temperature range of 20–550 °C. Samples of approximately 13 mg were used for the measurements.

Tensile tests

Tensile tests were carried out with an Instron Model 4468 universal testing machine (Digital Instruments). The crosshead speed was set to 80 mm/min. For each data point, five samples were tested and the average value was taken.

Surface contact angle tests

A 5-μL drop of pure distilled water was placed on the polymer blend film surface using a syringe with a 22-gauge needle. The static contact angle was measured with an optical contact angle meter CAM 200 (KSV Instrument, Finland). The measurements of each contact angle were performed within 10 s after each drop to ensure that the droplet did not soak into the compact. The surface contact angles were the mean of five determinations [16].

Water-resistant pressure tests

The water-resistant pressure (mm) tests of PVA/P(BA-*co*-MMA) blend films were carried out according to a conventional method. The sample films were made in a round shape with a diameter of 30 mm. The sample films were used to seal the mouth of a long round tube with graduation in millimeters (tube diameter: 10 mm). After the tube mouth was sealed with the film, it was upset, and deionized water was added into the long round tube drop by drop. As soon as the deionized water permeated through the film, the height of water column was written down.

Results and discussion

Morphology study

The surface morphologies of PVA/P(BA-*co*-MMA) blend films were evaluated by the SEM technique. Figure 1 shows the surface morphologies of PVA/P(BA-*co*-MMA) blend films with various P(BA-*co*-MMA) content: (a) 0, (b) 3, and (c) 7 mol% (magnification ×2,000). As it can be seen from Fig. 1, the surface morphologies of the polymer blend films are various with the introduction of P(BA-*co*-MMA). Figure 1a shows one uniform coarse surface, while Fig. 1b, c presents phase-separation phenomenon, which is caused by the interaction of the PVA chains and P(BA-*co*-MMA) segments. This phenomenon indicated that the change of the surface morphologies of the polymer blend films could be attributed to the introduction of P(BA-*co*-MMA).

As already known, the AFM height images indicated the surface roughness of polymer film [17–19]. Figure 2 presents the AFM 2D and 3D height images of PVA/P(BA-*co*-MMA) blend film surface with various P(BA-*co*-MMA) content:

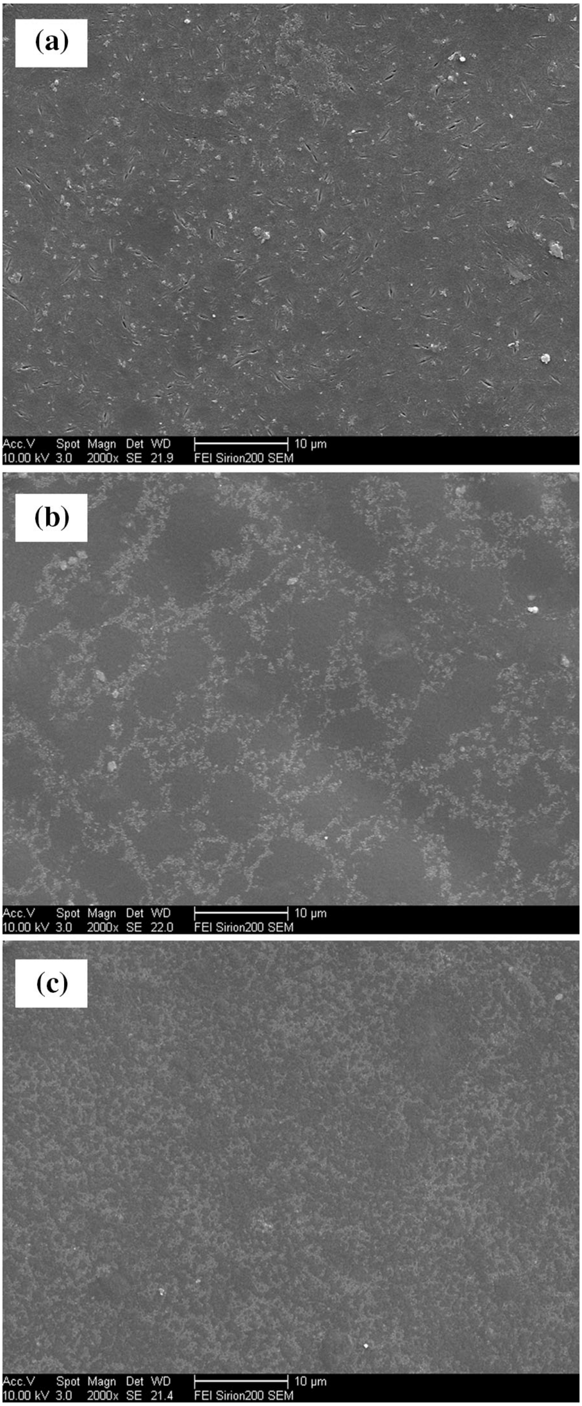


Fig. 1 SEM photographs of PVA/P(BA-*co*-MMA) blend film surface with various P(BA-*co*-MMA) content **a** 0, **b** 3, and **c** 7 mol% (magnification ×2,000)

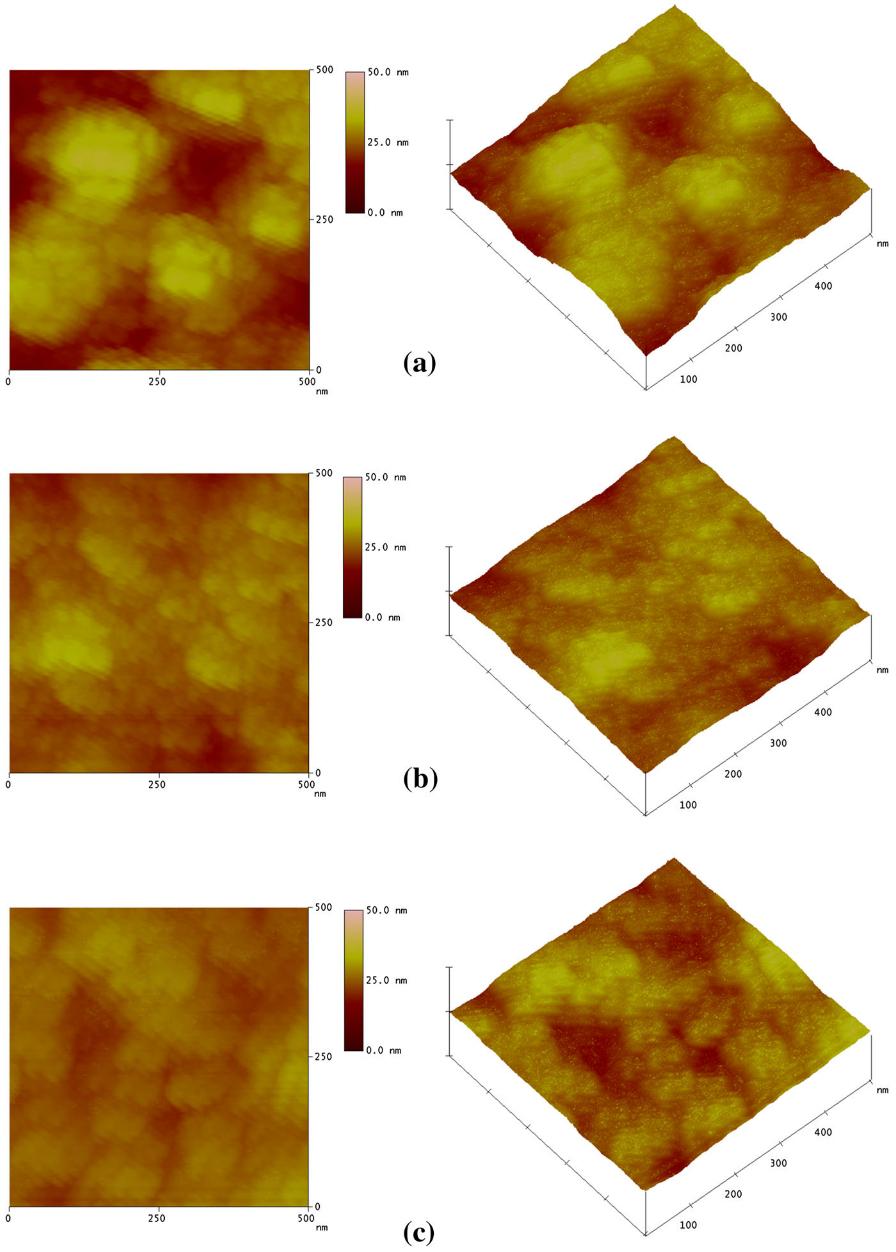


Fig. 2 AFM 2D and 3D height images of PVA/P(BA-*co*-MMA) blend film surface with various P(BA-*co*-MMA) content **a** 0, **b** 3, and **c** 7 mol%

(a) 0, (b) 3, and (c) 7 mol%. As seen from Fig. 2, the surface of the polymer blend film consists of both brighter domains (corresponding to the higher part) and darker domains (corresponding to the lower part) [18, 19]. Also, it is found that the ratio of

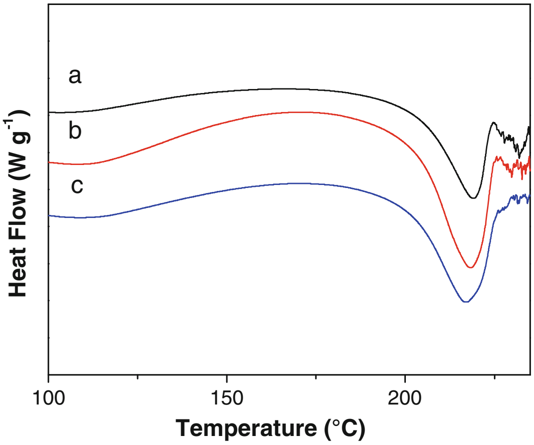


Fig. 3 DSC curves of PVA/P(BA-*co*-MMA) blends with various P(BA-*co*-MMA) content **a** 0, **b** 3, and **c** 7 mol%

Table 1 Melting temperature of PVA segments in polymer blends with various P(BA-*co*-MMA) content

P(BA-*co*-MMA) (mol%)	Melting temperature (°C)
0	218.8
3	218.0
7	217.1

brighter domains to darker domains is varied, indicating that the surface roughness of the polymer blend film is changing with the increase of P(BA-*co*-MMA) content [17–19]. This phenomenon showed that the introduction of the P(BA-*co*-MMA) segments changed the surface roughness of the polymer blend films.

Thermal properties

Figure 3 indicates the DSC curves of PVA/P(BA-*co*-MMA) blends with various P(BA-*co*-MMA) content: (a) 0, (b) 3, and (c) 7 mol%; the corresponding data are listed in Table 1. As is shown in Fig. 3 and Table 1, the melting temperature of PVA segments in the polymer blends decreased with the increase of P(BA-*co*-MMA) content. As already known, PVA chains and P(BA-*co*-MMA) segments could exert interaction by entanglement and by forming intermolecular hydrogen bonds, and the interaction could partially destroy the intermolecular or intramolecular hydrogen bonds of PVA chains, suggesting that the decrease of the melting temperature of PVA segments in the polymer blends could be attributed to the introduction of P(BA-*co*-MMA).

Figure 4 exhibits the TG curves of PVA/P(BA-*co*-MMA) blends with various P(BA-*co*-MMA) content: (a) 0, (b) 3, and (c) 7 mol%. As shown in Fig. 4, the initial decomposition temperature of the PVA segments in the polymer blends decreased with increasing P(BA-*co*-MMA) content. As mentioned above, the interaction between PVA chains and P(BA-*co*-MMA) segments could partially destroy the intermolecular or intramolecular hydrogen bonds of the PVA chains, indicating that

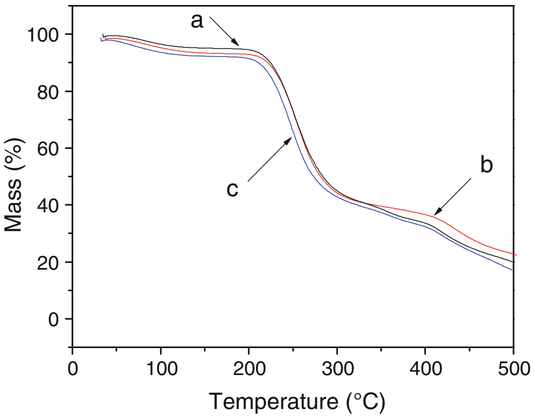


Fig. 4 TG curves of PVA/P(BA-*co*-MMA) blends with various P(BA-*co*-MMA) content **a** 0, **b** 3, and **c** 7 mol%

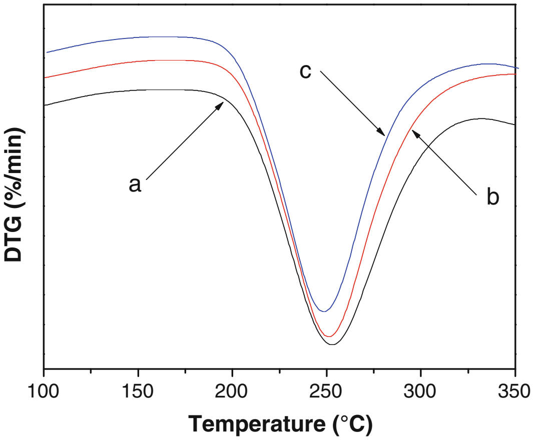


Fig. 5 DTG curves of PVA/P(BA-*co*-MMA) blends with various P(BA-*co*-MMA) content **a** 0, **b** 3 mol%, and **c** 7 mol%

Table 2 The maximum decomposition temperatures of PVA segments in polymer blends with various P(BA-*co*-MMA) content

P(BA-*co*-MMA) (mol%)	Maximum decomposition temperature (°C)
0	252.8
3	250.5
7	248.9

the decrease of the initial decomposition temperature of PVA chains in the polymer blends was related to the introduction of P(BA-*co*-MMA) segments.

Figure 5 presents the DTG curves of PVA/P(BA-*co*-MMA) blends with various P(BA-*co*-MMA) content: (a) 0, (b) 3, and (c) 7 mol%; the corresponding data are listed in Table 2. As shown in Fig. 5 and Table 2, the maximum decomposition temperature of PVA chains in the polymer blends decreased with the increase of P(BA-*co*-MMA) content. As discussed above, PVA chains and P(BA-*co*-MMA) segments could interact by entanglement and by forming intermolecular hydrogen

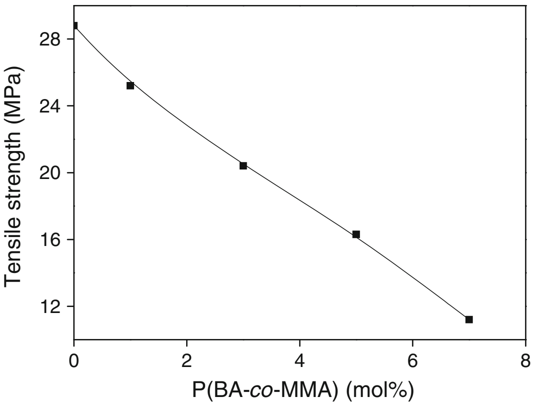


Fig. 6 Relationship between the tensile strength of PVA/P(BA-*co*-MMA) blend films and the P(BA-*co*-MMA) content

bonds, and the interaction could partially destroy the intermolecular or intramolecular hydrogen bonds of PVA chains, suggesting that the decrease of the maximum decomposition temperature of PVA chains in the polymer blends was also connected to the introduction of P(BA-*co*-MMA) segments.

Mechanical properties

Figure 6 shows the relationship between the tensile strength of PVA/P(BA-*co*-MMA) blend films and the P(BA-*co*-MMA) content. As can be seen from Fig. 6, the tensile strength of the polymer blend films decreased with the increase of P(BA-*co*-MMA) content. As mentioned above, the synthetic P(BA-*co*-MMA) (mole ratio of BA to MMA is 3:1) is flexible, suggesting that the interaction between PVA chains and flexible P(BA-*co*-MMA) segments could decrease the tensile strength of the polymer blend films. This phenomenon showed that the decrease of the tensile strength of the polymer blend films was concerned with the introduction of the flexible P(BA-*co*-MMA) segments. Under permitted P(BA-*co*-MMA) content, the higher the P(BA-*co*-MMA) content, the lower the tensile strength of the polymer blend films.

Water-resistant properties

Figure 7 indicates the relationship between the surface contact angle of PVA/P(BA-*co*-MMA) blend films and P(BA-*co*-MMA) content. As can be seen from Fig. 7, the surface contact angle of PVA/P(BA-*co*-MMA) blend films increased with increasing the P(BA-*co*-MMA) content, suggesting that the hydrophobicity of the polymer blend films increased. As already known, P(BA-*co*-MMA) segments are hydrophobic. The introduction of P(BA-*co*-MMA) segments could promote the hydrophobicity of the polymer blend films. This phenomenon proved that the increase of the surface contact angle of the polymer blend films was also concerned with the introduction of the hydrophobic P(BA-*co*-MMA) segments. Under permitted P(BA-*co*-MMA) content, the higher the P(BA-*co*-MMA) content, the higher the surface contact angle of the polymer blend films.

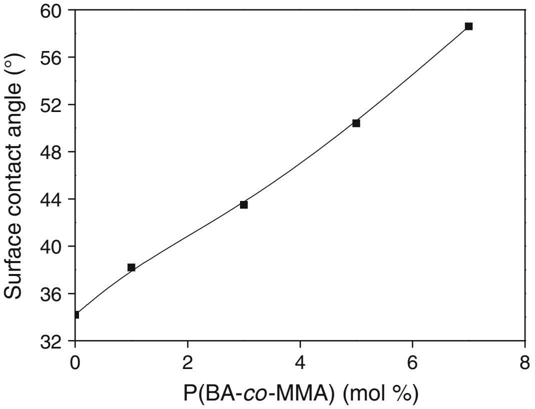


Fig. 7 Relationship between the surface contact angle of PVA/P(BA-*co*-MMA) blend films and the P(BA-*co*-MMA) content

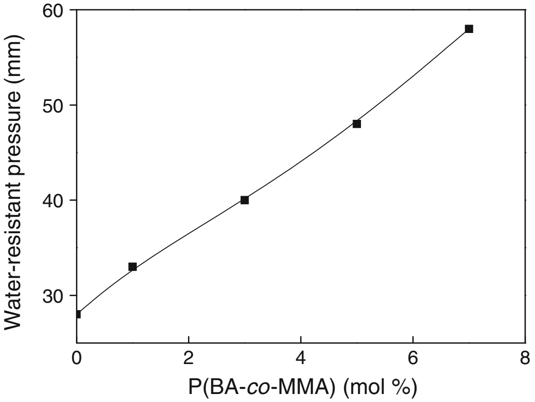


Fig. 8 Relationship between the water-resistant pressure of PVA/P(BA-*co*-MMA) blend films and the P(BA-*co*-MMA) content

Figure 8 shows the relationship between the water-resistant pressure (mm) of PVA/P(BA-*co*-MMA) blend films and the P(BA-*co*-MMA) content. As seen from Fig. 8, the water-resistant pressure (mm) of PVA/P(BA-*co*-MMA) blend films increased with the increase in P(BA-*co*-MMA) content, indicating that the hydrophobicity of the polymer blend films increased. This phenomenon demonstrated that the introduction of the hydrophobic P(BA-*co*-MMA) segments also promoted the water-resistant pressure of the polymer blend films.

Conclusions

A series of PVA/P(BA-*co*-MMA) blend films with various P(BA-*co*-MMA) content were prepared by the solution casting method. SEM, AFM, DSC, TGA, tensile tests, and surface contact angle tests were used to investigate the morphologies and the properties of PVA/P(BA-*co*-MMA) blend films. SEM photographs indicated that the introduction of P(BA-*co*-MMA) changed the surface morphologies of the PVA films. AFM images showed that the introduction of P(BA-*co*-MMA) changed the surface roughness of the PVA films. DSC measurements demonstrated that the introduction of P(BA-*co*-MMA) decreased the melting temperature of PVA segments in the polymer blends. TG measurements verified that the introduction of P(BA-*co*-MMA) decreased both the initial decomposition temperature and the maximum decomposition temperature of PVA segments in the polymer blends. Tensile tests presented that the tensile strength of the polymer blend films decreased with the increase of P(BA-*co*-MMA) content. Both the surface contact angle tests and the water-resistant pressure measurements proved that the introduction of P(BA-*co*-MMA) increased the hydrophobicity of the polymer blend films.

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References

1. J.S. Park, J.W. Park, E. Ruckenstein, Polymer **42**, 4271 (2001)
2. T.F. Shen, M.G. Lu, D.W. Zhou, L.Y. Liang, Iran. Polym. J. **21**, 317 (2012)
3. J.K. Duan, S.X. Shao, Y. Li, L.F. Wang, P.K. Jiang, B.P. Liu, Iran. Polym. J. **21**, 109 (2012)
4. L. Wang, X.L. Li, M.F. Huang, Z.S. Xu, C.F. Yi, Iran. Polym. J. **21**, 343 (2012)
5. Y. Nishio, R. Manley, Macromolecules **21**, 1270 (1988)
6. T. Kondo, C. Sawatari, R. Manley, D.G. Gray, Macromolecules **27**, 210 (1994)
7. C. Sawatari, T. Kondo, Macromolecules **32**, 1949 (1999)
8. K. Lio, N. Minoura, M. Nagura, Polymer **36**, 2579 (1995)
9. A. Papancea, A.J.M. Valente, S. Patachia, M.G. Miguel, B. Lindman, Langmuir **24**, 273 (2008)
10. C.C. DeMerlis, D.R. Schoneker, Food Chem. Toxicol. **41**, 319 (2003)
11. C.K. Chua, K.F. Leong, K.H. Tan, F.E. Wiria, C.M. Cheah, J. Mater. Sci. Mater. Med. **15**, 1113 (2004)
12. S.H. Hyon, W.I. Cha, Y. Ikada, M. Kita, Y. Ogura, Y. Honda, J. Biomater. Sci. Polym. Ed. **5**, 397 (1994)
13. W.S. Dai, T.A. Barbari, Biomaterials **21**, 1363 (2000)
14. M.L. Coluccio, G. Ciardelli, F. Bertoni, D. Silvestri, C. Cristallini, P. Giusti, N. Barbani, Macromol. Biosci. **6**, 403 (2006)
15. R.M. Hodge, G.H. Edward, G.P. Simon, Polymer **37**, 1371 (1996)
16. L.Q. Bai, L.J. Zhu, S.J. Min, L. Liu, Y.R. Cai, J.M. Yao, Appl. Surf. Sci. **254**, 2988 (2008)
17. S. Yamamoto, Y. Tsujii, T. Fukuda, Polymer **42**, 2007 (2001)
18. M.Y. Lee, S.H. Kim, H.S. Ganapathy, S.W. Kim, K.T. Lim, Ultramicroscopy **108**, 1210 (2008)
19. M.J. Fasolka, A.M. Mayes, S.N. Magonov, Ultramicroscopy **90**, 21 (2001)