Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2008) 5659–5663
www.elsevier.com/locate/tsf

Plasma surface graft of acrylic acid and biodegradation of poly(butylene succinate) films

Hong-Ping Zhao [a], Jin-Tang Zhu [b], Zhong-Yu Fu [b], Xi-Qiao Feng [a,*], Yue Shao [a], Ruo-Teng Ma [a]

[a] Department of Engineering Mechanics, Tsinghua University, Beijing 100084, PR China
[b] Department of Materials Engineering, Beijing Institute of Clothing Technology, Beijing 100029, PR China

Available online 13 July 2007

Abstract

The effect of plasma surface graft of acrylic acid (AAc) on the biodegradation and physical properties of poly(butylene succinate) (PBS) films was investigated in the present paper. The surface microstructures and compositions of the grafted PBS films were characterized by atomic force microscopy (AFM), high-resolution X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR). Water contact angle measurements and biodegradation tests under compost conditions were also carried out to study the wettability and biodegradability of the films. It is found that the biodegradation rates of the PBS films can be evidently accelerated by plasma surface graft of AAc. The present study might be helpful to produce the PBS films with enhanced biodegradability.

Keywords: Poly(butylene succinate) film; Plasma treatment; Acrylic acid; Graft polymerization; Biodegradation

1. Introduction

As a biodegradable aliphatic polyester with superior mechanical properties and thermal stability, poly(butylene succinate) (PBS) holds a promise for a wide range of applications (e.g., mulch film, packaging film, bag and hygiene products) [1]. The hydro-biodegradability of PBS is associated with its thermal characteristics, crystallinity, molecular weight and wettability. However, the poor wettability and higher molecular weight of PBS films decrease their enzymatic biodegradability and, therefore, limit their extension of commercialization and application. Therefore, various approaches have been proposed to modify the surface properties of PBS films. For instance, PBS is often blended with other compounds (e.g., short sisal fibres [2], organically modified layered silicate [3], poly(ethylene oxide) [4], starch [5], adipate copolymers [6], and cellulose triacetate [7]), copolymerized with mandelic acid [8], succinic acid and 2-methylsuccnic acid [9], treated by plasma, [10] or peroxide modification [11], printed with gravure inks [12], or produced in variable polymer concentration and zone drawing [13]. Hirotsu et al. [10] reported that PBS sheet surfaces become more wettable after modification with continuous plasma and pulsed plasma, but they did not observe evident promotion of biodegradation in the plasma treated sheets of PBS.

A widely accepted route to enhance the surface hydrophilicity of PBS is the formation of functional groups on its surface with chemical graft polymerization. As a kind of convenient monomer for plasma processes, acrylic acid (AAc) is volatile, soluble in water and can be polymerized effectively in a short time. The molar ratio of carboxyl group in AAc molecule is high, indicating that it may be adopted to enhance the surface wettability of a polymer substrate. Recently, plasma polymerization and graft of acrylic acid on some polymeric surfaces have been reported to improve their surface properties [14–16]. The mechanism of this kind of reaction involves the generation of free radicals from the main chain of polymeric surfaces in the processing of plasma treatment. Acrylic acid monomers polymerize with free radicals and thereby graft on the surfaces of the substrate.

In this study, PBS films were treated by glow discharge plasmas for surface activation and grafted with acrylic acid in

* Corresponding author. Tel.: +86 10 6277 2934; fax: +86 10 6278 1824.
E-mail address: fengxq@tsinghua.edu.cn (X.-Q. Feng).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.07.074

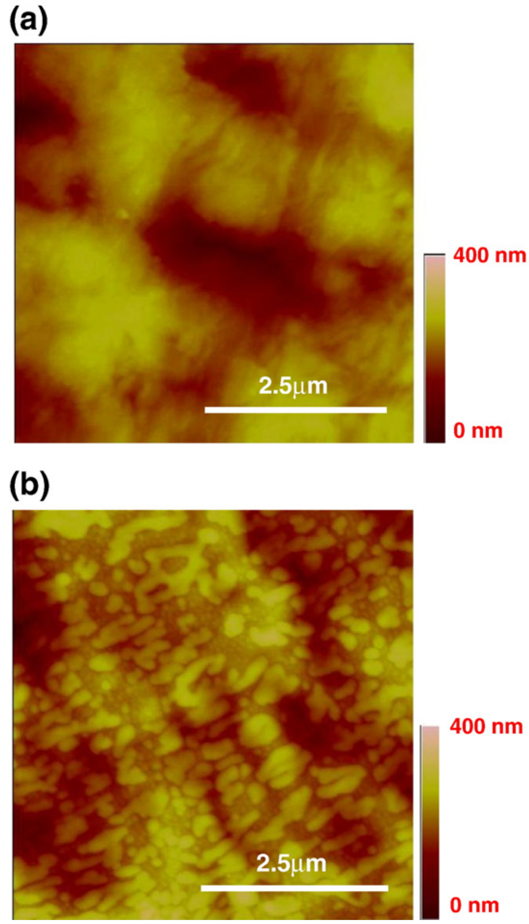

Fig. 1. AFM images of (a) a pristine PBS surface and (b) a grafted PBS surface.

vapor phase with the atmospheric–pressure plasma chemical reactor. The surface microstructure and composition of grafted PBS films were characterized by atomic force microscopy (AFM), high-resolution X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy (FTIR). Water contact angle measurements and biodegradation tests under compost conditions were also performed to measure the wettability and the biodegradability of grafted PBS films. It is found that the biodegradation rates of PBS films are influenced pronouncedly by plasma surface graft of AAc. The present study might be helpful to produce the PBS films with good biodegradability demanded in various applications.

2. Experiments

PBS films with a thickness of about 20 μm and a density of 1.25 g/cm^3 and the chemical pure monomer AAc were obtained commercially in China. Plasma treatments were carried out in an atmospheric–pressure plasma chemical reactor (Institute of Optics and Electronics, Chinese Academy of Sciences). A voltage of 125 V was applied between the discharge and induction electrodes in the reactor. Argon gas with the flow rate of 2000 cm^3/min was introduced via a carrier pipe into the reactor chamber. The carrier pipe had a branching pipe through which acrylic acid monomer vapor was added. The plasma activation and AAc grafting time for three groups of PBS films are chosen to be 30 s, 90 s and 150 s, and the corresponding samples will be referred to as PBS1, PBS2 and PBS3, respectively, in the sequel.

The surface microstructure topographies of pristine and treated PBS films were observed with AFM (DI-3100, USA) in the contact mode with a scanning scope of 5 μm and a scanning rate of 2 Hz. XPS measurements were carried out on a PHI 5100 ESCA System (Perkin Elmer, USA) using Mg Kα X-ray source with energy intensity of 1253.6 eV. The X-ray source power was set to be 240 W. The pressure in the analysis chamber was maintained at 5×10^{-6} Pa. FTIR characterizations were performed at ambient temperature with a 170SX FTIR spectroscopy (Nicolet, USA) by the attenuated total reflection (ATR) technique, with 4 cm^{-1} resolution and 64 accumulations. The contact angles of grafted PBS samples were measured using OCA20 contact anglemeter (Dataphysics, Germany) at room temperature. The water droplets made of 2 μl distilled water were dropped at five different positions on each sample, and the measured contact angles were averaged as the Young's contact angle of the sample. We buried the pristine and grafted PBS films in the composts for 10 days in order to determine their biodegradability by biodegradation tests (Beijing Nangong Compost Factory, China). The compost temperature was controlled at about 25 °C. Surface morphologies of the biodegraded PBS films were observed by scanning electron microscopy (SEM) (JSM-6360LV, JEOL, Japan).

3. Results and discussions

The AFM images of pristine and AAc-grafted PBS films were shown in Fig. 1. The pristine PBS surface has an average surface roughness value R_a of about 41 nm. After the Ar plasma-induced graft polymerization treated with AAc on the PBS film surface, the film surface has nanosized morphology and becomes smoother, with the R_a value reduced to be about 37 nm. In other words, the surface morphology of the PBS film was modified as a result of AAc graft treated with the plasma.

Fig. 2 gives the Young's contact angles of the different PBS film samples with water. The pristine PBS film surface is

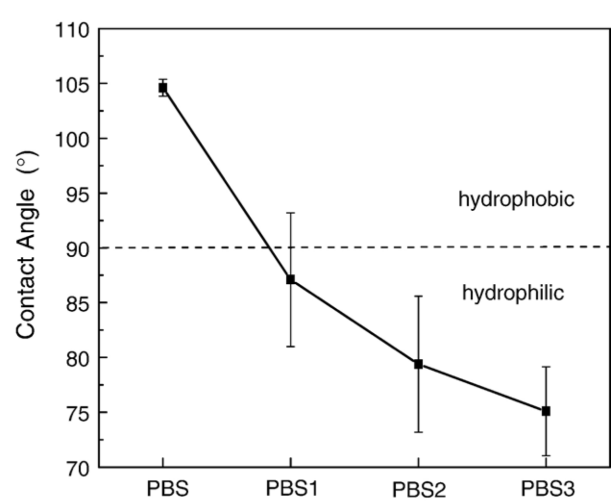

Fig. 2. Water contact angles of the pristine and grafted PBS films.

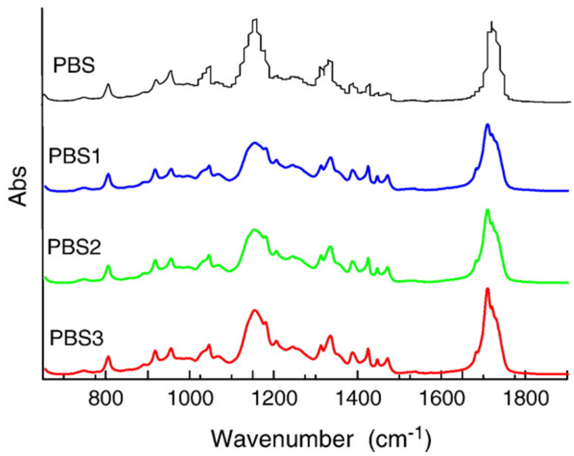

Fig. 3. ATR–FTIR spectra of the pristine and grafted PBS films.

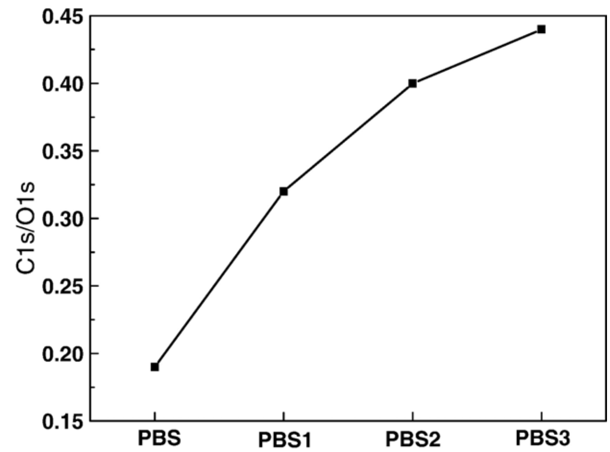

Fig. 5. The ratio between C1s and O1s of the pristine and grafted PBS films.

hydrophobic with a contact angle of about 105°, but it becomes hydrophilic after the plasma treatment and AAc graft polymerization. It is seen that the PBS surface became more wettable with the increase in the grafting time. Corresponding to the grafting time of 30 s, 90 s and 150 s, the contact angle of PBS1, PBS2 and PBS3 were about 87°, 80° and 75°, respectively. This change is attributed to the increase in the number of the hydrophilic group (–COOH).

The compositions of pristine and grafted PBS film surfaces were analyzed by ATR–FTIR and XPS, as shown in Figs. 3, 4 and 5. It can be seen from Fig. 3 that the ATR–FTIR spectra of the PBS film before and after AAc grafting have no evident difference. In fact, the absorption peak corresponding to carboxyl group (1710 cm^{-1}) is very close to that of the ester groups (1720 cm^{-1}) in PBS. The bands at 1100–1200 cm^{-1} and 1600–1800 cm^{-1} of the grafted PBS are broader and obtuser than those of the pristine PBS due to the hydrogen bonds and other molecular interactions between carboxyl of AAc and the free radicals on the treated PBS surface. This demonstrates that AAc had been grafted onto the PBS surface, as is also confirmed by the XPS spectra in Fig. 4 and the water contact angle changes in Fig. 2. From the XPS spectra of the pristine and

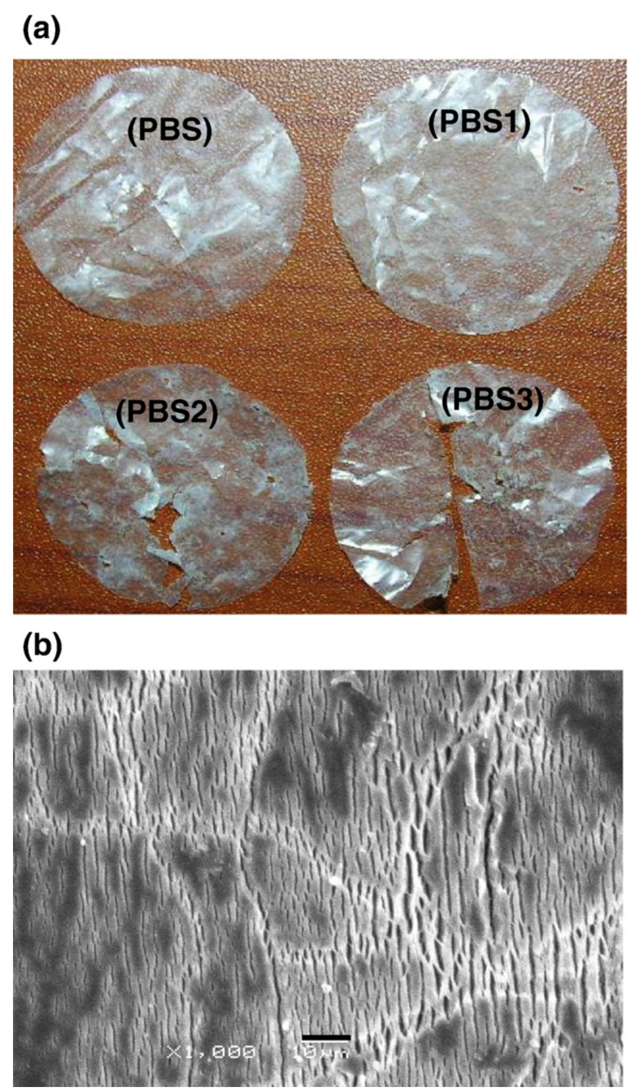

Fig. 6. (a) Photos of the pristine and grafted PBS films after buried in the compost for 10 days; and (b) an SEM image showing the microcracked surface (Scale bar: 10 μm).

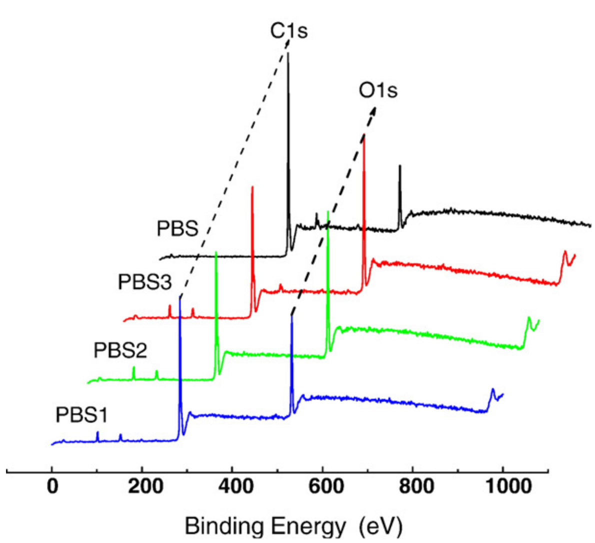

Fig. 4. XPS spectra of the pristine and grafted PBS films.

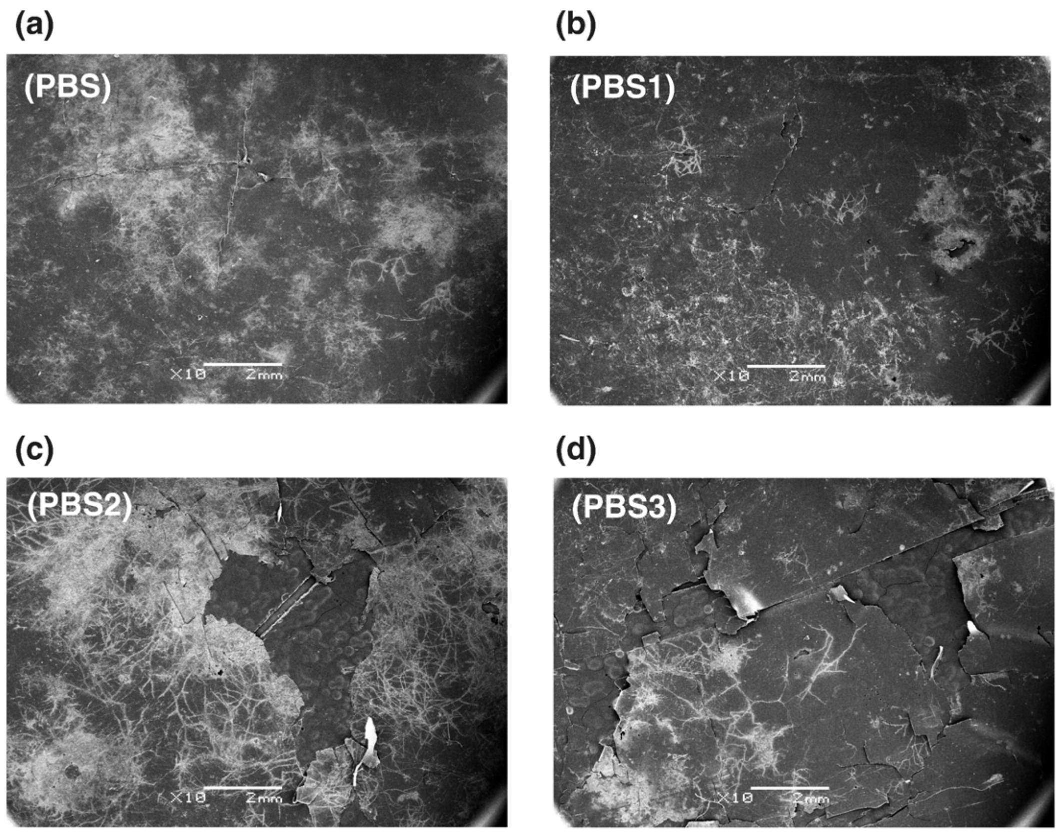

Fig. 7. SEM images of PBS films after buried in the composts for 10 days: (a) without grafting, and with grafting for (b) 30 s, (c) 90 s and (d) 150 s. (Scale bar: 2 mm).

grafted PBS samples in Fig. 4, two obvious peaks can be found for all the PBS samples, corresponding to C1s (284.6 eV) and O1s (523.3 eV), respectively. The small peaks at 100 eV and 175 eV in the XPS analysis correspond to Si and Cl elements, respectively, indicating that there are some impurities on the surface of PBS film. The chemical composition ratio between C1s and O1s is calculated from the XPS spectra, as shown in Fig. 5. It is found that compared to the pristine PBS film, the oxygen content of the grafted PBS films was increased as a result of the addition of AAc and the introduction of oxygen onto PBS film surface. The longer the grafting time, the higher the oxygen content. Furthermore, the C1s/O1s ratio also increased, indicating the enhancement of grafting content with the treatment time.

Figs. 6 and 7 show the photos and the SEM micrographs of the biodegraded PBS films, respectively. The circular PBS film samples were buried in the compost for 10 days. The biodegradation process of PBS was divided by Zhao et al. [17] into three phases with different degradation rates, namely, the lag phase, the biodegradation phase and the plateau phase. The PBS films, after buried in the compost for 10 days, were in the biodegradation phase. Some random hydrolytic cleavages of ester linkages had happened in the films. The pristine PBS film after composted was almost complete while some holes and fragmentary areas had appeared in the grafted PBS films, as shown in Figs. 6(a) and 7. It is estimated that the biodegradation rate of PBS films increased with the increasing AAc grafting time under the composting conditions in our tests. The PBS3 sample showed the best biodegradability due to the highest grafting degree and the surface hydrophilicity. Furthermore, Fig. 6(b) shows a typical biodegradation pattern with microcracked and fragmented structures on the sample.

4. Conclusions

PBS films were functionalized by plasma surface graft of AAc. AFM, water contact angle test, XPS, FTIR and biodegradation test under compost conditions demonstrated the presence of AAC grafting onto the PBS film surface, resulting in a copolymer PBS-g-AAc. The PBS films become more wettable and more biodegradable after the grafting treatment. The present study might be helpful to produce PBS films with good biodegradability, which are of interest for various applications. The plasma surface graft method presented in this paper may also be used for many other biodegradable polymers to enhance their biodegradability.

Acknowledgements

The supports from the National Natural Science Foundation of China (Grant Nos. 10402017, 10525210 and 10121202), the 973 project (2003CB615603) and Beijing Key Laboratory of Clothing Materials R&D and Assessment (2006ZK-05) are acknowledged. The authors also thank Prof. X. Zhang for his kind help in the experiments.

References

[1] D.R. Ishioka, E. Kitakuni, Y. Ichikawa, in: Y. Doi, A. Steinbüchel (Eds.), Biopolymers, vol. 4, Wiley-VCH, Weinheim, 2002, p. 275.
[2] M. Shibata, R. Makino, R. Yosomiya, H. Takeishi, Polym. Polym. Compos. 9 (2001) 333.
[3] S.S. Ray, K. Okamoto, M. Okamoto, Macromolecules 36 (2003) 2355.
[4] Z.B. Qiu, T. Ikehara, T. Nishi, Polymer 44 (2003) 3095.
[5] A. Sen, M. Bhattacharya, Polymer 41 (2000) 9177.
[6] M.Q. Ren, J.B. Song, C.L. Song, H.L. Zhang, X.H. Sun, Q.Y. Chen, H.F. Zhang, Z.S. Mo, J. Polym. Sci., Part B, Polym. Phys. 43 (2005) 3231.
[7] T. Uesakaa, K. Nakanea, S. Maedab, T. Ogiharaa, N. Ogataa, Polymer 41 (2000) 8449.
[8] H.J. Jin, B.Y. Lee, M.N. Kim, J.S. Yoon, J. Polym. Sci., Part B, Polym. Phys. 38 (2000) 1504.
[9] J.W. Park, D.K. Kim, S.S. Im, Polym. Int. 51 (2002) 239.
[10] T. Hirotsu, T. Tsujisaka, T. Masuda, K. Nakayama, J. Appl. Polym. Sci. 78 (2000) 1121.
[11] D.J. Kim, W.S. Kim, D.H. Lee, K.E. Min, L.S. Park, I.K. Kang, I.R. Jeon, K.H. Seo, J. Appl. Polym. Sci. 81 (2001) 1115.
[12] H. Akira, K. Shinzou, F. Kenji, S. Shigeichi, K. Makoto, Soil Sci. Plant Nutr. 49 (2003) 903.
[13] W.S. Lyoo, J.H. Kim, W.S. Yoon, B.C. Ji, J.H. Choi, J. Cho, J. Lee, S.B. Yang, Y. Yoo, Polymer 41 (2000) 9055.
[14] P.A. Tamirisa, J. Koskinen, D.W. Hess, Thin Solid Films 515 (2006) 2618.
[15] T. Hirotsu, C. Tagaki, Thin Solid Films 457 (2004) 20.
[16] J.G. Wang, K.G. Neoh, E.T. Kang, Thin Solid Films 446 (2004) 205.
[17] J.H. Zhao, X.Q. Wang, J. Zeng, G. Yang, F.H. Shi, Q. Yan, J. Appl. Polym. Sci. 97 (2005) 2273.