Plasma Surface Treatments of Melt-Extruded Uniaxial Blend Sheets of PLLA/PBS

Toshihiro Hirotsu, Kazuo Nakayama, Chie Tagaki,^a and Toichi Watanabe^b

National Institute of Advanced Industrial Science and Technology
AIST-Tsukuba Central 5, Tsukuba 305-8565, Japan

^a Precision Technology Research Institute of Nagano Prefectures
Okaya, Nagano Pref. 394-0084, Japan

^b Kyodo Chemicals Co., Setagaya-ku, Tokyo 156-0052, Japan
t-hirotsu@aist.go.jp

Uniaxial polymer blend sheets were produced by melt-extruding from a mixture of poly(L-lactic acid) (PLLA) with poly(butylene succinate) (PBS). These sheets were treated by use of O₂- or Ar-plasma, and the surface effects were examined by the plasma susceptibility. Mass loss by plasma etching depended on the polymer blend ratio; the etching was greater in the blend sheets with higher ratio of PBS. Microstructures were formed on the surface as a result, and the sheets treated with Ar-plasma had a finer morphology than these treated with O₂-plasma. A new IR absorption peak appeared at 1616 cm⁻¹ in the PLLA portions in the polymer blends after the O₂-plasma treatments. Plasma treatments increased the surface wetting of these polymer blends. PBS sheet was biologically degraded, but the degradation decreased substantially by the blending of PLLA even after the plasma treatments.

Keywords: Uniaxial polymer blend sheets, PLLA, PBS, plasma treatments, contact angles, biodegradation

1. Introduction

Plasma processing is a useful tool for the surface-specific modification of polymers. Both the reactivity of plasma gas source and the plasma intensity determine the effects on the polymer surface functions, and the control of the reaction will help designing the functions.

The plasma treatments are applied to the biodegradable polymer molds to control the surface chemistry. Aliphatic polyesters are in general biologically degraded to be used as environmental-friendly materials. The physical property evaluations have been studied from the practical aspects [1-8]. Poly (L-lactic acid)

(PLLA), which is produced from starch, is biodegradable. The chemical structure is shown in Fig. 1. The industrial use is interested for some of the advantages, e.g., toughness and thermal stabilities. PLLA may be used for the substitutes of engineering plastics.

Fig. 1 Chemical structure of PLLA.

The biodegradation rate is, however, slower compared to other conventional aliphatic polyesters such as poly (butylene succinate) (PBS) and poly(caprolactone). Ways to control the polymer performance as well as the biodegradation have been sought. One method is to fabricate the networked structure. The polymer blends will provide the advantageous bulk and surface properties that the individual polymers do not have originally.

Uniaxial-blend polymer sheets were prepared by the melt-extrusion of PLLA/PBS, and the sheet surface was treated by the different types of plasmas from Ar or O₂. PLLA and PBS are different from each other in the physical property; PLLA is much less degraded than PBS, while PBS is not so stable thermally. Overcome of these disadvantages in each polymer is expected by forming the blends.

Plasma modifications were made with these blend sheets. We previously reported the surface morphology changes in PLLA after plasma treatments [9]. The purpose of the present work is to examine the plasma treatments' effects of the PLLA/PBS blended sheets with regard to the mass loss and the changes in both chemical and physical structures on the surface.

2. Experimental

2.1 Polymer blend sheets

The polymers used in the present work are commercially available pellets of PLLA (Lacty™-2000) and PBS (Bionolle™; Showa Highpolymer Co. Ltd., Tokyo, Japan). Uniaxial sheets were produced from various PBS-ratios to PLLA by a twin-screw extruder (Labo Plastomill; Toyo Seiki Co., Tokyo, Japan). The processing details of melt-extrusion have been described in previous reports [10-12]. The blend sheets are identified according to their PLLA/PBS ratios: 0/100, 25/75, 50/50, 75/25, and 100/0.

2.2 Plasma treatments

The plasma treatments method is principally the same as those described previously [9, 13]. Glow discharge plasma was generated by the inductively coupling procedure under reduced pressure at 13.56 MHz by an RF generator

(HFS-005; Nihon Koshuha Co. Ltd., Yokohama, Japan). Argon or O₂ was introduced into the system, and the flow pressure was controlled by the opening of a valve (SS-4BMC, Swagelok).

A piece of blend sheet (2.5 cm x 2.0 cm) was placed in a reactor made of Pyrex glass tubing (4.4 cm- ϕ x 26 cm), and the plasma treatments were carried out under the predetermined plasma conditions. The surface etching was evaluated quantitatively by use of the mass loss rates (R_{et} , mg/cm² min) obtained from the equation of $R_{et} = W_t / t$, where W_t (mg/cm²) is the mass loss at the time of t (min). W_t was followed at 10 minute intervals for up to 40 minutes, and the etching tendency was analyzed quantitatively with these polymer blend sheets. R_{et} is to be a plasma susceptibility parameter.

3. Results and Discussion

3.1 Polymer blend sheets

Uniaxial polymer-blend sheets were produced by melt-extrusion of the blend of PLLA/PBS, and the 450-670 μ m-thick blend sheets were obtained under the present conditions of melt-extrusion. Whereas the PLLA sheets looked clear, the PBS sheets were opaque due to the microspheres that were formed during processing. The greater the PBS content in the blend sheets, the lower the transparency. This suggested that the microspheres of PBS remained in these blends.

The thermal behaviors of these blend sheets were evaluated by differential scanning calorimetry (DSC), and the effects of polymer blending were investigated before and after the plasma treatments. DSC was scanned with the differential scanning calorimeter (DSC-50; Shimadzu Co. Ltd., Kyoto, Japan) at the heating rate of 10 °C/min in nitrogen flow, and the data were processed with the thermal analyzer (TA-60WS, Shimadzu Co. Ltd.).

The DSC curves for PLLA and PBS appeared separately in the blends. The two polymers were thus immiscible, although they formed the polymer composites at the various blend ratios. The DSC profiles were unchanged after the present plasma treatments,

and the bulk crystalloid was unaffected in these treated blends.

The melting enthalpies (δH_m , J/g) for PLLA were obtained from the DSC data of the blends. The relationships between δH_m and the PBS-ratio are shown in Fig. 2, respectively for the untreated sheets and the plasma treated sheets by O₂ and Ar (30Pa, 50W, 10 min). δH_m decreased with the increase in the PBS-blending, and the decrease was more or less the same after the plasma treatments.

The net value of δH_m for the PLLA part can be obtained by taking the PLLA ratio in the blend into consideration. They were estimated at 30.6-37.3 J/g for PLLA. The crystalline percentage is related with δH_m , and the crystallinity (χ , %) of PLLA in the blends can be provided by the equation;

$$\chi = 100 \times (\delta H_m / 93.7).$$

The PLLA crystallinity is estimated at 32.7%-39.8% in these blends, and this is the same level as reported for PLLA [14].

Fig. 2 Melting enthalpy (J/g) of PLLA vs. the PBS fraction in PLLA/PBS blends.

3.2 Infrared spectroscopic analyses

IR spectra were taken by the reflection mode, and the chemical structure on the surface was analyzed from the absorption peak profiles. Fig. 3 shows the IR spectra for the region of carbonyls' absorption in the PLLA/PBS blends 100/0 (a), 75/25 (b), 50/50 (c), and 0/100 (d); that is, the blends at the PBS ratios of 0, 0.25, 0.5, and 1.0. The peak at 1754 cm⁻¹ is for the ester carbonyl of PLLA,

Fig. 3 Refraction IR spectra of blend sheets of PLLA/PBS blends; 100/0 (a), 75/25 (b), 50/50 (c), 0/100 (d).

and that at 1714 cm⁻¹ is for that of PBS

The spectral profile shows that the peak at 1754 cm⁻¹ decreased with the increase in the PBS fraction, and the peak intensity change was proportional to the polymer blend ratio. This also indicated that the polymer supply used in preparing the blend sheets reflected the composition in the vicinity of the surface.

3.3 Plasma treatments

Plasma susceptibility of the blend sheet was judged by use of the R_{et} parameter. Fig. 4 shows the R_{et} dependence on the PBS-ratio in the blend sheets. PBS was more easily etched, especially when exposed to the oxidative O₂-plasma. The O₂-plasma etching was two times greater for PBS than that of PLLA according to the R_{et} data. Characteristic morphologies are formed as a result of surface etching of polymer sheets. Plasma susceptibility should be affected not only by the polymer types but also by the physical factors or the blending states.

The plasma treatment effects influenced also the chemical structure of the surfaces. IR spectra were taken for the blend sheets treated by the O₂- or Ar-plasmas (30 Pa, 50 W, 10 min). The relative peak intensity for carbonyl absorption decreased by the detachment of the group during plasma exposure. After the plasma treatments, the peak at 1616 cm⁻¹,

which should be attributable to the vibration of C=C or diketone form, became greater than Before in the PLLA portions.

Fig. 4 R_{et} vs. the PBS-ratio in the blend sheets treated by O₂- or Ar-plasma (30 Pa, 50 W).

3.4 Polymer surface morphology

The polymer surface was observed with scanning probe microscopy (JSPM-4200; JEOL, Tokyo, Japan) in the AC-mode. Surface structure of the melt-extruded sheets should have been arisen from the shrinkage during the processing of the melted polymers. The morphology was naturally changed after the plasma treatments.

Figs. 5 and 6 show the three-dimensional (3-D) images of the surfaces of the 75/25 blend sheet after the treatments by O₂- and Ar-plasma (30Pa, 50 W), respectively. The etching degree was controlled at the mass loss of ca. 0.3mg/cm². The plasma reactivity appeared to affect the generated surface morphology, and the finer structures were observed on surfaces treated with the non-oxidative Ar-plasma.

Morphology changes appeared similarly in other blend polymer sheets with different compositions after the plasma treatments. The size of granules changed with the plasma treatment time, and the average diameter finally reached 80-100 nm on the blend sheets after the Ar-plasma treatment time longer than 10 minutes. The diameter was greater when the sheets were treated with O₂-plasmas.

Fig. 5 3-D images of the O₂-plasma-treated surface of a 75/25 blend sheet.

Fig. 6 3-D images of the Ar-plasma-treated surface of a 75/25 blend sheet.

The finer morphology should generate the increase in the effective surface area. The relative surface area (S/S_0) was taken to examine the surface morphology generated by plasma treatments. Fig. 7 shows the Ar-plasma treatment time dependences of S/S_0 for these polymer blend sheets. Here, S_0 is the original surface area of a sheet, and S is the one calculated from the SPM profiles.

The results revealed that the surface areas doubled from their original sizes. The increase in the surface area was greater in the blend sheets with the greater content of PBS parts. This is correspondent to the results of plasma etching treatments; that is the mass loss was greater in the blend with the more PBS part. It

is thus supposed that the plasma etching would remove PBS parts selectively to form the characteristic morphologies in these polymer blend sheets. The changes in the relative surface area were observed in the blend sheets treated by O₂-plasmas.

Fig. 7 Relative surface area (S/S_0) of the blend sheets treated by Ar-plasmas (30 Pa, 50W).

3.4 Surface hydrophilic changes

The polymer surface was evaluated by the contact angles before and after the plasma treatments, and the effects were examined by the changes in surface wetting. Advancing contact angles of fresh water (θ_a , degree) were measured on the surface of the blend polymer sheets by a scissile method using a goniometer (Erma Co., Tokyo, Japan). The measurements were made at room temperature.

Fig. 8 shows the relationship between θ_a and the PBS composition for the original sheets and for the plasma-treated sheets with O₂ and Ar (30 Pa, 50 W). The plasma treatment time was kept short for 1.0 min to prevent the etching degradation on the surface, but the time is long enough to change the surface chemistry of these polymer sheets under the present plasma conditions. The θ_a values decreased from ca. 82–90° to 48–56° after the plasma treatments, and the wetting effects by plasma treatments were indicated from the change. The sheets of PBS and the PBS-rich blends showed a little greater θ_a than the PLLA sheet.

The oxidative plasma treatments looked a little more effective to increase the surface wetting than the Ar-plasma treatments. That should be due to the oxidative reactions on the surface to introduce the polar groups at the higher density. The morphology changes as observed in the SPM studies should have played the role on the surface property changes.

Figures 8 Relationship between θ_a and the PBS ratio in the polymer blend sheets; untreated and plasma-treated sheets with O₂ or Ar (30 Pa, 50 W).

3.5 Biodegradation

The hydrophilic changes should increase the compatibility of bio-organisms on the polymer surface. In order to examine the effects on the biodegradation, the polymer sheets were tested by the soil burial. That is, sheet samples (2 cm x 5 cm) were embedded in soil collected in a forest (AIST Campus, Tsukuba, Japan), and were left at 42 °C for 3 months. The experiments were carried out at this relatively high temperature to accelerate the degradation. The extent of biological degradation was judged according to the degree to which the sheets lost mass after burial in soil. The biodegradation was investigated with regard to the effects of polymer blending and the surface treatments.

The mass loss after the 3-month burial is shown in Fig. 9 by the blend ratio dependences for the original sheets and the plasma treated sheets for 1.0 minute. At first, the biodegradation was much dependent on the

polymer blend ratio; the mass loss by biological degradation was much greater in the PBS sheets. The mass loss or the biodegradation decreased substantially in the blends, and became negligible with the blend sheets with the PBS contents smaller than 0.5.

The mass loss looked slightly greater in the blend sheet of 10/90 and the PBS sheet treated with oxidative O_2 -plasma. However, the increase was negligible in other blend sheets. The plasma treatments of both types were not so effective at increasing the biodegradation rates of these blend sheets, even though the surface changed more wettable.

Figure 9 Mass loss of the blend sheets with the various PBS-ratios by the biological degradation after 3-month burial in soil at 42 °C.

4. Conclusion

Surface phenomena of the PLLA/PBS blend sheets were investigated after the Ar- and O_2 -plasma treatments, and the following points were made clear in this work. The mass loss by etching and the surface wetting changes was promoted in PBS and the blends with more content of PBS. Plasma reactivity also affected

the surface phenomena; the finer morphologies were generated by the non-oxidative Ar-plasma treatments, and the relative surface area doubled. Plasma treatments increased surface hydrophilicity of these blend-sheets, but the enhancement of biodegradation was practically not observed.

References

1. S. Li, H. Garreau and M. Vert, *J. Mater. Sci. Mater. Med.* **1** (1990) 198.
2. H. Tsuji and Y. Ikada, *Polym. Degrad. Stabl.* **67** (2000) 179.
3. E. Blumm and A. J. Owen, *Polymer* **36** (1995) 4077.
4. B. P. M. Ferreira, C. A. C. Zavaglia and E. A. R. Duek, *Mater. Res.* **4** (2001) 34.
5. S. Iannace, L. Ambrosio, S. J. Huang and L. Nicolais, *J. Appl. Polym. Sci.* **54** (1994) 1525.
6. H. Tsuji, R. Smith, W. Bonfield and Y. Ikada, *J. Appl. Polym. Sci.* **75**, (2000) 629.
7. C. Nakafuji, *Polym. J.* **26** (1994) 680.
8. M. Sheth, R. A. Kumar, V. Dave, R. A. Gross and S. P. McCapthy, *J. Appl. Polym. Sci.* **66** (1997) 1495.
9. T. Hirotsu, T. Masuda, Y. Matsumura and M. Takahashi, *J. Photopolym. Sci. Technol.* **10** (1997) 123.
10. K. Qi and K. Nakayama, *Polym. Polym. Composites* **6** (1998) 473.
11. K. Qi and K. Nakayama, *Polym. Polym. Composites* **8** (2000) 187.
12. A. A. J. Ketelaars, Y. Papantonion and K. Nakayama, *J. Appl. Polym. Sci.* **66** (1997) 921.
13. T. Hirotsu, T. Tsujisaka, T. Masuda and K. Nakayama, *J. Appl. Polym. Sci.* **78** (2000) 1121.
14. E. W. Fisher, H. J. Sterzel and G. Wegner, *J. Kolloid-Z. Z. Polymere* **251** (1973) 980.