

Plasma Surface Treatments and Biodegradation of Poly(butylene succinate) Sheets

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ABSTRACT: The sheets prepared by the extrusion of the melt of poly(butylene succinate) were treated with inorganic gas plasmas. Bionolle, the commercially available polyester, was also used, and the treatment effects were compared. Plasma susceptibility by the continuous plasma of 13.56 MHz and by pulsed plasmas was evaluated by the weight loss rates by etching. Advancing and receding contact angles of water (θ_a , θ_r) on the plasma-treated sheets were obtained by the Wilhelmy method. Decay of hydrophilicity was considerable in θ_a , but θ_r was less changed. The biodegradation was examined by the preliminary soil-burial tests. The polymer sheets were biologically degraded, and the characteristic morphology appeared on the surface according to the SEM observation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1121–1129, 2000

Key words: poly(butylene succinate); plasma treatments; contact angles; SEM; biodegradation

INTRODUCTION

Plasma treatments are useful processes for finishing of polymers from the aspects of industrial application.^{1,2} The surface layer is etched by plasma, and the surface properties are changed. Application of glow discharge plasmas to the modification of biodegradable polymers has been attempted recently. Poly (butyric acid-3-hydroxyvalerate) sheets produced by a casting method were modified by oxidative and nonoxidative plasmas.^{3, 4} The surface phenomena were discussed with respect to the rearrangement of the chemical networks based on the contact angle results as well as ESCA studies. Poly (L-lactic acid) was treated with inorganic gas plasmas,⁵ and the generation of characteristic surface morphologies was observed by SEM, indicating loss of the skin

layer. Surface coating of the biodegradable polymers also has been attempted using ultrathin plasma polymers with a crosslinked structure.^{6–9} Resistance to the deterioration by contact to water or water vapor was achieved with the hydrophobic polymer coating. Application to the biomedical materials is also possible, and hemo-compatible coating has been attempted by hydrophilic plasma polymers.

Aliphatic polyesters are biodegradable. Various types of the polyesters with a succinate component were synthesized, and among them poly(butylene succinate) (PBS) has been more interesting for its advantages in mechanical properties. Enzymatic degradation characteristics have been studied with respect to the influences of the thermal character and crystallinity of the polymers.^{10, 11}

In the present work, sheets of PBS with higher molecular weight were treated by glow discharge plasmas for surface activation. The polymer sheets were prepared by extrusion from the melt,

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and mechanically improved products were obtained by alignment of the polymer chains. Treatments were also attempted with the pulsed plasmas as well as continuous RF plasmas. The experimental results were compared with those of the commercially available poly(butylene succinate) (Bionolle), which has been produced with the crosslinked structure by urethane networks.

EXPERIMENTAL

Materials

Poly(butylene succinate) (PBS) was produced by condensation polymerization as follows: the mixture of dimethyl succinate (0.18 mol) and 1, 4-butanediol (0.187 mol) was heated up to 200°C for 20 h, and then reacted at 215°C in a vacuum to remove generated methanol and unreacted monomers.¹⁰ Titanium tetraisopropoxide (0.05 mol % to dimethyl succinate) was added as a catalyst. Average molecular weight (M_n) was 34–50 K. Commercially available poly(butylene succinate) (Bionolle^{TR} 1010, Showa Highpolymer Co. Ltd., Japan) was also used for comparison.

Polymer Sheets

PBS sheets were produced using a twin screw extruder (Labo Plastomill, Toyo Seiki Co.)¹² operated at 30 rpm with a die temperature of 140°C. The sheets were cooled in water and kept in air. The thickness of the sheet was about 0.75 mm. The sheets were also produced from Bionolle similarly, at the screw speed of 50 rpm.

Plasma Treatments

Plasma was generated by inductively coupled discharges at 13.56 MHz using a RF generator (HFS 005, Nihon Koshuha Co. Ltd., Japan). Pulse plasmas were generated in the same apparatus at various plasma on-off ratios of discharges. Plasma surface treatments were carried out in a reactor made of Pyrex glass tubing (4.4-cm id × 26 cm) using O₂, N₂, He, etc. Symmetry and shape of the system are the same as those reported before.⁵ Gas supply was controlled by the opening of a valve (SS-4BMG, Nupro Co., USA), and monitored by a pressure meter (type 270, MK-Baratron Co., USA).

SEM

Surface morphology of the sheets was observed by scanning electron microscopy (SEM) at 15 kV

with an apparatus of FE-SEM (DS-720, Topcon Co. Ltd., Japan).

Contact Angles

Advancing and receding contact angles of water (θ_a , θ_r) were obtained by the Wilhelmy method.^{13–15} Polymer sheets with the size of 1.0 × 3.5 cm were used, and the surface tensions in the advancing receding states to water were measured with a contact angle meter (ST1S, Shimadzu Co. Ltd., Japan). The contact angles were calculated by use of the equation:

$$\cos \theta_a = \gamma_w/k \times (l/2), \text{ and } \cos \theta_r = \gamma_r/k \times (l/2).$$

Here, γ_a and γ_r are the surface tensions (mN/m) in the sample dipping and taking out processes, respectively. The constant of k is the surface energy of water (e.g., 72.75 mN/cm at 25°C), and l is the perimeter of a polymer sample contacting to water.

γ_s^p and γ_s^d

Advancing contact angles on the sheets were also measured by a sessile method. The contact angle data were processed by the Kaelble method,^{16,17} and polar (γ_s^p) and dispersion (γ_s^d) contributions to the total surface energy (γ_s) were determined. Liquids used for the contact angle measurements in the present work were; water, ethylene glycol, methylene iodide, etc.

Biodegradation Tests

The polymer sheets were subjected to preliminary biodegradation tests in the soil, and the biodegradability was determined. The soil collected in the forest near the NIMC campus (Tsukuba, Japan) was used, and the temperature was controlled at 42°C in a water bath. The polymer sheet samples were taken out at 1-month intervals, and the weight of the dried polymer sheets was measured to judge the biodegradation.

RESULTS AND DISCUSSION

Plasma Treatments

The weight loss by etching was followed, and the plasma susceptibility was investigated with respect to the effects of reactivity of gases in plasma and also to the plasma intensity.

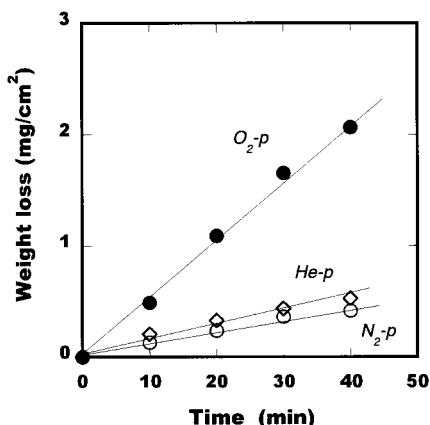


Figure 1 Weight loss dependence of PBS sheets on the plasma treatment time of O₂, N₂, and He (30 Pa, 50 W).

Weight Loss by Plasma Etching

The surface of a polymer sheet (2.2 × 2.5 cm) was exposed to glow discharge plasmas, and the weight was measured before and after the treatments. Figure 1 shows the weight loss dependence of PBS sheets on the plasma treatment time with O₂, N₂, and He (30 Pa, 50 W), respectively. Here, the flow rate of plasma gas sources was estimated to be 0.26 sccm for the system pressure condition, and intense enough glows for the surface treatments were obtained at 50 W.

Polymer sheets were etched from the surface, and the weight decreased linearly with the plasma treatment time. The weight loss was naturally greater by the oxidative treatments using O₂ plasma. When the weight loss was compared among the treatment by the nonoxidative plasmas, the polymer etching degree by He plasma was somewhat greater than that by N₂ plasma. The order should be related to the plasma intensity, which is reciprocally related to the molecular weight of a plasma gas. The molecular weight of He is smaller, and the relative glow is stronger as a result.

Weight Loss Rates by Etching

The etching rate (R_{et} , mg/cm² min) was calculated from the linear relationship between the weight loss and the plasma exposure time, as shown in Figure 1. Plasma susceptibility was determined by the size of R_{et} . Figure 2 summarizes the data of R_{et} for PBS and Bionolle by the continuous plasma treatments with He, O₂, and N₂ (30 Pa, 50 W), respectively. The rates were compared with

those for the PET film (Mylar). The etching degree was more or less the same between the PBS and Bionolle sheets. The etching rate was smaller for PET, which is composed of aromatic ester structure, and this suggests resistance by PET to glow discharge plasmas.

Etching by Pulse Plasmas

Plasma etching experiments were also carried out with the pulsed discharges, and the treatment effects were compared with those by the continuous discharges. Pulse plasmas were generated by changing the ratio of duty time of discharges at the frequency of 13.56 MHz. The plasma on-time was fixed in the order of 10⁻⁴ s, and the off-time was changed to determine the on-off ratio of discharges. If the plasma gas reactivity is retained during the off-time, the plasma surface treatments may be effectively achieved with relatively smaller applied power. This should be beneficial for polymers such as the biodegradable polymers, as the surface treatment effects are expected to take place with prevention of bulk degradation.

Figure 3 shows the plasma on-ratio dependence of R_{et} by O₂ (30 Pa, 50 W) for the sheets of PBS and Bionolle, respectively. The plasma duty is related to the plasma intensity, and R_{et} increases with the on-ratio in these sheets. Similar dependencies were obtained with other plasma gas sources, although the degree R_{et} is different due to differing reactivity. Figure 4 shows the dependence of R_{et} on the plasma for the three types of gases. Oxidative etching effects by O₂ were greater among the whole range of on-ratio. The polymer sheets were etched even with the

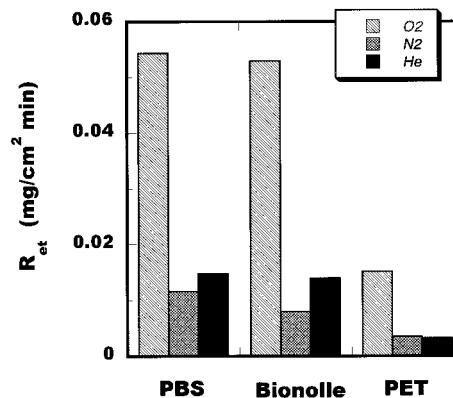


Figure 2 Weight loss rates (R_{et}) of PBS and Bionolle by the continuous plasma etching by O₂, N₂, and He (30 Pa, 50 W).

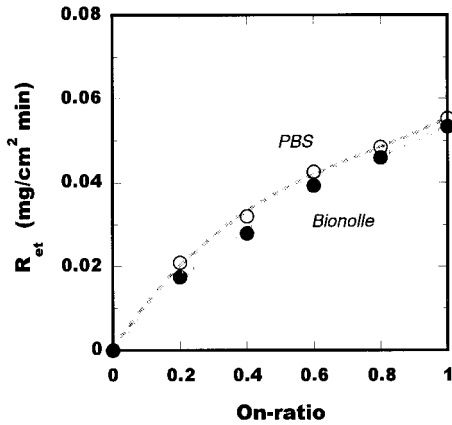


Figure 3 Dependence of etching rate (R_{et}) for PBS and Bionolle on the on-ratio of pulsed plasmas of O_2 (30 Pa, 50 W).

pulsed plasmas, which were slightly less effective compared with the linear relationship to the applied power level.

The on-ratio should be related to the applied energy of plasmas, and the reaction energy naturally should increase with increasing on-ratio. The results are comparable with the power changes. Figure 5 shows the power dependence of R_{et} for the plasma etching by O_2 , N_2 , and He (30 Pa, 50 W). The etching degree increased with power, with a similar tendency in the pulse plasmas.

Surface Hydrophilicity

The hydrophilicity of the polymers changes with plasma treatments, and the surfaces become wet-

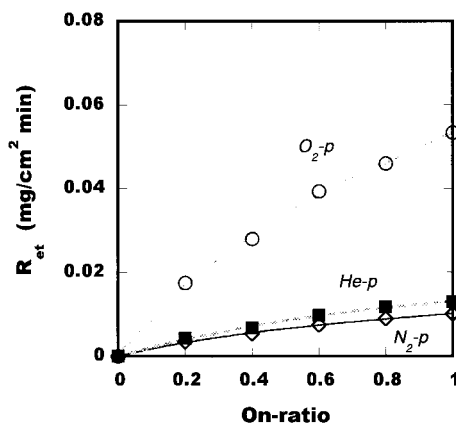


Figure 4 Dependence of etching rate (R_{et}) for PBS on the on-ratio of pulsed plasmas of O_2 , N_2 , and He (30 Pa, 50 W).

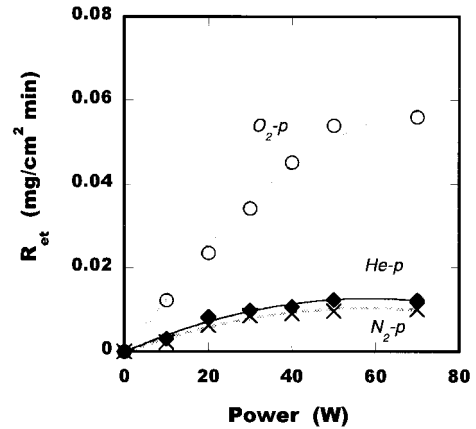


Figure 5 Discharge power dependence of etching rate (R_{et}) by the continuous plasma treatments of O_2 , N_2 , and He.

table in general. Advancing and receding contact angles (θ_a , θ_r) provide information on the dried surfaces and the wet surfaces, respectively. The Wilhelmy method is a convenient procedure to obtain the values of θ_a and θ_r on solid surfaces. Surface characterization of the plasma-treated surfaces of the PBS and Bionolle sheets was made with θ_a and θ_r .

θ_a and θ_r

Plasma treatment time for the modification of these sheets was changed, and the effects on the surface hydrophilicity were examined with θ_a and θ_r . Figure 6 shows the plasma exposure time dependencies of contact angles of water on PBS

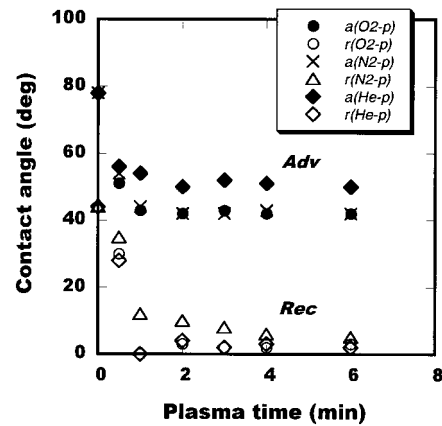


Figure 6 Plasma treatment time dependence of advancing (a) and receding contact angles (r) for water on the PBS sheets with O_2 , N_2 , and He-plasmas (30 Pa, 50 W).

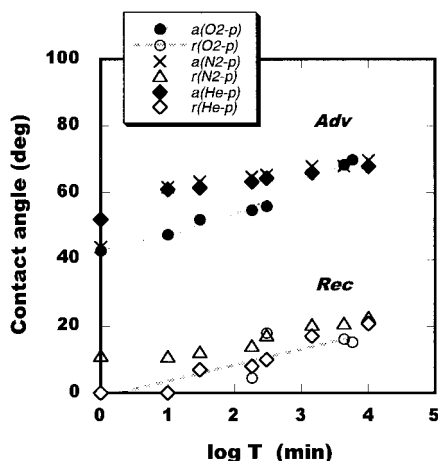


Figure 7 Aging of advancing (a) and receding contact angles (r) for water on the PBS sheets treated with O₂, N₂, and He plasma (30 Pa, 50 W, 1.0 min).

sheets, respectively, by the treatments with O₂, N₂, and He plasmas (30 Pa, 50 W). Here, the contact angle measurements were made just after the plasma treatments of the samples, and the results are based on fresh modified surfaces.

Both contact angles became smaller in 0.5 min, and the hydrophilicity reached equilibrated levels of surface wetting after 1 min of plasma exposure in these treatments. The weight loss by etching is estimated at 5.43, 1.16, and 1.47×10^{-2} mg/cm² after 1 min exposure to O₂, N₂, and He plasmas (30 Pa, 50 W, respectively). As the weight loss was small, the surface morphology changes on the polymer surfaces should be negligible. Thus, the hydrophilic changes should be due to chemical changes of surfaces by plasma exposure.

Recession of Contact Angles

The hydrophilicity brought by the surface treatment decreases with time after finishing. However, these discussions are based on advancing contact angles, and details for receding contact angles, or the wet state of surfaces, have not been provided as far as the authors know. In the present work, the measurements of θ_r were repeated, and the aging behaviors are compared with those of θ_a .

Figure 7 shows the results for the aging of θ_a and θ_r on the O₂, N₂, and He plasma-treated PBS sheets, respectively. In the figure, the logarithmic value is taken for the elapsed time after plasma treatments. The samples, which were treated

with plasmas (30 Pa, 20 W, 1.0 min) were kept dry, and the contact angle measurements were repeated. Similar behaviors were observed in the changes on the Bionolle sheets, although the contact angles were a little greater.

Among the treatments, O₂ plasma was more effective to decrease the contact angles, and the hydrophilicity increased more. However, the value of θ_a increased again, indicating a decrease in the hydrophilicity. Similar contact angle phenomena were observed in other types of plasma treatments, although the rates for the recovering of hydrophobicity were dependent on the plasmas.

The effect of plasma treatments has been prominently observed in the receding contact angles (θ_r), which reached almost zero degrees on the O₂ plasma-treated PBS sheets. The recession was much slower, and θ_r remained smaller for a long time. The angles were smaller than 44° for the untreated PBS sheet. The data of θ_r are related to the information on the solid surface that is contacting water. Thus, the results indicated above confirmed that the hydrophilicity on the plasma-treated sheets is still effective in the wet state even on the θ_a -recovered surfaces after longer storage.

Figure 8 shows the results for the pulsed O₂ plasma-treated PBS sheets. Pulsed plasmas were also effective for the change of surface hydrophilicity, and the treatments provided more or less the same effects as the continuous plasma treat-

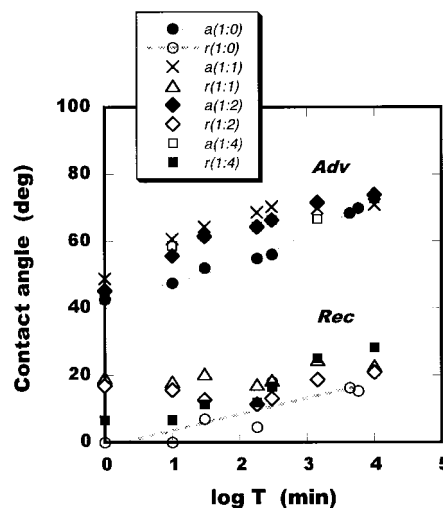


Figure 8 Aging of advancing (a) and receding contact angles (r) for water on the PBS sheets treated by pulsed O₂-plasmas with the on-off ratios of 1 : 0, 1 : 1, and 1 : 4, respectively (30 Pa, 50 W, 1.0 min).

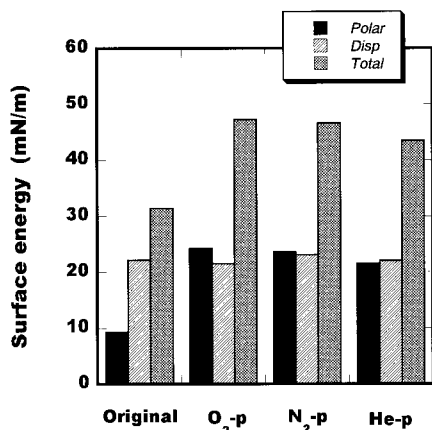


Figure 9 Polar, dispersion, and total surface energies for the original PBS sheet and the plasma treated sheets with O₂, N₂, and He (30 Pa, 50 W, 1.0 min).

ments. Application of the pulsed plasmas is thus advantageous with respect to the treatments for the surface changes without influence on the bulk through restriction to etching of the polymers.

Surface Energy

Polar (γ_s^p) and dispersion components (γ_s^d) of surface energies were obtained by Kaelble's method, respectively, and the surface phenomena of the plasma-treated sheets were analyzed for contributions. Figure 9 summarizes the data, respectively, for the original and the treated sheets by O₂, N₂, and He plasmas (30 Pa, 50 W, 1.0 min). The data were collected just after plasma treatments, and the results are compared with those of PET.

Increase in the value of γ_s^p was prominent on the plasma-treated surfaces, while γ_s^d did not change much. As a result, the change of total surface energy ($\gamma_s = \gamma_s^p + \gamma_s^d$) is due mainly to the increase in γ_s^p . Hydrophilic changes of the polymer surfaces after plasma treatments are related to the increase in the value of γ_s^p .

Surface energy data were also obtained 2 days later with the plasma-treated polymer sheets. The increased value of γ_s^p by plasma surface treatments decreased slightly, for example, from 24.2 to 22.4 mN/m in the O₂ plasma-treated PBS sheet. The decrease should have resulted in reduction of hydrophilicity. However, the value of γ_s^p is still greater than that for the original PBS sheets (i.e., 9.3 mN/m), and the retention of hydrophilicity in the wet state; i.e., the smaller θ_r , as seen in Figure 7 should be attributable to the phenomena.

Biodegradation

Polymer sheets were subjected to the burial tests in soil, and the degradability was investigated with respect to the surface hydrophilicity brought by the plasma treatments.

Weight Loss by Biodegradation

The polymer sheets buried in soil were taken out at 1-month intervals, and the degradation by bio-organisms was checked. The polymer sheet was digested from the surface, and the weight was lost gradually. The digested products and the soil attached to the surface were removed, and the remaining polymer sheets were weighed to measure the degradation amounts. The biodegradability of the sheets was estimated from the changes in the weight of the dried samples.

Figure 10 shows the weight loss dependence on the burial time of the PBS and Bionolle sheets, respectively. The sheet area was obtained from both faces of the sheet, and the weight loss amounts are shown in mg/cm². The soil bed temperature was kept high at 42°C to activate the micro-organisms for biodegradation. The polymer sheets were degraded, and the degree was almost the same between PBS and Bionolle.

The plasma-pretreated sheets were also subjected to the biodegradation by the soil burial, but no apparent changes in the degradation tendencies were observed. We had at first expected the promotion of biodegradation with these samples, as the hydrophilic surface may promote the contact of bio-organisms to increase the reactivity. However, the degradation degree was more or less the same as those for the untreated sheets,

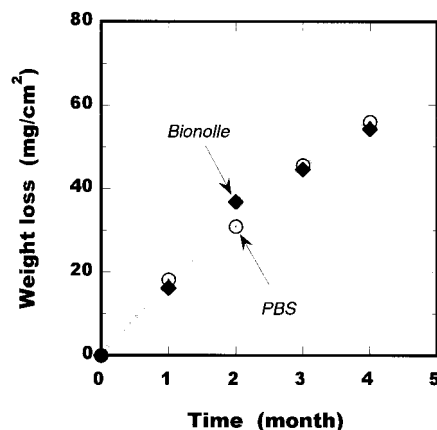


Figure 10 Biodegradation of the PBS and Bionolle sheets in soil at 42°C.

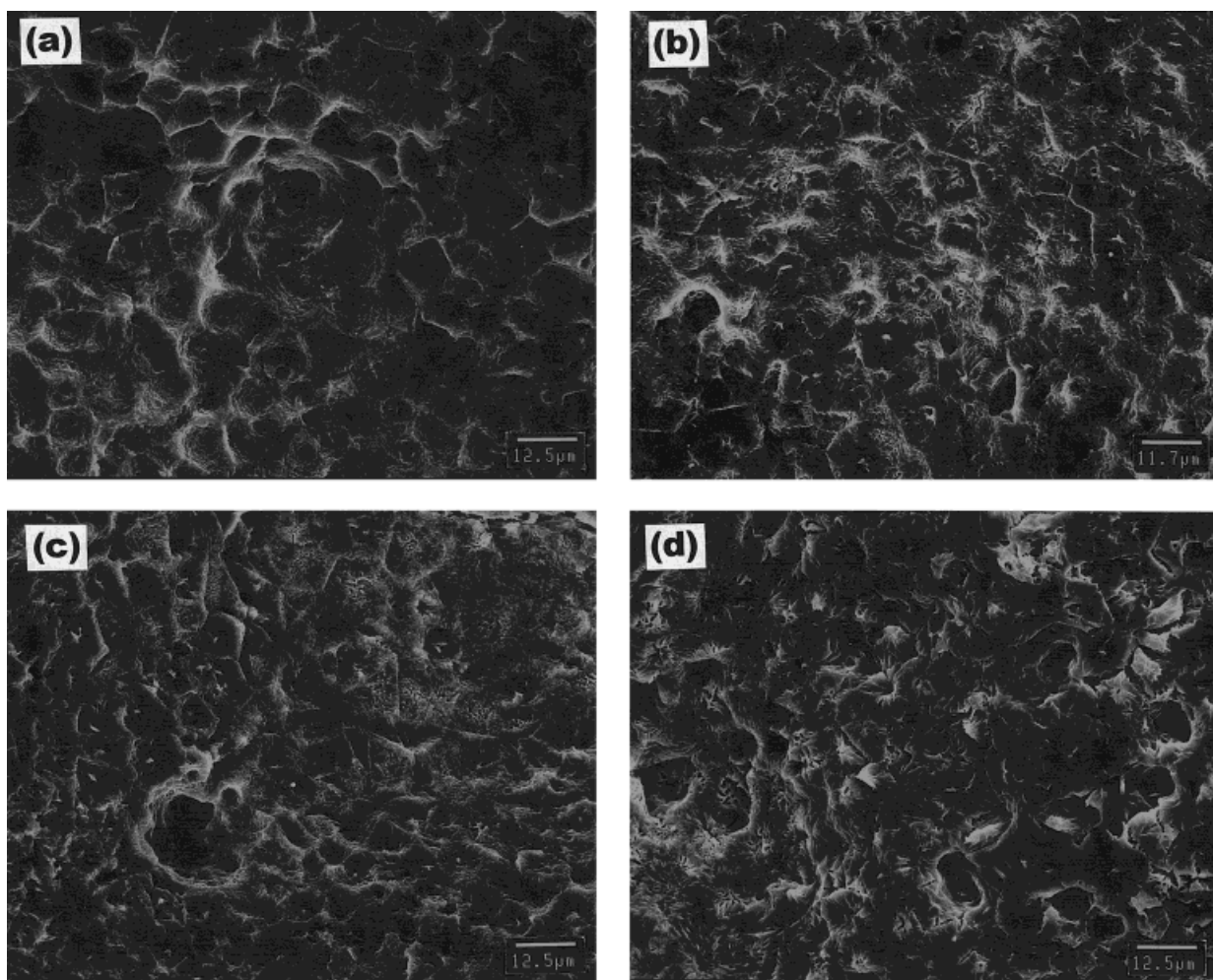


Figure 11 SEM pictures for the PBS sheets after burial in soil at 42°C for 2 months, respectively, for the untreated original sheet (a), and the plasma-pretreated sheets by the discharges of O₂ (b), N₂ (c), and He (d) (30 Pa, 50 W).

and the present plasma treatments were not effective actually to increase the biodegradability of the polymer sheets.

Surface Morphology by SEM

Figure 11 shows the SEM pictures of the biodegraded PBS surfaces, respectively, for the original sheet (a) and for those treated by O₂ (b), N₂ (c), and He plasma (d), respectively. Figure 12 shows those for the biodegraded Bionolle surfaces. Polymer sheets were pretreated by the plasmas at 50 W for 1.0 min, and subjected to the burial tests. The samples were buried in soil for 2 months, and the degradation degree was estimated about 30 mg/cm² for the polymer sheets.

New and clear patterns on the surfaces of these sheets were observed after degradation with both

sheets. The morphology was similar between PBS and Bionolle, but was different from those of the untreated smooth surfaces.

CONCLUSION

Polymer sheets of PBS and Bionolle were prepared by extrusion from the melts, and the surfaces were treated by continuous RF plasmas and pulsed plasmas from different types of gas sources. Plasma susceptibility was evaluated from the etching rates, which depended on the reactivity of plasma gas and also the intensity. The polymer sheets were etched more by the oxidative plasmas from O₂, and the etching was suppressed with the pulsed plasma treatments.

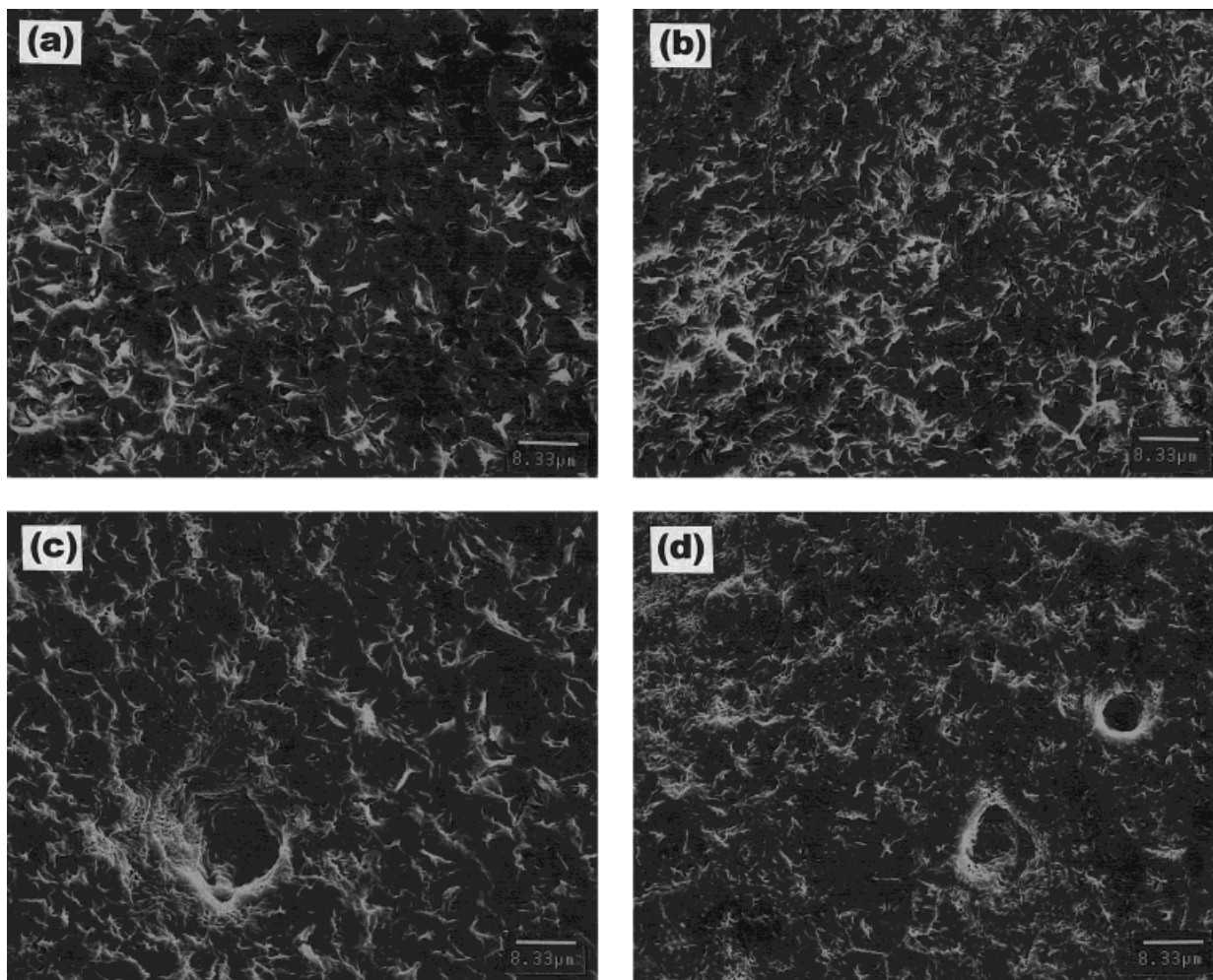


Figure 12 SEM pictures for the Bionolle sheets; notations are the same as in Figure 11.

The surface became wettable, and the plasma treatment effects more prominently appeared in the receding contact angles, i.e., the contact angle was 0° and the time-decay was much smaller. The biodegradation was investigated by soil burial tests. The sheets were degraded biologically, and characteristic morphology was observed on the surface. Promotion of biodegradation of the plasma-treated sheets of PBS and Bionolle was not necessarily observed, even though the surface was changed in hydrophilicity.

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