

Effects of Aromatic Groups in Polymer Chains on Plasma Surface Modification

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ABSTRACT: Three polyester films with different repeating units—poly(lactic acid) (PLA), poly(ethylene terephthalate) (PET), and poly(oxybenzoate-co-oxynaphthoate) (PBN)—were modified by plasma, and the way in which the chemical compositions of the polymer chains influenced the plasma modification was investigated with contact-angle measurements and X-ray photoelectron spectroscopy (XPS). There were large differences in the compensated rates of weight loss among the three polyester films when they were exposed to Ar and O₂ plasmas. The PLA film showed the highest rate for weight loss of the three films, and the PBN film showed the lowest rate. The PET and PBN film surfaces were modified to become more hydrophilic by either argon

or oxygen plasma. However, the PLA film surface was not made more hydrophilic by the plasmas. XPS spectra showed that the PLA film surface was not modified in its chemical composition, but the PBN film surface was modified in its chemical composition to form C—O groups in the PBN polymer chains. The reason that the PLA film surface was not modified but the PBN film surface was modified was examined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 96–103, 2003

Key words: cold plasma; ESCA; XPS; polyester; surface; modification

INTRODUCTION

Plasma containing electrons, ions, radicals, and neutral molecules strongly interacts with polymer surfaces, and as a result, chemical and physical modifications occur on the surfaces.^{1,2} Modification from a hydrophobic surface to a hydrophilic surface with oxygen plasma and modification from a hydrophilic surface to a hydrophobic surface with CF₄ plasma are good examples of chemical modification by plasma.¹ Moreover, physical modification by argon-plasma exposure is often used on the surfaces of fluoropolymers to roughen them and to improve their adhesion with other materials with epoxy glue.¹ Chemical modification entails reactions introducing hydrophilic or hydrophobic groups onto the polymer surfaces, whereas physical modification involves degradation reactions of the polymer chains on the surfaces.¹ We believe that these chemical introduction and degradation reactions are initiated by hydrogen abstraction from polymer chains and by the carbon-carbon bond scission of polymer chains, respectively. The chemical introduction and degradation reactions do not occur separately but occur simultaneously in the plasma-exposure procedure.³ We can never avoid degradation reactions

as long as plasma is used for modification. From the conception of plasma modification, we believe that a key factor in effective surface modification is minimizing degradation reactions occurring in the plasma-exposure procedure.

Degradation reactions that are triggered on polymer surfaces by plasma may depend on the polymer composition and the plasma conditions, including the kind of plasma, the radio-frequency (rf) power for discharging plasma, and the flow rate of the plasma gas. Plasma bombards polymer surfaces, causing C—C or C—O bond scission in the polymer chains. As a result, carbon or oxygen radicals will be formed at the ends of the polymer chains, and then degradation reactions will start from these radicals. Therefore, we believe that the degradation reactions depend strongly on what bond scission reaction occurs in the polymer chains and also on how the degradation reactions proceed from the carbon or oxygen radicals.

In this study, the influence of the chemical compositions of polymer chains on surface modification was investigated with three polyesters: poly(lactic acid) (PLA), poly(oxybenzoate-co-oxynaphthoate) (PBN), and poly(ethylene terephthalate) (PET). PLA is composed of aliphatic carbon chains and ester groups. PBN consists of aromatic carbon chains and ester groups. PET is composed of a mixture of aliphatic and aromatic carbon chains and ester groups. Our interest is in how aliphatic or aromatic carbon chains contribute to modification reactions.

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EXPERIMENTAL

Materials

Three commercially available polyester films were used: PLA (Ecoloju SFP, Mitsubishi Plastics, Inc., Tokyo, Japan; biaxially stretched and 20 μm thick), PET (Bobet, Toyobo Co., Ltd., Osaka, Japan; biaxially stretched and 38 μm thick), and PBN (Vecstar FA, Kuraray Co., Ltd., Osaka, Japan; inflated and 50 μm thick). These films were cut to a size of 12 mm \times 90 mm, washed with ethanol or acetone for 1 min with an ultrasonic washer (Bransonic-B1210J, Yamato Scientific Co., Ltd., Tokyo, Japan) for the removal of the residual oils, and dried at room temperature *in vacuo*. The argon and oxygen gases were pure-grade (99.995%).

Surface modification of the polyester films by the plasmas

A special reactor was used for argon- and oxygen-plasma treatments of the three polyester films. The reactor has been described in detail in a previous article.⁴ It consisted of a cylindrical Pyrex glass tube (45 mm in diameter and 1000 mm long) and a columnar stainless steel chamber (300 mm in diameter and 300 mm high). The Pyrex glass tube had two gas inlets for the injection of argon gas and a copper coil of nine turns for the energy input of the rf power (13.56-MHz frequency). The stainless steel chamber contained a Barocel pressure sensor (type 622, Edwards, England) and a vacuum system composed of a combination of a rotary pump (320 L/min) and a diffusion pump (550 L/s; type YH-350A, Ulvac Co., Tokyo, Japan). A Viton O-ring flange was used to join the Pyrex glass tube to the chamber.

The polyester films were positioned just under the center of the copper coil and exposed to the argon and oxygen plasmas. First, air in the reactor was displaced with argon. Afterward, the reactor was evacuated to approximately 1.3×10^{-2} Pa, and then argon or oxygen was introduced into the Pyrex glass tube with a flow rate of 10 cm^3 (STP)/min adjusted by a mass-flow controller. The argon and oxygen plasmas were operated at rf powers of 25–100 W at a 13.56-MHz frequency at a system pressure of 13.3 Pa for given times (5–180 s).

Contact angle of water on the plasma-treated film surfaces

With the sessile drop method,⁵ the contact angles of water on the polyester film surfaces treated with the plasmas were measured at 20°C with a contact-angle meter with a goniometer (model G-1, Erma Co., Ltd., Tokyo, Japan). An average contact angle was deter-

mined from 10 measurements with an experimental error of 3–4°.

X-ray photoelectron spectroscopy (XPS) of the plasma-treated films

XPS spectra of the Ar- and O₂-plasma-treated film surfaces were obtained on a Shimadzu ESCA 3400 spectrometer (Kyoto, Japan) with a nonmonochromatic Mg K α photon source. The anode voltage was 10 kV, the anode current was 20 mA, and the background pressure in the analysis chamber was 1.0×10^{-6} Pa. The spectra were deconvoluted by the fitting of a Gaussian–Lorentzian mixture function (80:20 ratio) to experimental curves with a nonlinear, least-squares curve-fitting program (ESCAPAC) supplied by Shimadzu. The binding energies were corrected by the reference of the lowest binding energy component of CH, CH₂, and CH₃ groups to 285.0 eV for the elimination of charge effects. The atomic compositions of the plasma-modified film surfaces was estimated from the relative intensities of C1s and O1s spectra. $S(\text{C1s}) = 1.00$ and $S(\text{O1s}) = 2.85$, as sensitivity factors of the C1s and O1s core levels, were used for the estimation.

RESULTS AND DISCUSSION

Plasma exposure, as explained in the introduction, makes two essentially different modifications to polymer surfaces: physical and chemical. The physical modification means degradation reactions of the polymer chain. In the physical modification process, bond scission of the polymer chains will occur, and some degradation products will be deposited on the polymer surfaces, or the topmost layer of the polymer specimens will be stripped off. As a result, rinsing the plasma-treated surface with organic solvents will lead to weight losses of the specimens. The chemical modification involves the introduction of functional groups onto the polymer surfaces, and as a result, the chemical compositions of the polymer surfaces will be modified. The modification will lead to a certain decrease in the water contact angle on the polymer surfaces. The weight-loss rate and changes in the water contact angle were evaluated as typical indices for the degradation and chemical introduction reactions, respectively, as functions of the rf power of the plasma and the kind of plasma. Furthermore, the plasma-treated film surfaces were also analyzed by XPS for the determination of what interaction reactions had occurred.

Weight-loss rate of the polyester films by Ar- and O₂-plasma exposures

Figures 1–4 show typical results for the weight loss ($\mu\text{g}/\text{cm}^2$) of PLA and PBN films as a function of the

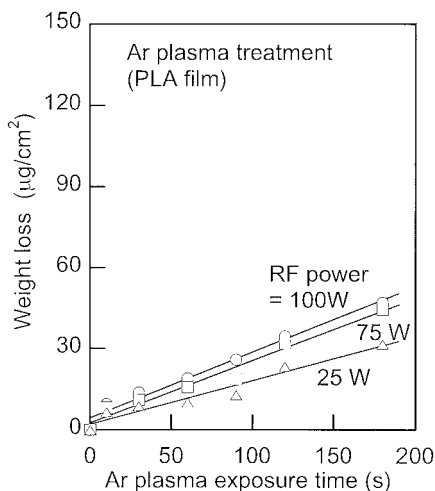


Figure 1 Weight loss of PLA films under argon-plasma exposure as a function of the plasma-exposure time and rf power.

argon- or oxygen-plasma-exposure time. The weight loss, as shown in Figures 1–4, has a linear relationship with the plasma-exposure time. From this linear relationship, we calculated the weight-loss rate ($\mu\text{g}/\text{cm}^2 \text{ s}$) for PLA, PET, and PBN films in the argon- or oxygen-plasma-exposure processes. The rates are summarized in Table I as functions of the kind of plasma and the rf power.

We believe that the weight-loss rate is an index of susceptibility to plasma. With this viewpoint in mind, we compare the weight losses of the three polyester films (PLA, PET, and PBN). Although the weight-loss rate is conventionally estimated as a dimension of $\mu\text{g}/\text{cm}^2 \text{ s}$, this is not an adequate index for an evaluation of plasma susceptibility. Plasma susceptibility does not mean how many weight degradation products were formed during the plasma exposure, but how many C—C bond scissions occurred during the plasma exposure. We believe that when one molecule (degradation product) is split from a polymer chain by bond scission, the molecular weight of the product from the PBN film, being composed of large repeating units (290 g/mol), might be larger than that for PLA, which is composed of small repeating units (78

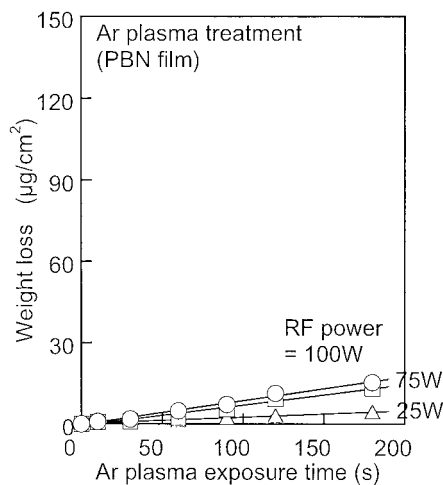


Figure 2 Weight loss of PBN films by argon-plasma exposure as a function of the plasma-exposure time and rf power.

g/mol). To compensate for the large differences in the repeating units of the three polyester films (PLA, PET, and PBN films), for which the molecular weights of the repeating units are 78, 192, and 290 g/mol, respectively, we divide the weight-loss rate ($\mu\text{g}/\text{cm}^2 \text{ s}$) by the molecular weight of the repeating unit for each polyester film. This compensation never completely solves large differences in repeating units and does not lead to an accurate concentration of the degradation products formed on polyester film surfaces by plasma exposure. We believe that the compensated rate rather than the noncompensated rate could be used as a preferable index of plasma susceptibility in a comparison of PLA, PET, and PBN films.

The compensated rates for PLA, PET, and PBN films are appended to Table I as functions of the kinds of plasmas and the rf power. There are large differences in the compensated rates among the three polyester films. The PLA film shows the highest rate for weight loss, even when argon or oxygen plasma is used at rf powers of 25–100 W. The PLA film shows a compensated rate about 15 times higher than that of the PBN film. The PET film also shows a rate about 2 times higher than that of the PBN film. However, the PBN film shows the lowest rate for weight loss. From this

TABLE I
Weight-Loss Rate of PLA, PET, and PBN Films by Ar- and O₂-Plasma Exposures

Plasma exposure conditions		Weight-loss rate ($\mu\text{g}/\text{cm}^2\text{-s}$)			Weight-loss rate in ($10^{-9} \text{ mol}/\text{cm}^2\text{-s}$)		
Plasma	RF power (W)	PBN	PET	PLA	PBN	PET	PLA
Ar plasma	25	0.025	0.085	0.161	0.080	0.443	2.78
	75	0.076	0.130	0.229	0.242	0.677	3.94
	100	0.088	0.123	0.242	0.280	0.641	4.17
O ₂ plasma	25	0.241	0.287	0.303	0.768	1.50	5.22
	75	0.478	0.527	0.950	1.52	2.75	16.4
	100	0.674	0.670	1.79	2.17	3.49	30.9

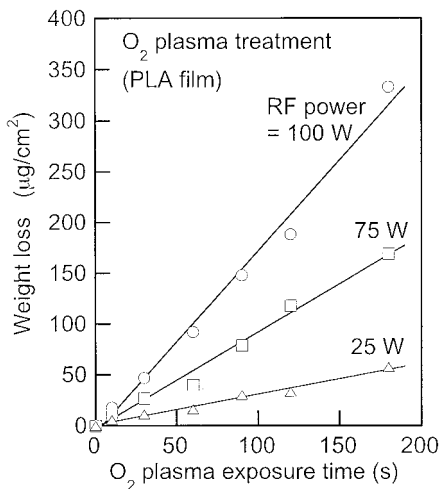


Figure 3 Weight loss of PLA films by oxygen-plasma exposure as a function of the plasma-exposure time and rf power.

comparison, we conclude that the PLA film is easy to subject to degradation reactions and that the PBN film is difficult to subject to degradation reactions. This conclusion means that the plasma susceptibility is related to the chemical composition of the polymer chains. Polyester chains containing aliphatic groups are susceptible to plasma and weight-loss reactions. However, polyester chains containing aromatic groups are not as susceptible to plasmas and are more resistant to weight-loss reactions.

Contact angle of water on the polyester film surfaces treated with the argon and oxygen plasmas

The contact angle of water on the plasma-treated polyester film surfaces was measured so that their modi-

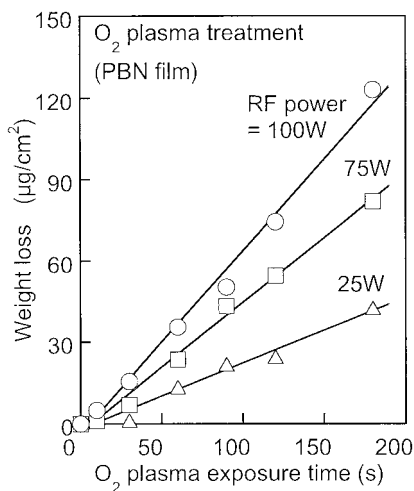


Figure 4 Weight loss of PBN films by oxygen-plasma exposure as a function of the plasma-exposure time and rf power.

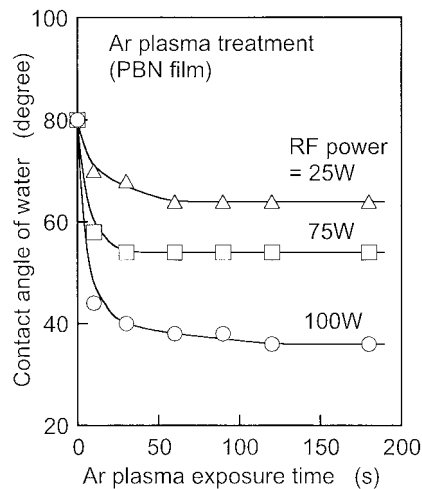


Figure 5 Contact angle of water on PBN film surfaces treated with argon plasma as a function of the plasma-exposure time and rf power.

fications by the plasmas could be determined. Three polyester films (PLA, PET, and PBN) were exposed to argon or oxygen plasma at rf powers of 25–100 W for 10–180 s, and then the film surfaces were rinsed with ethanol or acetone for the removal of degradation products deposited on the surfaces. Afterwards, against the plasma-treated and rinsed film surfaces, the water contact angle was measured as a function of the plasma-exposure time and rf power. Figure 5 shows typical results for water contact angles on argon-plasma-treated PBN film surfaces as functions of the argon-plasma-exposure time and rf power. The argon-plasma exposure for a short time of 10 s leads to a large decrease in the contact angle. The contact angle, as shown in Figure 5, decreases from 80 (unexposed film) to 58° (10-s exposure). Afterward, the contact angle continues to show a small decrease with increasing exposure time, and it reaches a constant level (54°) at an exposure time of 120 s. For an evaluation of the effects of the plasma exposure on the surface modification reactions, the contact angles for the three polyester (PLA, PET, and PBN) films treated with argon and oxygen plasmas for 120 s are summarized in Table II as functions of the kind of plasma and rf power. The contact angles for the original (not yet plasma-treated) PLA, PET, and PBN films are 74, 78, and 80°, respectively. There is not a large difference in the contact angles of the three original films. Once these films are exposed to argon or oxygen plasmas, there is a large difference in the contact angles of the plasma-exposed films. PLA shows no change in the contact angle from the argon- and oxygen-plasma exposures, even at an rf power of 100 W. However, PET films show a large decrease in the contact angle from the argon- and oxygen-plasma exposures. For example, the contact angle for PET films decreases from 78

TABLE II
Contact Angle of Water on PLA, PET, and PBN Films
Treated with Ar and O₂ Plasmas for 120 s

Plasma-exposure conditions			Contact angle of water (°)		
Plasma	RF power (W)	Exposure time (s)	PLA	PET	PBN
Not treated	—	—	74	78	80
Ar plasma	25	120	74	32	64
	75	120	74	28	54
	100	120	74	24	36
O ₂ plasma	25	120	74	26	56
	75	120	74	16	52
	100	120	74	16	44

(for the original PET film) to 28 and 16° after exposure to the argon and oxygen plasmas at 75 W. The PBN films also show some decrease in the contact angle from the argon- and oxygen-plasma exposures, but the magnitude of the decrease is not as large as that for the PET films. The contact angles for the PBN films treated with argon- and oxygen-plasma exposure are 54 and 52°, respectively.

These comparisons show that PET and PBN film surfaces are effectively modified to become more hydrophilic by either the argon or oxygen plasma. However, the PLA film surface is never modified even by argon and oxygen plasmas. The reason that the PLA film contact angles are never changed by plasma exposure, even though PLA films have significant weight-loss reactions, is discussed later on the basis of the results from XPS analyses.

Chemical compositions of the polyester film surfaces treated with the argon and oxygen plasmas

From the weight-loss rate and contact-angle measurements, we observe that the PLA film is distinguished from the PET and PBN films with respect to the interaction reactions with argon and oxygen plasmas. When PLA films are exposed to argon and oxygen plasmas, degradation reactions are initiated on the film surfaces, but the surfaces are not made more hydrophilic. However, the PET and PBN films show hydrophilic modification and a weight-loss process. There is one main difference in the chemical compositions of the PLA film and the PET and PBN films. The PLA film is composed of aliphatic carbon chains and ester groups and contains no aromatic group in the polymer chains. The PET and PBN films contain aromatic groups in the polymer chains, although the PET film contains aliphatic carbons. To investigate the influence of this difference on film surfaces treated with plasmas, we analyzed them with XPS.

The C1s and O1s spectra for the original PLA film surfaces, as shown in Figures 6 and 7, are composed of three and two main components, respectively. The three decomposed components are illustrated as dotted lines in the figures. The three components for the C1s spectrum are assigned to CH groups, C—O groups in ester linkages, and C=O groups in ester linkages at 285.0, 287.0, and 289.0 eV, respectively.⁶ The concentrations of these CH, C—O, and C=O components have been estimated from the peak areas to be 36, 31, and 33%, respectively, corresponding well to the expected values (33.3% each for CH, C—O, and C=O groups) calculated from the repeat unit of the PLA film (Table III). However, the two components for the O1s spectrum are due to O=C and O—C groups at 532.3 and 533.9 eV, respectively.⁶ The concentrations of the O=C and O—C groups are 49 and 51%, respectively, corresponding well to the values (50 and 50%) calculated from the repeat unit of the PLA film (Table III). The argon-plasma-treated PLA film surface shows similar C1s and O1s spectra, which are decomposed into three and two components, respectively (Figs. 6 and 7). The O/C atom ratio for the argon-plasma-treated PLA film is 0.61, which is unchanged in comparison with that for the original PLA (O/C atom ratio = 0.59). The concentrations of CH, C—O, and C=O groups are 41, 30, and 29%, respectively; and those of O=C and O—C groups are 49 and 51%, respectively (Table III). These spectral results indicate that the argon-plasma-treated PLA film surface may almost be the same in its chemical composition as that of the original PLA film surface, even though the film surface is exposed to argon plasma at an rf power of 75 W for 120 s. From these results, we believe that argon-plasma exposure always leads to a fresh surface for the PLA film, and as a result, the argon-plasma-treated film surface shows the same chemical composition as the original PLA film surface.

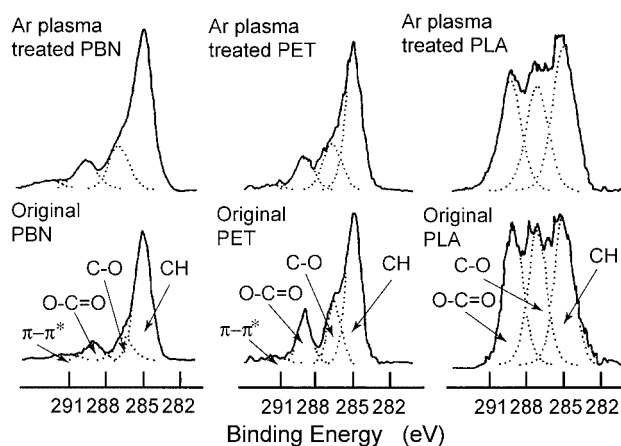


Figure 6 XPS (C1s) spectra for PLA, PET, and PBN film surfaces treated with argon plasma.

TABLE III
Chemical Compositions of PLA, PET, and PBN Film Surfaces Treated with Argon and Oxygen Plasmas at 75 W for 120 s

Polymer	O/C atomic ratio	C1s component (%) ^a			O1s component (%) ^b	
		1	2	3	1	2
Original PLA	0.59	36	31	33	49	51
Ar-plasma-treated PLA	0.61	41	30	29	49	51
Original PET	0.34	58	22	20	50	50
Ar-plasma-treated PET	0.31	59	24	17	47	53
O ₂ -plasma-treated PET	0.35	62	19	19	52	48
Original PBN	0.24	75	13	12	51	49
Ar-plasma-treated PBN	0.30	69	19	14	47	53
O ₂ -plasma-treated PBN	0.34	69	21	10	45	55

^a C1s component 1 at 285.0 eV due to CH₃, CH₂, and CH components. C1s component 2 at 286.6–287.0 eV due to the C—O component. C1s component 3 at 288.9–289.1 eV due to the C=O component. C1s component 4 at 291.4–291.8 eV due to the π - π^* component.

^b O1s component 1 at 531.9–532.3 eV due to the O=C component. O1s component 2 at 533.5–533.9 eV due to the O—C component.

The PBN film surfaces treated with argon and oxygen plasmas show increases in the O/C atom ratio from 0.24 for the original PBN film to 0.30 and 0.34, respectively (Table III). This increase indicates the formation of some oxygen functional groups on the PBN film surface by the argon- and oxygen-plasma exposures. The C1s spectrum for the original PBN film is decomposed into four components due to CH (at 285.0 eV), C—O (at 286.6), and C=O groups (at 289.1 eV) and a π - π^* shake-up satellite (at 291.4 eV; Fig. 6). The O1s spectrum also is decomposed into two components due to O=C (at 532.2 eV) and O—C groups (at 533.9 eV). The argon- and oxygen-plasma-treated PBN film surfaces show C1s and O1s spectra similar to those for the original PBN film surface. These spectra are decomposed into four components for the C1s spectra and two components for the O1s spectra. Their concentrations are summarized in Table III. The C—O

component (at 286.6–287.0 eV) for the plasma-treated PBN films has a larger concentration than that for the original PBN film; this indicates that new C—O groups are formed on the PBN film surfaces by the plasma exposure. The relative concentration of the π - π^* shake-up satellite (at 291.4–291.8 eV) is within an experimental error of $\pm 1\%$. The concentration of the π - π^* shake-up satellite is 4.9% for the original PBN film and 4.5 and 4.3% for the argon- and oxygen-plasma-treated PBN films, respectively. This indicates that most of the aromatic groups in the PBN polymer chains are not broken down by plasma exposure and that C—O groups are formed in the PBN polymer chains.

From the results, we can conclude that the PLA film surface is not modified in its chemical composition. However, the PBN film surfaces are modified in their chemical compositions. C—O groups are formed in the PBN polymer chains.

This is the main difference in modification reactions occurring with the PLA and PBN film surfaces. This difference may be due to the chemical compositions of the polymer chains. The PLA film is composed of aliphatic carbon chains and ester groups, whereas the PBN film consists of aromatic carbon chains and ester groups.

Now we discuss why the PLA film surface is not modified but the PBN film surface is modified to form C—O groups on the film surfaces. It is well known that during the exposure of polyesters to high-energy radiation such as γ and ionizing rays, C—O bonds in the ester groups are scissored to form radicals at the ends of the polymer chains.^{7,8} Degradation reactions are initiated from the radicals, and degradation products with low molecular weights are deposited on the surface. A similar bond scission will occur during

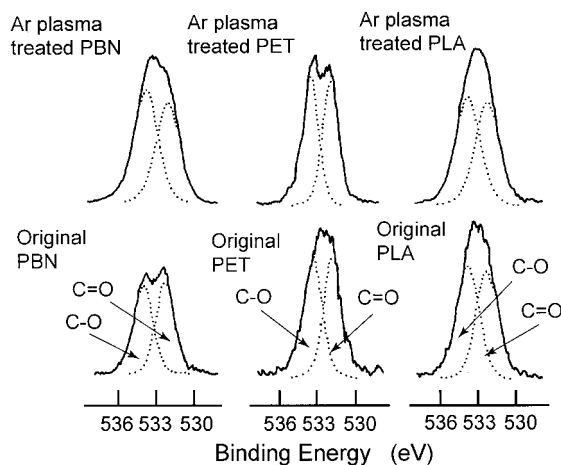


Figure 7 XPS (O1s) spectra for PLA, PET, and PBN film surfaces treated with argon plasma.

plasma exposure, and radicals will be formed at the ends of the polymer chains. Typical degradation reactions are shown in Figure 8 for the PLA film and in Figure 9 for the PBN film. In degradation reactions for the PLA film (Fig. 8), the C—O bond scission will lead to the formation of two radicals, A1 and A2, at the polymer chain ends. Subsequently, A1 and A2 will transform into A3 and A4 radicals, respectively, with the elimination of small molecules such as CO₂ and CH₂=CH₂. A3 and A4 radicals will transform into A5 and A2 radicals, respectively. The A5 radical will transform into an A3 radical for the elimination of CO. Once C—O bond scission in the PLA film occurs, chain reactions (A1—A3—A5—A1 and A2—A4—A2) will be initiated from the polymer chain ends. The chain reactions will continue as long as the radicals exist at the polymer chain ends. Consequently, when these reactions proceed completely, no radical will remain on the PLA film surface after the plasma exposure is finished. Therefore, no oxygen functional group will form on the PLA film surface. We believe that the oxygen functional groups formed by the plasma exposure may be due to a postoxidation of the radicals remaining on the film surfaces. The plasma-treated PLA film surface shows no improvement in the hydrophilic properties in comparison with the original film surface. This is our interpretation of the modification of the PLA film surface by plasma irradiation.

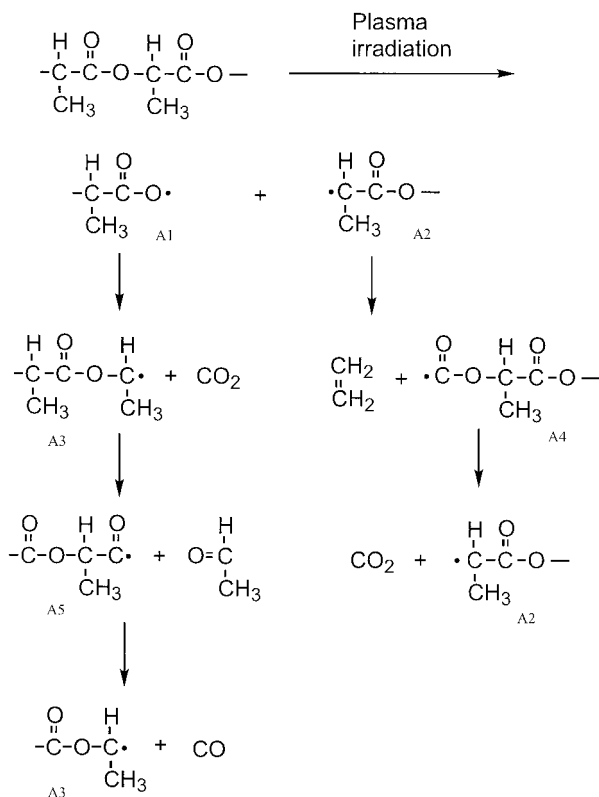


Figure 8 Possible degradation reactions occurring on PLA film surfaces during plasma irradiation.

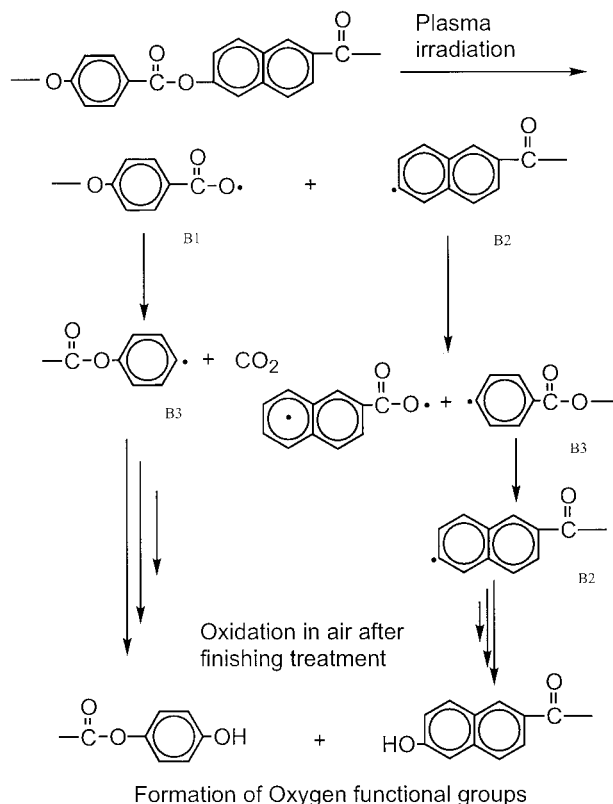


Figure 9 Possible degradation reactions occurring on PBN film surfaces during plasma irradiation.

The instability of radicals such as A2 and A3 may be the cause of the PLA film surfaces not being made hydrophilic by the plasma exposure.

However, PBN films also undergo the scission of ester groups to form two radicals, B1 and B2 (Fig. 9). Each of these radicals will subsequently convert into B3 radicals with the elimination of small molecules such as CO₂. Some B2 and B3 radicals will remain on the PBN film surface because of their high stability due to delocalization. The B2 and B3 radicals will be oxidized to form oxygen functional groups. The PBN film surface is modified to become more hydrophilic (low water contact angle).

CONCLUSIONS

Three polyester films, composed of different repeating units (PLA, PET, and PBN), were used as specimens, and their modification by plasma was investigated from the viewpoint of how the chemical compositions of the polymer chains influenced the plasma modification. The main results can be summarized as follows:

1. There are large differences in the compensated rates of weight loss of the three polyester films. The PLA film shows the highest rate for the

weight-loss process, and the PBN film shows the lowest rate. The plasma susceptibility is related to the chemical composition of the polymer chains. Polyester chains containing aliphatic groups are susceptible to plasma and weight-loss reactions. However, polyester chains containing aromatic groups are not as susceptible to plasmas and are more resistant to weight-loss reactions.

2. PET and PBN film surfaces can effectively be modified to become more hydrophilic with either argon or oxygen plasma. However, the PLA film surface is not made more hydrophilic by the plasmas. Its contact angle (74°) is the same as that of the original (74°).
3. XPS spectra show that the PLA film surface is not modified in its chemical composition, but the PBN film surfaces are modified in their chemical composition, forming C—O groups in the PBN polymer chains.
4. Aromatic groups in the polymer chains play an important role in modification by plasmas. The

delocalization and stabilization of radicals by aromatic groups may contribute to the formation of oxygen functional groups such as C—O groups in polyester polymer chains.

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