Comparative Studies on Surface Modification of Poly(ethylene terephthalate) by Remote and Direct Argon Plasmas

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ABSTRACT: Surface modification of poly(ethylene terephthalate) (PET) film by an argon (Ar) plasma was investigated as a function of the distance from the Ar plasma zone. Changes in distance between the PET film and the Ar plasma zone had a strong influence on the surface modification of the film. The direct Ar plasma treatment (distance between the PET film and Ar plasma zone = 0 cm) was effective in hydrophilic surface modification, but heavy etching reactions occurred during the modification. On the other hand, the remote Ar plasma treatment (distance between the PET film and Ar plasma zone = 80 cm) modified the PET film surfaces to be hydrophilic without heavy etching reactions, although the hydrophilicity of the PET was lower than that by the direct Ar plasma. The remote Ar plasma treatment was distinguished from the direct Ar plasma treatment from the viewpoint of degradation reactions. The remote Ar plasma treatment rather than the direct Ar plasma treatment was an adequate procedure for surface modification and caused less polymer degradation on the film surface. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 808–815, 2001

Key words: surface modification; poly(ethylene terephthalate); remote and direct argon plasmas

INTRODUCTION

Plasma containing electrons, ions, and radicals can interact with polymer surfaces and modify their chemical and physical properties. Surface modification is mainly due to the formation of functional groups on their surfaces (process I) and the etching of their surfaces (process II). In process I the radicals in the plasma abstract hydrogen atoms from the polymer surface to form carbon radicals on the surface. The carbon radicals combine with other radicals in the plasma to form new functional groups on the polymer surface.

This is an essential reaction for the formation of functional groups on the polymer surface.[1] On the other hand, in process II the electrons and ions bombard the polymer surface, causing C—C bond scission of polymer chains to form carbon radicals at the end of the polymer chains. Degradation reactions of the polymers are initiated from the carbon radicals at the polymer chain ends. Degradation products with low molecular weight and an injured layer (weak boundary layer) are formed on the polymer surface. This is an essential reaction for the etching of the polymer surfaces.[1] The etching of polymer surfaces is not usable for surface modification, because degradation products with low molecular weight are formed on the polymer surfaces by the etching. As long as plasma is used to develop reactive species for modification of polymer surfaces, the etching pro-
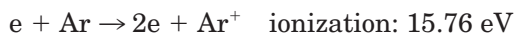
cess is unavoidable during the modification reactions.

We pointed out a large difference in the lifetime between a hydrogen radical (H) and electron or hydrogen ions (H^+ and H_2^+) in a hydrogen plasma.[2] Hydrogen radicals have longer lifetimes than electrons and hydrogen ions. As a result, the hydrogen radical is a predominant component at a special distance far from the plasma zone, and it plays an important role in the surface modification process. The electron and hydrogen ion are minor components at this position, and the etching reaction becomes negligible. This is a basic concept of "remote plasma treatment." We call the conventional plasma treatment "the direct plasma treatment" to distinguish it from the remote plasma treatment. The difference between the remote and direct plasma treatments is the relative position of the polymer samples from the plasma zone. The effects that differentiate the remote and direct plasma treatments were experimentally shown in the case of poly(tetrafluoroethylene) (PTFE). PTFE films were treated by the remote (at an 80-cm distance from the hydrogen plasma zone) and direct (at a 0-cm distance) hydrogen plasmas (at an RF power of 100 W), and their surface topology was compared.[3] Figure 1 shows typical SEM pictures for the remote and direct hydrogen plasma treated PTFE film surfaces. The remote hydrogen plasma produced less damage on the PTFE film surface; its surface topology was similar to that of the original PTFE film. On the other hand, the direct hydrogen plasma injured the PTFE film surface, and the surface topology was apparently different from that of the original PTFE. This comparison shows that the ion and electron bombardments lead to extensive surface modification of polymers.
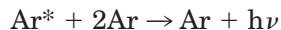
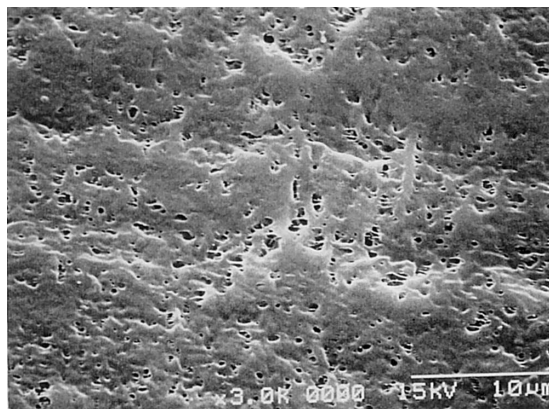The essential processes occurring in an argon (Ar) plasma are ionization,

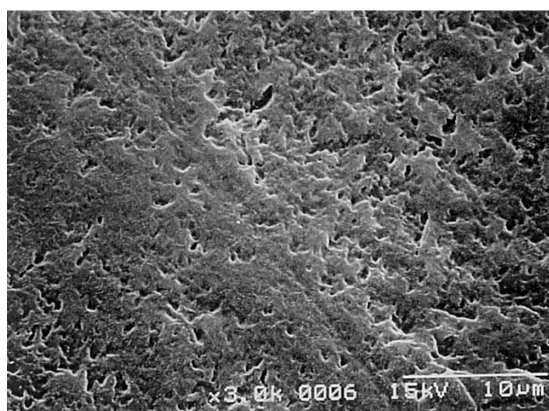$$e + Ar \rightarrow 2e + Ar^+ \quad \text{ionization: 15.76 eV}$$

excitation,

$$e + Ar \rightarrow e + Ar^* \quad \text{excitation to 2p: 11.56 eV}$$

relaxation,
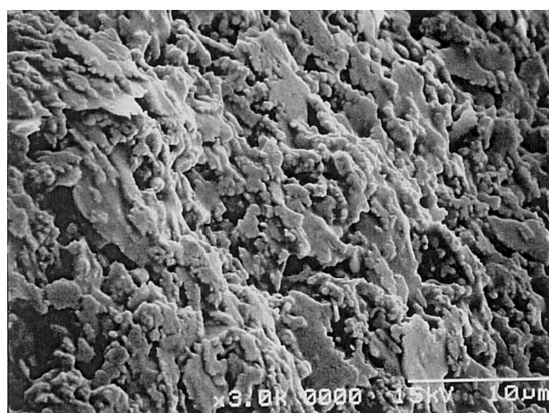
$$Ar^* + 2Ar \rightarrow Ar + h\nu$$

and charge transfer,
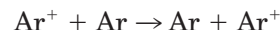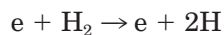

(a)

(b)

(c)

Figure 1 SEM pictures of PTFE surfaces treated with the remote and direct H_2 plasmas: (a) original PTFE, (b) treated with the remote H_2 plasma at 100 W for 120 s, and (c) treated with the direct H_2 plasma at 100 W for 30 s.

$$Ar^+ + Ar \rightarrow Ar + Ar^+$$

These are essential processes in the Ar plasma.[4] In the Ar plasma there is no dissociation,

$$e + H_2 \rightarrow e + 2H$$

that makes radicals such as H radicals in H_2 plasma. This is the essential difference between a noble gas plasma such as Ar and a diatomic-molecule plasma such as H_2 and O_2. When polymer materials are exposed to an Ar plasma, electrons, argon ions (Ar^+), and argon excimers (Ar^*) interact with the polymer surface, but there is never an interaction with radicals. As a result, etching reactions become predominant, C—H and C—C bonds in the polymer chains are broken, and there is carbon radical formation on the polymer surface. A new functional group is never formed by recombination reactions between the carbon radical formed in the polymer chains and other radicals, because there is no radical in the Ar plasma, although oxidized groups are formed when the carbon radicals are exposed to air. Therefore, we believe that the Ar plasma treatment shows surface modification by etching reactions. An analysis of the effects of the Ar plasma treatment may give us important insight into how to control plasma for surface modification without etching reactions.

In this study we investigated how the Ar plasma modified the polymer surfaces. For practical reasons, a poly(ethylene terephthalate) (PET) film was used as a polymer material for the surface modification; the surface modification was evaluated as a function of the distance from the Ar plasma zone.

EXPERIMENTAL

Materials

The PET film was received from Toyobo Co. (trade name BOPET, a film thickness = 38 μm) and was cut to 12 × 90 mm dimensions to be used as specimens for surface modification experiments. Prior to the surface modification experiment, the PET films were washed with acetone in an ultrasonic washer and dried at room temperature under a vacuum. The Ar (99.995% purity) was purchased from Teikoku Sanso Co. and used without further purification.

Remote and Direct Ar Plasma Treatments of PET Sheets

A special reactor was used for the remote and direct Ar plasma treatments of the PET sheets.

The details of the reactor were described in a previous article.[5] The reactor consists of a cylindrical Pyrex glass tube (45-mm diameter, 1000-mm length) and a columnar stainless steel chamber (300-mm diameter, 300-mm height). The Pyrex glass tube has two gas inlets for the injection of argon gas and a copper coil (nine turns) for the energy input RF power (13.56-MHz frequency). The stainless steel chamber contains a Barocel pressure sensor (model 622, Edwards) and a vacuum system composed of a combination of a rotary pump (320 L/min) and a diffusion pump (550 L/s, YH-350A, Ulvac Co.). A Viton O ring flange is used to join the Pyrex glass tube to the chamber.

The PET films were positioned at a constant distance of 0 (direct Ar plasma treatment), 40, and 80 cm (remote Ar plasma treatment) from the center of the copper coil and exposed to the argon plasma. First the air in the reactor was displaced with argon. Afterward, the reactor was evacuated to approximately 1.3×10^{-2} Pa, and then argon was introduced into the Pyrex glass tube with a flow rate of 10 mL (STP)/min adjusted by a mass flow controller. The Ar plasma was operated at RF powers of 75 W at a 13.56-MHz frequency at a system pressure of 13.3 Pa for 5–180 s.
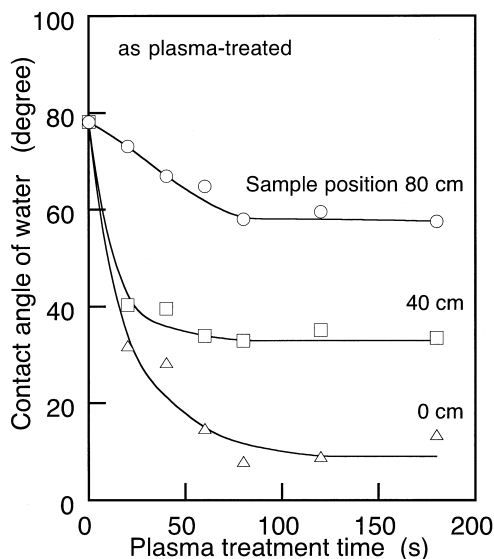
Contact Angle of Water on Ar Plasma Treated PET Film Surfaces

Using the sessile drop method,[6] the contact angles of the water on the PET film surfaces treated with the remote and direct Ar plasmas were measured at 20°C using a contact angle meter with a goniometer (model G-1, Erma Co. Ltd.). An average contact angle was determined from 10 measurements with an experimental error of 3–4°.

X-Ray Photoelectron Spectroscopy (XPS) of Ar Plasma Treated PET Films

XPS spectra for PET film surfaces treated with the remote and direct Ar plasmas were obtained on a Shimadzu ESCA K1 spectrometer using a nonmonochromatic MgKα photon source at a 12-kV anode voltage, a 20-mA anode current, and a 1.5×10^{-6} Pa pressure in the analytical chamber. The XPS spectra were referenced with respect to the 285.0 eV carbon 1s core level to eliminate charging effects. The spectra were not modified by the smoothing procedure. The C_{1s} and O_{1s} spectra were deconvoluted by fitting a Gaussian–Lorentzian mixture function (mixture ratio = 80 :

Figure 2 The contact angle of water on PET film surfaces treated with the Ar plasma at 75 W as functions of the sample position from the plasma zone and plasma treatment time.

20) to an experimental curve using a nonlinear least squares curve-fitting program (ESCAPAC) supplied by Shimadzu. Sensitivity factors (S) for the C_{1s}, O_{1s}, and N_{1s} core-level spectra were $S(C_{1s}) = 1.00$, $S(O_{1s}) = 2.85$, and $S(N_{1s}) = 1.77$. The O/C and N/C atomic ratios were calculated from the C_{1s}, O_{1s}, and N_{1s} intensities; their experimental error was within 0.03.

Peroxide Concentration on Ar Plasma Treated PET Film Surfaces

Peroxide groups formed on PET film surfaces by the remote and direct Ar plasma treatments and then exposed to air were analyzed by the iodide method.[7] The treated PET film surfaces were immersed in a 2-propanol/benzene (6 : 1 volume ratio) solution of sodium iodide, which contained a trace of ferric chloride (1 ppm), at 60°C for 10 min. The peroxide groups were reduced with iodide ions; as a result, iodine was formed in the mixture solution. The concentration of peroxide groups on the PET film surfaces was determined from the absorption intensity of iodine liberated in the mixture solution at 360 nm.

RESULTS AND DISCUSSION

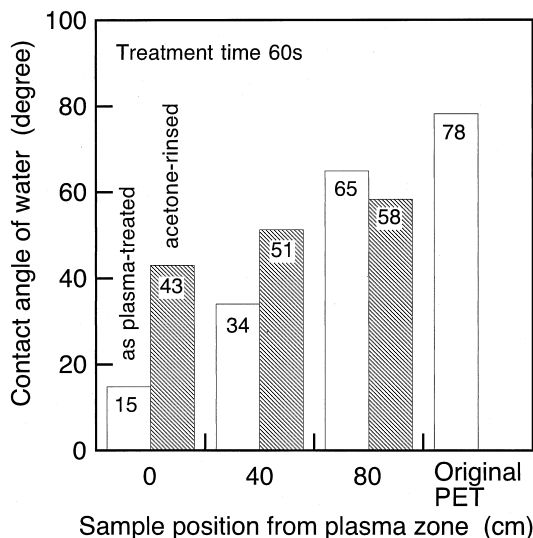### Contact Angle of Water on PET Film Surfaces Treated with Remote and Direct Ar Plasmas

The PET films were positioned at 0, 40, and 80 cm from the Ar plasma zone and treated with the Ar

plasma at 75 W as a function of treatment times of 20–180 s. The plasma treated PET films were divided into two groups for the contact angle measurements. Group A was the plasma treated PET films, and group B was the PET films treated with the Ar plasma and then rinsed with acetone using an ultrasonic washer for 5 min. Figures 2 and 3 show the contact angle of water on the two categorized PET film surfaces (groups A and B) as functions of the sample position and treatment time. For group A the contact angle decreased with increasing plasma treatment time and reached a constant level for treatment times of 60–80 s (Fig. 2). The constant level was strongly related to the sample position. The contact angle at a treatment time of 60 s was 15° at a sample position of 0 cm, 34° at 40 cm, and 65° at 80 cm. This comparison shows that the direct Ar plasma is more effective in hydrophilic surface modification than the remote Ar plasma.

For group B the contact angle also decreased with increasing plasma treatment time and leveled off after a plasma treatment time of 60 s, except for the PET films treated at a sample position of 0 cm (direct Ar plasma treatment, Fig. 3). A comparison of Figures 2 and 3 shows a large difference in the contact angle between groups A and B. Group B always had a larger contact angle than group A. A typical comparison is shown in Figure 4; here changes from the acetone rinsing
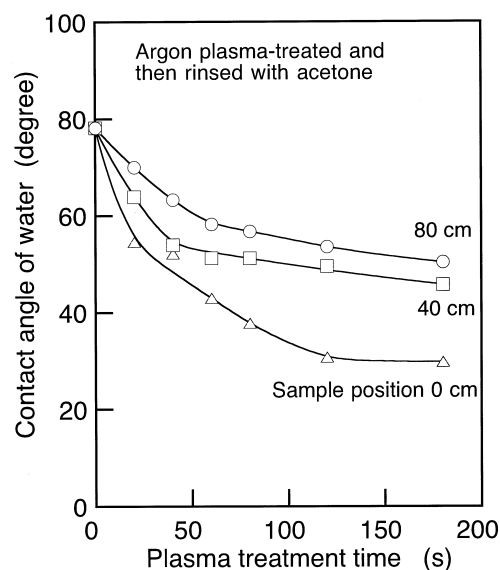
Figure 3 The contact angle of water on PET film surfaces treated with the Ar plasma at 75 W and rinsed with acetone as functions of the sample position from the plasma zone and plasma treatment time.

Figure 4 The contact angle of water on PET film surfaces treated with the Ar plasma at 75 W for 60 s as functions of the sample position from the plasma zone and acetone rinsing.

are illustrated for the PET films treated with the Ar plasma for 60 s. At a sample position of 0 cm (the direct plasma treatment), the contact angle was increased from 15 to 43° (28° difference) by the acetone rinsing; the contact angle of the 40-cm sample was also increased from 34 to 51° (17° difference). On the other hand, the change for the 80-cm sample was very small. The contact angle before the acetone rinsing was 65° and that after the acetone rinsing was 58°. These changes indicate that some products were formed on the PET film surfaces by the Ar plasma treatment. Products were removed from the PET film surfaces by the acetone rinsing. As a result, a large difference in the contact angle resulted between the PET film surfaces before and after the acetone rinsing. We believe that the products may be small molecules that were formed by the degradation reactions of the PET polymers. From this viewpoint, the difference in the contact angle between the PET film surfaces before and after the acetone rinsing may be evaluated as an indicator of the extent of the etching reactions occurring during the Ar plasma treatment. In this sense, the direct Ar plasma treatment leads to strong hydrophilic surface modification but with heavy etching reactions occurring. On the other hand, although the remote Ar plasma treatment is less effective in hydrophilic surface modification than the direct Ar plasma treatment, more limited etching reactions occur in the remote plasma treatment process.

From these results we can conclude that the direct Ar plasma treatment is effective in hydrophilic surface modification, but heavy etching reactions occur during the plasma treatment process. The directly plasma treated PET films have damaged surfaces, which are etched and contain many degradation products that are easily removed by acetone rinsing. On the other hand, the remote Ar plasma treatment makes PET film surfaces hydrophilic without heavy etching reactions. Deposition of degradation products on the surface is small.

Peroxide Groups Formed on PET Film Surfaces by Remote and Direct Ar Plasma Treatment

When electrons and ions with high energy bombard PET film surfaces, C—O bond scission in the ester groups and decarboxylation occur and rupture the PET polymer chains. As a result, carbon radicals are formed at the polymer chain ends and degradation products, which are pieces of the PET polymer chains and of low molecular weight, are deposited on the PET film surfaces. The carbon radicals are oxidized into peroxides when the PET films are taken out of the plasma reactor and exposed to air. This is an essential process for the peroxide formation. If electrons and ions with high energy do not touch the PET film surface, no peroxide or degradation product will be formed on the PET film surface. From this viewpoint, we believe that peroxide concentration is an indicator of whether electrons and ions interact with PET film surfaces.

The peroxide concentrations on the PET film surfaces, when the surfaces were treated with the remote and direct Ar plasmas, were determined and are summarized in Table I. The peroxide

Table I   Peroxide Concentration on Ar Plasma Treated PET Film Surfaces

Plasma Treatment				
RF Power (W)	Time (s)	Sample Position (cm)	Acetone Rinsed	Peroxide Conc ($\times 10^{15}$ numbers/cm^2)
75	60	80	No	2.8
			Yes	2.8
75	60	0	No	2.7
			Yes	2.7

Table II   Atom Composition and Relative Concentration of C_{1s} and O_{1s} Components for Ar Plasma Treated PET Film Surfaces

| Plasma Treatment | | | | Atom Composition O/C Atom Ratio | C_{1s} Components (%) | | | O_{1s} Components (%) | |
RF Power (W)	Time (s)	Sample Position (cm)	Acetone Rinsed		CH_2	C—O	C=O	O=C	O—C
Original			Yes	0.34	58 (1.4)[a]	22 (1.2)	20 (1.2)	50 (1.5)	50 (1.6)
75	60	80	No	0.34					
			Yes	0.33	67 (1.5)	16 (1.2)	17 (1.2)	52 (1.6)	48 (1.5)
75	60	0	No	0.42					
			Yes	0.31	59 (1.5)	24 (1.8)	17 (1.8)	47 (1.7)	53 (1.9)

[a] Full-width at half-maximum (eV).

concentrations were $2.7–2.8 \times 10^{15}$ numbers/cm^2, which are higher than those for low-density PE film ($6.0–6.3 \times 10^{14}$ numbers/cm^2)[7] and polyimide film ($4.4–4.6 \times 10^{14}$ numbers/cm^2).[8] Ester groups in the PET films may contribute this high concentration of peroxide groups.

The peroxide concentration as shown in Table I is 2.8×10^{15} numbers/cm^2 for the PET film surface treated with the remote Ar plasma and 2.7×10^{15} numbers/cm^2 for the PET film surface treated with the direct Ar plasma. There was little difference in the peroxide concentration between the two plasma treated PET film surfaces. This indicates that electrons and ions touched the PET film surface, which was positioned at a distance of 80 cm from the plasma zone, and peroxide groups were formed on the surface. The efficiency of the formation of peroxide groups by the electron and ion bombardment is almost the same at positions of 80 cm (remote Ar plasma treatment) and 0 cm (the direct Ar plasma treatment). This is surprising evidence because there was a large difference in the water contact angle between the PET film surfaces treated at sample positions of 80 and 0 cm with the Ar plasma (Fig. 4). Another surprising observation was that the peroxide groups formed on the PET film surfaces were never lost by the acetone-rinsing procedure. In the remote Ar plasma treatment, the PET film surface after the acetone rinsing showed a peroxide concentration of 2.8×10^{15} numbers/cm^2, which corresponded to that before the acetone rinsing. Similarly, in the direct Ar plasma treatment the peroxide concentration on the PET film surface after the acetone rinsing was 2.7×10^{15} numbers/cm^2, which corresponded to that before

the acetone rinsing. This comparison shows that all peroxide groups existed on the PET polymer chains and never existed on the degradation products, which were easily removed from the PET film surface by the acetone rinsing.

Chemical Composition for Remote and Direct Ar Plasma Treated PET Film Surfaces

The remote and direct Ar plasmas each showed different effects on the surface modification of PET films. The change in the chemical composition on the PET film surfaces occurring in both remote and direct Ar plasma treatment processes was investigated by XPS. The specimens for the investigation were the PET films treated with the remote (at 80 cm) and direct (at 0 cm) Ar plasmas at 75 W for 60 s. Table II shows the atom composition of the two plasma treated PET film surfaces. The O/C atom ratio for the original PET was 0.34, which was smaller than the calculated ratio (0.40) from the repeating unit ($C_{10}H_8O_4$) of the PET. We cannot interpret why there is a difference between the O/C atom ratios determined by XPS and calculated from the repeating unit. The remote Ar plasma treatment gave less change in the atom composition on the PET film surface, although the surface showed some decrease in the water contact angle. The O/C atom ratios were 0.34 before and 0.33 after the acetone rinsing. On the other hand, the direct Ar plasma treatment gave a large increase in the O/C atom ratio (0.42) for the PET film surface that was Ar plasma treated. However, when the treated PET film surface was rinsed with acetone, the O/C atom ratio decreased from 0.42 to 0.31. This com-
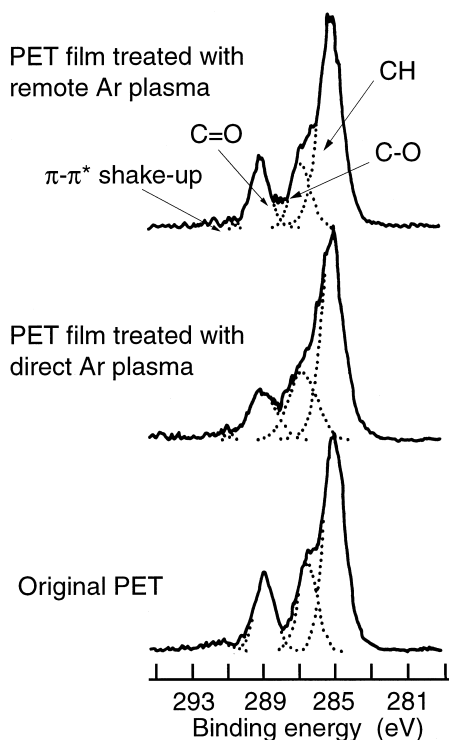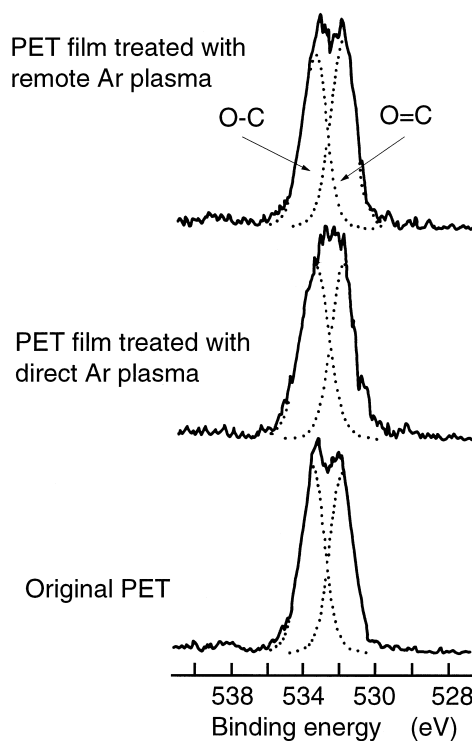
Figure 5 C_{1s} spectra for PET film surfaces treated with the remote and direct Ar plasma at 75 W for 60 s and rinsed with acetone. $(\cdot\cdot\cdot)$ The decomposed components.

parison indicates that the remote Ar plasma treatment did not form a distinguishable oxygen functional group, but the direct Ar plasma treatment formed oxygen functional groups on the PET film surface. However, most of the oxygen functional groups were easily removed from the PET film surface by the acetone rinsing. The oxygen functional groups may be low molecular weight fragments from the degradation of PET polymers. Therefore, the remote Ar plasma treatment is distinguished from the direct Ar plasma treatment by the degradation occurring on the PET film surface. The remote Ar plasma treatment is not effective in the surface modification, but it never injures the PET film surface. The direct Ar plasma treatment is effective, but it injures the film surface by etching reactions.

To discuss the details of the modification reactions by the remote and direct Ar plasmas, the C_{1s} and O_{1s} spectra were decomposed into special components. The specimens for the XPS measurements were the PET films treated with the remote (at 80 cm) and direct Ar plasmas (at 0 cm) at 75 W for 60 s and then rinsed with acetone. The C_{1s} and O_{1s} spectra are shown in Figures 5 and 6,

respectively, and the decomposed components are illustrated. The C_{1s} spectra consisted of three components: $\underline{C}H_2$ groups at 285.0 eV, $\underline{C}$—O groups at 286.5–286.7 eV, $\underline{C}$=O groups at 288.9–289.0 eV, and a π–π^* shake-up satellite near 290–292 eV.[9] The underlined letter is the objective atom for the assignment. The O_{1s} spectra also consisted of two components: $\underline{O}$=C groups at 531.9–532.1 eV and $\underline{O}$—C groups at 533.5–533.6 eV. The relative concentrations of these C_{1s} and O_{1s} components are listed in Table II. The relative concentrations of the CH_2, C—O, and C=O groups for the original PET film were 58, 22, and 20%, respectively, which corresponded well with those calculated from the repeating unit of the PET film (CH_2 group = 60%, C—O group = 20%, and C=O groups = 20%). For the PET films treated with the remote and direct Ar plasmas, there was no new C_{1s} and O_{1s} components besides the three components of the $\underline{C}H_2$, $\underline{C}$—O, and $\underline{C}$=O groups in the C_{1s} spectra and also besides the two components of the $\underline{O}$=C and $\underline{O}$—C groups in the O_{1s} spectra. There was only a small change in the relative concentration of the C_{1s} and O_{1s} components for the remote and direct Ar plasma treated

Figure 6 O_{1s} spectra for PET film surfaces treated with the remote and direct Ar plasma at 75 W for 60 s and rinsed with acetone. $(\cdot\cdot\cdot)$ The decomposed components.

PET film surfaces. For the PET film surface treated with the remote Ar plasma, some increase in the CH_2 concentration from 58 to 67% and only a few decreases in the C—O and C=O concentrations from 22 to 16% and 20 to 17%, respectively, were observed. For the O_{1s} spectrum the O=C and O—C components were merely changed from 50 to 52% and 50 to 48%, respectively. On the other hand, for the PET film surface treated with the direct Ar plasma, the CH_2 component was unchanged, the C—O component increased from 22 to 24%, and the C=O component decreased from 20 to 17%. The O=C component decreased from 50 to 47%, and the O—C component increased from 50 to 53%. As interpreted above, changes in the C_{1s} and O_{1s} components by the remote and direct Ar plasma treatments were small, although the treated PET film surfaces showed distinguished decreases in the water contact angle. For example, the remote and direct Ar plasma treated PET film surfaces, contact angle decreased from 78 to 58 and 43°.

From these results, it is hard to discuss which functional groups contribute to decreases in the water contact angle, because changes in the chemical composition of the PET film surfaces by the remote and direct Ar plasma treatments are not large enough to assign new functional groups.

CONCLUSION

Surface modification of PET film by an Ar plasma was investigated as a function of the distance from the Ar plasma zone. The relative distance between the PET film and the Ar plasma zone strongly influenced the surface modification of the film. The surface modification procedures at distances of 80 and 0 cm from the Ar plasma zone were done as typical experiments to investigate the influences of the relative distance. The surface modification procedures at relative distances of 80 and 0 cm from the Ar plasma zone were called remote and direct Ar plasma treatments, respectively, for convenience. The influences are summarized as follows:

1. The direct Ar plasma treatment was effective in hydrophilic surface modification, but heavy etching reactions occurred during the modification. The PET films treated with the direct AR plasma gave surfaces containing many degradation products that were formed by etching reactions and were easily removed by acetone rinsing. On the other hand, the remote Ar plasma treatment was able to modify the PET film surfaces' hydrophilicity without heavy etching reactions, although the hydrophilicity of the PET was lower than that by the direct Ar plasma.

2. Peroxide groups were formed on the PET film surface by the remote Ar plasma and the direct Ar plasma. All peroxide groups existed on the PET polymer chains and never existed on the degradation products that were easily removed from the PET film surface by the acetone rinsing.

In conclusion, the remote Ar plasma treatment is distinguished from the direct Ar plasma treatment by the degradation reactions. The remote Ar plasma treatment, rather than the direct Ar plasma treatment, is an adequate procedure for surface modification; it causes less polymer degradation on the film surface.

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