

Surface Modification of Aromatic Polyamide Film by Remote Oxygen Plasma

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ABSTRACT: Surface modification of poly(*p*-phenylene terephthalamide) (PPTA) film by a remote oxygen plasma treatment has been investigated from a viewpoint of comparison with a direct oxygen plasma treatment. We call the modification procedure in a space far away from the oxygen plasma zone "the remote oxygen plasma treatment," and the modification procedure in a space just in the oxygen plasma zone (a conventional oxygen plasma treatment) "the direct oxygen plasma treatment." In a space far away from the plasma zone, oxygen radicals rather than electrons and oxygen ions are predominant, and the PPTA film can be modified by the remote oxygen plasma treatment into a hydrophilic surface without heavy degradation of the PPTA film. The PPTA film surfaces modified by the remote oxygen plasma treatment were analyzed with contact angle measurement, scanning microscopy, atomic force microscopy, and X-ray photoelectron spectroscopy. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 831–840, 1997

Key words: surface modification; aromatic polyamide; remote plasma; plasma treatment; hydrophilic modification; XPS; contact angle

INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) is one of the most effective materials used as reinforcements for composites. Poor adhesion between the PPTA fiber and polymer matrices such as epoxy resins impedes application of the PPTA fiber as a reinforcement to polymer composites. Adhesion of the PPTA fiber has been improved by several methods.^{1–9} Plasma treatment is one of the effective surface modifications of polymeric materials for adhesion improvement. The plasma treatment is not effective for the PPTA fiber, but is effective for polyolefins and poly(ethylene terephthalate).^{2,8} The ineffectiveness is considered to be due to bond scission of the PPTA fiber occurring by the plasma treatment.¹⁰

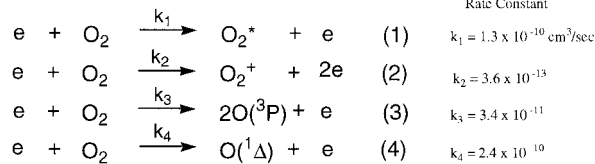
Plasma contains electrons, ions, and radicals (atoms) in a gas phase. These species are able to

interact with surfaces of polymeric materials to initiate chemical reactions such as hydrogen abstraction, bond scission, and radical formation. As a result, the surfaces are modified, e.g., from hydrophobic to hydrophilic. This is an essential mechanism of the plasma treatment. Hydrophilic surface modification by oxygen plasma is due to oxidation reactions with oxygen radicals. Oxygen ions and electrons in oxygen plasma are troublesome species for hydrophilic surface modification because their heavy collision with the polymer surface leads to the bond scission of the polymer chains. As a result, degradation products (oligomers) are formed at the surface and act as a weak boundary layer deteriorating the adhesion. Both oxidation and degradation reactions always occur in oxygen plasma treatment.¹¹ Although an extent of the degradation depends on the plasma operating conditions, such as rf input power and kind of plasma gasses, the plasma treatment never escapes from the degradation occurring at the surface. The hydrophilic surface modification

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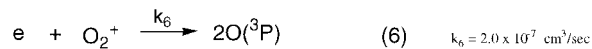
1. Generation of active species



2. Radiative decay of excimers



3. Recombination between electron and oxygen ion



4. Recombination between oxygen radicals

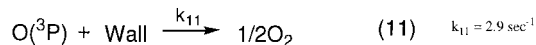
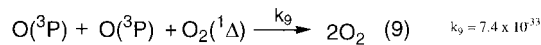
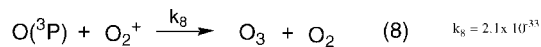
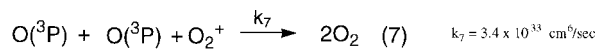


Figure 1 Elemental reaction in oxygen plasma.

by oxygen plasma is a key to how oxygen radicals in oxygen plasma interacts effectively with the polymeric materials without heavy attacks of oxygen ions and electrons.

Plasma is a mixture of electrons, ions, and radicals. These species disappear in the processes of electron–positive ion recombination, positive ion–negative ion recombination, and radical–radical recombination. The rate constant of these reactions is in the order of $10^{-7} \text{ cm}^3/\text{sec}$, $10^{-7} \text{ cm}^3/\text{sec}$, and $10^{-33} \text{ cm}^6/\text{s}$, respectively.¹² Therefore, radicals possess much longer lifetimes than electrons and ions. We expect that a radical concentration at a position far away from the plasma zone will become predominantly higher than electron and radical concentrations because of the lifetime difference. This is the concept of a remote plasma treatment. The remote plasma treatment is different from conventional plasma treatment with respect to relative distance of the sample position against the plasma zone: the sample in the remote plasma treatment is positioned away from the plasma zone, and the sample in the conventional plasma treatment is positioned just in the plasma zone. We call the usual plasma treatment the “direct plasma treatment” to distinguish it from the remote plasma treatment. In this study, we have investigated whether the remote

oxygen plasma treatment is able to modify PPTA surface without electron and ion attack or not.

THEORETICAL BACKGROUND OF REMOTE PLASMA TREATMENT

Activated species in oxygen plasma (that is, oxygen radicals, oxygen ions, and electrons) decay in manners of radioactive decay, recombination between electron and ion, and recombination between radicals. Essential reactions in the oxygen plasma are shown in Figure 1.^{13–17} When the recombination reactions between electrons and ions are faster than those between radicals, the oxygen radicals will have a longer lifetime than electrons and ions. Is this expectation true? We simulated the kinetics of oxygen plasma. A model shown in Figure 2 was applied for simulating the kinetics of oxygen plasma. A cylindrical tube is connected at one end to the oxygen plasma zone. Oxygen gas flows at a constant velocity of $V \text{ cm/s}$ from the plasma zone to the other end of the tube. The concentrations of oxygen radicals (C_r), oxygen ions (C_i), and electrons (C_e) at a distance of $z \text{ cm}$ from the edge of the plasma zone are simulated from the model. We consider the one-dimensional mass balance between positions of z and $z + dz$. The mass balance of the oxygen radicals is represented by two basic equations, eqs. (1) and (2). The differential coefficient (dJ_r/dz) of the oxygen radical flux (J_r) at a position of z is equal to the generation rate of oxygen radicals (R_r) in a space of dz .

$$\frac{dJ_r}{dz} = R_r \quad (1)$$

The J_r at z is given by two modes of the radical drifting (oxygen flux and diffusion):

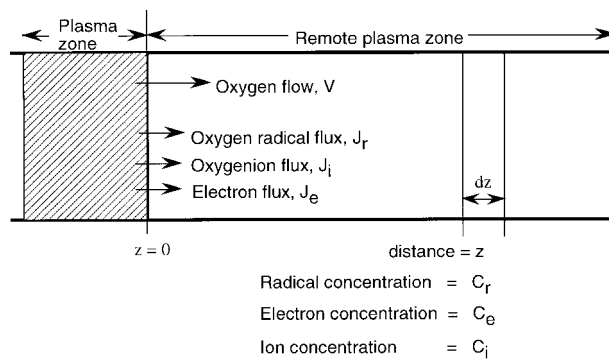


Figure 2 Model used for simulating the kinetics of oxygen plasma.

$$J_r = C_r V - D_r \frac{dC_r}{dz} \quad (2)$$

where C_r , V , and D_r are the oxygen radical concentration, the velocity of the oxygen flow, and the diffusion coefficient of the oxygen radicals, respectively. Since the diffusion velocity is much faster than the oxygen flux, eq. (2) is modified to become eq. (3):

$$J_r = D_r \frac{dC_r}{dz} \quad (3)$$

Combination of eqs. (1) and (3) gives the oxygen radical concentration as a function of the distance, z . Details of the simulation procedure are not described here because the procedure has been reported elsewhere.¹⁸ Consequently, the oxygen radical concentration (C_r) is written in eq. (4) as

$$C_r = C_r^0 \exp \left\{ - \left(\frac{k_{11}}{D_r} \right)^{0.5} z \right\} \quad (4)$$

where C_r^0 is the oxygen radical concentration at $z = 0$, and $(k_{11}/D_r)^{0.5}$ is $3.2 \times 10^{-2} \text{ cm}^{-1}$.

On the other hand, the electron and ion concentrations also are simulated in similar simulation procedures using the model shown in Figure 2. The electron (C_e) and oxygen ion concentrations (C_i) are written as follows:

$$C_e = C_e = C_i = \frac{C_c^0}{\left\{ 1 + \left(\frac{C_c^0 k_6}{6D_c} \right)^{0.5} z \right\}^2} \quad (5)$$

where C_c^0 is the electron and oxygen ion concentration at $z = 0$, and $(k_6/6D_c)^{0.5}$ is $1.3 \times 10^{-6} \text{ cm}^{-1}$.

Figure 3 shows the relative concentrations of oxygen radicals (C_r), oxygen ions, and electrons (C_e) as a function of the distance, z , which are calculated from eqs. (4) and (5). The oxygen ions and electrons decrease faster than the oxygen radical: for example, the relative concentration of the oxygen ions and electrons at a distance of 20 cm against the original concentrations in the plasma zone is only 1.2%, while that of the oxygen radicals is 53%. At a distance of 60 cm, the relative concentration of the oxygen ions and electrons is 0.15% and that of the oxygen radicals is 15%. The oxygen radical concentration (C_r^0) at a distance of zero ($z = 0$) is 10^5 to 10^6 times higher than the charged species concentration (C_c^0).¹⁹ Therefore,

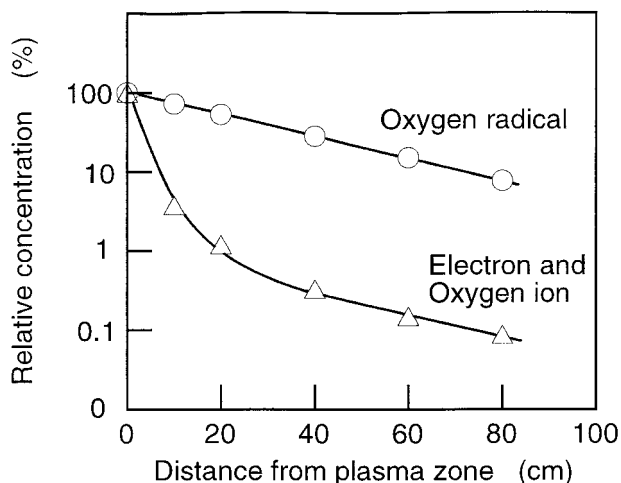


Figure 3 Relative concentration of oxygen radicals, and electrons and oxygen ions as a function of distance from the plasma zone.

we believe that the oxygen radicals become predominant species in spaces far away from the oxygen plasma zone. We expect a possibility that predominant interactions between oxygen radicals and the polymer surface will occur in a space far away from the oxygen plasma zone. We call the procedure in a space far away from the oxygen plasma zone a “remote oxygen plasma treatment,” and the procedure in a space just in the oxygen plasma zone (a conventional oxygen plasma treatment) a “direct oxygen plasma treatment.”

EXPERIMENTAL

Materials

Aramika™, kindly provided in the form of film 500 mm wide and 25 μm thick by Asahi Chemical Ind. Co. Ltd., Japan, was used as the PPTA sample. The PPTA film was washed with acetone in an ultrasonic washer prior to the surface modification experiments.

Plasma Reactor for Remote Oxygen Plasma Treatment

A special reactor was used for the remote oxygen plasma treatment. 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). One end of the Pyrex glass tube was jointed with the chamber by a Viton O-ring flange; at the other end of

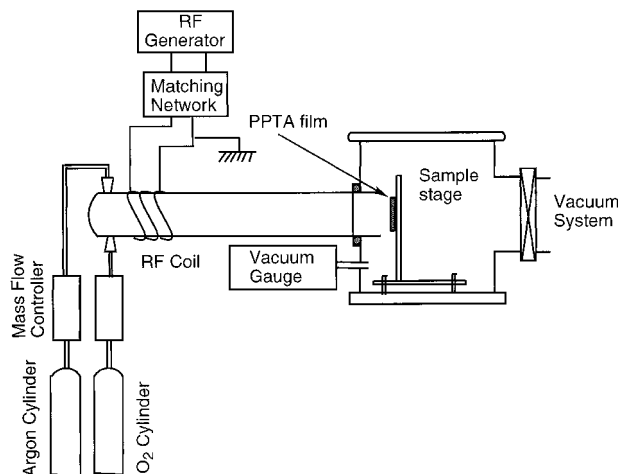


Figure 4 Schematic representation of remote plasma reactor.

the tube were two gas inlets for the injection of oxygen and argon gases and a copper coil of nine turns for the energy input of rf power (13.56 MHz frequency). In the stainless-steel chamber were a sample stage positioned at 80 cm from the copper coil for the rf power input; a Barocel pressure sensor (type 622, Edwards, England); and a vacuum system with a combination of a rotary pump (320 L/min) and a diffusion pump (550 L/s). The vacuum system can depress a pressure in the reaction chamber to an order of 10^{-3} Pa. A schematic diagram of the plasma reactor for the remote oxygen plasma treatment is shown in Figure 4.

Remote Oxygen Plasma Treatment

The PPTA films were mounted on the sample stage in the reaction chamber. Air in the reaction chamber was displaced with argon, and the reaction chamber was evacuated to approximately 0.13 Pa. Afterwards, oxygen gas whose flow rate was adjusted to 10 cm^3 (STP)/min by a mass flow controller (model SEC-400 MARK3; Estec Co., Japan) was introduced into the reaction chamber. The remote oxygen plasma treatment was performed at a system pressure of 13.3 Pa at an rf power of 50 W for 1 to 20 min.

Contact Angle of Water on the Remote Oxygen Plasma-Treated PPTA Films

Using the sessile drop method,²⁰ contact angles of water on the oxygen plasma-treated PPTA film surfaces were measured at 20°C using a contact-angle meter with a goniometer (Erma Co, Japan, model

G-1). A drop ($1 \mu\text{l}$) of water pushed out of a microsyringe was transferred to the surface of the PPTA specimens, and the height (h) and width (w) of the drop on the PPTA surface were measured using a telescope with a scale. A contact angle (θ) of the drop was estimated from the equation, $\theta/2 = \tan^{-1}(2h/w)$. The contact angle was determined from an average of ten measurements with a standard deviation of 1 degree. The contact angle determined by the sessile drop method is static, and is distinguished from dynamic contact angles such as advancing and receding contact angles.

X-ray Photoelectron Spectra (XPS)

XPS spectra of the surface of the PPTA films were obtained on a Shimadzu ESCA K1 (Japan) using a non-monochromatic MgK_{α} photon source. The anode voltage was 10 kV, the anode current was 30 mA, and the background pressure in the analytical chamber was 1.5×10^{-6} Pa. The X-ray spot was 2 mm in diameter, and take-off angle of photoelectrons was 90 degrees with respect to the sample surface. The XPS spectra were referenced with respect to the 285.0 eV carbon 1s level observed for hydrocarbon to eliminate charge effects. The smoothing procedure of the spectra was not done. The C_{1s} , and O_{1s} spectra were decomposed by fitting a Gaussian-Lorentzian mixture function (mixture ratio, 80:20) to an experimental curve using a nonlinear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. Sensitivity factors (S) for the core levels were $S(\text{C}_{1s}) = 1.00$, $S(\text{N}_{1s}) = 1.77$, and $S(\text{O}_{1s}) = 2.85$. O/C and N/C atomic ratios at the PPTA film surface were estimated from the relative intensity of the O_{1s} or N_{1s} core level against the C_{1s} core level within an experimental error of ± 0.01 .

Atomic Force Microscopy

The oxygen plasma-treated PPTA film surfaces were scanned with atomic force microscopy (AFM; Seiko Instrument, Japan, SFA-300) to observe their surface morphology. A triangular-pyramidal silicon nitride tip was used as a probe, and an area of $2 \times 2 \mu\text{m}^2$ square was scanned under a probe pressure of $8.7 \times 10^{-11} \text{ N/m}^2$. An arithmetic mean of the surface roughness (R_a) and a root mean square of the surface roughness (R_{ms}) were calculated from the roughness profile determined by AFM. When a roughness profile is written as a function of $Z(x)$, R_a and R_{ms} are defined by the following equations:

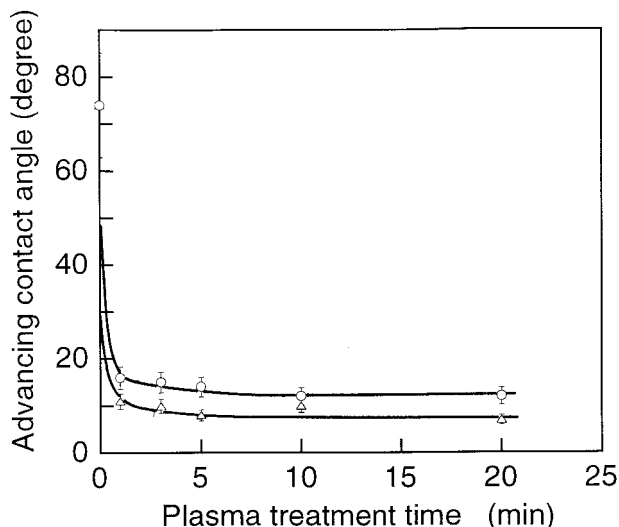


Figure 5 Contact angle of water against PPTA film surface treated with the remote and the direct oxygen plasma at 50 W as a function of plasma treatment time; (○) treated with the remote oxygen plasma; (△) treated with the direct oxygen plasma.

$$R_a = \frac{1}{L} \int_0^L |Z(x)| dx \quad (6)$$

$$R_{ms} = \sqrt{\frac{1}{L} \int_0^L Z(x)^2 dx} \quad (7)$$

where L is the scanning distance ($2 \mu\text{m}$).

RESULTS AND DISCUSSION

Contact Angle of Water Against Remote Oxygen Plasma-Treated PPTA Films

When the PPTA films were mounted at the sample stage (80 cm away from the rf input zone) and treated with the remote oxygen plasma, their surface property changed from hydrophobic to hydrophilic. Figure 5 shows typical results for the contact angle of water against the PPTA film surface treated with the remote oxygen plasma at an rf power of 50 W as a function of the plasma treatment time. A short time treatment of 1 min, as shown in Figure 5, shows a large decrease in contact angle from 74 to 16 degrees. After this initial large decrease, the contact angle continues to decrease but the decrease is small: the contact angle at a plasma treatment time of 3 min is 15 degrees, and that at 20 min is 12 degrees.

When the PPTA films are treated with the direct oxygen plasma using the same plasma reac-

tor and under the same plasma operating conditions as those in the remote oxygen plasma treatment, the contact angle of water is 11 degrees at a plasma treatment time of 1 min, 10 degrees at 3 min, and 7 degrees at 20 min (Fig. 5). There is no large difference in contact angle between the PPTA films treated with the remote and the direct oxygen plasmas. Therefore, we conclude that (1) the remote oxygen plasma can modify the PPTA film into a hydrophilic surface as powerfully as the direct oxygen plasma, and (2) a great part of the hydrophilic surface modification process by the remote oxygen plasma is accomplished within a treatment time as short as 1 min.

Surface Morphology of Remote Plasma-Treated PPTA Film Surface

The contact angle measurement shows that the remote oxygen plasma is able to modify the PPTA film surface into hydrophilic. A main difference between the remote and direct oxygen plasmas, as described in the theoretical background section, is a relative concentration between oxygen radicals and charged species such as oxygen ions and electrons. The oxygen radicals in the remote oxygen plasma zone are in higher concentration than the charged species. On the other hand, both charged species and oxygen radicals in the direct oxygen plasma zone are in high concentration. Therefore, we expect that the surface modification with the remote oxygen plasma will escape from degradation of the PPTA film surface initiated by heavy collision of the charged species.

Surface morphology of the PPTA film treated with the remote oxygen plasma was examined with scanning electron microscopy (SEM) and AFM in order to investigate how the PPTA film surface was damaged by the plasma treatment. The PPTA films which were treated with the remote and direct oxygen plasmas at 50 W for 1 min and then rinsed with ethanol to eliminate degradation products from the film surfaces were used as specimens for SEM and AFM measurements. Figure 6 shows SEM pictures of the PPTA film surfaces treated with the remote and direct oxygen plasmas. The remote oxygen plasma-treated PPTA film surface is as smooth as the original PPTA film, but the direct oxygen plasma-treated PPTA film shows a rougher surface. There are numerous lumps (less than $0.1 \mu\text{m}$ diameter) all over the surface of the direct oxygen plasma-treated PPTA film. In order to evaluate the surface roughness, roughness profiles of the oxygen

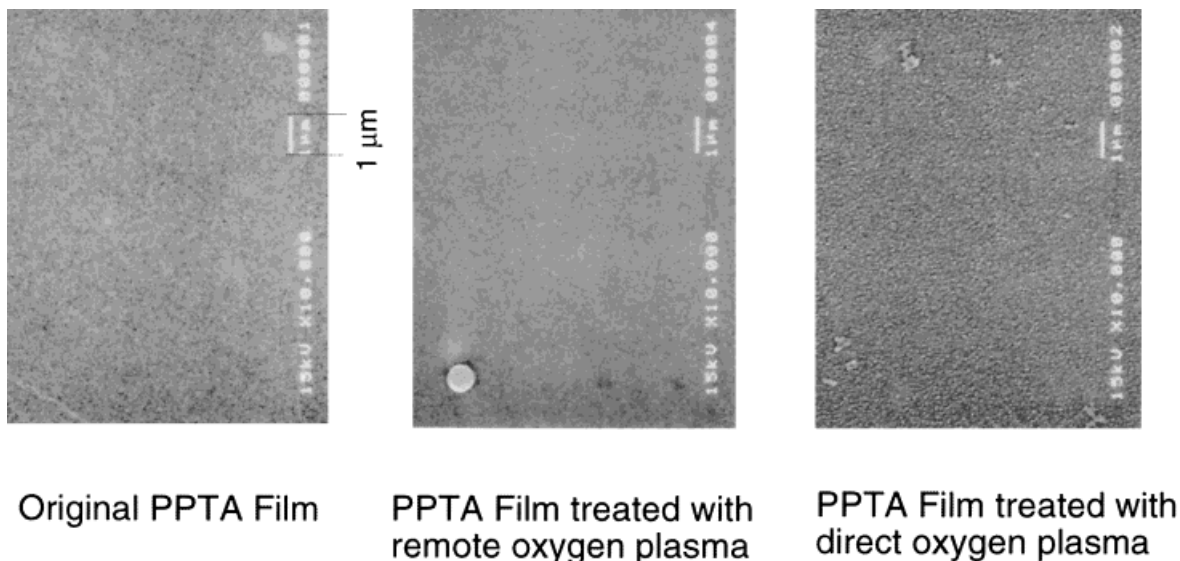


Figure 6 SEM pictures of PPTA film surfaces treated with the remote and the direct oxygen plasma at 50 W for 1 min.

plasma-treated PPTA film surfaces were measured by AFM (Fig. 7). From the AFM pictures, an arithmetic mean of the surface roughness (R_a) and a root mean square of the surface roughness (R_{ms}) are calculated in Table I. R_a and R_{ms} values for the remote oxygen plasma-treated PPTA film surface are 1.2 and 1.7 nm, respectively, which are comparable to those of the original PPTA film surface, 1.0 and 1.4 nm, respectively. On the other hand, R_a and R_{ms} values for the direct oxygen plasma-treated PPTA film surface are 9.7 and 12.5 nm, respectively, which are greatly larger than those of the remote oxygen plasma-treated PPTA film. This comparison shows that the remote oxygen plasma treatment caused no change in surface morphology, but the direct oxygen plasma treatment led to a large change in surface morphology. Therefore, we conclude that the remote oxygen plasma does not initiate remarkable degradation on the PPTA film surface with hydrophilic modification. On the other hand, the direct oxygen plasma initiates heavy degradation on the PPTA film surface with hydrophilic modification.

Chemical Composition of Remote Oxygen Plasma-Treated PPTA Film Surface

Atomic composition of the PPTA films treated with the remote oxygen plasma was determined by XPS in order to investigate what oxygen functionalities were formed on the PPTA film surface by the remote oxygen plasma. Specimens used for

the XPS measurement were the PPTA films which were treated with the remote and direct oxygen plasma at an rf power of 50 W for 1 min. Table II shows the O/C and N/C atomic ratios for the remote and direct oxygen plasma-treated PPTA films. The O/C and N/C atomic ratios for the original PPTA film, as shown in Table II, are 0.14 and 0.13, respectively, which correspond with the ratios (0.143) calculated from the repeating unit of the PPTA film, $C_{14}H_{10}N_2O_2$, within an experimental error of ± 0.01 . This good correspondence indicates that the XPS analytical procedure was performed appropriately. The remote oxygen plasma treatment, as shown in Table II, leads to a large increase in O/C atomic ratio (0.23) and a small increase in N/C atomic ratio (0.16). Of course, the direct oxygen plasma treatment also leads to a large increase in O/C atomic ratio (0.29) and a small increase in N/C atomic ratio (0.15). Large increases in the O/C atomic ratio indicate that some oxygen functionalities were formed by the remote oxygen plasma treatment as well as by the direct oxygen plasma treatment.

The remote and direct oxygen plasma-treated PPTA film surfaces were rinsed with ethanol to eliminate low-molecular-weight degradation products, and their surface compositions before and after the rinsing were analyzed with XPS (Table II). If there is a large difference in atomic ratios, especially in the O/C atomic ratio, between the oxygen plasma-treated PPTA films before and after the rinsing, low-molecular-weight degrada-

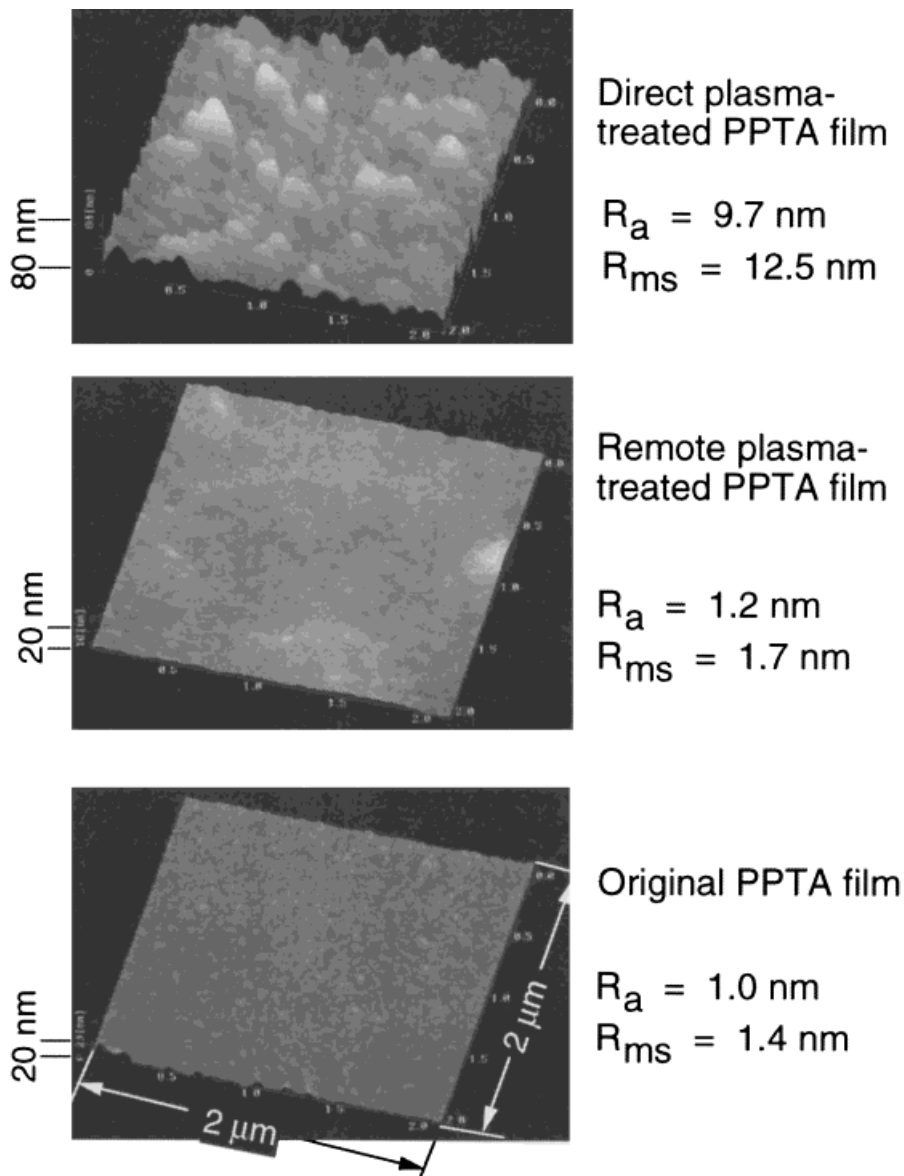


Figure 7 AFM pictures of PPTA film surfaces treated with the remote and the direct oxygen plasma at 50 W for 1 min.

tion products may have been formed on the surface of the PPTA film by the oxygen plasma treatment. Table II compares O/C and N/C atomic ratios before and after the rinsing. For the remote oxygen plasma-treated PPTA films, there is less difference in O/C and N/C atomic ratios before and after the rinsing the PPTA films: the O/C and N/C atomic ratios before the rinsing are 0.23 and 0.16, respectively, and those after the rinsing are 0.25 and 0.16, respectively. On the other hand, for the direct oxygen plasma-treated PPTA films, there are large differences in O/C atomic ratios before and after the rinsing but less difference in

the N/C atomic ratios: the O/C and N/C atomic ratios before the rinsing are 0.29 and 0.15, respectively, and those after the rinsing are 0.18 and 0.14, respectively. A large decrease in O/C atomic ratio indicates that the direct oxygen plasma treatment formed low-molecular-weight products (degradation products) as well as oxygen functionalities on the PPTA film surface. From the comparison, we can conclude that (1) not only the direct oxygen plasma treatment but also the remote oxygen plasma treatment are able to form oxygen functionalities on the PPTA film surface; and (2) the remote oxygen plasma treatment

Table I Surface Roughness of PPTA Films Treated with the Remote and the Direct Oxygen Plasmas

PPTA Film	Surface Roughness (nm)	
	R_a	R_{ms}
Original PPTA film	1.0	1.4
Remote oxygen plasma-treated PPTA film	1.2	1.7
Direct oxygen plasma-treated PPTA film	9.7	12.5

Treated at 50 W for 1 min.

forms little degradation product on the PPTA film surface, but the direct oxygen plasma treatment forms some low-molecular-weight degradation products. This conclusion is supported by the experimental evidence obtained from the contact angle and AFM measurements.

What oxygen functionalities were formed by the remote oxygen plasma treatment is investigated from XPS spectra. The PPTA films treated with the remote and the direct oxygen plasmas at 50 W for 1 min and rinsed with ethanol were used as specimens for the XPS measurement. C_{1s} , O_{1s} , and N_{1s} spectra for the specimens are shown in Figures 8 and 9. The original PPTA film, as shown in Figure 8, shows a complex C_{1s} spectrum which is deconvoluted into five components: CH groups at 285.0 eV; C—N groups in amides at 286.2 eV; C=O groups in amides at 288.0 eV; C(O)O groups at 289.0 eV; and $\pi-\pi^*$ shake-up satellite at 291.0 eV.²¹ The relative concentrations of the four components other than the $\pi-\pi^*$ shake-up satellite are 73, 13, 11, and 3%, respectively, which corresponds with three of the four compo-

nents calculated from the repeating unit of the PPTA (71.4% for CH groups, 14.3% for C—N groups in amides, 14.3% for C=O groups in amides). The presence of the C(O)O groups in the C_{1s} spectrum indicates that a part of the amide groups in the original PPTA film has already been hydrolyzed before the oxygen plasma treatment. This supposition is supported by the O_{1s} spectrum. The O_{1s} spectrum for the original PPTA film in Figure 9 shows two oxygen functionalities due to O=C groups in amides and carboxylates at 531.8 eV and O—C(O) groups in carboxylates at 533.6 eV.²¹ The relative concentrations of the two functionalities are 81 and 19%, respectively. This indicates that an amide group of 24% ($19/[62 + 19] = 0.24$) in the PPTA film has been hydrolyzed into carboxylate groups, because the C=O group in the amides is $81 - 19 = 62$, and the C=O groups in the carboxylates is 19.

The remote and direct oxygen plasma-treated PPTA films show some changes in C_{1s} and O_{1s} spectra, but no change in the N_{1s} spectrum (Figs. 8 and 9). No change in N_{1s} spectrum indicates that oxidation reactions by the remote and direct oxygen plasma treatments did not occur at nitrogen atoms in the PPTA film but occurred at carbon atoms because if nitrogen atoms were oxidized into nitroso (NO), nitro (NO_2), or nitrate (ONO_2), a large chemical shift (5–8 eV) would be observed in the N_{1s} spectrum.²¹ The C_{1s} spectra for the remote and direct oxygen plasma-treated PPTA films, as shown in Figure 8, are deconvoluted into five components: CH groups at 285.0 eV; C—N and C—O groups at 286.0–286.2 eV; C=O groups at 288.0–288.3 eV; C(O)O groups at 289.0–289.5 eV; and $\pi-\pi^*$ shake-up satellite at 291.0–291.9 eV.²¹ The relative concentrations of the four components other than the $\pi-\pi^*$ shake-up satellite are summarized in Table III. The remote and direct oxygen plasma-treated

Table II Atomic Composition of PPTA Film Surfaces Treated with the Remote and the Direct Oxygen Plasmas

Plasma Treatment Conditions				Atomic Composition			
				Before EtOH Washing		After EtOH Washing	
Kind of Plasma	Radio Frequency Power (W)	Exposure Time (min)	O/C	N/C	O/C	N/C	
No	—	—	0.14	0.13	0.14	0.13	
Remote	50	1	0.23	0.16	0.25	0.16	
Direct	50	1	0.29	0.15	0.18	0.14	

C_{1s} spectra

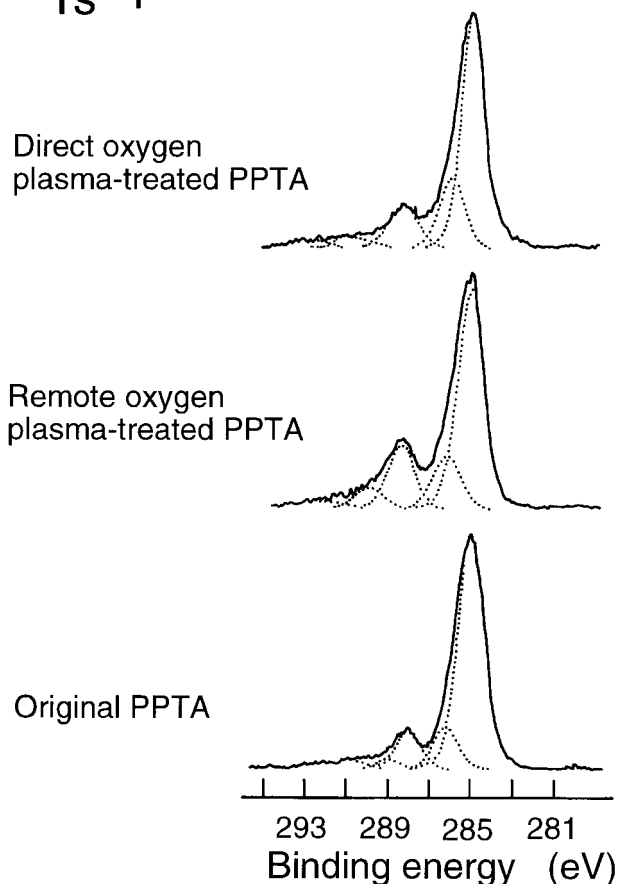


Figure 8 C_{1s} spectra of PPTA film surfaces treated with the remote and the direct oxygen plasma at 50 W for 1 min.

PPTA films, as shown in Table III, show a large decrease in the CH groups and increases in the C—N, C—O, and C=O groups. Although the component at 286.0–286.2 eV involves a C—N functionality due to amide groups and a C—O functionality due to alcohols, ethers, and esters,²⁰ the increase in the component may be due mainly to C—O groups because the amide concentration in the oxygen plasma-treated PPTA films is considered to be changeless from the almost-constant N/C atomic ratio in Table II even after the remote and direct oxygen plasma treatments.

The O_{1s} spectra show oxygen functionalities formed on PPTA film surfaces by the remote and direct oxygen plasma treatments. The O_{1s} spectra are deconvoluted into two components: O=C groups in amides, carbonyls, and carboxylates at 531.7–531.9 eV; and O—C groups in alcohols, ethers, and carboxylates at 533.3–533.6 eV.²¹ The relative concentrations of the two components are summarized

in Table III. The remote and direct oxygen plasma treatments lead to distribution of oxygen functionalities, decrease in O=C groups, and increase in O—C groups. This indicates that a predominant oxygen functionality formed by the remote and direct plasma treatments may be O—C groups.

CONCLUSION

Surface modification of the PPTA film by the remote oxygen plasma treatment has been investigated from a viewpoint of comparison with the direct oxygen plasma treatment. Results are summarized as follows:

1. The remote oxygen plasma can modify the PPTA film into a hydrophilic surface as powerfully as the direct oxygen plasma.
2. The hydrophilic surface modification process by remote oxygen plasma is accomplished within a treatment time as short as 1 min.
3. The remote oxygen plasma does not give

O_{1s} Spectra

N_{1s} Spectra

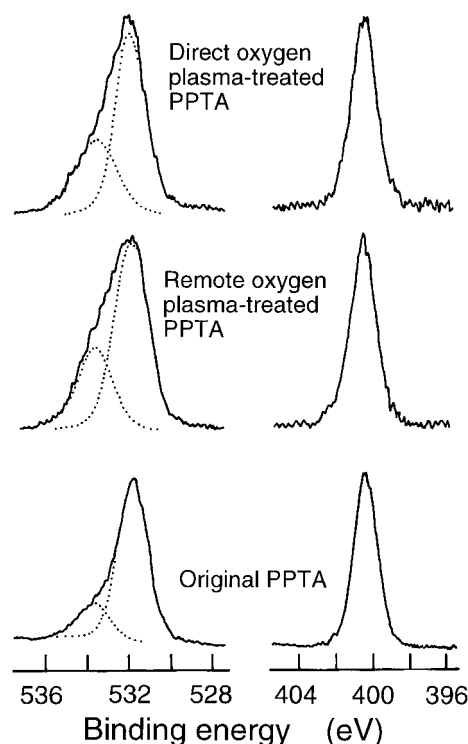


Figure 9 C_{1s} and N_{1s} spectra of PPTA film surfaces treated with the remote and the direct oxygen plasma at 50 W for 1 min.

Table III C_{1s} and O_{1s} Spectra of PPTA Films Treated with the Remote and the Direct Oxygen Plasmas

Plasma Treatment Conditions			C _{1s} Components (%)			
Kind of Plasma	RF Power (W)	Treatment Time (min)	C—N ^a			
			CH	C—O	C=O ^b	C(O)O ^c
No	—	—	73	13	11	3
Remote	50	1	60	17	18	5
Direct	50	1	61	20	13	5
			O _{1s} Components (%)			
			O=C ^d O—C ^e			
No	—	—			81	19
Remote	50	1			69	31
Direct	50	1			63	37

^a CH groups at 285.0 eV.^b C—N and C—O groups at 286.0–286.4 eV.^c C=O groups at 288.2–288.3 eV, C(O)O groups at 289.8–290.1 eV.^d O=C groups at 531.7–531.9 eV.^e O—C groups at 533.3–533.6 eV.

remarkable degradation on the PPTA film surface with hydrophilic modification. On the other hand, the direct oxygen plasma gives heavy degradation on the PPTA film surface with hydrophilic modification.

- The remote oxygen plasma treatment as well as the direct oxygen plasma treatment forms oxygen functionalities on the PPTA film surface.
- Main oxygen functionalities formed by the remote oxygen plasma treatment are C—O and C=O groups.

REFERENCES

- M. Takayanagi and T. Katayose, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1133 (1981).
- M. R. Wertheimer and H. P. Schreiber, *J. Appl. Polym. Sci.*, **26**, 2087 (1981).
- M. Takayanagi, *Pure Appl. Chem.*, **55**, 819 (1983).
- L. S. Penn, F. A. Bystry, and H. J. Marchionni, *J. Polym. Comp.*, **4**, 26 (1983).
- Y. Wu and G. C. Tesoro, *J. Appl. Polym. Sci.*, **31**, 1041 (1986).
- L. S. Penn, T. J. Byerley, and T. K. Liao, *J. Adhesion*, **23**, 163 (1987).
- M. Takayanagi, S. Ueta, W.-Y. Lei, and K. Koga, *Polym. J.*, **19**, 467 (1987).
- K. Küpper and P. Schwartzu, *J. Adhesion Sci. Technol.*, **5**, 165 (1991).
- E. G. Chatzi, S. L. Tidrick, and J. L. Koenig, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 1585 (1988).
- N. Inagaki, S. Tasaka, and H. Kawai, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 2001 (1995).
- N. Inagaki, *Plasma Surface Modification and Plasma Polymerization*, Technomic Pub., Lancaster, PA, 1996.
- A. Goldman and J. Amourouz, in *Electrical Breakdown and Discharge in Gases, Macroscopic Processes and Discharge*, E. E. Kunhardt and L. H. Luessen, Eds., Plenum Press, New York, 1983, p. 293.
- M. J. Kushmer, *J. Appl. Polym. Phys.*, **63**, 2532 (1988).
- C.-H. Chou, T.-C. Wei, and J. Phillips, *J. Appl. Phys.*, **72**, 870 (1992).
- T.-C. Wei and T.-C. Phillips, *J. Appl. Phys.*, **74**, 825 (1993).
- H. Rau and F. Picht, *J. Phys. D: Appl. Phys.*, **26**, 1260 (1993).
- J. Deson, F. Halous, C. Lalo, C. Rousseau, and V. Veniard, *J. Phys. D: Appl. Phys.*, **27**, 2320 (1994).
- Y. Yamada, T. Yamada, S. Tasaka, and N. Inagaki, *Macromolecules*, **29**, 4331 (1996).
- Y. Osada, Ed., *Plasma Polymerization*, Tokyo Kagaku Dojin, Tokyo, 1986, p. 40.
- F. Garbassi, M. Morra, E. Occhiello, *Polymer Surfaces from Physics to Technology*, Wiley, Chichester (England), 1994, p. 166.
- G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers, The Scienta ESCA300 Database*, Wiley, New York, 1992.