Surface Modification of Poly(aryl ether ether ketone) Film by Remote Oxygen Plasma

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ABSTRACT: Surface modification of poly(aryl ether ether ketone)(PEEK) film surfaces by oxygen plasma treatment was investigated. Two procedures, the direct plasma treatment and the remote oxygen plasma treatment, were used as oxygen plasma treatments, and the efficiency of the hydrophilic modification was discussed. The direct and remote oxygen plasma treatments lead to degradation of the PEEK film as well as hydrophilic surface modification. The degradation disturbs the surface modification. The remote oxygen plasma treatment rather than the direct oxygen plasma is suitable for the hydrophilic surface modification of the PEEK film. The remote oxygen plasma treatment at 10 W for 60 s forms predominantly C—O groups rather than C═O groups as an oxygen-containing group on the PEEK surface and gives a highly hydrophilic surface with a contact angle of 44 degrees. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 271–279, 1998

INTRODUCTION

Poly(aryl ether ether ketone)(PEEK) is a thermoplastic and crystalline polymer, made up of the following repeating unit:
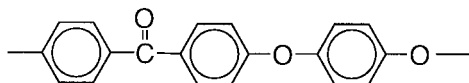

PEEK has good mechanical properties, high thermal stability, and outstanding chemical properties, such as high hydrolysis resistance, low flammability, and low toxic gas emission. As a consequence of these advantages, PEEK can be used in a wide variety of fields, such as the aerospace, automotive, electrical, electronics, and medicine industries in types of not only molding but also of composites and laminates. In laminate structures, surface modification is requested to emphasize the adhesion between layer surfaces of the laminae. We believe that plasma treatment is a powerful way used for the adhesion improvement.

In plasma chemistry, PEEK possesses interesting units, a phenyl ether group,
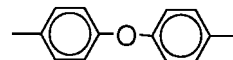
and a benzophenone group
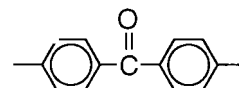
which may be susceptible to plasma actions, electron and ion bombardments, and ultraviolet (UV) irradiation. These interactions of oxygen plasma with PEEK surface will bring about bond scissions of the C—O bond in the phenyl ether group and the C(O)—O bond in the benzophenone group, as well as surface modification by introducing oxygen functional groups into the PEEK surface. We believe that the surface modification and degradation may be in a competitive state in the

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oxygen plasma treatment of PEEK. Therefore, when the degradation becomes predominant, degradation products will cover completely the PEEK surface, and PEEK surface will be never modified into hydrophilic surface.

Many modifications of PEEK with high-energy species, such as plasma, ozone, UV light, electrons, and gamma rays, have been reported reported.[1-5] Pawson et al.[1] and Jama et al.[2] have separately investigated the PEEK surface modified by plasma treatment using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF–SIMS). They observed that degradation products were formed on the PEEK surface by the plasma treatment and pointed out the following important aspect on the surface modification of PEEK by the oxygen plasma: PEEK is susceptible to plasma actions, and, as a result, the degradation of PEEK, as well as the introduction of oxygen functionalities, occur simultaneously on the PEEK film surface. Effective modification of PEEK surfaces should be carried out without degradation of the PEEK surface.

A remote plasma treatment is a way to minimize the bombardment of electrons and ions onto polymer surfaces. Plasma is a mixture of electrons, ions, and radicals. These species disappear in processes of the electron–positive ion recombination, the positive ion–negative ion recombination, and the radical–radical recombination. The rate constant of these reactions is in an order of 10^{-7} and 10^{-7} cm^3/s and 10^{-33} cm^6/s (the dimension of the rate constant in the radical–radical recombination is not cm^3/s but cm^6/s because of the following three-body reactions: $2O^\bullet + O_2 \rightarrow 2O_2$; and $3O^\bullet \rightarrow O^\bullet + O_2$.), respectively.[6] Radicals can possess extremely longer lifetime than electrons and ions. Therefore, we expect that the collision of electrons and ions with polymer surfaces would be reduced by keeping the polymer surface away from a plasma zone. This is the concept of a remote plasma treatment. The remote plasma treatment is different from a conventional plasma treatment with respect to the relative distance between the polymer sample position and the plasma zone: the polymer sample in the remote plasma treatment is positioned away from the plasma zone, and the polymer sample in the conventional plasma treatment is positioned just in the plasma zone. In the remote plasma treatment, reactions of radicals with the polymer surfaces will occur predominantly, but electron and ion bombardment will occur scarcely. In this study,

to distinguish the remote plasma treatment from the conventional plasma treatment, the conventional plasma treatment is called the direct plasma treatment. We have investigated the following question: "Can the remote oxygen plasma treatment modify PEEK surface into hydrophilic without degradation of the PEEK surface?"

EXPERIMENTAL

Materials

PEEK, kindly provided in a form of film (250 μm thickness) by Sumitomo Kasei. Co. Ltd. (trade name, Sumilight FS-1100C), was used for surface modification experiments as a specimen whose size was 10 mm wide × 20 mm long. The PEEK film was washed with acetone in an ultrasonic washer prior to the surface modification experiments.

Plasma Reactor for Direct and Remote Oxygen Plasma Treatment

The same reactor was used for the direct and remote oxygen plasma treatment. Details of the reactor has been reported elsewhere.[7] The reactor consists of a cylindrical Pyrex glass tube (45 mm diameter and 1000 mm long) and a columnar stainless steel chamber (300 mm diameter and 300 mm height). An end of the Pyrex glass tube is jointed with the columnar chamber in a manner of Viton O ring flange, and at the other end of the Pyrex glass tube, there are two gas inlets for the injection of oxygen and argon gases and a pair of copper electrodes for the energy input of rf power (13.56 MHz frequency). In the stainless steel chamber, there are a sample stage positioned at 0 and 80 cm from the copper electrodes for the rf power input, a Barocel pressure sensor (type 622, Edwards), 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 is shown in Figure 1.

Direct and Remote Oxygen Plasma Treatment

The PEEK films were mounted on a given sample stage in the reaction chamber. The sample stage for the direct oxygen plasma treatment was at 0 cm from the copper electrode, and that for the remote
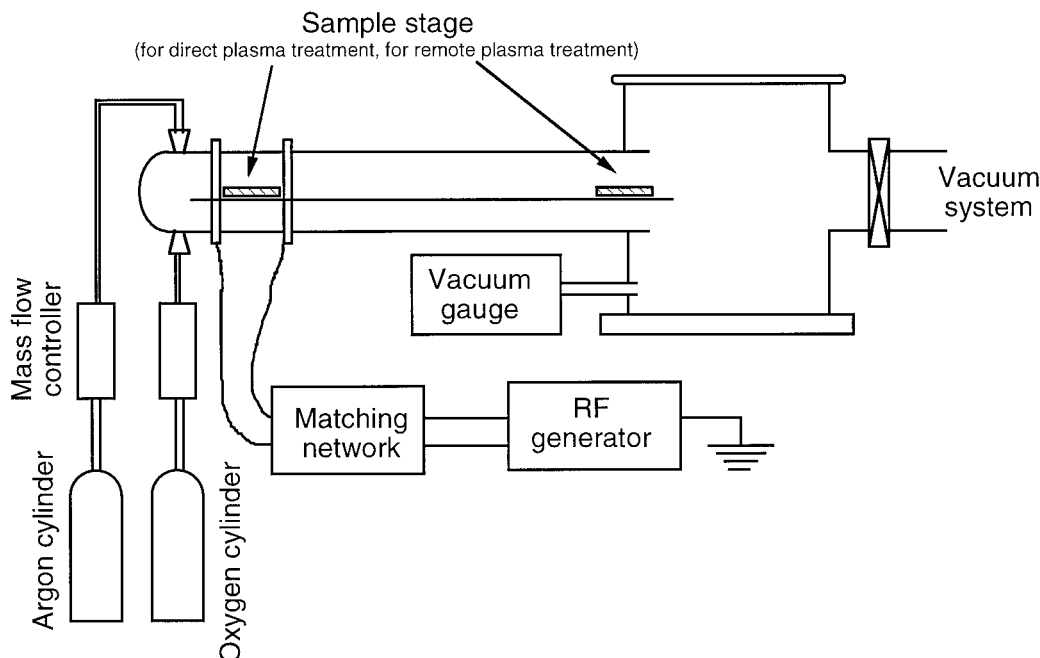
Sample stage
(for direct plasma treatment, for remote plasma treatment)

Figure 1 Schematic representation of the direct and remote plasma reactor.

oxygen plasma treatment was at 80 cm. Air in the reaction chamber was displaced with argon, and the reaction chamber was evacuated to approximately 0.13 Pa. Afterward, oxygen gas whose flow rate was adjusted to 10 cm^3 (STP)/min by a mass flow controller (Estec Co., Japan, model SEC-400 MARK3) was introduced into the reaction chamber. The direct and remote oxygen plasma treatments were performed at a system pressure of 13.3 Pa at a given radio frequency (rf) power of 5 to 60 W for a given time of 10 to 120 s.

Contact Angle of Water on the Plasma-Treated PEEK Films

Contact angles of water on the oxygen plasma-treated PEEK film surfaces were measured according to the sessile drop method.[8] The measurement was carried out at 20°C using an contact-angle meter with a goniometer (Erma Co., Japan, model G-1). The contact angle was determined from an average of 10 measurements with a standard deviation of 1 degree.

X-ray Photoelectron Spectra

XPS spectra of the surface of the PEEK films were obtained on a Shimadzu ESCA K1 using a non-monochromatic MgK$_\alpha$ 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. A size of the X-ray spot was 2 mm diameter, and a 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 (the mixture ratio was 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 $S(C_{1s}) = 1.00$ and $S(O_{1s}) = 2.85$. The O/C atomic ratio at the PEEK film surface was estimated from the relative intensity of the O_{1s} core level against the C_{1s} core level within an experimental error of ± 0.01.

RESULTS AND DISCUSSION

Contact Angle of Water on Direct Oxygen Plasma-Treated PEEK Surface

PEEK films were treated with the direct oxygen plasma operating at an rf power of 20−80 W, and the contact angle of water against the direct oxygen plasma-treated PEEK film surfaces was mea-
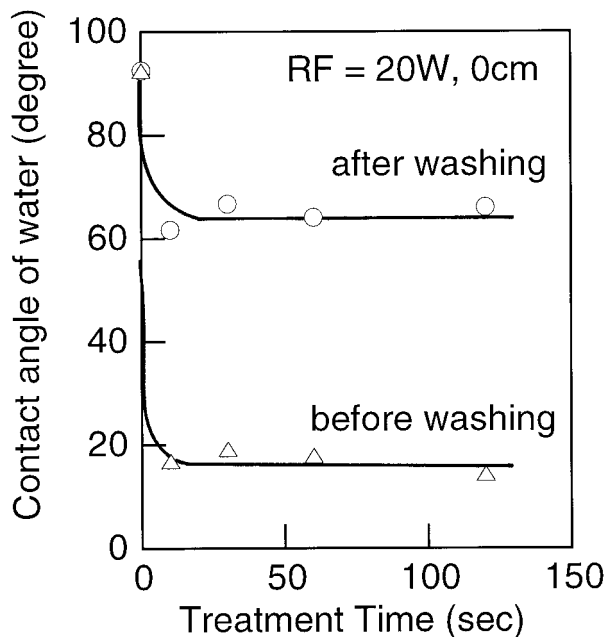
Figure 2 Contact angle of water on the PEEK film surface treated with the direct oxygen plasma at 20 W as a function of treatment time.

sured as a function of the treatment time. Figures 2 and 3 show typical results of the contact angle of water on the PEEK film surfaces, which were treated with the direct oxygen plasmas at rf powers of 20 and 60 W, respectively. The direct oxygen plasma treatment, as shown in Figs. 2 and 3, leads to large decrease in the contact angle within a few seconds after exposing the PEEK surface to the direct oxygen plasma. A longer plasma treatment time than 10 s does not give additional hydrophilicity, and, after that treatment time, the contact angle shows a constant value of 17° at 20 W and 10° at 60 W.

Once these hydrophilic PEEK film surfaces modified by the direct oxygen plasma were washed with acetone, the contact angle increase (Figs. 2 and 3), and the hydrophilicity is lost as follows: for the PEEK film surface plasma-treated at 20 W for 10 s, the contact angle is increased from 17 to 67° by the acetone-washing; for the film surface modified at 60 W for 10 s, the contact angle is increased from 10 to 75°. These large increases in contact angle infers that hydrophilicity is lost from the PEEK film surface by the acetone washing, and the PEEK film surface turns back to the hydrophobic surface. The loss of the hydrophilicity may be due to either of removing of degradation products from the PEEK film surface by the acetone washing or chemical modification of

hydrophilic groups into hydrophobic groups by the acetone washing. We believe that the removing of degradation products is a possible factor for the hydrophilicity loss because of less reactivity of the hydrophilic groups with acetone. The PEEK film surface before the acetone washing shows a false surface that is contaminated by the degradation products. The PEEK film surface after the acetone washing shows a true PEEK film surface modified by the oxygen plasma.

From these results, we conclude that the direct oxygen plasma treatment is not suitable for hydrophilic surface modification of the PEEK films. The action of the direct oxygen plasma is so strong that the degradation of the PEEK film rather than the introduction of hydrophilic groups into the PEEK surface predominantly occurs. As a result, the surface remains still hydrophobic.

Contact Angle of Water Against Remote Oxygen Plasma-Treated PEEK Surface

To minimize the degradation of the PEEK film, the modification by the remote oxygen plasma treatment was investigated. Operational conditions for the remote oxygen plasma treatment were the same as those for the direct oxygen plasma treatment except for the position of the sample stage. In the remote oxygen plasma treat-
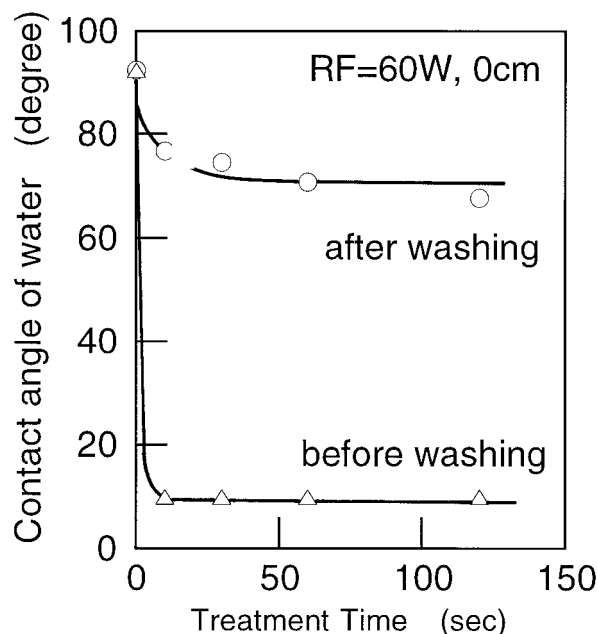

Figure 3 Contact angle of water on the PEEK film surface treated with the direct oxygen plasma at 60 W as a function of treatment time.
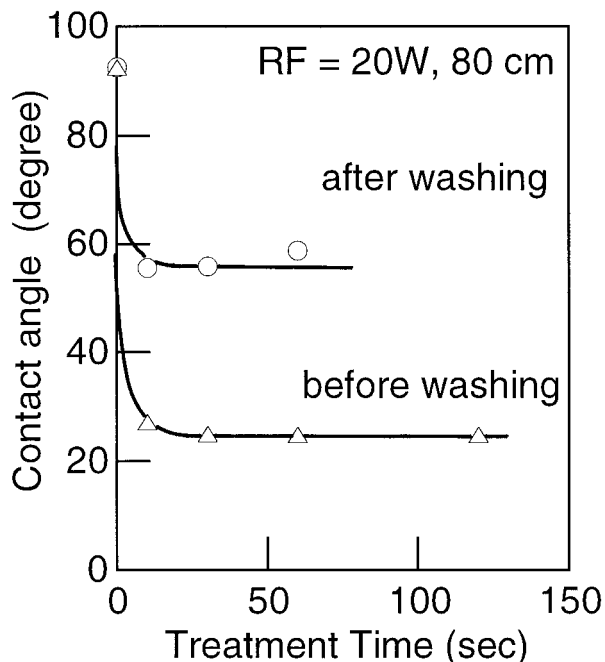
Figure 4 Contact angle of water on the PEEK film surface treated with the remote oxygen plasma at 20 W as a function of treatment time.

ment, the PEEK film samples were positioned at a distance of 80 cm from the copper electrode in the Pyrex reactor.

Figures 4 and 5 show typical results of the contact angle of water against the PEEK film surfaces treated with the remote oxygen plasma at 20 and 60 W, respectively. The contact angle, as shown in Figures 4 and 5, shows large decrease at an initial treatment time within 30 s after exposing the film surfaces to the remote oxygen plasma, and, after that treatment time, the constant angle levels off at an angle of 25° (at 20 W) and 22° (at 60 W). Furthermore, these PEEK film surfaces were washed with acetone, and the contact angle of water against the acetone-washed PEEK film surfaces was inspected from the viewpoint of the degradation of the PEEK film. Figures 4 and 5 show the contact angle of water against the acetone-washed PEEK film surfaces. For the PEEK film surface treated with the remote oxygen plasma at 20 W for 30 s, as shown in Figure 4, the contact angle of water increases from 25 to 56° by the acetone washing. For the PEEK film surface treated with the remote oxygen plasma at 60 W for 30 s also, an increases from 22 to 78° is shown in Figure 5. These increases indicate that some degradation products of the PEEK film are

formed on the film surface, even by the remote oxygen plasma.

Table I shows the contact angle for the PEEK film surfaces, which were treated with the direct and remote oxygen plasmas at an rf power of 20–60 W for 30 s and then washed with acetone to remove degradation products from the surfaces. The table shows the following hydrophilic modification effects by the direct and remote plasmas.

1. Both direct and remote oxygen plasma treatments are effective for hydrophilic modification of the PEEK film surface. The PEEK film surfaces treated with the direct and remote oxygen plasmas show lower contact angle (56–78°) than that for the untreated surface (93°).
2. The remote oxygen plasma treatment is more effective in hydrophilic modification than the direct oxygen plasma treatment. The PEEK film surfaces treated with the remote oxygen plasma possess lower contact angle (56°) than those treated with the direct oxygen plasma (67°).
3. The remote oxygen plasma at a low rf power is more effective than that at a high rf power: The contact angle for the PEEK film surface treated at an rf power at 20 W is 56°, while
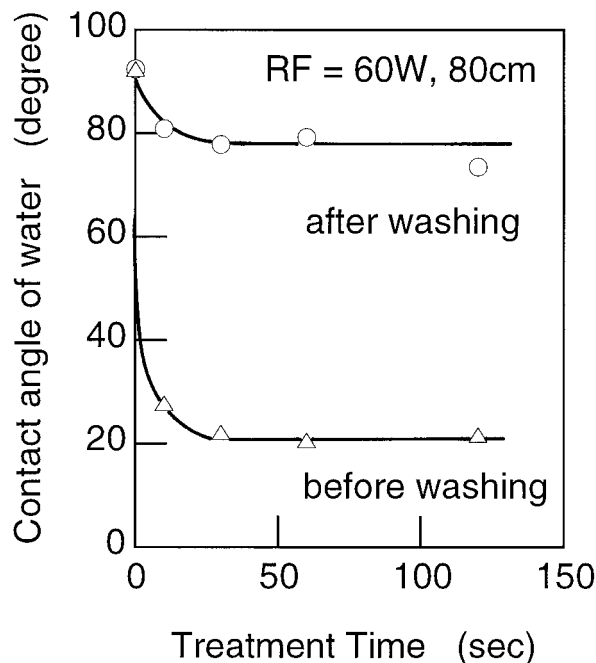

Figure 5 Contact angle of water on the PEEK film surface treated with the remote oxygen plasma at 60 W as a function of treatment time.

Table I   Contact Angle of Water on PEEK Film Surfaces Treated with the Direct and Remote Oxygen Plasmas and Washed with Acetone

Plasma Treatment Conditions			Contact Angle of Water on PEEK Film Surface Treated with Oxygen Plasma and Washed with Acetone (in degrees)
Kind of Plasmas	RF Power (W)	Treatment Time (s)	
None			93
Direct	20	30	67
Direct	40	30	75
Direct	60	30	75
Remote	20	30	56
Remote	40	30	67
Remote	60	30	78

the contact angle for the PEEK film surfaces treated at 40 and 60 W is 67 and 78°, respectively.

From above discussion, we conclude that the remote oxygen plasma rather than the direct oxygen plasma is suitable for hydrophilic surface modification of PEEK film. However, the modification by the remote oxygen plasma does not yet lead to satisfactory hydrophilicity.

Prior to highly hydrophilic surface modification, the question of how the photons in the oxygen plasma contribute to the hydrophilic surface modification was investigated. The PEEK films were sealed in a small box with a quartz or magnesium fluoride window. The box was positioned just under the copper electrode (at a distance of 0 cm from the copper electrode) in the Pyrex tube of the same plasma reactor as used for the direct and remote oxygen plasma treatments. The PEEK film surfaces were exposed for 60 s through the windows to vacuum ultraviolet (UV) light emitted from the oxygen plasma at 20 W. Quartz and magnesium fluoride windows cut off shorter

wavelength lights than 200 and 100 nm, respectively. Therefore, the PEEK film surfaces in the small box are isolated from attacks by electrons, oxygen ions, and oxygen radicals in the oxygen plasma but are irradiated to the vacuum UV lights with longer wavelengths than 200 (through quartz window) or 100 nm (through the MgF_2 window). The contact angle of water on the PEEK film surfaces irradiated to the vacuum UV lights is tabulated in Table II. The contact angle, as shown in Table II, is 92° (through quartz window) and 91° (through MgF_2 window), and 93° for the original PEEK film. This indicates no change in hydrophilicity by irradiation of the vacuum UV light.

Atomic analyses with XPS also show that no oxidation occurred in irradiating the PEEK film by the vacuum UV lights. The O/C atomic ratio, as shown in Table II, is 0.14 for the PEEK film irradiated by the vacuum UV light transmitted through quartz window and 0.13 for the PEEK film irradiated to the vacuum UV light transmitted through the MgF_2 window. The O/C atomic ratio for the original PEEK film is 0.13. On the

Table II   Contact Angle and Atomic Composition of PEEK Film Surfaces Treated with Vacuum Ultraviolet Light and Washed with Acetone

Oxygen Plasma Treatment Conditions				Modified PEEK Film Surfaces	
RF Power (W)	Treatment Time (s)	Position of Sample Stage (cm)	Window in Small Box	Contact Angle of Water (in degrees)	O/C Atomic Ratio Determined by XPS
None				93	0.13
20	60	0	Quartz	92	0.14
20	60	0	MgF_2	91	0.13
20	60	80	None	57	0.20

other hand, the O/C atomic ratio for the PEEK film surface treated with the remote oxygen plasma at 20 W is 0.20. From this comparison and the experimental evidence that the UV light intensity has fallen off considerably at 80 cm compared to 0 cm exposure distance, we conclude that the vacuum UV lights with longer wavelength than 100 or 200 nm have less contribution to hydrophilic modification of the PEEK film. We expect that highly hydrophilic surface modification may be accomplished by the remote oxygen plasma.

Hydrophilic Surface Modification with Remote Oxygen Plasma at Low RF Powers of Less Than 20 W

The remote oxygen plasmas, as described in a previous section, are able to modify the PEEK film surfaces into hydrophilic, but we are not satisfied with the hydrophilicity. The remote oxygen plasma treatment involves the following two main processes: oxidation, which forms hydrophilic groups on the PEEK film, and degradation, which formed low-molecular-weight products on the PEEK film surface. The first process contributes to the hydrophilic modification due to the formation of degradation products, and the other process disturbs the hydrophilic surface modification by the formation of the degradation products. The two processes are in a competitive situation. If the degradation becomes predominant, an outermost layer of the PEEK film will be always stripped off by the degradation, and the PEEK film surface will be covered with degradation products. Therefore, we believe that a key factor for highly hydrophilic surface modification is how to depress the degradation of the PEEK film.

To depress the degradation, the remote oxygen plasma treatment at low rf powers, especially less than 20 W, was investigated. Table III shows the typical results of the contact angle of water on the PEEK film surfaces, which were treated with the remote oxygen plasma at rf powers of 5–20 W for 60 s and rinsed with acetone. The contact angle of water, as shown in Table III, appears a minimum of 44 degrees when the PEEK film surface was modified with the remote oxygen plasma at an rf power of 10 W for 60 s. A shorter or longer exposure time than 60 s to the remote oxygen plasma did not give more hydrophilic surface with a contact angle of less than 44°. The remote oxygen plasma at 10 W for 60 s is the optimum condi-

Table III   Contact Angle and Atomic Composition of PEEK Film Surfaces Treated with Remote Oxygen Plasma and Washed with Acetone

Oxygen Plasma Treatement Conditions		Modified PEEK Film Surfaces	
RF Power (W)	Treatment Time (s)	Contact Angle of Water (in degrees)	O/C Atomic Ratio
None		93	0.13
5	60	51	0.23
10	60	44	0.21
15	60	57	0.19
20	60	59	0.20

tions in our experiment for modifying the PEEK film surface into hydrophilic.

What oxygen functionalities were formed by the remote oxygen plasma is investigated by XPS (Figs. 6 and 7). From increases in the O/C atomic ratio, as shown in Table III, it is obvious that the remote oxygen plasma treatment forms oxygen groups on the PEEK film surface. Figure 6 shows C_{1s} spectra of the PEEK film surface, which was treated with the remote oxygen plasma at 10 W for 60 s and rinsed with acetone. The C_{1s} spectrum for the original PEEK film, as shown in Figure 6, is decomposed into three main components at 285.0 (CH groups), 286.4 (C—O groups), and 287.2 eV (C=O groups) and two small components at 289.3 ($\pi - \pi^*$ shake-up satellite) and 291.8 eV ($\pi - \pi^*$ shake-up satellite).[9] The relative concentration of the CH, C—O, and C=O components for the original PEEK film is 72, 21, and 7%, respectively. The decomposition procedure is believable because the decomposed components, CH, C—O, and C=O groups, correspond to each (74, 21, and 5%) calculated from the repeating unit of the PEEK film within an experimental error (3%). The remote-oxygen-plasma-treated PEEK film shows a similar C_{1s} spectrum, which is decomposed into five components at 285.0 (C—H groups), 286.7 (C—O groups), 287.1 (C=O), 289.0 ($\pi - \pi^*$ shake-up satellite), and 291.7 eV ($\pi - \pi^*$ shake-up satellite).[9] These relative concentration of the CH, C—O, and C=O components for the plasma-treated PEEK film is 64, 32, and 4%, respectively. The remote-oxygen-plasma-treated PEEK film possesses higher concentration of the C—O groups than the original PEEK film. The O_{1s} spectrum for the original PEEK, as shown
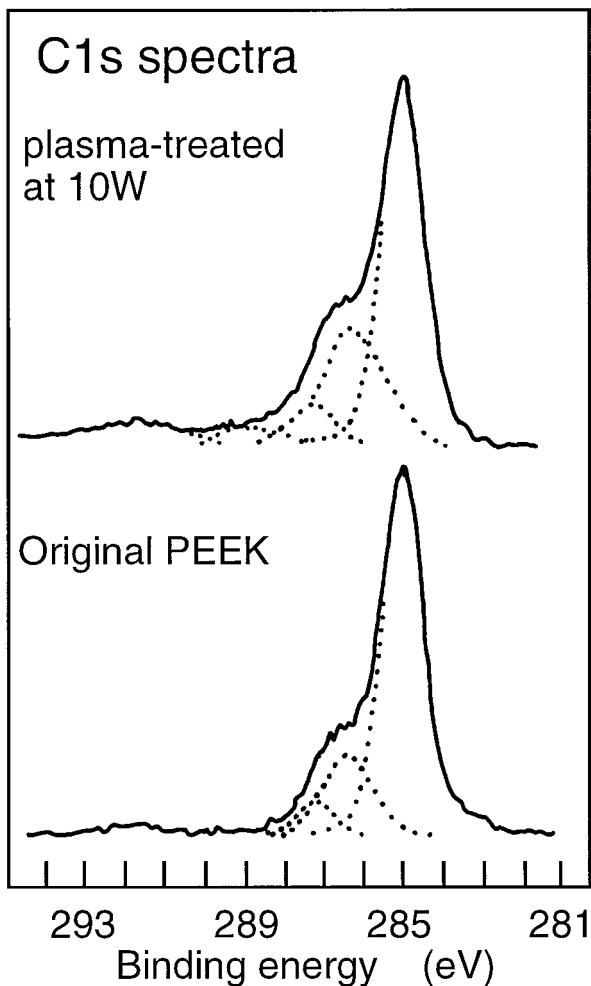
Figure 6 C_{1s} spectra of the original PEEK film and the PEEK film treated with the remote oxygen plasma at 10 W for 60 s.

groups, we can estimate the number of the C=O and C—O groups per 100 carbons on the PEEK film surface (Table IV). The estimation shows that the remote oxygen plasma treatment leads to increases by about two factors in the number of the C—O groups per 100 carbons on the surface from 8.8 to 15.3 numbers and to a small increase of the C=O groups per 100 carbons from 4.2 to 5.7 numbers. This estimation indicates that the remote oxygen plasma treatment forms predominantly C—O groups rather than C=O groups on the PEEK film surface. This formation of C—O groups on the PEEK film surface may contribute to the hydrophilic modification.

Consequently, we conclude that the remote oxygen plasma treatment at 10 W for 60 s can modify the PEEK film surface into hydrophilic. The treated PEEK film surface keeps hydrophilicity still after washing the film surface with acetone. The contact angle of water on the remote-oxygen-
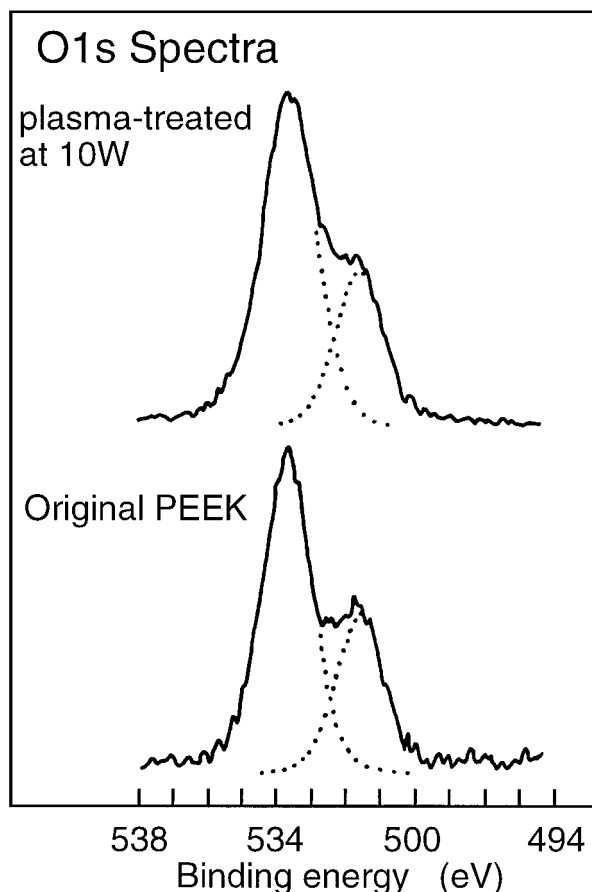
in Figure 7, is decomposed into two components, at 531.6 (C=O groups) and 533.7 eV (O—C groups).[8] The relative concentration of the C=O and O—C components is 32 and 68%, which correspond to each (33 and 67%) calculated from the repeating unit of the PEEK film. For the remote-oxygen-plasma-treated PEEK films, the O_{1s} spectrum also is decomposed into two components, at 531.6 eV (O=C groups) and 533.6 eV (C—O groups),[8] whose relative concentration is 27 and 73%, respectively. Comparison in the O_{1s} spectra shows that the remote-plasma-treated PEEK film possesses more concentration of the C—O groups than the original PEEK film and possesses slightly less concentration of the C=O groups. From combination of the O/C atomic ratio and the relative concentration of the O=C and O—C

Figure 7 O_{1s} spectra of the original PEEK film and the PEEK film treated with the remote oxygen plasma at 10 W for 60 s.

Table IV   C—O and C=O Groups Formed on the PEEK Film Surface by Remote Oxygen Plasma at 10 W for 60 s

Sample	O/C Atomic Ratio	O1s Component (%)		Concentration of Oxygen Groups per 100 Carbons on the PEEK Film Surface	
		C—O	C=O	C—O Group	C=O Group
Original PEEK	0.13	67	32	8.8	4.2
PEEK treated with remote oxygen plasma at 10 W for 60 s	0.21	73	27	15.3	5.7

plasma-treated and acetone-washed PEEK film surface is 44 degrees. C—O groups rather than C=O groups are formed predominantly as oxygen-containing groups on the PEEK film surface by the remote oxygen plasma treatment.

CONCLUSION

Surface modification of PEEK film surfaces by oxygen plasma treatment was investigated. Two procedures, the direct plasma treatment and the remote oxygen plasma treatment, were used for the oxygen plasma treatment in this study, and the efficiency of the hydrophilic modification was discussed. Results are summarized as follows.

1. The direct and remote oxygen plasma treatments led to degradation of the PEEK film, as well as to hydrophilic surface modification. The degradation disturbs the hydrophilic modification of the PEEK film surface.
2. The remote oxygen plasma treatment rather than the direct oxygen plasma is suitable for the hydrophilic surface modification of the PEEK film. The remote oxygen plasma treatment at 10 W for 60 s can give highly hydrophilic surface with a contact angle of 44°.
3. The remote oxygen plasma treatment forms predominantly C—O groups rather than C=O groups as oxygen-containing groups on the PEEK surface.

REFERENCES

1. D. J. Pawson, A. P. Ameen, R. D. Short, P. Denison, and F. R. Jones, *Surf. Interface Anal.,* **18,** 13 (1992).
2. C. Jama, O. Dessaux, P. Goudmand, L. Gengembre, and J. Grimblot, *Surf. Interface Anal.,* **18,** 751 (1992).
3. A. Baalmann, K. D. Vissing, E. Born, and A. Gross, *J. Adhes.,* **46,** 57 (1994).
4. I. Mathieson and R. H. Bradley, *J. Mater. Chem.,* **4,** 1157 (1994).
5. M. Oyabu, Y. Kobayashi, T. Seguchi, and T. Sasuga, *Bunseki Kagaku,* **44,** 195 (1995).
6. A. Goldman and J. Amouroux, *Electrical Breakdown and Discharge in Gases, Macroscopic Processes and Discharges,* E. E. Kunhardt and L. H. Luessen, Eds., Plenum, New York, 1983, p. 293.
7. Y. Yamada, T. Yamada, S. Tasaka, and N. Inagaki, *Macromolecules,* **29,** 4331 (1996).
8. F. Garbassi, M. Morra, and E. Occhiello, *Polymer Surfaces from Physics to Technology,* Wiley, Chichester, U.K., 1994, p. 166.
9. G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers, The Scienta ESCA300 Database,* Wiley, New York, 1992.