A New Approach for Selective Surface Modification of Fluoropolymers by Remote Plasmas

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ABSTRACT: Ethylene-*co*-tetrafluoroethylene (ETFE) and poly (vinylidene fluoride) (PVDF) films were exposed to the remote Ar, H_2, and O_2 plasmas. The modified polymer surfaces were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact angle measurement. The plasma exposure led to weight loss and changes in the chemical composition on the polymer surface. Selective surface modification of fluoropolymers introduces various functional groups without altering the bulk properties. The results may be summarized as follows: the remote hydrogen plasma was the most effective in alternation from C–F to C–H (abstraction of fluorine). On the other hand, the remote oxygen plasma was unfavorable to abstract fluorine atoms, but effective in dehydrogenation (abstraction of hydrogen). © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1012–1020, 2004

Key words: ethylene-*co*-tetrafluoroethylene (ETFE); poly (vinylidene fluoride) (PVDF); surface modification; remote plasma; X-ray photoelectron spectroscopy (XPS)

INTRODUCTION

In recent years, plasma surface modification (PSM) of polymeric materials has been intensively investigated. Plasma treatment affects the polymer surface to an extent of several hundred to several thousand angstrom, and the bulk of the polymer substrate is never modified due to its low penetration range.[1] The plasma initiated both chemical modification process and degradation reaction on every polymeric material. There are various active species such as highly excited electron, ion, and radical species in the plasma.[2] Therefore, it is an important technique to control highly active species in the plasma.

We have proposed a special technique for surface modification of fluoropolymers such as PTFE, FEP, and PFA sheet surfaces with less influence of ions and electrons.[3–6] This special technique is the remote plasma treatment. The concept of the treatment has been described earlier.

In this study, we investigated selective surface modification of fluoropolymers that consist of CF_2 and CH_2 components by remote plasma treatment. We changed plasma gases such as argon, hydrogen, and oxygen to introduce the various functional groups. There are large difference in bonding energy between C–F and C–H bond in the fluoropolymers such as ETFE and PVDF. If the chemical structure of polymers modified only the C–F component by plasma, it means defluorination (C–F bond scission) reaction occurring on the surface. On the other hand, if only a C–H component was modified by plasma, it means dehydrogenation (C–H bond scission) reaction occurring on the surface. If this plasma treatment can abstract some atoms in fluoropolymer surfaces selectively, that may introduce other desired functional groups such as carbonyl, carboxyl, hydroxyl, etc. Using this technique induced by plasma treatment, various polymeric materials properties can be controlled, for example, adhesion, wettability, and biocompatibility of polymers.

EXPERIMENTAL

Materials

Ethylene-*co*-tetrafluoroethylene (ETFE) (Asahi Glass Co. Ltd., Japan; trade name, Fluon ETFE, 100 μm thickness) and poly (vinylidene fluoride) (PVDF) films (Kureha Co., Japan; trade name, KF polymer, 60 μm thickness) were used in this study. The concentration of CH_2–CH_2 and CF_2–CF_2 components in the ETFE sheet was 47 and 53 mol %; CH_2 and CF_2 components in the PVDF sheet was 52 and 48 mol % respectively, which were estimated from the XPS analyses. These films were cut to a dimension of 10 mm ×50 mm for surface modification experiments. Prior to the surface modification experiment, ETFE and PVDF sheets were washed with ethanol in an ultrasonic washer and

dried at room temperature under vacuum. Argon, hydrogen, and oxygen were pure grade, and the purity was 99.9995%.

Plasma reactor and plasma treatments

A special reactor was used for the remote plasma treatments of the ETFE and PVDF films. The reactor consists of a cylindrical Pyrex glass tube (45 mm diameter, 1000 mm long) and a columnar stainless steel chamber (300 mm diameter, 300 mm height). The Pyrex glass tube has gas inlets for the injection of argon, hydrogen, and oxygen gases and a copper coil of nine turns for the energy input of radio frequency power (rf power: 13.56 MHz). The stainless steel chamber contains a Barocel pressure sensor (type 622, Edwards, Japan) and a vacuum system of a combination of a rotary pump (320 lit. /min) and a diffusion pump (550 lit. /s.) (type YH-350 A, Ulvac Co., Japan). The Pyrex glass tube is jointed with the chamber in a manner of Vilton O ring flange. Samples were positioned at a constant distance of 0 mm (direct plasma region) and 800 mm (remote plasma region) from the center of the copper coil, and were exposed to the argon, hydrogen, and oxygen plasmas separately. First, air in the reaction system was displaced with argon. Afterward, the reaction chamber was evacuated to approximately 1.3×10^{-2} Pa, and then argon, hydrogen, and oxygen whose flow rate was adjusted to 10 cm^3 (STP)/min by a mass flow controller was introduced into the Pyrex glass tube. The argon, hydrogen, and oxygen plasmas were operated at an rf power of 25, 50, 75, and 100 W at a system pressure of 13.3 Pa for given times (10 ~ 180 s).

Contact angle of water on the plasma treated etfe and pvdf films

Using the sessile drop method,[7] contact angles of water on the ETFE and PVDF films treated with the Ar, H_2, and O_2 plasmas were measured at 20°C using a contact angle meter with a goniometer (Erma Co. Ltd., Japan, model G-1). An average contact angle was determined from 10 measurements with an experimental error of 3–4 degrees.

X-ray photoelectron spectroscopy (xps)

XPS spectra of the surfaces of the ETFE and PVDF sheets treated with remote argon, hydrogen, and oxygen plasmas were obtained on a Shimadzu (Japan) ESCA 3400 spectrometer using a nonmonochromatic MgKα photon source at an anode voltage of 6 kV, an anode current of 20 mA, and a pressure of 5×10^{-6} Pa. The sample size of the analysis was a circular area of 6 mm diameter, and the take-off angle of photoelectrons was 70 degrees against the sample surface. The

XPS spectra were referenced with respect to the 688.65 eV fluorine 1s core lever to eliminate charging effects. The spectra were not modified by the smoothing procedure. The C1s and O1s 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 C1s, O1s, and F1s core level spectra were S (C1s) = 1.00, S (O1s) = 2.85, and S (F1s) = 4.26. The F/C and O/C atomic ratios were calculated from the F1s, O1s, and C1s intensities with an experimental error of less than 0.03.

Atomic Force Microscopy (AFM)

The topographic measurements of untreated ETFE and plasmas treated ETFE sheet surfaces were done on a Digital Instruments NanoScope IIIa type (US) to observe their surface configuration. A squared-pyramidal oxide-sharpened silicon nitride tip (V-shaped) was used as a probe, and an area of 2×2 μm square was scanned under a phase imaging method by tapping mode.

RESULTS AND DISCUSSION

Surface degradation and morphology of plasma treated etfe

Plasma contains electrons, ions, and radicals, which are able to play as active species in surface modification. When polymer surfaces are exposed to plasma, two main reactions are occurring simultaneously on the polymer surfaces. One is the introduction reaction of functional groups. The other is the degradation (etching reaction) of polymer chains to products with low molecular weight. Radicals contribute to the introduction reaction in the plasma. Ions and electrons mainly initiate the degradation reactions. The former reaction is a genuine process for the surface modification, but the latter reaction never contributes to surface modification. Which reaction is initiated by these species depends mainly on the nature of the plasma gases, as well as the energy level of the plasma and nature of the polymeric materials.[8] In this concept, we have to seek modification conditions for minimizing the degradation reactions.

We have proposed a special technique for the surface modification under less influence of ions and electrons.[3] In general, degradation products will be formed on the polymer surface when polymer surfaces are exposed to plasma. We believe that the remote plasma leads to less degradation products than the direct plasma (inside the glow region) treatment. Table I shows the change of contact angle on the plasma treated ETFE surfaces before and after the

TABLE I
Contact Angle Changed on Plasmas Treated ETFE Sheet Surfaces by Rinsing with Ethanol

Gas	Plasma treatment			Contact angle (deg.)		
	Sample position (mm)	Exposure time (s)	RF power (W)	After rinsing	Before rinsing	Def.
Untreated	-	-	-	106	106	0
Argon	800	10	100	78	77	1
	800	60	100	54	57	3
	800	180	100	58	58	0
Hydrogen	800	10	100	56	53	3
	800	60	100	44	42	2
	800	180	100	39	38	1
Oxygen	800	10	100	86	86	0
	800	60	100	80	77	3
	800	180	100	77	75	2
Argon	0	180	100	42	26	16
Hydrogen	0	180	100	62	45	17
Oxygen	0	180	100	82	63	19

ethanol rinsing. The table shows that contact angles of water on the remote plasma treated ETFE surfaces before and after ethanol rinsing had a small difference. However, the contact angle on the ETFE surface treated with direct plasma was more extensive (16–19°) between before and after rinsing. The small difference in the water contact angle before and after rinsing for ETFE surfaces treated with remote plasmas indicates that no degradation products formed on the ETFE surface by remote plasma treatments. On the other hand, the ETFE surfaces treated with direct plasmas contained a large amount of degradation products. This increase in water contact angle by ethanol rinsing may be due to removal of some degradation products from the treated film surface. Furthermore, we evaluated the degradation process by means of weight loss measurement. Figures 1 and 2 show the weight loss on ETFE sheet surfaces treated by three remote plasmas as a function of plasma exposure time at 100 W of rf power. The weight loss, as shown in

Figures 1 and 2, was nearly a linear relationship with the plasma exposure time. In the case of remote hydrogen plasma, weight loss was 7 μg at 60 s. However, weight loss was increased as highly as 2 times (16 μg) at the same exposure time when treated with direct hydrogen plasma. In the case of argon and oxygen plasmas, weight loss was higher than that of hydrogen plasma treatment. The weight loss was deeply related with degradation reaction. In the remote plasma zone, argon plasma treated ETFE showed the greatest weight loss, and oxygen plasma treated ETFE showed the greatest weight loss in the direct plasma. In the case of remote argon plasma, active species (electron and argon ions) mainly attacked the polymer surface due to argon plasma not containing radical species. In the case of direct plasma, argon plasma willing to act on crosslinking reaction and the heavy oxygen plasma initiated degradation reaction may be due to higher energy species attacks on the polymer surface. From these results, it is sure that the remote plasma treat-
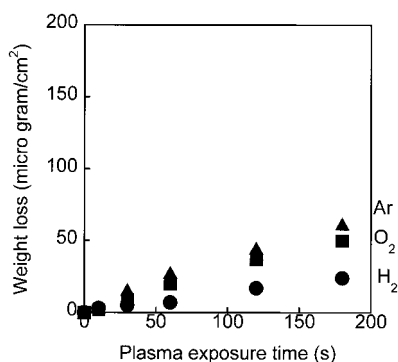

Figure 1 Weight loss on ETFE sheet surfaces treated with remote plasmas as a function of plasma exposure time (rf power: 100 W).
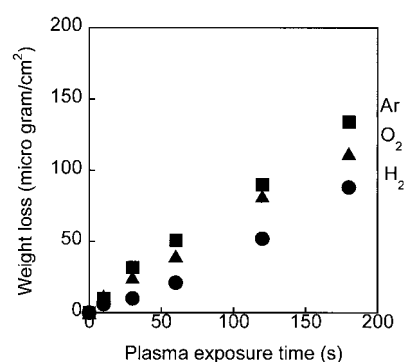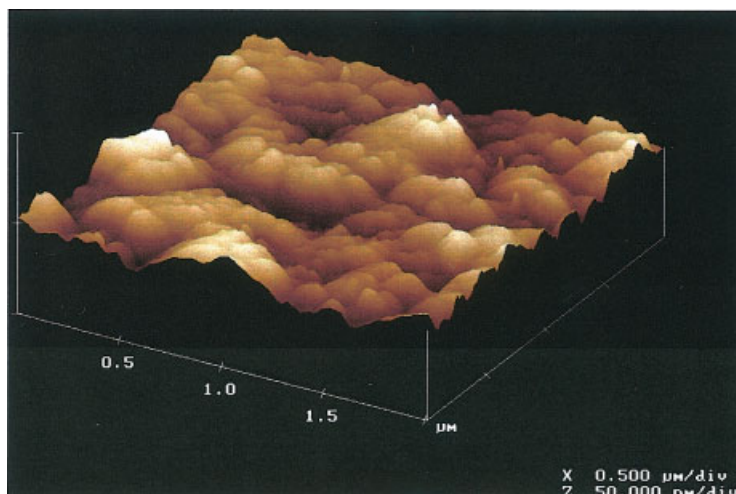

Figure 2 Weight loss on ETFE sheet surfaces treated with direct plasmas as a function of plasma exposure time (RF power: 100 W).
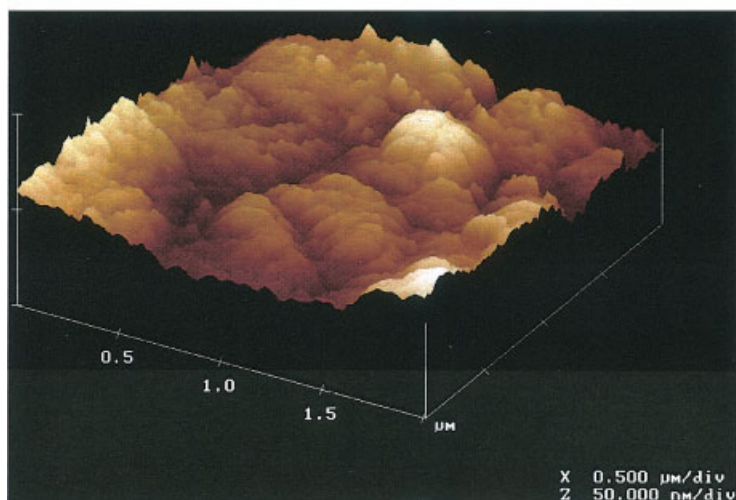
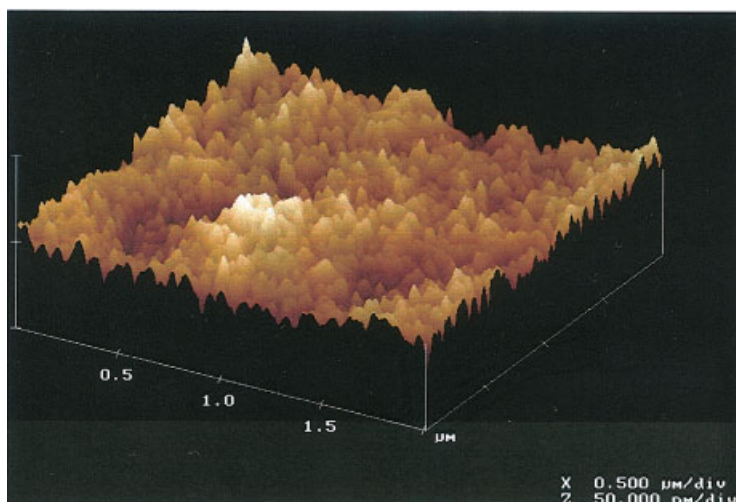**Figure 3** Comparison of typical AFM images between remote and direct hydrogen plasma treated ETFE sheet surface.

ment leads to a little damage on the ETFE sheet surface.

To investigate the surface morphology, the ETFE sheets were exposed to argon, hydrogen, and oxygen plasma (at an rf power of 100 W) at different positions from the plasma zone. Figure 3 shows the different AFM images between remote and direct plasma treated ETFE surfaces. In the remote hydrogen plasma, the surface morphology was less changed compared with the original surface. However, in the
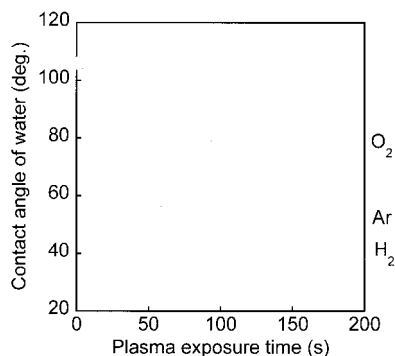
Figure 4 Contact angle of water on ETFE surfaces treated with remote argon, hydrogen, and oxygen plasmas as a function of plasma exposure time (RF power: 100 W).
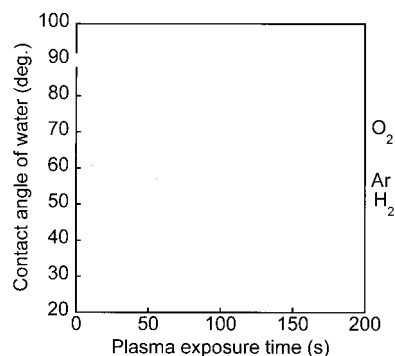

Figure 5 Contact angle of water on PVDF surfaces treated with remote argon, hydrogen, and oxygen plasmas as a function of plasma exposure time (RF power: 100 W).

direct hydrogen plasma, surface morphology was dreadfully changed when compared with the untreated ETFE surface. From this result, we confirmed that direct plasma led to a heavy etching reaction and remote plasma treatment led to mild surface modification.

Chemical composition of etfe and pvdf surfaces treated with remote plasmas

ETFE film is an alternating copolymer of CH_2–CH_2 and CF_2–CF_2 components and PVDF film is one of the simple additional fluorocarbon polymers containing the CH_2–CF_2 component. In the previous section, we concluded that the remote plasma could modify ETFE surfaces without degradation. In this section, we evaluate the formation of functional groups on the ETFE and PVDF sheet surfaces. The ETFE and PVDF sheet surfaces treated with the three remote plasmas at 100 W were evaluated by contact angle of water and XPS analysis.

Figure 4 compares the contact angle of water on ETFE surfaces treated with three remote plasmas, as a function of plasma exposure time at 100 W. On the remote argon, hydrogen, and oxygen plasmas treated ETFE sheet surface, as shown in Figure 4, contact angle decreased within a short plasma exposure time. Decrease in the water contact angle was the largest (44 degrees) in the case of hydrogen plasma, and was the smallest (80 degrees) in the case of the oxygen plasma. Thus, kind of plasma influenced the modification reactions of the copolymers. Figure 5 compares the contact angle of water on PVDF treated with remote argon, hydrogen, and oxygen plasmas at 100 W as a function of plasma exposure time. The figure shows that the remote hydrogen plasma was the most effective in the modification, but the remote oxygen plasma was not effective compared with the hydrogen and argon plasmas. It is clear that the remote oxygen

plasma initiated different reactions compared with the argon and hydrogen plasmas.

We ascertained the chemical changes that occur in ETFE and PVDF sheet surfaces as results of remote argon, hydrogen, and oxygen plasma treatments by XPS analyses. Figure 6 shows typical C1s and O1s
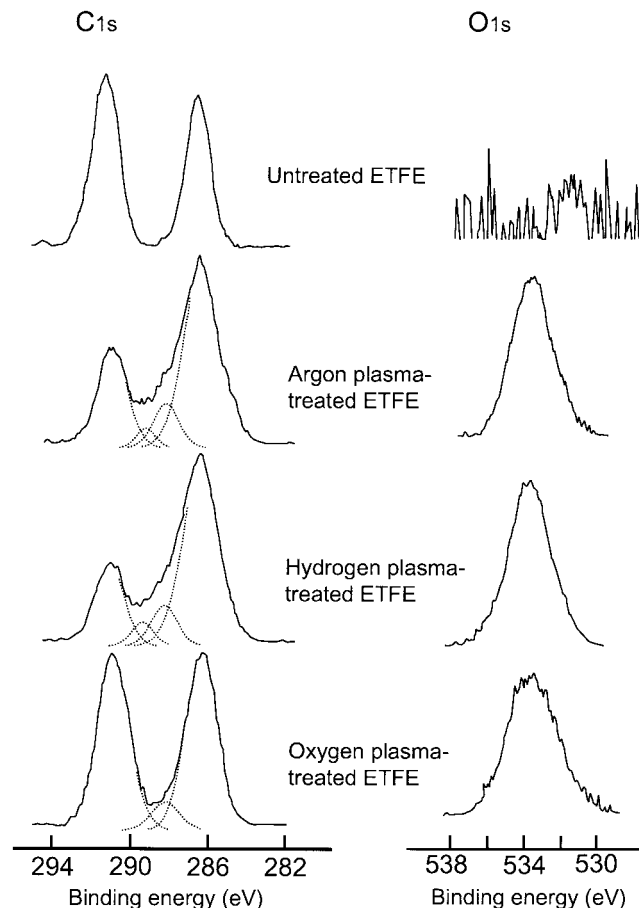

Figure 6 Typical C1s and O1s spectra of ETFE surfaces treated with remote argon, hydrogen, and oxygen plasmas at 100 W for 60 s.

TABLE II
C1s Components of ETFE Sheet Surfaces Exposed to Argon, Hydrogen, and Oxygen Plasmas at 100 W for 60 s

Plasma treatment		C1s components (mol %)			
Gas BE (eV)	Sample position (mm)	CH_2–$\underline{C}H_2$–CF_2 CH_2–$\underline{C}H_2$–CHF O–$\underline{C}H_2$–CH_2 286–286.4	CH_2–$\underline{C}HF$–CHF O–$\underline{C}H_2$–CF_2 288.3–288.7	CH_2–$\underline{C}HF$–CF_2 CHF–$\underline{C}HF$–CHF O–$\underline{C}HF$–CHF 289.3–289.5	–$\underline{C}F_2$–CH_2– 291.1–291.4
Untreated		46.2	0	0	53.8
Argon	800	59.5	10.7	3.6	26.2
Hydrogen	800	63.5	10.2	5.1	21.1
Oxygen	800	43.9	6.8		49.4

spectra for the ETFE sheet surfaces treated with the three remote plasmas. The untreated ETFE surface showed a simple two peaks at 291.2 eV (due to CF_2) and 286.2 eV (due to CH_2) components. The three remote plasmas treated ETFE surfaces showed complex C1s spectra, which were different from these for the untreated. The C1s spectra were decomposed into four components, which were the results of the decomposition, shown in Table II. The decomposed peaks were illustrated in dotted lines in Figure 6. The four components appeared at 286.0–286.4, 288.3–288.7, 289.3–289.5, and 291.1–291.4 eV, which were assigned to CH_2– CH_2–CHF and CH_2– CH_2–CF_2 groups; CH_2–CHF–CHF and O–CH_2–CF_2 groups; CH_2– CHF–CF_2, CHF–CHF–CHF, and O–CHF–CHF groups; and CF_2–CH_2, respectively. The italic C in these groups means the objective carbon. These assignments were done from the binding energy of carbon atoms. The binding energy was calculated from the primary (2.9 eV) and secondary effects (0.7 eV) of fluorine atoms and the primary effect (1.54 eV) of the oxygen atom.[9–11] Figure 6 indicates that CF_2 carbons were modified into CHF and CH_2 carbons and O–C carbons (O–CH_2 and O–CHF) by the plasma exposure. The reactive concentration of the decomposed groups is summarized in Table II. For ETFE sheet surfaces treated with remote argon and hydrogen plasmas, remarkably decreased –CF_2CH_2 – groups mean defluorination reaction occurred on the ETFE surfaces. In addition, remote oxygen plasma was not effective in defluorination that decreased only 8%. The original ETFE sheet, as shown in Figure 6, shows a poor O1s spectrum because of low oxygen concentration. The remote argon, hydrogen, and oxygen plasmas treated ETFE sheets showed vivid O1s spectra that appeared at 533.5–533.7 eV. These spectra mean they produced C–O groups on the ETFE surfaces. Three remote plasmas treated ETFE surfaces changed chemical structure as fluorocarbon or hydrocarbon are modified functional groups such as carbonyl groups.

Figure 7 shows similar results to ETFE treated with three remote plasmas. Typical C1s spectra resulted for the PVDF sheet surfaces treated with the remote argon, hydrogen, and oxygen plasmas. Although the

untreated PVDF surface showed a simple two peaks at 291.0 eV (due to CF_2) and 286.4 eV (due to CH_2) components, the remote plasma treated PVDF surfaces showed complex C1s spectra. These C1s spectra were decomposed into four components as shown in Table III. The four components appeared at 286.2–286.6, 288.3–288.7, 289.3–289.5, and 291.1–291.4 eV, which were assigned to –CH_2–CF_2–, CHF–CH_2–CHF, and –O–CH_2 – groups; CH_2– CHF–CH_2, CH_2–CHF–CHF, and O–CH_2–CF_2 groups; CH_2– CHF–CF_2, CHF–
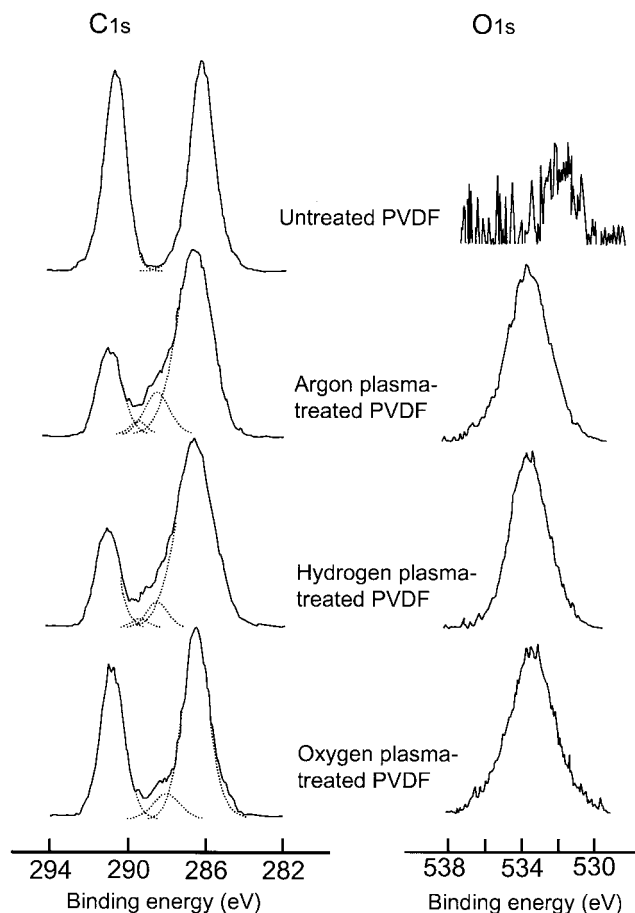

Figure 7 Typical C1s and O1s spectra of PVDF surfaces treated with remote argon, hydrogen, and oxygen plasmas at 100 W for 60 s.

TABLE III
C1s Components of PVDF Sheet Surfaces Exposed to Argon, Hydrogen, and Oxygen Plasmas at 100 W for 60 s

Plasma treatment		C1s components (mol %)			
Gas BE (eV)	Sample position (mm)	–$\underline{C}$H$_2$–CF$_2$– CHF–$\underline{C}$H$_2$–CHF O–$\underline{C}$H$_2$ 286.2–286.6	CH$_2$–$\underline{C}$HF–CH$_2$ CH$_2$–$\underline{C}$HF–CHF O–$\underline{C}$H$_2$–CF$_2$ 288.3–288.7	CH$_2$–$\underline{C}$HF–CF$_2$ CHF–$\underline{C}$HF–CHF O–$\underline{C}$HF–CHF 289.3–289.5	–$\underline{C}$F$_2$–CH$_2$– 291.1–291.4
Untreated		51.7	0	0	48.3
Argon	800	64.1	10.6	2.3	23.0
Hydrogen	800	69.9	5.9	1.7	22.5
Oxygen	800	49.1	7.5		43.4

CHF–CHF, and O–CHF–CHF groups; and CF$_2$–CH$_2$, respectively. The composition in Figure 7 indicates surely that CF$_2$ carbons were modified into CHF and CH$_2$ carbons and O–C carbons (O–CH$_2$ and O–CHF) during the plasma exposure. Effects of the plasma gases on these modifications show in Table III. The PVDF surfaces treated with remote argon and hydrogen plasmas showed a large decrease in –CF$_2$CH$_2$ – component. The decrease means that defluorination reactions occurred on the PVDF surfaces. The defluorination reaction occurred 10–53% at rf power of 100 W for 60 s. However, remote oxygen plasma treated PVDF sheet surface was not effective in defluorination (only 10%) compared with the other plasmas.

Golub et al. found that surface degradation and oxygen incorporation were found to be small for oxygen plasma treated PTFE. Fluoropolymers were resistant to oxygen attack.[12] However, we found some oxidation reactions occurred on the ETFE and PVDF sheet surfaces such as C–O groups relatively.

Selective surface modification for etfe and pvdf sheet surfaces

To investigate selective surface modification of fluoroethylene polymers, we compared the poly(tetrafluoroethylene) (PTFE) and poly(ethylene) (PE) films that were modified by three remote plasmas. Table IV compares the contact angle and chemical compositions among the PE, PTFE, and ETFE surfaces modified by the remote argon, hydrogen, and oxygen plasmas at 100 W for 60 s. Whichever we choose of the

three remote plasmas, the PE sheet surfaces were easily modified. The contact angle on the modified PE surfaces was 30 degrees by the remote argon plasma, 40 degrees by the remote hydrogen plasma, and 44 degrees by the remote oxygen plasma. From the O/C atom ratio, oxidation reaction occurred on the modified surfaces. In the case of PTFE sheet surface, remote hydrogen plasma was the most effective in hydrophilic modification. Remote argon and oxygen plasma treated PTFE sheet surfaces were little effected in hydrophilicity. From the F/C atom ratio, modified PTFE films showed defluorination reaction. Remote oxygen plasma treated PTFE sheet surface was unfavorable for defluorination and oxidation reactions compared with remote argon and hydrogen plasmas. In the case of ETFE and PVDF sheet surfaces, remote argon and hydrogen plasmas were favorable for defluorination and oxidation reactions. On the other hand, remote oxygen plasma treated ETFE and PVDF sheet surfaces show interesting results. In spite of a little defluorination reaction, remote oxygen plasma treated sheet surfaces showed oxidation reactions from the O/C atom ratio, where similar degrees (ETFE: 0.19, PVDF: 0.17) came out compared with argon (ETFE: 0.18, PVDF: 0.22) and hydrogen (ETFE: 0.20, PVDF: 0.18) plasmas.

The proportion of components in the remote plasmas treated ETFE sheet surfaces region can be estimated from the CF$_2$/CH$_2$ and C–O, CHF/CH$_2$ ratio calculated from XPS peak intensities. For clarity, these results are plotted versus different plasma gases in the histogram in Figure 8. Two results are clear. First,

TABLE IV
Comparison of Contact Angle and Chemical Composition on the Remote Plasmas Treated PE, PTFE, ETFE, and PVDF Sheet Surfaces at 100 W for 60 s

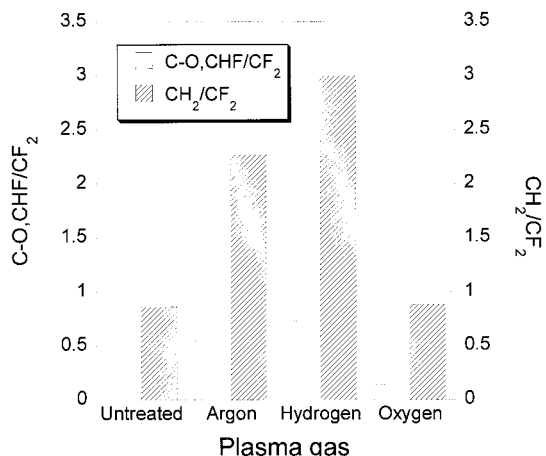| Kind of plasma	Contact angle of water (degree)				F/C ratio (mol %)			O/C ratio (mol %)			
	PE	PTFE	ETFE	PVDF	PTFE	ETFE	PVDF	PE	PTFE	ETFE	PVDF
None	101	121	106	90	1.90	1.17	0.93	< 0.02	< 0.03	< 0.03	< 0.03
Argon	30	102	54	55	1.37	0.48	0.51	0.22	0.24	0.18	0.22
Hydrogen	40	82	44	53	1.20	0.41	0.42	0.15	0.24	0.20	0.18
Oxygen	44	105	80	71	1.70	0.84	0.70	0.18	0.07	0.19	0.17

Figure 8 Defluorinated and oxidized carbons for ETFE surfaces treated with remote argon, hydrogen, and oxygen plasmas.

remote hydrogen plasma is the most effective in the hydrogen substitution after defluorination and that by argon plasma on the ETFE sheet surfaces. And remote oxygen plasma is not effective in defluorination reaction but oxidation reaction occurred on the ETFE sheet surface. From these results, we consider that each plasma processing is different and produces complicated chemical reactions with polymer surfaces.

If the remote plasma treatments could prevent degradation reactions entirely, we could propose the following mechanism based on the XPS results. A typical

mechanism on three remote plasmas treated ETFE sheet surfaces were shown in Scheme 1. From this mechanism, a possibility of selective surface modification was discussed.

In the case of remote argon plasma, ETFE film surface interacted with argon ion and electrons that are activated species in the argon plasma to make bond scission of C–F and C–H bonds. As a result, fluorine and hydrogen atoms will be removed from a polymer chain, and carbon radicals will be formed at the middle position of the polymer chain. These carbon radicals will be successively oxidized into oxygen functional groups such as hydroxyl, carbonyl, carboxyl groups, etc., when the polymer film is taken out from the plasma reactor.

A main process of ETFE in modification by remote hydrogen plasma change may be an alternation from fluorocarbon to hydrocarbon. Bond energy of C–F bond is higher than that of C–H and C–C bonds. The important factor in the modification is the stability of the product gas rather than the bond energy. The bond energy for F–F bonds is only 37 kcal/mol, and that for H–F bonds is 135 kcal/mol, and that for C–F bonds is 102 kcal/mol. High reactivity of hydrogen radicals toward fluorine atoms in the ETFE sheet also will contribute to the efficient elimination of fluorine atoms from the ETFE surface.

As shown in Scheme 1, remote oxygen plasma is not effective to abstract the fluorine atoms. In the oxygen plasma, oxygen species is difficult to abstract the flu-
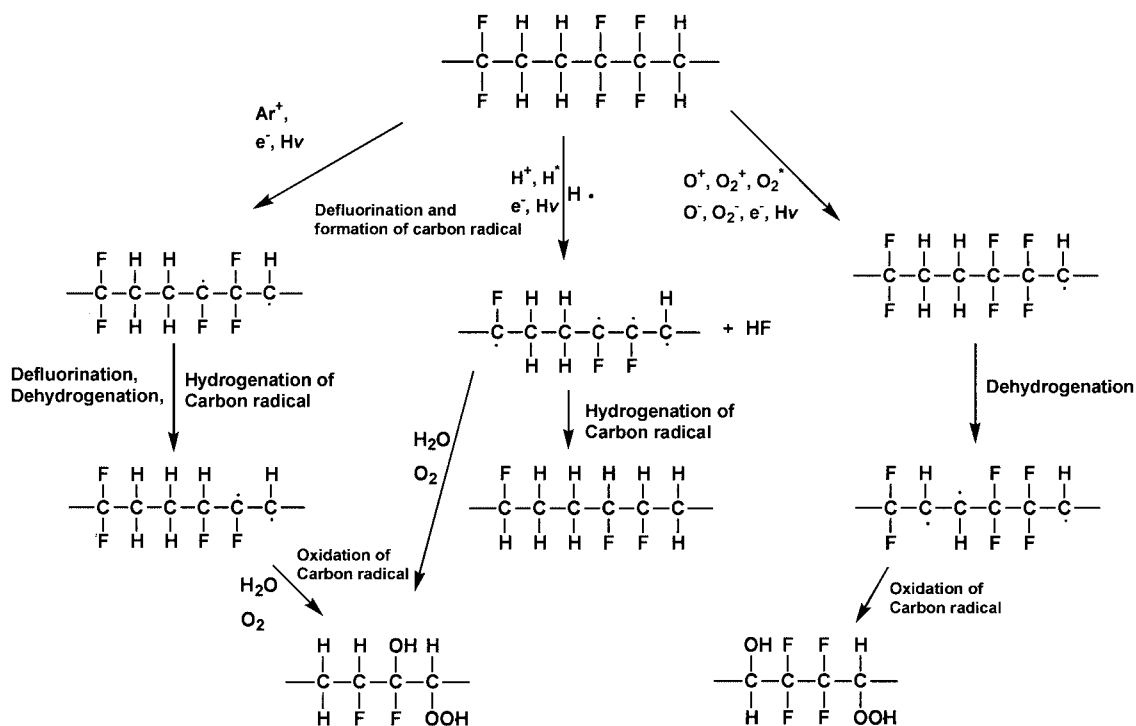
Scheme 1 A typical mechanism of ETFE sheet surface treated with remote argon, hydrogen, and oxygen plasmas.

orine atoms. Fluorine tends to recombine with carbon radicals even though oxygen species can eliminate the fluorine atoms, because remaining C radicals recombine with F radicals immediately (O–F bond energy is weaker than that of C–F bond).

CONCLUSION

A possibility of selective surface modification of fluoropolymers that consist of C–F and C–H components by three remote plasmas was investigated. The plasmas initiated degradation reaction and chemical modification process simultaneously. We confirmed the remote plasma treatment was effective in mild surface modification on the ETFE and PVDF sheet surfaces. If the remote plasma treatments could prevent degradation reactions entirely, we concluded as follows.

(1) The remote argon plasma treatment was effective in both defluorination and dehydrogenation (abstraction of fluorine and hydrogen).

(2) The remote hydrogen plasma was the most effective in alternation from fluorocarbon to hydrocarbon (abstraction of fluorine).

(3) The remote oxygen plasma treatment was not effective in defluorination but effective in dehydrogenation on the ETFE (abstraction of hydrogen).

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