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Surface modification of poly(vinylidene fluoride) film by remote Ar, H_2, and O_2 plasmas

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Abstract

The surface modification of poly(vinylidene fluoride) (PVDF) film induced by remote Ar, H_2, and O_2 plasmas have been investigated using contact angle measurement, X-ray photoelectron spectroscopy, and scanning probe microscope. The contact angle of water shows an improvement in the PVDF surface wettability during short plasma exposure time. Three remote plasmas treated PVDF sheet surfaces occurred dehydrofluorination and oxidation reactions simultaneously. Remote hydrogen plasma was the most effective in defluorination reactions and remote oxygen plasma was unfavorable to abstract fluorine atoms.

Keywords: Surface modification; Plasma; Poly(vinylidene fluoride)

1. Introduction

Fluoropolymers have unique properties such as chemical resistance, high temperature stability, low surface energy, mechanical stability, and excellent electrical resistance. These properties have been applied to various industrial fields, but pre-treatment of the polymers is normally required to achieve satisfactory adhesion. In order to increase the adhesion with other materials, many methods of pre-treatments for fluoropolymers have been reported [1].

The use of plasma treatments to produce surface modification in fluoropolymers has been studied by many researchers. Many kinds of gases are used as plasma gases for surface modification of polymers. They are argon, helium, hydrogen, nitrogen, ammonia, nitrous oxide, oxygen, carbon dioxide, sulfur dioxide, water, and tetrafluoromethane. Chemical nature of the plasma gases gives strong influences on surface modification reactions. For example, oxygen plasma is very effective in hydrophilic modification due to formation of oxygen functional groups. Nitrogen plasma is also effective in surface modification due to formation of nitrogen functionalities such as amino and amido groups. Fluorine plasma is effective in hydrophobic surface modification due to formation of fluorinated groups [2].

In the previous study, PTFE and FEP can easily be modified by plasma surface modification [3,4]. The remote plasma initiated chemical modification process on the PTFE and FEP sheet surfaces. The chemical modification involved defluorination and oxidation reactions. When polymer surfaces are exposed to plasma, two main reactions are initiated on the surfaces [5]. One is introduction reaction of functional groups such as carbonyl, carboxyl, etc., onto the polymer surfaces. As a result, the surface properties of the polymer materials are modified. The other is degradation reaction of polymer chains. The latter reaction is a burdensome process for the surface modification, because polymer chains on the surface are injured, and the surfaces are contaminated with degradation products. This injured layer (weak boundary layer) does not supply for the strong adhesion between polymeric surface and another materials.

In this study, we proposed the mild surface modification for fluoropolymers, which have CF_2 and CH_2 components by remote plasma treatments, and we also investigated the possibility of selective surface modification. If this plasma treatment can abstract some atoms (CF_2 component or CH_2 component) in fluoropolymer surfaces selectively, which may introduce other desired functional groups such as carbonyl,

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carboxyl, and hydroxyl, etc. Furthermore, we could make desired functional groups introduce on the polymeric surfaces without degradation reactions. These functional groups may be contributed to the adhesion between polymeric surfaces and other materials.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF), sheet (Kureha Co., Japan; trade name, KF polymer, 60 μm thickness) was commercially served as specimens for plasma surface modification experiments. The concentration of CH_2 and CF_2 components in the PVDF sheet was 52 and 48 mol%, respectively, which were estimated from the X-ray photoelectron spectroscopy (XPS) analyses. These films were cut to a dimension of 10 mm × 50 mm for surface modification experiments. Prior to the surface modification experiment, PVDF sheet was 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%.

2.2. Plasma reactor and plasma treatments

A special reactor for the remote plasma treatments of the PVDF sheet was used. 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 RF power (radio frequency: 13.56 MHz frequency). The stainless steel chamber contains a Barocel pressure sensor (type 622, Edwards) and a vacuum system of a combination of a rotary pump (320 l/min) and a diffusion pump (550 l/s) (type YH-350 A, Ulvac Co.). 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). The schematic diagram of the reactor is shown in Fig. 1.

2.3. Contact angle of water on the plasma-treated PVDF film

Using the sessile drop method [6], contact angles of water on the PVDF sheet 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 times measurement with an experimental error of 3–4°.

2.4. X-ray photoelectron spectra of the plasma-treated PVDF film

XPS spectra of the surfaces of the PVDF sheet treated with remote argon, hydrogen, and oxygen plasmas were obtained on a Shimadzu (Japan) ESCA 3400 spectrometer using a non-monochromatic Mg K_α photon source at an anode voltage of 6 kV, an anode current 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° against the sample surface. The XPS spectra were referenced with respect to the 688.65 eV fluorine 1s core level 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 non-linear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. Sensitivity factors (S) for the C1s, O1s, and F1s core level spectra were $S(\mathrm{C1s}) = 1.00$, $S(\mathrm{O1s}) = 2.85$, and $S(\mathrm{F1s}) = 4.26$. 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.

2.5. Scanning probe microscopy (SPM)

The topographic measurements of untreated PVDF and plasmas treated PVDF sheet surfaces were done on a Shimadzu SPM-9500 (Japan) to observe their surface configuration. A squared-pyramidal oxide-sharpened silicon nitride tip was used as a probe, and an area of 5×5 μm^2 was scanned under a phase imaging method by non-contact mode.

3. Results and discussion

3.1. Hydrophilic modification of the PVDF surface by remote plasmas

PVDF has a great balance of properties that make it suitable for many applications and one of the simple additional fluorocarbon polymers.

Figs. 2–4 show typical results of contact angle of water on the PVDF surfaces treated by remote argon, hydrogen, and oxygen plasmas as functions of the plasma exposure

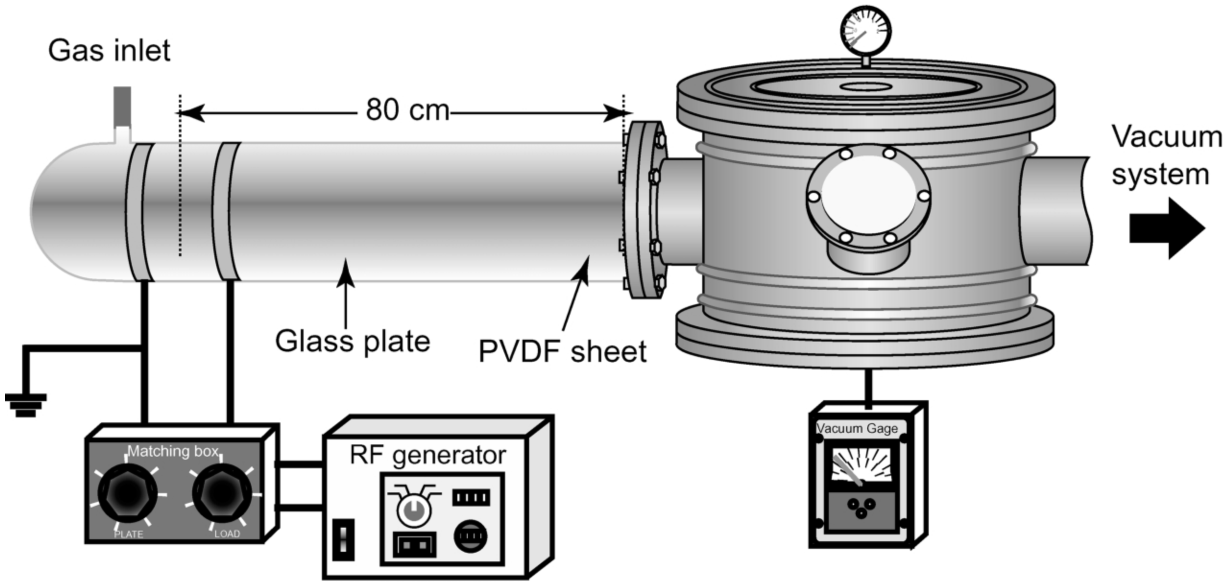

Fig. 1. Schematic representation of the remote plasma reactor.

time and RF power. Rapid decreasing in contact angle of water occurred during exposure time of 60 s, and the contact angle became a constant level after 60 s. This decrease in contact angle shows that the remote plasma treatments within a short time of 60 s can modify the PVDF surface from hydrophobic to hydrophilic. Fig. 2 shows the water contact angles of remote argon plasma-treated PVDF surfaces. In the remote argon plasma-treated PVDF, almost same values when treated at 25, 50, and 75 W, but large different at RF power of 100 W as shown in Fig. 2.

Fig. 3 shows contact angle of remote hydrogen plasma-treated PVDF surface for which contact angle depends on the RF power. Changes in water contact angle as shown in Fig. 3, at a plasma exposure time of 60 s, water contact angle decreased a constant level of 79°, 71°, 60°, and 53° at 25, 50, 75, and 100 W, respectively. The magnitude of the RF power also influences the decrease in the water contact angle. The contact angle at a plasma exposure time of 10–180 s that attained shows a linear decrease with increasing RF power.

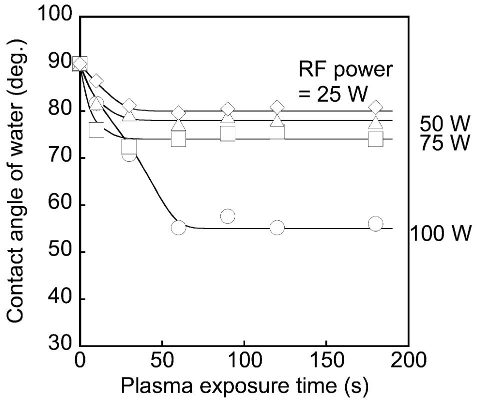

Fig. 2. Contact angle of water on PVDF surfaces treated with remote argon plasma as functions of plasma exposure time and RF power.

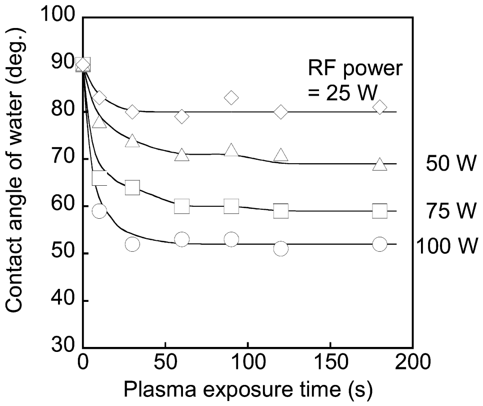

Fig. 3. Contact angle of water on PVDF surfaces treated with remote hydrogen plasma as functions of plasma exposure time and RF power.

Fig. 4 shows the contact angle of remote oxygen plasma-treated PVDF surfaces as functions of plasma exposure time and RF power. As shown in Fig. 4, remote oxygen plasma-treated PVDF sheet surface changed from 90° to 71° at 100 W for 60 s. Hydrophilicity of remote oxygen plasma-treated PVDF sheet was not good value that compared with other plasmas such as argon and hydrogen plasmas.

From theses results, there was a large difference in contact angle among the three remote plasmas. Remote hydrogen and argon plasmas were effective in hydrophilicity on PVDF sheet surface. However, remote oxygen plasma was not effective in decreasing contact angle of PVDF sheet surface.

3.2. Degradation reaction of PVDF sheet surfaces by plasma exposure

As mentioned in the previous section, plasma contains activated species able to initiate chemical and physical

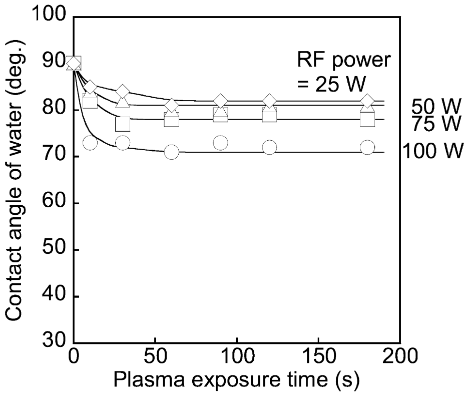

Fig. 4. Contact angle of water on PVDF surfaces treated with remote oxygen plasma as functions of plasma exposure time and RF power.

reactions at the solid surface of polymers, when it contacts with the surface of the polymers. When polymers are exposed to plasma, essentially initiated degradation reactions such as polymer chain scission and cross-linking. In general, degradation products will be formed on the polymer surface when polymer surfaces are exposed to plasma. We believe that the remote plasma (depart from the glow region) treatment leads to less degradation products than the direct plasma (inside the glow region) treatment. Table 1 shows the contact angle changes on the plasmas treated PVDF surfaces before and after the ethanol rinsing. This table showed that contact angles of water on the remote plasmas treated PVDF surfaces before and after ethanol rinsing had less difference (0–8°), but the contact angle on the PVDF surfaces treated with direct plasmas had large difference (17–25°) between before and after rinsing. Less difference for PVDF surfaces treated with remote plasmas in the water contact angle before and after rinsing indicates that degradation products were small. On the other hand, the PVDF surfaces treated with direct plasmas, contained large amount of degradation products.

Surface topography of PVDF sheets treated by three plasmas was investigated by means of SPM. SPM operating in non-contact mode was used to study the surface topography of untreated PVDF and three plasmas treated PVDF at 50 W for 60 s. Table 2 shows the surface roughness of the PVDF surfaces as a function of kind of plasma. The surface roughness (R_a) was estimated from the SPM images in $5 \times 5\ \mu m^2$. The direct argon plasma-treated PVDF sheet surface led to a large change in the surface roughness from 26.73 to 19.98 nm (−6.75 nm). On the other hand, the remote hydrogen and oxygen plasma-treated PVDF sheet surfaces never showed a large change (from 26.73 to 25.76–23.90). These large changes indicate that in the argon plasma, the etching process rather than the introduction process of functional groups may have been predominant.

From these results, we confirmed that direct plasma led heavy etching reaction and remote plasma could prevent the etching reaction relatively. Furthermore, hydrogen plasma was the most effective in mild surface modification that compared with other plasmas.

3.3. Chemical composition of PVDF surfaces treated by three remote plasmas

Atomic composition for the PVDF surfaces modified with the remote argon, hydrogen, and oxygen plasmas was estimated from relative intensities of C1s, F1s, and O1s core level spectra. Results of XPS analysis for the F/C and O/C atom ratios of PVDF surface treated with remote plasmas are summarized in Table 3. The F/C and O/C atom ratios for the untreated PVDF were 0.93 and <0.03, respectively. All plasma-treated PVDF surfaces showed lower F/C atom ratio than the untreated PVDF surface, and higher O/C atom

Table 1
Contact angle changed on plasmas treated PVDF sheet surfaces by rinsing with ethanol

Plasma treatment				Contact angle (°)		
Gas	Sample position (mm)	Exposure time (s)	RF power (W)	After rinsing	Before rinsing	Def.
Untreated	–	–	–	90	90	0
Argon	800	10	100	82	82	0
	800	60	100	55	50	5
	800	180	100	56	49	7
Hydrogen	800	10	100	59	55	4
	800	60	100	47	41	6
	800	180	100	49	41	8
Oxygen	800	10	100	73	73	0
	800	60	100	71	64	7
	800	180	100	72	66	6
Argon	0	180	100	59	34	25
Hydrogen	0	180	100	66	46	20
Oxygen	0	180	100	77	60	17

Table 2
Surface roughness of three plasmas treated PVDF film at 50 W for 60 s

Kind of plasma	Surface roughness (R_a[a]) (nm)
Untreated	26.73
Remote Ar	20.56
Direct Ar	19.98
Remote H_2	25.76
Direct H_2	24.67
Remote O_2	23.90
Direct O_2	19.87

[a] $R_a = \frac{1}{l}\int_c^1 |y|\mathrm{d}x$, where l is the roughness sampling length and y is the height of the roughness trace at a given point from the centerline.

ratio. These changes indicates that the plasma exposure led to defluorination and oxidation reactions on the PVDF surfaces. Defluorination estimated from the F/C atom ratio was 55% by the remote hydrogen plasma, 45% by the remote argon plasma, and 25% by the remote oxygen plasma at 100 W for 60 s. From these comparisons, the remote hydrogen plasma had high ability to abstract fluorine atoms from the PVDF.

To discuss defluorination and oxidation reactions for detail, we investigated from the data of narrow scanning C1s and O1s core level spectra. Fig. 5 shows typical C1s spectra 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 4. The decomposed peaks were illustrated in dotted lines in the figure. 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 $-\mathit{C}\mathrm{H}_2-\mathrm{CF}_2-$, $\mathrm{CHF}-\mathit{C}\mathrm{H}_2-\mathrm{CHF}$, and $-\mathrm{O}-\mathit{C}\mathrm{H}_2-$ groups; $\mathrm{CH}_2-\mathit{C}\mathrm{HF}-\mathrm{CH}_2$, $\mathrm{CH}_2-\mathrm{CHF}-\mathrm{CHF}$, and $\mathrm{O}-\mathit{C}\mathrm{H}_2-\mathrm{CF}_2$ groups; $\mathrm{CH}_2-\mathit{C}\mathrm{HF}-\mathrm{CF}_2$, $\mathrm{CHF}-\mathit{C}\mathrm{HF}-\mathrm{CHF}$,

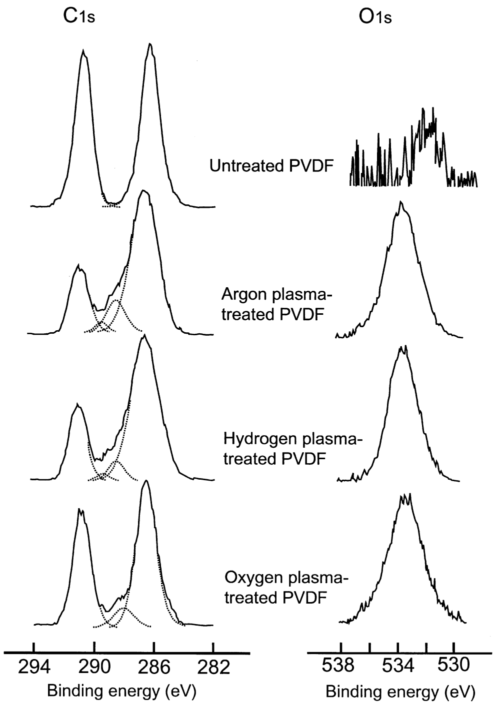

Fig. 5. Typical C1s and O1s spectra of PVDF surfaces treated with remote argon, hydrogen, and oxygen plasmas at 100 W for 60 s.

Table 3
Atom composition of PVDF sheet surfaces exposed to remote argon, hydrogen, and oxygen plasmas

Plasma treatment			Atomic ratio		Defluorination (%)
Gas	RF power (W)	Exposure time (s)	F/C	O/C	
Untreated	–	–	0.93	<0.03	0
Remote argon	100	10	0.49	0.18	47
		60	0.51	0.22	45
		180	0.42	0.23	55
	75	60	0.54	0.20	42
	50	60	0.55	0.21	41
	25	60	0.73	0.13	22
Remote hydrogen	100	10	0.49	0.17	47
		60	0.42	0.18	55
		180	0.28	0.17	70
	75	60	0.48	0.19	48
	50	60	0.56	0.16	40
	25	60	0.85	0.04	9
Remote oxygen	100	10	0.75	0.07	19
		60	0.70	0.17	25
		180	0.69	0.13	26
	75	60	0.64	0.16	31
	50	60	0.65	0.11	30
	25	60	0.75	0.14	19

Table 4
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	Sample position (mm)	$-\mathit{C}H_2{-}CF_2{-}$ $CHF{-}\mathit{C}H_2{-}CHF$ $O{-}\mathit{C}H_2$	$CH_2{-}\mathit{C}HF{-}CH_2$ $CH_2{-}\mathit{C}HF{-}CHF$ $O{-}\mathit{C}H_2{-}CF_2$	$CH_2{-}\mathit{C}HF{-}CF_2$ $CHF{-}\mathit{C}HF{-}CHF$ $O{-}\mathit{C}HF{-}CHF$	$-\mathit{C}F_2{-}CH_2{-}$
BE (eV)		286.2–286.6	288.3–288.7	289.3–289.5	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

and $O{-}\mathit{C}HF{-}CHF$ groups; and $\mathit{C}F_2{-}CH_2$, respectively. The italic C in these groups means the objective carbon. The composition in Fig. 5 indicates surely that CF_2 carbons were modified into $\mathit{C}HF$ and $\mathit{C}H_2$ carbons and $O{-}\mathit{C}$ carbons ($O{-}\mathit{C}H_2$ and $O{-}\mathit{C}HF$) during the plasma exposure. Effects of the plasma gases on these modifications are shown in Table 4. The PVDF surfaces treated with remote argon and hydrogen plasmas showed a large decrease in $-\mathit{C}F_2CH_2-$ component. Remote hydrogen plasma is the most effective in the hydrogen substitution after defluorination and that by remote argon plasma on the PVDF sheet surface as shown in Table 4. The defluorination reaction was 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.

Gloub et al. described that surface degradation and oxygen incorporation were found to be small for oxygen plasma-treated PTFE. Fluoropolymers were resistant to oxygen attack [7]. However, some oxidation reactions occurred on the PVDF sheet surfaces such as C–O groups relatively. In the oxygen plasma, oxygen species are difficult to abstract the fluorine atoms. Fluorine tends to recombine with carbon radicals even though oxygen species can eliminate the fluorine atoms. However, oxygen plasma can abstract to hydrogen atoms because eliminated hydrogen combine with oxygen atoms in stable. The important factor in the modification is the stability of the product gas rather than the bond energy.

From these results, we investigated possibility of selective surface modification of PVDF surface. In order to discuss the selective surface modification, we compared the poly(ethylene); PE film and poly(tetrafluoroethylene); PTFE films that treated by three remote plasmas. Table 5 compares the chemical compositions among the PE, PTFE, and PVDF surfaces modified by the remote argon, hydrogen, and oxygen plasmas at 100 W for 60 s. Whichever we choose the three remote plasmas, the PE sheet surfaces were easily modified from the results of O/C atom ratio. These results indicated that C–H bonds in the PVDF polymer were modified into C–O or C═O bonds by the remote plasma exposure. In the case of PTFE surface, remote argon and hydrogen plasmas were effective in defluorination and oxidation reactions. These oxidation reactions were due to the leaved carbon radicals were oxidized into oxygen functional groups when the PVDF films were taken out from the plasma reactor after finishing the modification procedure. However, remote oxygen plasma-treated PTFE sheet surface was unfavorable effect for defluorination and oxidation reactions that compared with remote argon and hydrogen plasmas. From the F/C atom ratio, remote hydrogen plasma was the most effective in defluorination reaction (F/C = 0.42) on the PVDF and that by remote argon plasma (F/C = 0.51). Remote oxygen plasma-treated PVDF sheet surfaces occurred lower defluorination reaction (F/C = 0.70) that compared with other plasmas. However, O/C atom ratios are very similar (0.17) to the other plasmas treated PVDF surfaces (Ar: 0.22, H_2: 0.18,) at 100 W for 60 s. This condition of the remote oxygen plasma, we believe that oxidation reaction is caused by dehydrogenation on the PVDF sheet surface because of oxygen plasma is difficult to abstract fluorine atoms. Unfortunately, details of the C–H modification are not clear because XPS gives us no information concerning the C–H chemistry.

4. Conclusions

PVDF surfaces were modified with the remote argon, hydrogen, and oxygen plasmas and a possibility of selective surface modification was investigated.

1. Remote hydrogen and argon plasmas were effective in hydrophilicity on PVDF sheet surface, but remote

Table 5
Comparison of chemical composition on the remote plasmas treated PE, PTFE, and PVDF sheet surfaces at 100 W for 60 s

Kind of plasma	F/C ratio (mol%)		O/C ratio (mol%)		
	PTFE	PVDF	PE	PTFE	PVDF
None	1.90	0.93	<0.02	<0.03	<0.03
Argon	1.37	0.51	0.22	0.24	0.22
Hydrogen	1.20	0.42	0.15	0.24	0.18
Oxygen	1.70	0.70	0.18	0.07	0.17

oxygen plasma was not effective in decreasing contact angle of PVDF sheet surface.

2. Remote plasma treatments were effective in mild surface modification on the PVDF sheet surface. Especially, hydrogen plasma could modify the PVDF sheet surface effectively without heavy etching reaction.
3. Remote argon, hydrogen, and oxygen plasmas treated PVDF sheet surfaces occurred dehydrofluorination and oxidation reactions simultaneously. Remote argon and hydrogen plasmas were effective in defluorination reaction and remote oxygen plasma was effective in dehydrogenation on the PVDF surface.

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