Surface Modification of Poly(tetrafluoroethylene) with Pulsed Hydrogen Plasma

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ABSTRACT: Surface modification of polymers by pulsed plasma has been investigated to minimize degradation reactions occurring at the same time as the surface modification reactions. The hydrogen radical, ion, and electron concentrations in the hydrogen plasma were simulated as a function of the elapsed time after turning off the discharge. The contact angle measurement showed that hydrogen plasma treatment, regardless of pulsed or continuous plasma, led to degradation reactions as well as defluorination and oxidation on PTFE surfaces. The degradation reactions of PTFE chains initiated by the pulsed hydrogen plasma were not as vigorous as those by the continuous hydrogen plasma. A combination of the on-time/off-time of $30/270\mu s$ in the pulsed hydrogen plasma was efficacious in modifying PTFE surfaces. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 340–348, 2002

Key words: poly(tetrafluoroethylene); surface modification; pulsed plasma treatment; defluorination; contact angle; XPS spectra

INTRODUCTION

Plasma containing electrons, ions, and radicals, can interact with polymer surfaces to modify their surfaces in chemical and physical properties. The surface modification is mainly due to the formation of functional groups on their surfaces (Process I) and the etching of their surfaces (Process II).[1] In Process I, radicals in the plasma remove hydrogen atoms when available from the polymer surface to form carbon radicals on the surface. Successively, the carbon radicals combine with other radicals in the plasma to form new functional groups on the polymer surface. This is an essential reaction for the formation of functional groups on the polymer surface. On the other hand, in Process II, electrons and ions bombard the polymer surface to make C—C bond scission of polymer chains and to form carbon radicals at the end of polymer chains. As a result, degradation reactions of the polymer chain initiate from the carbon radical to yield degradation products with low-molecular weight on the polymer surface. A part of the degradation products volatize from the surface, and weight-loss of the polymer substrate occurs. This is an essential reaction for the etching of the polymer surfaces. The etching process is not desirable for surface modification, because the surface is contaminated by degradation products. As long as plasma is used to develop reactive species for modification of polymer surface, the etching process is never avoided during the modification reactions. To avoid the etching process, charged species of electrons and ions should be removed from the plasma, and radicals

should be predominantly used as active species for the surface modification.

We have pointed out a large difference in the lifetime between hydrogen radical (H) and electron or hydrogen ions (H^+ and H_2^+) in hydrogen plasma.[2] Hydrogen radicals have a longer lifetime than electrons and hydrogen ions. If polymer substrates to be modified are separated from the hydrogen plasma, radicals, rather than electrons and ions, will attack predominantly the polymer surfaces, and surface modification without etching reactions will occur. The separation of the polymer substrate in a meaning of time is called pulsed plasma treatment, and the separation in a meaning of space is called remote plasma treatment. When hydrogen plasma being in equilibrium is turned off at a certain time, active species in the hydrogen plasma, hydrogen radicals, electrons, and hydrogen ions, start to dissipate in the reaction zone by means of recombination between two hydrogen radicals and between the hydrogen ion and electron. As a result, the concentration of the species decreases with elapsed time after turning-off the RF power. The dissipation of hydrogen radicals, electrons, and hydrogen ions does not proceed at the same rate, but the dissipation rate of electrons and hydrogen ions is faster than that of hydrogen radicals. This disparity is mainly due to the rate constant of the recombination reactions. The rate constant is 5.66×10^{-8} cm^3/s for the reaction between electron and H_2^+, 2.62×10^{-13} cm^3/s for the reaction between electron and H^+, and 8.3×10^{-33} cm^6/s for the reaction between hydrogen radicals.[3] Therefore, hydrogen radicals rather than electrons and hydrogen ions become predominant species after turning-off the RF power. Under such a situation, reactions by hydrogen radicals (Process I) will be major, and reactions by electrons and hydrogen ions (Process II, etching reaction) will be minor. This is a basic concept of "pulsed hydrogen plasma treatment."

In this study, we investigated whether the pulsed hydrogen plasma made surface modification of fluoropolymers with minimizing etching reaction possible or not. Practically, poly(tetrafluoroethylene), PTFE, film was used as a fluoropolymer substrate for the surface modification, and was modified using pulsed hydrogen plasma. The surface modification was evaluated from the
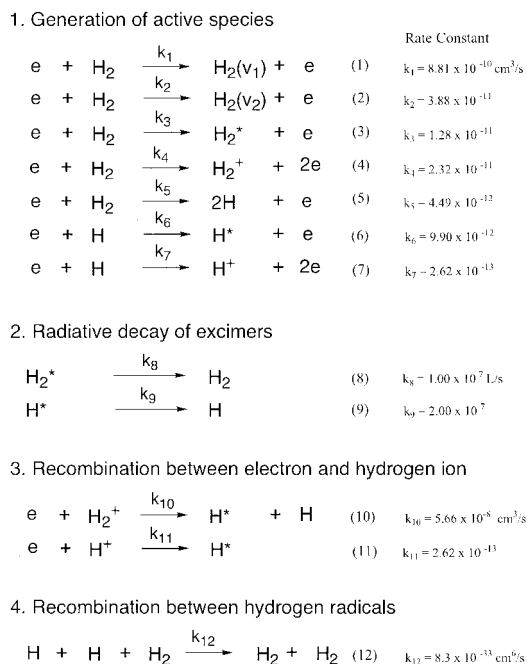
1. Generation of active species

$$e + H_2 \xrightarrow{k_1} H_2(v_1) + e \quad (1) \qquad k_1 = 8.81 \times 10^{-10}\ cm^3/s$$

$$e + H_2 \xrightarrow{k_2} H_2(v_2) + e \quad (2) \qquad k_2 = 3.88 \times 10^{-11}$$

$$e + H_2 \xrightarrow{k_3} H_2^* + e \quad (3) \qquad k_3 = 1.28 \times 10^{-11}$$

$$e + H_2 \xrightarrow{k_4} H_2^+ + 2e \quad (4) \qquad k_4 = 2.32 \times 10^{-11}$$

$$e + H_2 \xrightarrow{k_5} 2H + e \quad (5) \qquad k_5 = 4.49 \times 10^{-13}$$

$$e + H \xrightarrow{k_6} H^* + e \quad (6) \qquad k_6 = 9.90 \times 10^{-12}$$

$$e + H \xrightarrow{k_7} H^+ + 2e \quad (7) \qquad k_7 = 2.62 \times 10^{-13}$$

2. Radiative decay of excimers

$$H_2^* \xrightarrow{k_8} H_2 \quad (8) \qquad k_8 = 1.00 \times 10^7\ L/s$$

$$H^* \xrightarrow{k_9} H \quad (9) \qquad k_9 = 2.00 \times 10^7$$

3. Recombination between electron and hydrogen ion

$$e + H_2^+ \xrightarrow{k_{10}} H^* + H \quad (10) \qquad k_{10} = 5.66 \times 10^{-8}\ cm^3/s$$

$$e + H^+ \xrightarrow{k_{11}} H^* \quad (11) \qquad k_{11} = 2.62 \times 10^{-13}$$

4. Recombination between hydrogen radicals

$$H + H + H_2 \xrightarrow{k_{12}} H_2 + H_2 \quad (12) \qquad k_{12} = 8.3 \times 10^{-33}\ cm^6/s$$

Figure 1 Elemental reactions in hydrogen plasma; $H_2(v_1)$ and $H_2(v_2)$ mean the excited vibration states. H_2^* and H^* mean excimers.

contact angle on the modified surfaces and chemical composition of the modified surfaces as functions of the interval between turning-on and tuning-off of hydrogen plasma (on and off time) and RF power.

BACKGROUND OF PULSED HYDROGEN PLASMA TREATMENT

Hydrogen plasma is a mixture of hydrogen ions, hydrogen radicals, hydrogen excimer, and hydrogen molecules. Essential reactions occurring in hydrogen plasma are (1) generation of activated species by collision with electrons, (2) radiative decay of the excimer, (3) recombination between electrons and ions, and (4) recombination between two radicals. Details of these essential reactions are shown in Figure 1.[8] Although hydrogen plasma has many activated species, all of the species cannot interact with the PTFE surfaces. The hydrogen radical and hydrogen ions play important roles in the surface modification of PTFE. Hydrogen radicals modify PTFE surfaces by means of substitution of hydrogen atoms with fluorine atoms on PTFE surfaces.

PTFE   Hydrogen radical

Defluorinated PTFE
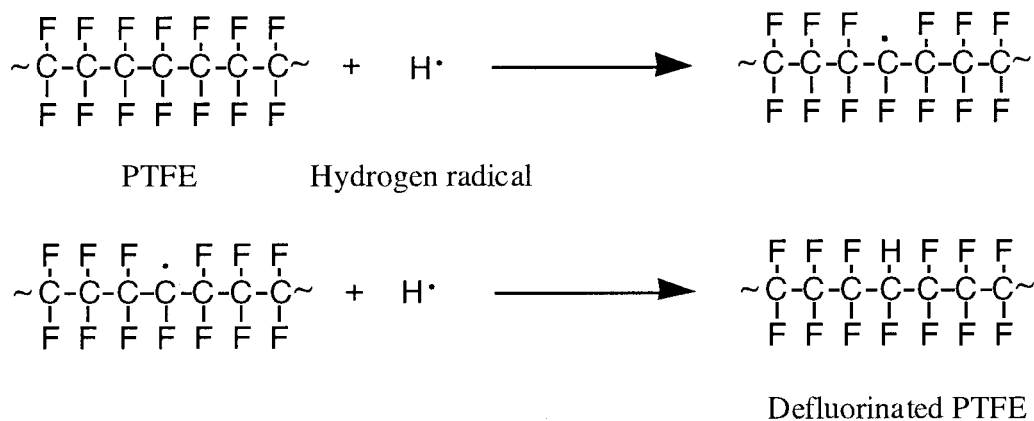
Hydrogen ions etch PTFE surfaces by means of ion bombardment to modify surface morphology.

PTFE

Hydrogen ions and Electrons

Bond scission

Degradation products
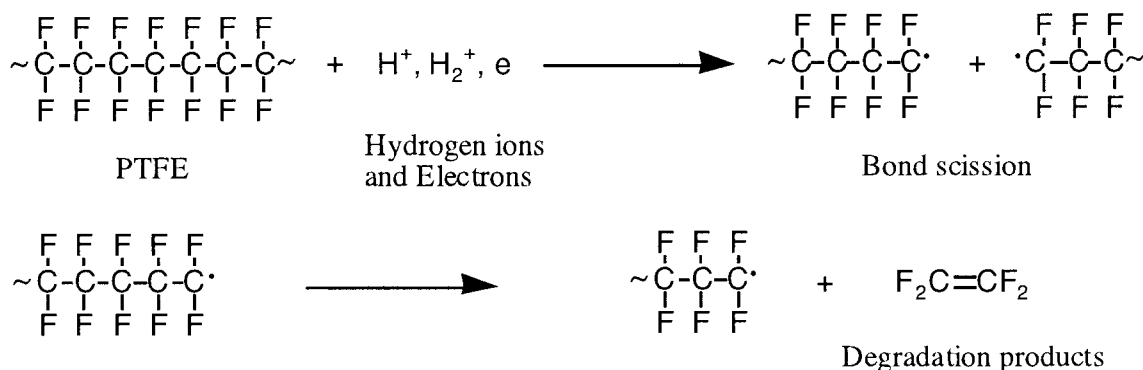
Therefore, we believe that the hydrogen radical and ion concentration in the system is an important factor to modify PTFE surface. Hydrogen radicals (H) are produced by Reaction 5, and are dissipated by Reactions 6, 7, and 12. Hydrogen ions (H_2^+ and H^+) are produced by Reactions 4 and 7, and are dissipated by Reactions 10 and 11. As long as the supply of RF power to the system continues, the production and dissipation of hydrogen radicals and ions are in equilibrium. The concentration of these species is kept constant. When the RF power is discontinued, the concentration of these species will decrease according to Reactions 10, 11, and 12. The decrease may be a function of the elapsed time after discontinuance of the RF power. We simulate the dissipation rate of hydrogen radicals and ions using a model of the pulsed hydrogen plasma treatment. The model consists of a space of hydrogen plasma and hydrogen gas flow at a constant flow rate (A). Hydrogen

gas flows at a flow rate of A in the reactor on the left side and flows out from the reactor on the right side. The hydrogen plasma expands into all spaces of the reactor, and the concentration of hydrogen radicals, hydrogen ions, and electrons is homogeneous in all spaces of the reactor. When the RF power is discontinued at time zero, the hydrogen radicals and hydrogen ions start to dissipate according to Reaction 12 and Reactions 10 and 11, respectively. The concentration (C_r) of the hydrogen radicals at an elapsed time of t is written as follows:

$$\frac{\partial C_r}{\partial t} = -k_{12}C_n(C_r)^2 + k_{10}(C_i)^2 - AC_r \qquad (1)$$

where k_{12}, and k_{10} are the rate constant of Reactions 12 and 10, respectively. C_i, C_n, and C_r are the concentrations of hydrogen ions, neutral hy-
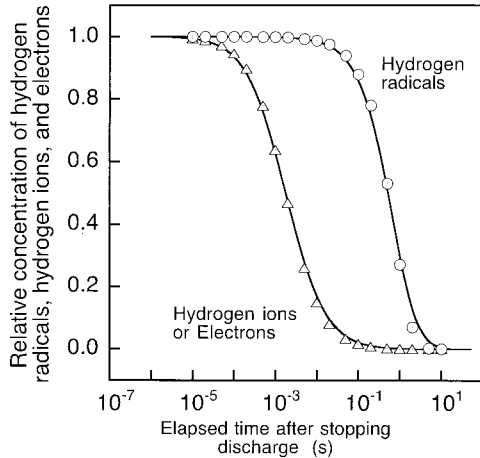
Figure 2 Relative concentration of hydrogen radicals, hydrogen ions, and electrons as a function of elapsed time after stopping discharge; ○, relative concentration of hydrogen radicals; △, relative concentration of hydrogen ions or electrons.

drogen molecules, and hydrogen radicals, respectively. The first term on the right side of eq. (1) is the dissipation rate of hydrogen radicals by Reaction 12. The second is the generation rate of hydrogen radicals by Reaction 10, and the last term is the traveling rate of hydrogen radicals by a hydrogen gas stream. A is the velocity of the hydrogen gas stream. Also, the concentration (C_i) of the hydrogen ions at the time of t is written in a similar formula. The first term is the dissipation rate of the hydrogen ions by Reactions 10 and 11. The second term is the traveling rate of hydrogen ions by the hydrogen stream.

$$\frac{\partial C_i}{\partial t} = -(k_{10} + k_{11})C_e C_i - AC_i \qquad (2)$$

where k_{10} and k_{11} are the rate constant of Reactions 10 and 11, respectively. C_e and C_i are the concentrations of electrons and hydrogen ions, respectively.

Using the Mathematica program (Wolfram Research Inc., ver. 2.2), numerical calculation of eqs. (1) and (2) was done with reference to the literature.[4,5] The following boundary conditions were taken into the numerical calculation from refs. 5 and 6. The C_r, C_i, and C_e concentrations at $t = 0$ were 10^{15}, 10^{10}, and 10^{10} cm^{-3}. A was 1.3 s^{-1}. The relative concentrations of hydrogen radicals, hydrogen ions, and electrons are plotted as functions of the elapsed time (Fig. 2). The relative

concentrations of hydrogen radicals, hydrogen ions, and electrons are 1.0 at an elapsed time of zero. The hydrogen radical concentration, as shown in Figure 2, shows less decrease up to an elapse time of 50 ms, and shows some decrease after 100 ms. On the other hand, the hydrogen ion and electron concentrations show some decrease even at 100 μs. Therefore, we believe that at elapsed times of more than 100 μs the hydrogen radical may be the main species, and radical reactions will proceed predominantly.

EXPERIMENTAL

Materials

A poly(tetrafluoroethylene) (PTFE) sheet that was received from Nitto Denko Co. (Nitofuron NO900UL) in a form of 300 mm wide and 1 μm thick, was used as a specimen for surface modification experiments. Prior to the modification experiment, the PTFE sheets were washed with acetone in an ultrasonic washer and dried at room temperature under vacuum.

Pulsed Hydrogen Plasma Reactor and Pulsed Plasma Treatment Procedure

A commercial vacuum deposition apparatus (Ulvac Co., Japan; model EBH6) consisting of a bell-jar chamber (400 mm diameter × 590 mm high) and a vacuum system with a combination of a rotary pump (320 L/min) and diffusion pump (550 L/s) was remodeled to be pulsed hydrogen plasma reactor. The reactor contained a diode planar electrode (100 × 100 mm) made of stainless steel for glow discharge, a sample stage (100 × 100 mm) made of stainless steel mesh, a hydrogen gas inlet, and a vacuum gauge were installed in the bell-jar chamber. The diode electrodes were separated by 100 mm from each other. The sample stage was positioned midway between the diode electrodes. A schematic diagram of the reactor is shown in Figure 3. Electric power at 13.56 MHz frequency was applied between the diode planar electrodes through a matching box (Adtec Co., Japan; model AMV-500SU) from a RF power source (Adtec Co., Japan; model AX-1000-P-1). The RF power was modulated using a function generator (Sony, Japan; model AFG310).

The PTFE sheets were positioned on the sample stage, and exposed to the pulsed hydrogen
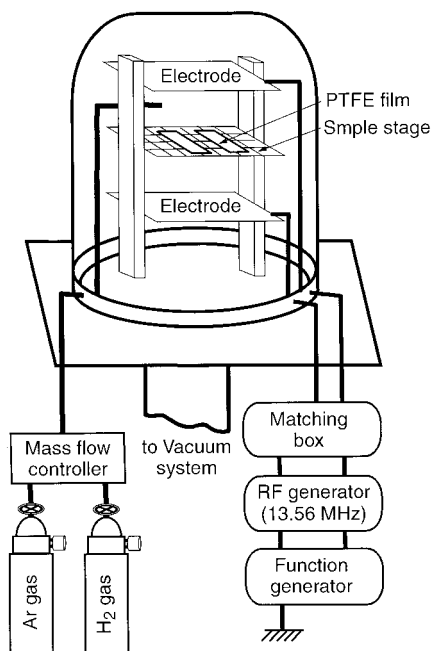
Figure 3 Schematic diagram of reactor for pulsed hydrogen plasma treatment.

plasma for a given period. First, air in the reactor was displaced with argon. Afterward, the reactor was evacuated to approximately 1.3×10^{-2} Pa, and then hydrogen, whose flow rate was adjusted to 10 cm^3 (STP)/min by a mass flow controller and was introduced into the reactor. The pulsed hydrogen plasma was operated at a RF power of 75 to 400 W at 13.56-MHz frequency at a system pressure of 13.3 Pa. The modulation of the pulsed cycle, on-time/off-time in μs, was 30/170, 30/270, 30/570, and 30/2970.

Contact Angle of Water on the Treated PTFE Surfaces

Using the sessile drop method,[7] contact angles of water on the treated PTFE surfaces 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. An experimental error for the contact angle measurement was 3–4°.

X-ray Photoelectron Spectra

XPS spectra for the PTFE surfaces treated with the pulsed hydrogen plasma were obtained on a Shimadzu ESCA K1 using a nonmonochromatic MgK$_\alpha$ photon source. The anode voltage was 12

kV, the anode current 20 mA, and the background pressure in the analytical chamber 1.5×10^{-6} Pa. The XPS spectra were referenced with respect to the 690.0 eV fluorine 1s core level to eliminate the charge effect. 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. The sensitivity factors (S) for the core levels were $S(C_{1s}) = 1.00$, $S(O_{1s}) = 2.85$, and $S(F_{1s}) = 4.26$. Experimental error for the estimation of F/C and O/C atom ratios from the relative F_{1s}, O_{1s}, and C_{1s} intensities was within 0.03.

RESULTS AND DISCUSSION

Degradation Reactions of PTFE Surfaces Initiated by Pulsed Hydrogen Plasma

When PTFE surfaces are exposed to hydrogen plasma, hydrogen radicals in the hydrogen plasma will cause defluorination of their surfaces, while hydrogen ions and electrons in the hydrogen plasma will cause C—C bond scission in the PTFE polymer chains to form radicals at the polymer chain ends. As a result, degradation reactions will initiate from the radicals, and some degradation products will deposit on their surfaces. Therefore, the PTFE surfaces just after the treatment by hydrogen plasma are not genuine surfaces but ones stained with some degradation products. These degradation products should be removed from the surface. We believe that, if some degradation reactions occur, there will be some difference in the contact angle between the PTFE surfaces before and after removing degradation products. The difference is an indicator as to how much degradation product the hydrogen plasma formed. Thus, surface modification of PTFE by the pulsed hydrogen plasma was assessed from a viewpoint of the contact angle.

The PTFE surfaces were treated with the pulsed hydrogen plasma at a RF power of 100 W at an off-time of 2970, 570, 270, and 170 μs for a treatment time of 900 s. The on-time in the pulsed plasma cycle was kept a constant of 30 μs. The duty cycle, which is a ratio of the on-time and off-time, was 0.01 to 0.15. The treatment time

Table I Difference in Water Contact Angle between Pulsed or Continuous Plasma-Treated PTFE Surfaces before and after Acetone Rinsing

| | | | | Water Contact Angle on Plasma-Treated PTFE Surfaces (Degree) | | |
| | Treatment by Pulsed or Continuous Hydrogen Plasma | | | | | |
Kind of Plasma	RF Power (W)	On/Off Time (μs)	Treatment Time (s) (Net Exposure Time, s)	Before Acetone Rinsing	After Acetone Rinsing	Difference
Pulsed	100	30/2970	900 (9)	101	100	−1
		30/570	900 (45)	76	82	6
		30/270	900 (90)	74	80	6
		30/170	900 (135)	74	85	11
Continuous	100		10 (10)	62	90	28
			40 (40)	67	84	17
			90 (90)	67	86	19
			120 (120)	67	88	21
Untreated PTFE				118	118	

(900 s) does not mean the net exposure time to hydrogen plasma, but how much time the PTFE films were treated by the cycle of the on-time and off-time. The net exposure time is a product of the duty cycle (0.01 to 0.15) and treatment time (900 s). Successively, the treated PTFE sheet surfaces were rinsed with acetone using an ultrasonic washer to remove degradation products on the PTFE surfaces. The PTFE surfaces just after the treatment by the hydrogen plasma are called the treated PTFE surfaces before the acetone rinsing. The PTFE surfaces treated with the hydrogen plasma and rinsed with acetone are referred to as the treated PTFE surfaces after the rinsing. The contact angle of water on the treated PTFE sheet surfaces before and after the acetone rinsing was measured. Table I compares the water contact angles for the treated PTFE sheet surfaces before and after the acetone rinsing as a function of the off-time.

The pulsed hydrogen plasma treatment, as shown in Table I, showed large decreases in the contact angle from 118 degrees for the original PTFE surface to 74–76 degrees for the treated PTFE surfaces except for one treated at an off-time of 2970 μs. Once these PTFE surfaces were rinsed with acetone, the surfaces showed some increases in the contact angle, with the one treated at an off-time of 2970 μs again the exception. The increase was in the range of 6–11 degrees (Table I). This indicates that some change occurred on the PTFE surfaces by the acetone rinsing. We believe that the change may be due to

removing degradation products from the PTFE surfaces. Similarly, in the continuous hydrogen plasma treatment, the treated PTFE surfaces before the acetone rinsing showed some increases of 17–28 degrees by acetone rinsing (Table I). The difference (17–28 degrees) for the continuous hydrogen plasma-treated PTFE surfaces before and after acetone rinsing is larger than that (6–11 degrees) for the pulsed hydrogen plasma-treated PTFE surfaces before and after the acetone rinsing. This comparison indicates that the pulsed hydrogen plasma made less degradation product on the PTFE surfaces than the continuous hydrogen plasma.

The pulsed hydrogen plasma also was compared with the continuous hydrogen plasma with regard to the contact angle on the treated PTFE surface after acetone rinsing. The contact angle on the pulsed hydrogen plasma-treated PTFE surfaces after the acetone rinsing, as shown in Table I, was 80–85 degrees, excluding the long off-time example. While the contact angle on the continuous hydrogen plasma-treated PTFE surfaces after the acetone rinsing was 84–90 degrees. This comparison shows that the contact angle on the PTFE surfaces treated with the pulsed hydrogen generally on the low side of that for the continuous hydrogen plasmas. A combination of the on-time/off-time of 30/270 μs in the pulsed hydrogen plasma is efficacious in modifying PTFE surfaces, and showed the lowest contact angle of 80 degrees.

Table II Atom Composition of PTFE Surfaces Treated with Pulsed and Continuous Hydrogen Plasmas

| Kind of Plasma | Pulsed and Continuous Hydrogen Plasma Treatment | | | Atom Composition of Treated PTFE | |
	RF Power (W)	On/Off Time (μs)	Treatment Time (s) (Net Exposure Time, s)	F/C Atom Ratio	O/C Atom Ratio
Pulsed	25	30/270	900 (90)	1.6	<0.05
	75	30/270	900 (90)	0.76	0.12
	100	30/270	900 (90)	0.74	0.11
	200	30/270	900 (90)	0.57	0.14
	300	30/270	900 (90)	0.42	0.18
	400	30/270	900 (90)	0.72	0.10
Continuous	75		120 (120)	0.60	0.07
Untreated PTFE				1.9	<0.05

Chemical Composition of PTFE Surfaces Treated with Pulsed Hydrogen Plasma

The surface modification by the pulsed hydrogen plasma was assessed from a viewpoint of the atom composition. The atom composition (F/C and O/C atom ratios) on the treated PTFE surfaces was analyzed with XPS. The specimens for the analysis were the PTFE surfaces treated with the pulsed hydrogen plasma at an on-time/off-time cycles of 30/270 μs for a treatment time of 900 s at RF power of 25–300 W. Prior to the XPS analysis, the treated PTFE sheet surfaces were rinsed with acetone to remove degradation products from the surfaces. Table II shows the F/C and O/C atom ratios for the PTFE surfaces treated with the pulsed hydrogen plasma. There are large decreases in the F/C ratio from 1.9 to 0.42–0.76 and some increase in the O/C atom ratio from <0.05 to 0.10–0.18 for the treated PTFE surfaces except for the surface treated at an RF power of 25 W. These changes in atom composition indicates that defluorination and oxidation occurred on the PTFE surfaces. The defluorination may be due to a combination of two reactions: hydrogen radicals in the pulsed hydrogen plasma removed fluorine atoms on the PTFE surface to form a carbon radical, and the carbon radical recombined with another hydrogen radical in the pulsed hydrogen plasma. Some of the carbon radicals reacted with oxygen in air when the PTFE surface was taken out from the plasma reactor after finishing the plasma treatment. This may be a mechanism of the oxidation.

The F/C and O/C atom ratios in Table II are shown graphically as a function of the rf power in Figure 4. The F/C atom ratio decreased linearly with increasing rf power except at 25 W. On the other hand, the O/C atom ratio increased with increasing the rf power. This indicates undoubtedly that defluorination and oxidation reactions were strongly influenced by magnitude of the rf power. Is there any difference in modification reactions at low and high rf powers such as 75 and 300 W? The surface modification by hydrogen plasma, as described in the Introduction, is based on two competitive processes—substitution reaction of fluorine atoms on the PTFE surfaces by hydrogen radicals (Process I) and degradation reactions of the PTFE surface by electron and hy-
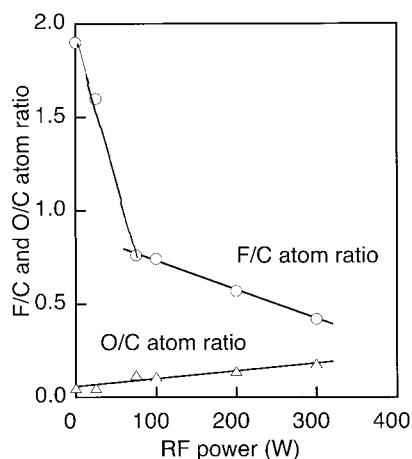

Figure 4 F/C and O/C atom ratios for PTFE surfaces treated with pulsed hydrogen plasma (at an on-time/off-time cycle of 30/270 μs for treatment time of 900 s) as a function of rf power; ○, F/C atom ratio; △ O/C atom ratio.

Figure 5 XPS (C1s) spectra for PTFE surfaces untreated and treated with pulsed hydrogen plasma at an on-time/off-time cycle of 30/270 μs and a rf power of 75, 100, and 300 W for a treatment time of 900 s.

drogen-ion bombardment (Process II). Therefore, the F/C atom ratio is a result of Processes I and II. If Process I rather than Process II predominantes, the substitution reaction will lead to a large decrease in the F/C atom ratio: defluorinated carbons species such as CFH and CH_2 groups will appear in the PTFE polymer chains. On the other hand, if Process II predominates, C—C bond scission of PTFE polymer chains will form carbon radicals at chain ends: degradation reactions will initiate from the chain ends, CF_3 groups will ap-

pear at the chain end, and fragments with low-molecular weight (degradation products) will deposit on the PTFE surface. Therefore, we can evaluate how Process I and II operate in the pulsed hydrogen plasma treatment from XPS spectroscopy. The formation of defluorinated carbons such as CFH and CH_2 groups is due to Process I, and the formation of CF_3 groups is due to Process II.

Three PTFE specimens, which were treated with the pulsed hydrogen plasma at rf powers of 75, 100, and 300 W, at an on-time/off-time cycle of 30/270 μs, were chosen for XPS analysis. C1s spectra for the specimens are shown in Figure 5. The C1s spectra were decomposed into five components at 285.9–286.0, 287.6–287.9, 289.6–289.8, 293.5, and 294.9 eV, which were assigned to CH_2—CHF, CHF—CH_2 and C=O, CH(OR)—CHF, CF_2—CF_2, and CF_3—CF_2 groups, respectively, from the first and secondary effects of fluorine and oxygen atoms on chemical shifts of the C1s spectra.[8–10] The underlined carbons are the objective carbons for the assignment. The relative concentration of the components is listed in Table III. C1s components such as CH_2—CHF and CHF—CH_2 are products of substitution reactions of hydrogen atoms for fluorine atoms on the PTFE surface. CH(OR)—CHF and C=O components are due to oxidation reactions. The CF_3—CF_2 component is a product of the CF_2—CF_2 bond scission in the PTFE polymer.

The PTFE surfaces treated with the pulsed hydrogen plasma at 75 and 100 W, as shown in Table III, show similar distribution of the C1s components. A relative concentration of the CF_2—CF_2 component was 45 and 44% at rf pow-

Table III Chemical Composition of PTFE Surfaces Treated with Pulsed and Continuous Hydrogen Plasmas

Kind of Plasma	Pulsed or Continuous Hydrogen Plasma Treatments			C1s Components (Relative Concentration in %)				
	RF Power (W)	On/Off Time (μs)	Treatment Time (s) (Net Exposure Time, s)	CH_2—CHF	CHF—CH_2 C=O	CH(OR)—CHF	CF_2—CF_2	CF_3—CF_2
Pulsed	75	30/270	900 (45)	34	11	10	45	0
	100	30/270	900 (45)	34	12	10	44	0
	300	30/270	900 (45)	56	8	12	18	6
Continuous	75		120 (120)	55	12	5	26	2
Untreated PTFE							100	

ers of 75 and 100 W, respectively. Therefore, the CF_2—CF_2 units at 55 (at 75 W) and 56 mol % (at 100 W) in the PTFE chains was modified into CH_2—CHF (34 mol %), CHF—CH_2 and C=O units (11% at 75 W and 12 mol % at 100 W) and CH(OR)—CHF units (10 mol %). These surfaces never contained CF_3—CF_2 groups. On the other hand, the PTFE surface treated at 300 W is different in the C1s component from the former two surfaces. On the C1s spectrum, a new CF_3—CF_2 group appeared, although similar C1s components such as CF_2—CF_2 (18 mol %), CH_2—CHF (56 mol %), CHF—CH_2 and C=O (8 mol %), and CH(OR)—CHF units (12 mol %) were also contained. The relative concentration of the CF_3—CF_2 group was 6 mol % of the total carbon units on the surface. This comparison points out that there is an essential difference between the pulsed hydrogen plasma treatments at 75 or 100 and 300 W. In the treatment at 75 and 100 W, the bond scission of CF_2—CF_2 units rarely occurred, while in the treatment at 300 W, bond scission did occur. A continuous hydrogen plasma, even if the rf power was as small as 75 W, led to the CF_2—CF_2 bond scission. The relative concentration of the CF_3—CF_2 groups was 2 mol %.

From these results, we can conclude that the pulsed hydrogen plasma, preferably at a low rf power of less than 100 W, is capable of removing fluorine atoms from PTFE surfaces with less degradation of the PTFE surface. The modification of the PTFE surface by the pulsed hydrogen plasma is superior to that by the continuous plasma from the viewpoint of minimizing the surface degradation.

CONCLUSION

Surface modification of polymers by pulsed plasma has been investigated to minimize degradation reactions occurring at the same time as the surface modification reactions. The kinetics of hydrogen plasma just after turning off discharge was simulated to distinguish pulsed plasma treatment from continuous hydrogen plasma. Experimentally, PTFE was used as a specimen for the surface modification. Hydrogen substitution processes of PTFE by the pulsed and continuous hydrogen plasma were assessed from the viewpoint of contact angle and chemical composition. Experimental results are summarized as follows:

1. The simulation showed that at elapsed times of more than 100 μs, hydrogen radi-

cals rather than hydrogen ions and electrons could contribute predominantly to the surface modification reactions of PTFE.
2. The contact angle measurement showed that hydrogen plasma treatment, regardless of pulsed or continuous plasma, led to degradation reactions as well as defluorination and oxidation on PTFE surfaces. The pulsed hydrogen plasma made less degradation product on the PTFE surfaces than did the continuous hydrogen plasma.
3. XPS measurement showed that the pulsed hydrogen plasma, if the rf power was less than 300 W, did not cause frequent bond scission of PTFE polymer chains, while the continuous hydrogen plasma, even with the rf power at 75 W, did cause frequent bond scission.
4. The contact angle on the PTFE surfaces treated with the pulsed hydrogen plasma was almost the same as or somewhat less than that for the continuous hydrogen plasmas. A combination of the on-time/off-time of 30/270 μs in the pulsed hydrogen plasma was efficacious in modifying PTFE surfaces.

From these results, we conclude that the surface modification of PTFE by pulsed hydrogen plasma is superior to that by continuous plasma.

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