Surface Modification of PET Films by Pulsed Argon Plasma

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ABSTRACT: The rf power was modulated (discharge on-time of 10 μs and discharge off-time of 50–500 μs), for pulsed argon (Ar) and oxygen (O_2) plasmas used to irradiate PET film surfaces to modify the film surfaces. From data regarding the contact angle for the modified PET film surfaces and chemical analyses with XPS, effects of the rf power modulation on the surface modification are discussed. The pulsed Ar and O_2 plasmas are effective in modification of the PET film surface. There is no difference in the contact angle between the pulsed plasma and the continuous plasma. Furthermore, the pulsed Ar plasma is advantageous in formation of hydroxyl groups on the PET film surfaces. The rf power modulation has a possibility to modify into peculiar surfaces. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2845–2852, 2002

Key words: films; surfaces; modification; irradiation

INTRODUCTION

To modify hydrophobic surfaces of polymer materials to become hydrophilic, many people frequently use argon plasma as well as oxygen plasma.[1] In the modification process, active species such as electrons and argon ions in the argon plasma interact with the polymer surfaces, and as a result, the polymer surfaces become hydrophilic. The hydrophilic modification by the argon plasma is mainly due to the formation of oxygen functional groups on their surfaces, even though the argon plasma does not contain oxygen atoms. The oxidation reactions occur at the carbon radicals after finishing irradiation of the argon plasma.

A mechanism of the modification of poly(ethylene terephthalate), PET, by the argon plasma is believed to be as follows [Fig. 1(a)–(e)].[2] Figure 1(a)–(e) show typical interaction reactions between argon plasma and PET film surface. Argon ions and electrons in the argon plasma bombard the PET surface, and then cause C—H bond scission in CH_2 units of PET polymer chains (Route A), C—O bond scission in CH_2—O—C(O) units (Route B and C), and C—C bond scission in C(O)—Ph units (Route D) [Fig. 1(a)]. As a result, many kinds of carbon and oxygen radicals may be formed on the PET surface: radical A by the Route A, radicals B-1 and B-2 by the Route B, radicals C-1 and C-2 by the Route C, and radicals D-1 and D-2 by the Route D. These radicals are reactive enough to initiate subsequent chemical reactions. The chemical reactions involve oxidation of radicals A and B-2 by oxygen in air, hydrogen abstraction of radicals B-1 and C-2 from other PET polymer chains, elimination of carbon monoxide from radical C-1, and elimination of carbon dioxide from radical D-2. Finally, oxygen functional groups such as hydroxyl and carboxyl groups are formed on the PET surface. Possible reactions of the radicals A, B-1, B-2, C-1, C-2, D-1, and D-2 are shown in Figure 1(b)–(e), respectively. These figures show that, once the radicals were formed on PET surface by the argon plasma, the formed radicals can initiate spontaneously special reac-

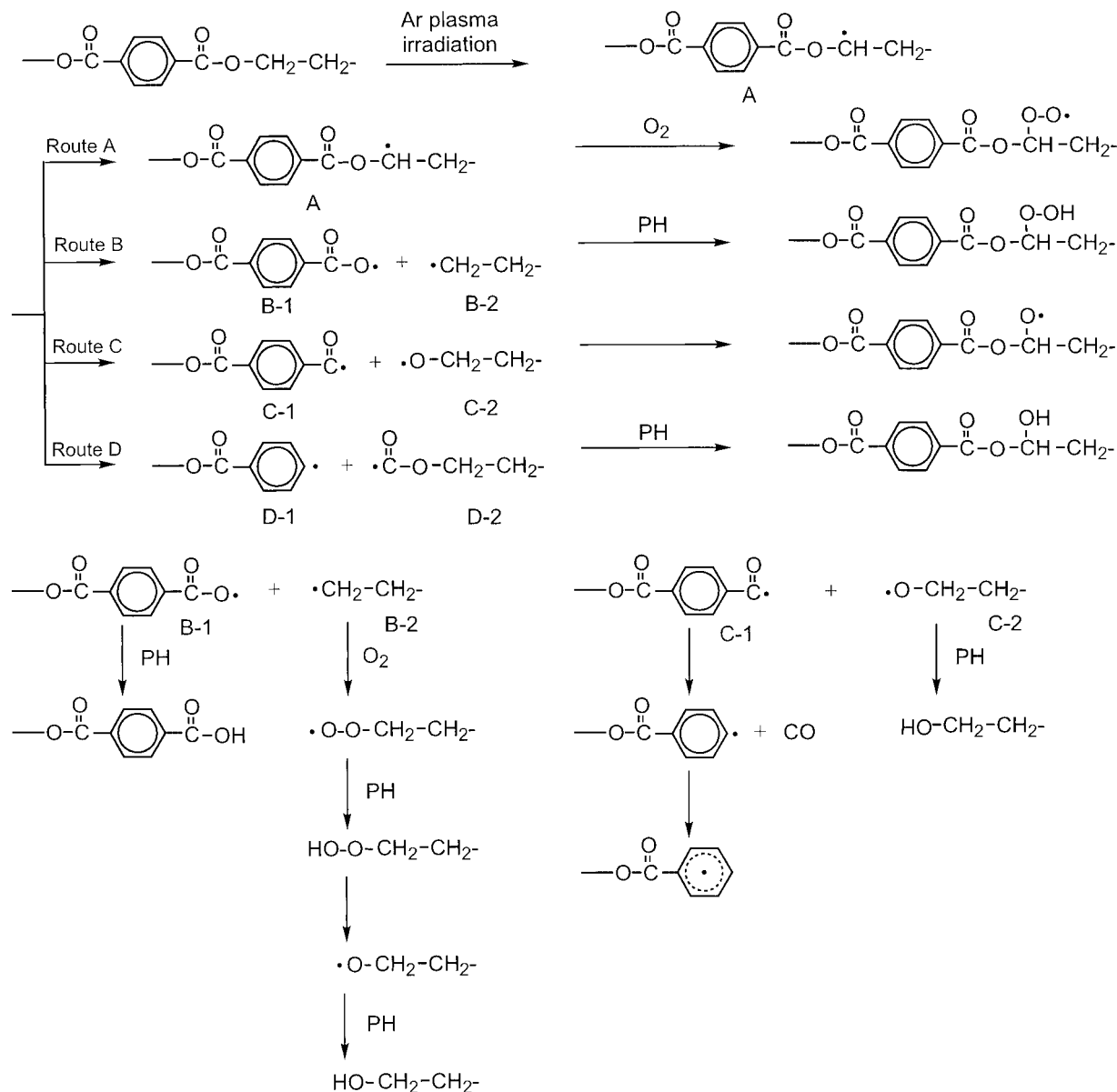*Correspondence to:* N. Inagaki (tcninag@mat.eng.shizuoka.ac.jp).

Figure 1 (a) Possible reactions initiated by Ar plasma irradiation. (b) Possible reactions of radical A after Ar plasma irradiation. (c) Possible reactions of radicals B-1 and B-2 after Ar plasma irradiation. (d) Possible reactions of radicals C-1 and C-2 after Ar plasma irradiation. (e) Possible reactions of radicals D-1 and D-2 after Ar plasma irradiation.

tions that lead to the formation of oxygen functional groups. In this step, the argon plasma no longer contributes to the formation of such oxygen functional groups. If the argon plasma contributes only to the radical formation on the PET surface, the argon plasma irradiation time should be reduced from a few minutes to a few seconds or even a few milliseconds, because the radicals can be formed as soon as the plasma is irradiated.

From this viewpoint, we have a lot of questions regarding the conventional procedure of the argon plasma treatment. How long a time is needed for the argon plasma irradiation for the surface modification? When the plasma irradiation is reduced to a few seconds, is modification performed? What chemistry forms the oxygen functional groups?

To answer our questions, we propose here use of a new technique of the pulsed argon plasma

treatment. The pulsed argon plasma means that for a certain period, the argon plasma is discharged, and is undischarged for another period. To make a cycle of discharged and undischarged period, the rf power is modulated at a certain frequency. The pulsed argon plasma is irradiated PET surfaces for a given period. We call here the period of the discharged plasma "on-time," and the period of the undischarged plasma "off-time." The treatment using the pulsed plasma leads to shortening of actual period exposed to the plasma. When PET surface is exposed to the pulsed plasma with an on-time of 10 μs and an off-time of 500 μs for 60 s, the irradiation period is not 60 s but 1.18 s [$60 \times \{10/(10 + 500)\} = 60 \times 0.0196 = 1.176$]. In this study, we have investigated on what effects the pulsed argon plasma brings about regarding the modification of PET surface.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate), PET, film received from Toyobo Co., Japan (trade name, BOPET, with film thickness of 38 μm) was cut to a dimension of 20 $\times$ 50 mm, and used as specimens for

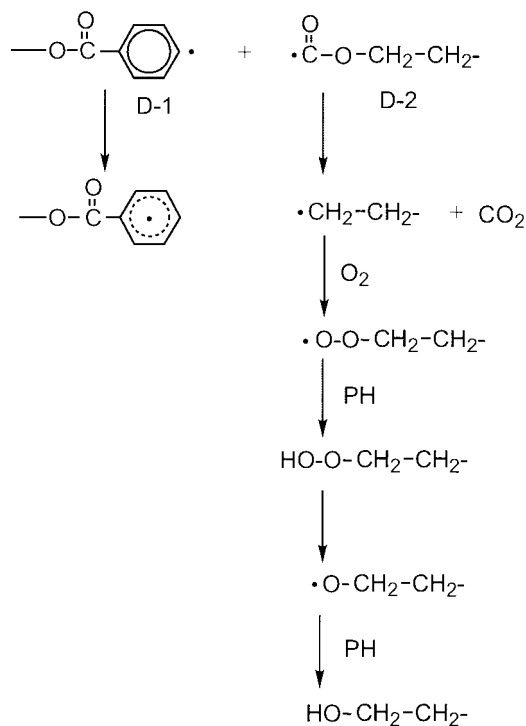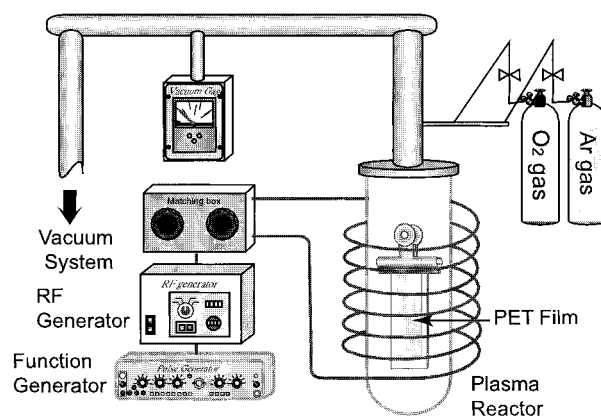**Figure 2** Schematic diagram of reactor used for pulsed plasma treatment.

surface modification experiments. Prior to the surface modification experiment, the PET films were washed with acetone in an ultrasonic washer and dried at room temperature under vacuum. Argon (Ar) and oxygen (O_2) (purity 99.95%) was purchased from Teikoku Sanso Co, Japan, and used without further purification.

Pulsed Ar and O_2 Plasma Treatments of PET Film Surfaces

A home-made reactor was used for the pulsed argon and oxygen plasma treatments of the PET films. The reactor consists of a cylindrical Pyrex glass tube (32 mm diameter, 400 mm long), and the reactor is connected with a vacuum system (model, DS-A212W; Daia Vacuum Engineering Co., Japan) of a combination of a diffusion and rotary pumps. The Pyrex glass tube has a gas inlet for the injection of argon and oxygen gases and a copper coil of seven turns for the energy input of rf power at 13.56 MHz frequency (model, RFG-300; Samuco International Inc., Japan). The rf power at 13.56 MHz was modulated using a pulse generator (model MG411B, Anritsu Co., Japan), and inputted into the reactor by a capacitive coupling system. The on-time of the modulated rf power was a constant of 10 μs, and the off-time was varied from 10 to 500 μs. A diagram of the reactor is shown in Figure 2.

The PET films (20 $\times$ 50 mm) used for the pulsed plasma treatment were fastened on slide glass (26 $\times$ 76 mm, 0.8–1.0 mm thickness) using clips, and positioned vertically in the reactor. First, air in the reactor was displaced with argon. Afterward, the reactor was evacuated to approximately 1.3 $\times$ 10^{-2} Pa, and then argon or oxygen

Figure 1 (*Continued from the previous page*)

was introduced into the Pyrex glass tube with a flow rate of 10 cm^3 (STP)/min adjusted by a mass flow controller. The Ar and O$_2$ plasmas were operated at rf powers of 30 W at 13.56 MHz frequency at a system pressure of 13.3 Pa for given times (5–120 s).

Contact Angle of Water on the PET Film Surfaces treated with Pulsed Ar and O$_2$ Plasmas
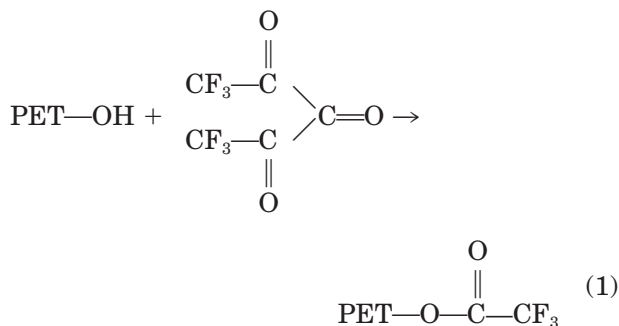
Using the sessile drop method,[3] contact angles of water on the PET film surfaces treated with the pulsed plasmas were measured at 20°C using a contact angle meter with a goniometer (Erma Co. Ltd., Japan, model G-1). An average contact angle was determined from 10 measurements with an experimental error of 3–4°.

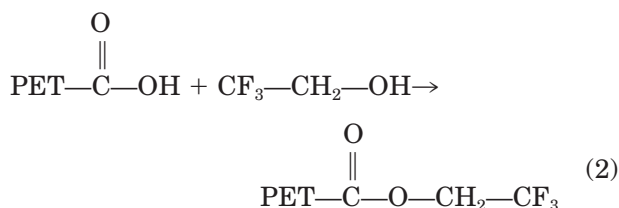### X-ray Photoelectron Spectra of the PET Film Surfaces treated with Pulsed Ar and O$_2$ Plasmas

XPS spectra for the PET film surfaces treated with the pulsed Ar and O$_2$ plasmas were obtained on a Shimadzu ESCA 3400 spectrometer using a nonmonochromatic MgKá photon source at an anode voltage of 10 kV, an anode current of 20 mA, and a pressure in the analytical chamber of 1.0 × 10^{-6} Pa. The XPS spectra were referenced with respect to the carbon 1s core level at 285.0 eV to eliminate charging effects. The spectra were not modified by the smoothing procedure. The C$_{1s}$ spectra were decomposed into three components 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 and O$_{1s}$ core level spectra were S(C$_{1s}$) = 1.00 and S(O$_{1s}$) = 2.85, respectively. The O/C atomic ratio was calculated from the C$_{1s}$ and O$_{1s}$ intensities with an experimental error of less than 0.03.

Determination of Hydroxyl and Carboxyl Groups formed on the PET Film Surfaces by Pulsed Ar and O$_2$ Plasmas

To analyze hydroxyl and carboxyl groups formed on the PET film surfaces by the pulsed Ar and O$_2$ plasmas, these groups were chemically modified into the corresponding fluorinated esters with trifluoroacetic anhydride (TFA) or trifluoroethanol (TFE).[4] The modification of hydroxyl groups (PET-OH) into fluorinated esters is as follows.

$$\text{PET—OH} + \begin{matrix} CF_3\text{—C} \\ CF_3\text{—C} \end{matrix} \underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{\Big\rangle}} C{=}O \rightarrow$$

$$\text{PET—O—}\overset{\overset{O}{\parallel}}{C}\text{—CF}_3 \tag{1}$$

The modification of carboxyl groups (PET—C(O)OH) into fluorinated esters is as follows.

$$\text{PET—}\overset{\overset{O}{\parallel}}{C}\text{—OH} + CF_3\text{—CH}_2\text{—OH} \rightarrow$$

$$\text{PET—}\overset{\overset{O}{\parallel}}{C}\text{—O—CH}_2\text{—CF}_3 \tag{2}$$

The two modification reactions were carried out at 20°C for 2 h in the gas phase system. The details of the modification procedure have been described in the ref. 4.

After finishing these modifications, the modified PET films were analyzed with an XPS to determine the F/C atomic ratio. The concentrations of hydroxyl groups (X in number per 100 carbons on the PET film surface) and carboxyl groups (Y in number per 100 carbons on the PET film surface) were estimated from the F/C atomic ratio according to following eqs. (3) and (4), respectively.

$$X = \frac{100a}{3 - 2a} \tag{3}$$

$$Y = \frac{100b}{3 - 2b} \tag{4}$$

where a and b are F/C atomic ratios determined from the PET film surfaces modified by the reactions 1 and 2, respectively.

RESULTS AND DISCUSSION

Contact Angle of Water on the PET Film Surfaces treated with Pulsed Ar and O$_2$ Plasmas

PET films were treated with the pulsed Ar plasma at an rf power of 30 W, which was modu-
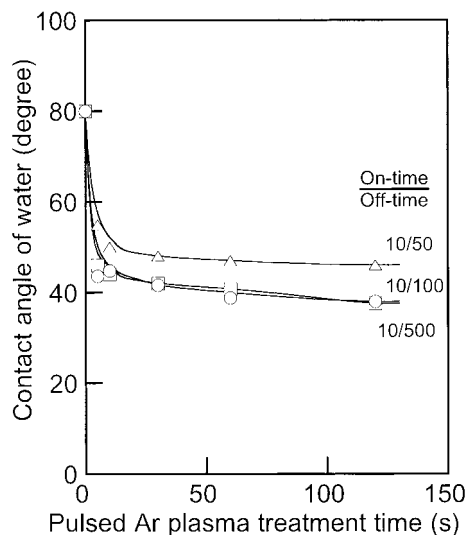
Figure 3 Contact angle of water on PET film surfaces treated with pulsed Ar plasma as functions of plasma treatment time and on-time/off-time ratio.

lated at a cycle of the on-time and off-time. The on-time was a constant of 10 μs, and the off-time was 50, 100, and 500 μs. After finishing the plasma treatment, the PET surfaces were rinsed with acetone to remove some degradation products, and then the contact angle of water on the acetone-rinsed PET surfaces was measured. Figure 3 shows typical results of the contact angle of water against the acetone-rinsed PET surfaces as functions of the plasma treatment time and the on-time/off-time ratio. The plasma treatment time means the residence time of the PET films in the plasma reactor. The plasma treatment time is distinguished from the plasma exposure time. The plasma exposure time is the actual period for the PET surfaces to be exposed to the plasma. The plasma exposure time (τ) is calculated from the plasma treatment time (t) and the on-time/off-time ratio (R).

$$\hat{o} = t \times \frac{R}{R+1} \qquad (5)$$

The contact angle, as shown in Figure 3, showed large decreases at a plasma treatment time within 10 s, and small decrease continued up to 60 s. At a plasma treatment time of 10 s, the contact angle of water was 50, 44, and 45° for the PET surfaces treated at R ratios of 0.2 (on-time/off-time = 10 μs/50 μs), 0.1 (10/100), and 0.02 (10/500), respectively. At a plasma treatment

time of 60 s, the contact angle was 47, 41, and 39° at R ratios of 0.2, 0.1, and 0.02, respectively. These results indicate that the pulsed Ar plasma was able to modify the PET surface, and the modification reaction was almost completed within 10 s, because the prolongation of the plasma treatment time up to 60 s led to less decrease in contact angle.

The surface modification by the pulsed Ar plasma was compared with that by the continuous Ar plasma. The same surface modification procedures except for the modulation of the rf power were carried out using the same plasma reactor, and the contact angle of water was evaluated. Table I compares the water contact angle between the pulsed and continuous Ar plasma-treated PET surfaces. The water contact angle on the continuous Ar plasma-treated PET surfaces was 46 and 46° at plasma treatment times of 10 and 60 s, respectively. There is negligible difference in the contact angle between the PET surfaces treated with the pulsed and continuous Ar plasmas, although there is large difference in the plasma exposure time between the two plasma treatments. The plasma exposure time (τ) is the actual time for the PET surfaces to be exposed to the Ar plasma. A plasma treatment time of 10 s corresponds to a plasma exposure time (τ) of 2.4, 0.9, and 0.2 s at R ratios of 0.2, 0.1, and 0.02, respectively. It is surprising that even when the plasma exposure time (τ) was as short as 0.02–0.2 s, the contact angle for the PET film surfaces treated with the pulsed Ar plasma was as low as that for those treated with the continuous Ar plasma. This may be due to that surface modification reactions by the Ar plasma were completed within a few milliseconds.

Similarly, we investigated the modification of the PET surfaces by the pulsed and continuous O_2 plasmas from a viewpoint of the water contact angle. Typical results in the water contact angle are listed in Table I. The pulsed O_2 plasma, as shown in Table I, led to a large decrease in the contact angle by a plasma treatment time of 10 s, and the contact angle for the pulsed O_2 plasma-treated PET surfaces was as low as those treated with the continuous O_2 plasma. Like the pulsed Ar plasma, the pulsed O_2 plasma was able to modify the PET surface, and the modification reaction was almost completed within 10 s. Another experimental evidence that there was less difference in the water contact angle between the PET surfaces treated with the pulsed O_2 and Ar plasmas indicates that the modification reactions do

Table I   Contact Angle of Water on PET Films Surfaces Treated with the Pulsed Ar and O$_2$ Plasmas

Kind of Plasma	On Time/Off Time (μs)	Plasma Treatment Time (s)	Exposure Time (s)	Contact Angle of Water (Degree)
Pulsed Ar	10/50	10	2.4	50
		60	14.4	47
	10/100	10	0.9	44
		60	5.5	41
	10/500	10	0.2	45
		60	1.2	39
Continuous Ar		10	10	46
		60	60	46
Pulsed O$_2$	10/50	10	2.4	42
		60	14.4	42
	10/100	10	0.9	46
		60	5.5	40
	10/500	10	0.2	51
		60	1.2	49
Continuous O$_2$		10	10	50
		60	60	44
(Original PET)				78

not always require the presence of oxygen and the plasma irradiation at the same time. We will discuss in a next section on "Is there any difference in chemical composition between the PET surfaces treated with the pulsed Ar and O$_2$ plasmas?" from a viewpoint of chemistry of functional groups formed on the PET surfaces.

Chemical Composition of PET Film Surfaces treated with Pulsed Ar and O$_2$ Plasmas

The PET film surfaces that were treated with the pulsed Ar and O$_2$ plasmas were analyzed with XPS. Table II shows the chemical composition of the plasma-treated PET surfaces as functions of a kind of the plasmas and on-time/off-time ratio. Prior to the XPS measurement, the plasma-treated PET film surfaces were rinsed with acetone to remove degradation products. The O/C atom ratio was estimated from relative intensities of the C$_{1s}$ and O$_{1s}$ spectra, and is listed in Table II. The PET films surfaces treated with the pulsed Ar and O$_2$ plasma showed a similar O/C atom ratio (0.35–0.41), which is slightly higher than that for the original PET film (0.33). An O/C atom ratio of 0.33 determined for the original PET

Table II   Chemical Composition of PET Surfaces Treated with Pulsed Ar and O$_2$ Plasmas

	Plasma Treatment Conditions			Cls Components (%)		
Kind of Plasma	On Time/Off Time (μs)	Plasma Treatment Time (s)	O/C Atom Ratio	Comp. 1	Comp. 2	Comp. 3
Pulsed Ar	10/50	60	0.38	61	21	18
	10/100	60	0.40	49	29	22
	10/500	60	0.41	55	26	20
Continuous Ar		60	0.35	61	20	19
Pulsed O$_2$	10/50	60	0.37	60	18	22
	10/100	60	0.38	61	21	18
	10/500	60	0.40	58	23	19
Continuous O$_2$		60	0.35	62	19	19
(Original PET)			0.33	67	16	17

Table III Hydroxyl and Carboxyl Concentrations for PET Surfaces Treated with Pulsed Ar and O_2 Plasmas

Plasma Treatment Conditions			Concentration of Hydroxyl Groups	Concentration of Carboxyl Groups	Ratio of OH and COOH
Kind of Plasma	On Time/ Off Time (μs)	Plasma Treatment Time (s)	(Number/100 Carbons)		
Pulsed Ar	10/50	60	2.6	0.8	3.3
	10/100	60	2.9	0.9	3.2
	10/500	60	2.8	0.9	3.1
Continuous Ar		60	1.4	0.8	1.8
Pulsed O_2	10/50	60	1.7	1.1	1.6
	10/100	60	1.9	1.2	1.6
	10/500	60	1.9	1.4	1.4
Continuous O_2		60	1.2	1.0	1.2

film is slightly lower than the ratio of 0.40, which is calculated from the repeating unit of the PET polymer chains, although the PET film surface was carefully rinsed with acetone to remove some contamination. There is not a large difference in O/C atom ratio between the PET surfaces treated with the pulsed Ar and O_2 plasmas. There is no doubt that some oxygen functional groups were formed on the PET surfaces by the pulsed Ar and O_2 plasmas. To elucidate the oxygen functional groups the C_{1s} spectra were decomposed into three components, and the relative concentration of these components were estimated (Table II). The components 1, 2, and 3 were assigned to CH at 285.0 eV, C—O at 286.5–286.8 eV, and C=O groups at 288.9–289.1 eV, respectively.[5] Assuredly, the pulsed Ar and O_2 plasma treatments led to a decrease in component 1 and an increase in components 2 and 3. However, Table II does not show details of chemistry of the oxygen functional groups.

We speculate about possible reactions occurring on the PET film surfaces in the Ar plasma treatment, and summarize them in Figure 1(a)–(e). According to our speculation, possible oxygen functional groups formed on the PET surfaces may be hydroxyl and carboxyl groups. From this viewpoint we determined the concentration of hydroxyl and carboxyl groups formed on the PET film surfaces by the pulsed and continuous Ar plasmas, and pulsed and continuous O_2 plasmas. The hydroxyl and carboxyl concentrations formed on the PET film surfaces treated by the plasmas were determined according to the procedures described in the Experimental section. Results are

summarized in Table III. It is worth noting the difference in chemical meaning between the O/C atom ratio in Table II and hydroxyl and carboxyl concentrations in Table III. The O/C atom ratio does not mean the oxygen groups formed by the plasmas but means the whole of the oxygen functional groups on the PET film surfaces. Especially, ester groups in the PET polymer chains are properly involved in the modulation, made the hydroxyl and carboxyl groups. The concentration of hydroxyl groups was in the 1.2–2.9 numbers per 100 carbons on the PET film surface, and that of carboxyl groups was in 0.8–1.4 numbers per 100 carbons. Modulation of the rf power, the pulsed Ar and O_2 plasmas, was effective in the formation of hydroxyl groups, but no effective in the formation of carboxyl groups. Especially, the pulsed Ar plasma irradiation yielded higher concentration of hydroxyl groups (2.8–2.9 numbers per 100 carbons) than the continuous Ar plasma as well as the pulsed and continuous O_2 plasma irradiations (1.2–1.9 numbers per 100 carbons). Furthermore, the pulsed Ar plasma irradiation yielded lower concentration of carboxyl groups (0.8–0.9 numbers per 100 carbons) than the other three plasma irradiations (1.0–1.4 numbers per 100 carbons). It is clear that the rf power modulation, especially pulsed Ar plasma, contributes to the formation of hydroxyl groups rather then that of carboxyl groups. A ratio of the hydroxyl groups and carboxyl groups formed on the PET film surfaces was 3.1–3.3 in the pulsed Ar plasma treatment, and 1.8 in the continuous Ar plasma treatment (Table III). This may be due to that the pulsed Ar plasma plays part in formation of rad-

icals alone. We predict that if the speculation is true, a ratio of the formation of hydroxyl groups and carboxyl groups will be 3 : 1 from Figure 1(b)–(e). Radical B-2, C-2, and D-2 will form hydroxyl groups, and radical B-1 will form carboxyl groups.

From these results, we can conclude that the pulsed Ar plasma is advantageous in the formation of hydroxyl groups on the PET film surfaces.

CONCLUSION

The rf power was modulated at a cycle of the on-time of 10 μs and the off-time of 50–500 μs, and pulsed argon (Ar) and oxygen (O$_2$) plasmas were irradiated to PET film surfaces to modify the film surfaces. Effects of the modulation on the modification of the PET film surface were investigated by means of the contact angle measurement and chemical analyses with XPS. Results are summarized as follows.

1. The pulsed Ar and O$_2$ plasmas are effective in modification of the PET film surface.
2. There is no difference in the contact angle between the pulsed plasma and the continuous plasma.
3. Chemistry of the oxygen functional groups formed on the PET film surfaces shows strong dependence on what kind of the plasmas was used for the modification.
4. Modulation of the rf power, the pulsed Ar and O$_2$ plasmas, was effective in the formation of hydroxyl groups, but no effective in the formation of carboxyl groups.
5. The pulsed Ar plasma is advantageous in formation of hydroxyl groups on the PET film surfaces.

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