Studies on the Surface Free Energy and Surface Structure of PTFE Film Treated with Low Temperature Plasma

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ABSTRACT: The surface free energy and surface structure of poly(tetrafluoroethylene) (PTFE) film treated with low temperature plasma in O_2, Ar, He, H_2, NH_3, and CH_4 gases are studied. The contact angles of the samples were measured, and the critical surface tension γ_c (Zisman) and γ_c (max) were determined on the basis of the Zisman's plots. Furthermore, the values of nonpolar dispersion force γ_s^a, dipole force γ_s^b, and hydrogen bonding force γ_s^c to the surface tensions for the plasma-treated samples were evaluated by the extended Fowkes equation. Mainly because of the contribution of polar force, the surface free energy and surface wettability of PTFE film which was treated with H_2, He, NH_3, Ar, and CH_4 for a short time increased greatly. Electron spectroscopy for chemical analysis (ESCA) shows that the reason was the decrease of fluorine and the increase of oxygen or nitrogen polar functional group on the surface of PTFE. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1733–1739, 1997

Key words: low temperature plasma; PTFE; surface free energy; surface structure

INTRODUCTION

The wettability of the surface of polymer materials is tightly related to many fields, such as adhesion, coating, printing, dyeing, and fabrication of fibers. PTFE has a very extensive use as a kind of good polymer material with electric insulating property, thermal stability, climate hardiness, and corrosion resistance. Although the fluoropolymers of polyalkene do not contain polar groups, their use in technology is restrained by low surface free energy, hydrophobic properties, and poor adhesive properties. Therefore, the sub-

ject of improving their properties and enlarging their scope is required. Some chemical sculpture methods like alkali metal solution treatment,[1] alkali metal amalgam process,[2] and electrolytic reduction process[3] had already been studied in improving the surface wettability of PTFE film, metal steam plating,[4] corona discharge, glow discharge, and plasma treatment were also studied.[5–7] It is reported that plasma etching can effectively improve the surface adhesive properties of PTFE, and successive treatment has already been used in industry.[8]

PTFE was treated with low temperature plasma in various gases, such as O_2, Ar, He, H_2, NH_3, and CH_4. The contact angle, the critical surface tension, and the surface elements of the sample were measured; and the surface properties of the sample were studied. The correlation between

the change in surface free energy of the plasma-treated PTFE films and their surface chemical compositions were discussed.

EXPERIMENTAL

The commercial PTFE films (Toray Co., 15 μm thickness) were soaked with toluene for 3 h, then were scoured with acetone for 5 min, and finally washed repeatedly with distilled water and dried in air.

The low temperature plasma apparatus is a Yamato PR 501 (made in Japan), which is a capacitively coupled reactor with an internal electrode; and the volume of the plasma chamber is 215 mm (inside diameter) $\times$ 275 mm (length). The conditions of low temperature plasma reaction were gas sources, O_2, Ar, He, H_2, NH_3, and CH_4; pressures in the reaction chamber were 10^{-2} Pa; power was 300 W; frequency was 13.56 MHz; and irradiating time was 10–180 s. The plasma treated samples were put in a desiccator 24 h later, and the contact angles were measured.

The contact angle was measured according to the method of drop with an apparatus CA-A FACE made in Shimadzu, Japan. To avoid the effect of gravity, the volume of every drop was about 0.2 cc. The measurement was carried out at a temperature of 20°C and at a humidity of 45% RH; the size of the sample is 15 $\times$ 15 mm. Each sample was measured at different points for 18 times, and the result was determined by their average values.[6,9,10]

The liquids used in measuring the contact angle of the film are shown in Table I. The surface tension γ_L of the liquid can be divided into three components: nonpolar dispersion force γ_L^a, dipole force γ_L^b, and hydrogen bonding force γ_L^c; their values are known and are listed in Table I. The liquids of series A, B, C, and D are classified as a type of $\gamma_L = \gamma_L^a$, $\gamma_L = \gamma_L^a + \gamma_L^b$, $\gamma_L = \gamma_L^a + \gamma_L^b + \gamma_L^c$, and $\gamma_L = \gamma_L^a + \gamma_L^c$, respectively.

The Zisman's plots, $\cos \theta$ versus γ_L, where θ and γ_L represent contact angle and surface tension of liquid. The extrapolation of the linear $\cos \theta$ versus γ_L plot to $\cos \theta = 1$ gives the surface tension of a liquid as the critical surface tension γ_c of a solid sample. The critical surface tensions obtained by the liquids of series A, B, C, and D are marked as γ_c (A), γ_c (B), γ_c (C), and γ_c (D), respectively. The lowest value obtained refers to γ_c (Zisman) and the highest one to γ_c (max). Furthermore, the γ_c (max) corresponds highly with the surface tension γ_s of the solid.[11–13]

The surface tension of PTFE evaluated by the extended Fowkes equation was shown as follows:

Table I   Surface Tensions of Liquids for Measuring Contact Angle at 20°C[11]

Series	Liquids	Surface Tension ($\times 10^{-5}$ N·cm^{-1})			
		γ_L	γ_L^a	γ_L^b	γ_L^c
A	Tetradecane	26.7	26.7	0	0
	Dodecane	25.4	25.4	0	0
	Undecane	24.7	24.7	0	0
	Decane	23.9	23.9	0	0
B	1,1,2,2-Tetrabronoethane	47.5	44.3	3.2	0
	1-Bronomaphthalene	44.6	44.4	0.2	0
	1,1,2,3,4,4-Hexachloro, 1,3-butadiene	36.0	35.8	0.2	0
C	Water	72.8	29.1	1.3	42.4
	Glycerin	63.4	37.4	0.2	25.8
	Formamide	58.2	35.1	1.6	21.5
	2,2'-Thiobisethanol	54.0	39.2	1.4	13.4
D	Ethyleneglycol	47.7	30.1	0	17.6
	Diethyleneglycol	44.4	31.7	0	12.7
	Polyethyleneglycol 200	43.5	29.9	0.1	13.5
	Dipropyleneglycol	33.9	29.4	0	4.5

$$\gamma_{sL}$$
$$= \gamma_s + \gamma_L - 2(\sqrt{\gamma_s^a\,\gamma_L^a} + \sqrt{\gamma_s^b\,\gamma_L^b} + \sqrt{\gamma_s^c\,\gamma_L^c}) \quad (1)$$

In addition, adhesive work is as follows:

$$W_a = \gamma_s + \gamma_L - \gamma_{sL} \quad (2)$$

According to the Young equation,

$$\gamma_s = \gamma_{sL} + \gamma_L \cdot \cos\theta \quad (3)$$

Equations (2) and (3) were substituted in eq. (1) and obtained the following:

$$\gamma_L(1 + \cos\theta)$$
$$= 2(\sqrt{\gamma_s^a\,\gamma_L^a} + \sqrt{\gamma_s^b\,\gamma_L^b} + \sqrt{\gamma_L^b\,\gamma_L^c}) \quad (4)$$

The three components γ_S^a, γ_S^b, and γ_S^c of the solid surface tension can be calculated by eq. (4), then the surface tension γ_S of the solid sample can be obtained by the following equation:

$$\gamma_S = \gamma_S^a + \gamma_S^b + \gamma_S^c \quad (5)$$

The chemical compositions of the PTFE film surface were characterized by shimadzu ESCA 750 at Mg-Kα x-ray, at a pressure lower than 10^{-5} Pa, an electric pressure of 8 KV, and an electric current of 30 mA.

RESULTS AND DISCUSSION

Table II shows contact angle's average values and standard deviations of all samples. It can be learned from the data that functions of PTFE treated by plasma were quite even.

The Zisman's plots of PTFE films treated with low temperature plasma in O_2, Ar, He, H_2, NH_3, and CH_4 are shown in Figure 1; and the untreated sample is also included in Figure 1. It is evident from Figure 1(a) that the surface of the untreated PTFE film were not wetted thoroughly by all series of liquids and existed γ_c (A) = γ_c (B) = γ_c (C) = γ_c (D). So the value of γ_c (Zisman) is equal to γ_c (max) and is approximately 20×10^{-5} N·cm^{-1}. The result of the O_2 plasma-treated film [Fig. 1(b)] was similar to the untreated sample. They both have the following character, γ_c (Zisman) = γ_c (max) = 20×10^{-5} N·cm^{-1}, and the surface tension is unchanged. That is contrary to the common fact that the surface free energy and the wettability of the O_2 plasma-treated polymer material will be improved.[13–14] This phenomenon is important for the study of surface modification mechanism of O_2 plasma-treated polymer. Figure 1(c) and (d) are the results of Ar and He plasma-treated films, respectively. The changing regularity of these two kinds of treated films was very similar, and it showed γ_c (A) = γ_c (B) = γ_c (Zisman), and γ_c (C) = γ_c (D) = γ_c (max). The surface tension has a remarkable increase. The values of γ_c (Zisman) are 22×10^{-5} N·cm^{-1} and 24×10^{-5} N·cm^{-1}, respectively; but they are still lower than the surface tension of all used liquids. Thus, the surface of the films were not wetted thor-

Table II   Average Value (θ) and Standard Deviations (S) of Contact Angles[a]

	Liquids	Blank	O_2	Ar	He [θ (S)]	NH_3	H_2	CH_4
A	Tetradecane	43.1 (0.97)	43.7 (0.76)	43.2 (0.57)	36.5 (0.54)	0 (0)	0 (0)	0 (0)
	Dodecane	39.3 (0.82)	40.0 (1.05)	36.1 (0.95)	32.5 (0.65)	0 (0)	0 (0)	0 (0)
	Undecane	35.4 (0.79)	36.4 (0.86)	33.1 (1.08)	23.6 (0.73)	0 (0)	0 (0)	0 (0)
	Dodecane	30.4 (0.57)	32.0 (1.08)	31.0 (0.80)	0 (0)	0 (0)	0 (0)	
B	1,1,2,2-Tetrabronoethane	80.4 (1.35)	79.0 (1.09)	73.1 (0.65)	73.0 (0.89)	61.5 (1.16)	51.2 (0.99)	45.0 (0.87)
	1-Bronomaphthalene	74.8 (0.95)	74.9 (1.22)	67.9 (0.92)	67.3 (0.65)	56.2 (0.85)	47.3 (0.67)	37.0 (0.57)
	1,1,2,3,4,4-Hexachloro,1,3-butadiene	62.2 (1.01)	60.5 (0.96)	56.6 (1.07)	53.2 (0.80)	36.8 (0.74)	20.8 (1.07)	0 (0)
C	Water	114.0 (0.98)	110.0 (0.93)	102.0 (0.66)	98.0 (1.03)	102.0 (0.82)	88.0 (0.95)	103.0 (0.54)
	Glycerin	106.9 (0.94)	101.6 (0.95)	94.7 (0.80)	90.5 (0.64)	91.2 (0.33)	82.2 (1.00)	92.6 (0.82)
	Formamide	98.6 (1.26)	92.5 (1.08)	84.3 (0.75)	76.4 (0.72)	83.6 (0.50)	69.4 (0.75)	82.9 (1.10)
	2,2,'-Thiobisethanol	93.0 (1.34)	85.3 (1.07)	78.4 (1.49)	72.3 (1.11)	79.5 (0.69)	64.0 (0.87)	71.8 (0.72)
D	Ethyleneglycol	94.3 (0.51)	83.4 (0.90)	74.6 (0.97)	65.2 (0.85)	65.8 (0.99)	60.2 (1.09)	73.0 (0.60)
	Diethyleneglycol	90.3 (0.81)	80.3 (1.43)	67.1 (0.94)	55.4 (0.86)	57.5 (0.80)	49.5 (1.20)	65.1 (0.89)
	Polyethylene-glycol 200	89.5 (1.54)	75.8 (0.79)	61.8 (0.89)	54.7 (0.97)	53.8 (1.04)	48.7 (0.38)	62.4 (1.09)
	Dipropyleneglycol	69.0 (0.84)	59.7 (1.05)	40.8 (0.47)	22.0 (0.94)	29.7 (1.21)	0 (0)	34.9 (0.99)

[a] Plasma treatment was carried out for 180 s. 0 (0): PTFE film was wetted thoroughly by the liquid.
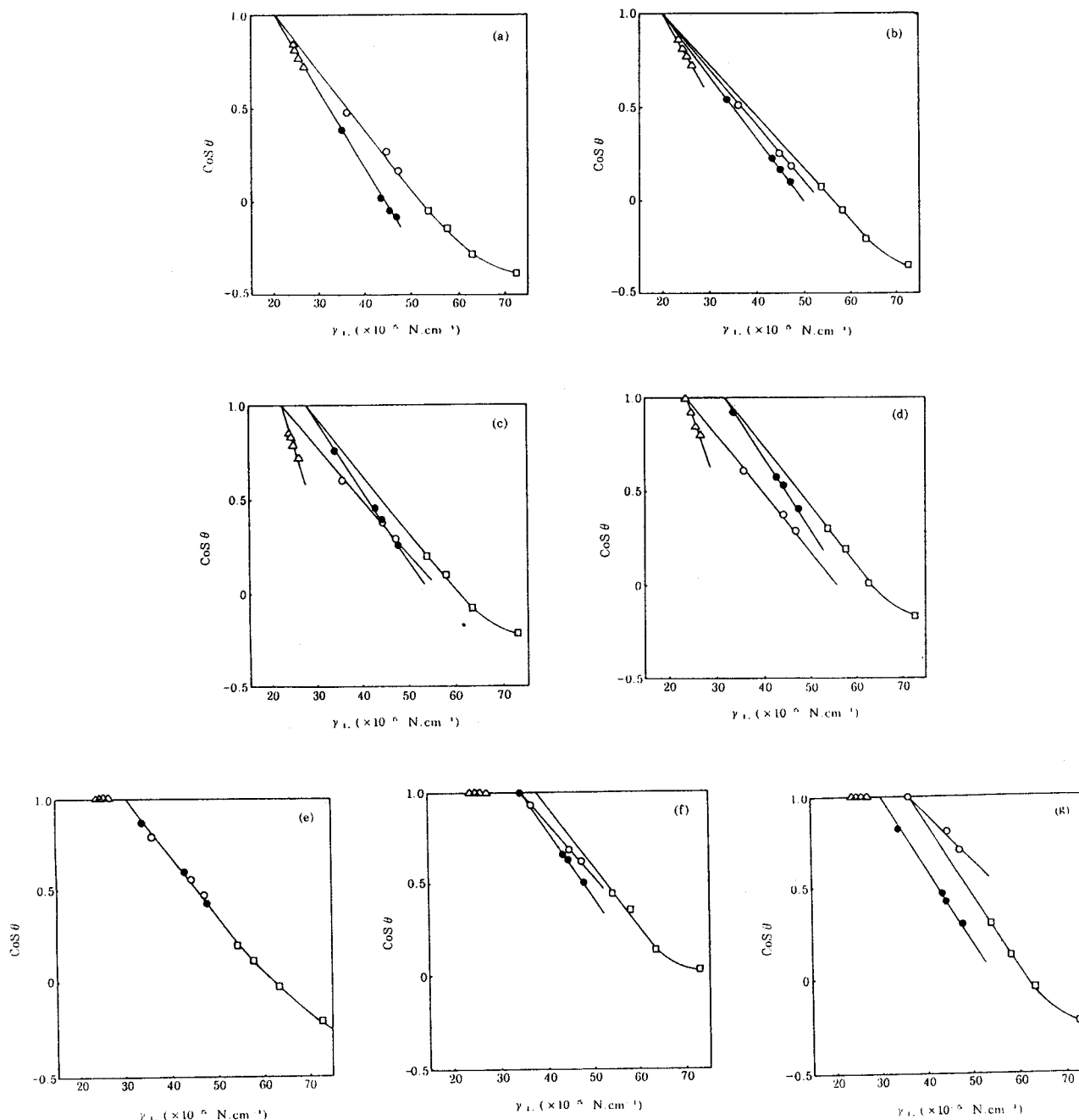
Figure 1 Zisman's plots of PTFE treated with low temperature plasma: (a) untreated, (b) O_2 plasma, (c) Ar plasma, (d) He plasma, (e) NH_3 plasma, (f) H_2 plasma, and (g) CH_4 plasma. $\triangle$ represents A series of liquids; $\bigcirc$, B series of liquids; $\square$, C series of liquids; and $\bullet$, D series of liquids. Plasma treatment was carried out for 180 s.

oughly by each liquid. The value of γ_c (max) increased to 28×10^{-5} N·cm^{-1} and 32.5×10^{-5} N·cm^{-1}, respectively. Figure 1 (e)–(g) are the results of NH_3, H_2, and CH_4 plasma-treated films, respectively. The surfaces of these three kinds of

films were wetted thoroughly by the liquids of series A. This indicated that the critical surface tension γ_c (Zisman) of the three kinds of films are all greater than γ_L (A). The NH_3 plasma-treated film [Fig. 1(e)] showed γ_c (B) $= \gamma_c$ (C) $= \gamma_c$ (D)

Table III   Surface Tension of PTFE Treated with Low-Temperature Plasmas[a]

Plasma Treatment	Zisman Plot γ_c (max)	Surface Tension ($\times 10^{-5}$ N·cm^{-1})			
		Extended Fowkes Equation			
		γ_s (C)	γ_s^a	γ_s^b	γ_s^c
Untreated	20.0	20.4	20.0	0.4	0.0
O_2	20.0	20.1	19.8	0.3	0.0
Ar	28.0	28.1	19.7	5.9	2.5
NH_3	31.0	32.1	23.7	5.8	2.6
He	32.5	32.7	23.8	6.1	2.8
CH_4	35.5	33.9	26.6	5.4	1.9
H_2	37.5	37.6	25.3	6.9	5.4

[a] Plasma treatment discharge for 180 s.

$= \gamma_c$ (Zisman) $= \gamma_c$ (max) $= 31.5 \times 10^{-5}$ N·cm^{-1}. The H_2 plasma-treated film [Fig. 1(f)] showed γ_c (B) $= \gamma_c$ (D) $= \gamma_c$ (Zisman) $= 34 \times 10^{-5}$ N·cm^{-1}, γ_c (C) $= \gamma_c$ (max) $= 37.5 \times 10^{-5}$ N·cm^{-1}; the surface free energy of the sample increased remarkably. The CH_4 plasma-treated film [Fig. 1(g)] showed γ_c (D) $= \gamma_c$ (Zisman) $= 30 \times 10^{-5}$ N·cm^{-1}, and γ_c (B) $= \gamma_c$ (C) $= \gamma_c$ (max) $= 35.5 \times 10^{-5}$ N·cm^{-1}; the increase of the surface free energy of the sample is only secondary to the H_2 plasma-treated film. It can be concluded that the surface free energy of the PTFE film treated with plasma in varlous gases increased in the following order: untreated $= O_2 < $ Ar $<$ NH_3 $<$ He $<$ CH_4 $<$ H_2.

As shown in Figure 1, the PTFE films treated with plasma in six kinds of gases have the following similarity: γ_c (C) $= \gamma_c$ (max), so we selected the liquids of series C as a reference.[10] The results of the surface tension γ_S (C) and its three components γ_S^a, γ_S^b, γ_S^c of the PTFE film obtained by the extended Fowkes equation are summarized in Table III. From the data in Table III, it is evident

that the value of the surface tension γ_S (C) of PTFE film obtained by extended Fowkes equation corresponds highly to γ_c (max) of Zisman's plots. The values of the three components of the surface tension were almost unchanged in the O_2 plasma-treated film, so the surface of the film is still in a low-energy state. The dipole force γ_S^b and hydrogen bonding force γ_S^c all increased highly by the plasma treatments with Ar, He, H_2, NH_3, and CH_4, especially the polar force component by the H_2 plasma treatment. Therefore, it is apparent that an increase in surface free energy by these plasmas is due to the substantial increase in the polar force component.

The smaller the contact angle to water on the polymer material, the better its wettability. The improving degree of the wettability of the PTFE treated with various kinds of plasmas was estimated by measuring the contact angle to water ($\theta_{H_2O}^\circ$) on the PTFE film. The results are shown in Table IV. From the data, it is evident that the surface wettability of the PTFE film treated with plasma in various gases increased in the following

Table IV   Contact Angles to Water and the Polar Force of Surface Tension of PTFE Treated with Low-Temperature Plasmas[a]

Palsma Treatment	Untreated	O_2	CH_4	Ar	NH_3	He	H_2
Contact Angles ($\theta_{H_2O}^\circ$)	114	110	103	102	102	98	88
Polar force ($\gamma_s^b + \gamma_s^c$) ($\times 10^{-5}$ N·cm^{-1})	0.4	0.3	7.3	8.4	8.4	8.9	12.3

[a] Plasma treatment discharge for 180 s.

order: $O_2 < CH_4 < Ar = NH_3 < He < H_2$. This changing rule is the same as that of the polar force components γ_S^b and γ_S^c of the sample's surface tension. The increase of the polar force components γ_S^b and γ_S^c of the surface tension of CH_4 plasma-treated PTFE is less than that of Ar, NH_3, and He plasma-treated PTFE. Therefore, the surface wettability of the PTFE film treated with CH_4 plasma is lower than of Ar, NH_3, and He plasma-treated PTFE film. This is different from the changing order of the surface free energy mentioned above. The polar force components $\gamma_S^b + \gamma_S^c$ are important to improve modification on PTFE surface.

The further step regarding the effect of the plasma treatment time on the wettability of the surface of PTFE was also studied. The relationships between the water contact angle of PTFE and the plasma treatment time are represented in Figure 2. As is readily evident in Figure 2, a decrease in contact angle is attributable to an increase in the treatment time with any kinds of plasmas, but the degree of the decrease in contact angle has a remarkable difference in various gases. The contact angle of O_2 plasma-treated samples decreased slightly. After treatment for 30 s, the contact angle tended to be stable. The contact angle of H_2 plasma-treated samples decreased greatly: it decreased to 88 degrees after treatment for 180 s. It shows that the surface wet-
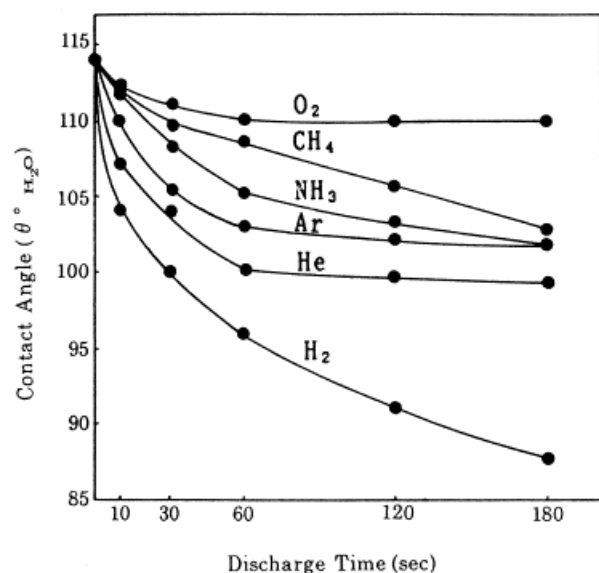
Table V   ESCA Relative Intensity of Surface Atoms of PTFE Films Treated with Low-temperature Plasma[a]

Plasma Treatment	Chemical Composition of Surface (%)			
	C1s	F1s	O1s	N1s
Untreated	38.5	60.5	1.0	0.0
O_2	34.0	65.5	0.5	0.0
Ar	38.2	58.2	3.3	0.2
He	40.0	56.0	3.8	0.2
NH_3	42.6	55.5	1.1	0.8
H_2	52.8	43.0	4.0	0.2
CH_4	71.3	25.3	2.6	0.9

[a] Plasma treatment discharge for 180 s.

tability of H_2 plasma-treated PTFE film can be effectively improved with a short time.

The chemical compositions of PTFE surface treated with various plasmas were measured by ESCA, as shown in Table V, and C1s spectra was shown in Figure 3. It can be seen from Table V that the increase of surface free energy of Ar, He, NH_3, CH_4, and H_2 plasma-treated PTFE is due chiefly to the decrease of fluorine and the increase of oxygen and nitrogen on PTFE surface. It is obvious from Figure 3 that the untreated sample showed a strong peak in the neighborhood of 293
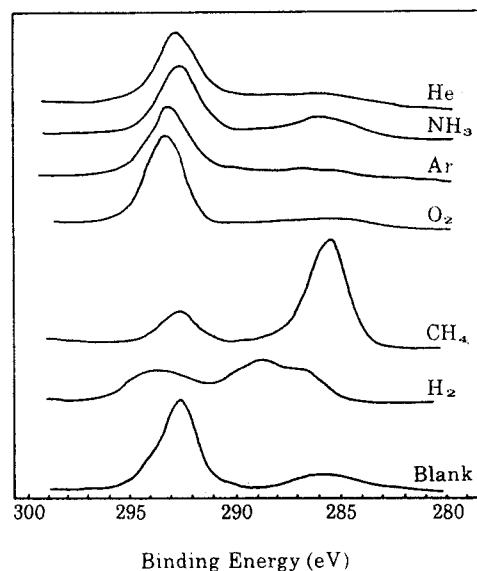

Figure 2   Effect of plasma treatment time on the contact angles to water of PTFE.

Figure 3   Relative intensities of C1s spectra in ESCA measurement of PTFE treated with low-temperature plasma. Plasma treatment discharged for 180 s.

eV, which corresponds to the fluorine containing groups. The O_2 plasma-treated sample also showed the same spectrum of the untreated with the same fluorine intensity. Ar, NH_3, and He plasma treatment somewhat decreased the fluorine intensity, while CH_4 plasma treatment decreased the fluorine intensity and —CH— intensity at about 285 eV increased greatly. The H_2 plasma-treated sample showed a relatively small fluorine intensity; and the intensity of —CO— and —CN— at 286.5 eV, and that of —COO— and —CON— at 289.5 eV, became obviously greater. This greatly contributes to an increase of surface free energy and wettability of the PTFE film. The blank PTFE shows a weak peak around 285 eV, which can only be attributed to hydrocarbon contaminant. Plasma treatment by O_2, Ar, and He seem to clean this contamination layer. Probably because of the organic contamination from toluene or acetone, the untreated PTFE has incorporated oxygen, and O_2 plasma treatment seems to remove the organic contamination.

CONCLUSIONS

The results of the study shows the following.

1) The surface free energy of PTFE film treated with six plasma increase in the following order: untreated $= O_2 <$ Ar $<$ NH_3 $<$ He $<$ CH_4 $<$ H_2.
2) The surface wettability of the PTFE film treated with six plasmas increased in the following order: O_2 $<$ CH_4 $<$ Ar $=$ NH_3 $<$ He $<$ H_2. This changing rule is the same as that of the polar force components γ_S^b $+$ γ_S^c of surface tension, which shows that the polar force component of surface tension contributes greatly to the surface wettability of PTFE film.
3) The result of ESCA measurement shows that the increase of surface free energy of PTFE film treated with Ar, NH_3, He, CH_4, and H_2 plasmas is chiefly due to the decrease of fluorine and the increase of oxygen and nitrogen on PTFE surface. H_2 plasma treatment is an efficient means of improving the surface energy and wettability of PTFE film.
4) The surface wettability of O_2 plasma-treated PTFE film remained unchanged, and the oxygen content decreased. These are important for the study of surface modification mechanism of O_2 plasma-treated polymer.

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