Wettability of Poly(ethylene Terephthalate) Film Treated with Low-Temperature Plasma and Their Surface Analysis by ESCA

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ABSTRACT: The surface of poly(ethylene terephthalate) (PET) film was modified by low-temperature plasma with O_2, N_2, He, Ar, H_2, and CH_4 gases, respectively. After being treated by low-temperature plasma, their surface wettability and chemical composition were investigated by means of electron spectroscopy for chemical analysis (ESCA) and contact angle measurement. The result shows that the surface wettability of PET can be improved by low-temperature plasma, and the effect of the modification is due mainly to the kind of the gases. Mainly because of the contribution of hydrogen bonding force γ_S^c, the surface wettability of PET treated with O_2, N_2, He, and Ar plasma for a short time (3 min) increase sharply, and the surface wettability is also improved by H_2 plasma treatment; but the CH_4 plasma treatment does not improve the wettability of PET. ESCA shows that the effect of wettability of PET is tightly related to the presence of polar functional groups that reside in the outermost surface layer of PET.
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Key words: low-temperature plasma; poly(ethylene terephthalate) film; wettability; surface analysis by electron spectroscopy for chemical analysis

INTRODUCTION

The surface wettability of polymer materials is tightly related to many fields, such as in printing, spray, adhesion, and dyeing. But the molecular structure of the poly(ethylene terephthalate) (PET) lacks polar groups, such as —COOH and —OH, which causes it to have low surface-free energy and poor wettability. A hydrophilicity process is required for improving the processing properties of PET, but some chemical methods damage the polymer matrix and require the disposal of a great deal of devil water; besides, they consume a large amount of fuels and processing cost. The technique of gas-discharge low-temperature plasma is an effective way to overcome the defects mentioned above. The modification of polymer materials by low-temperature plasma is a dry reaction system in the gas–solid phase. This kind of method saves water and energy and does not pollute the environment. Just touching upon the shallow surface of the materials, it can give the material some new characters while keeps its original qualities. Its improvements of the surface wettability, dyeing property, adhesive, and anti-fouling properties of PET have been reported for

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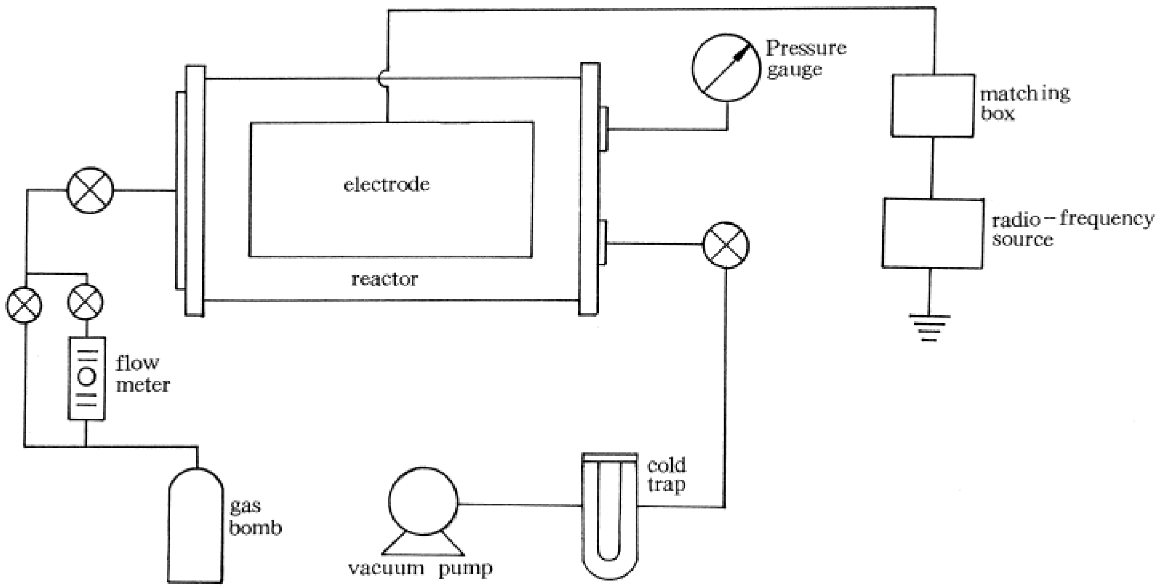

Figure 1 Schematic representation of the plasma reactor system.

many years,[1–4] but studies on the mechanism of modification are not adequate.[5]

In this article, the mechanism of the improvement of the surface wettability of the PET treated by low-temperature plasma is studied. According to the measurement of the contact angle and the evaluation of the surface tension, the effect of the changing rule of surface-free energy and the interfacial intermolecular force on surface wettability of the PET treated with O_2, N_2, He, Ar, H_2, and CH_4 plasma is discussed systematically. The relationship between the surface wettability and the surface structure of PET is investigated by electron spectroscopy for chemical analysis (ESCA).

EXPERIMENTAL

The PET films (15 μm thickness) were soaked with toluene and acetone and finally washed repeatedly with distilled water and dried in air.

Table I Surface Tensions of Liquids for Measuring Contact Angle (20°C)

Series	Liquids	γ_L	γ_L^a	γ_L^b	γ_L^c
A	*n*-Hexadecane	27.6	27.6	0	0
	n-Dodecane	25.4	25.4	0	0
	n-Decane	23.9	23.9	0	0
	n-Hexane	18.4	18.4	0	0
B	Tetrabromoethane	47.5	44.3	3.2	0
	α-Bromonaphthalene	44.6	44.4	0.2	0
	Tetrachloroethane	36.3	33.2	3.1	0
	Hexachlorobutadiene	36.0	35.8	0.2	0
C	Water	72.8	29.1	1.3	42.4
	Glycerol	63.4	37.4	0.2	25.8
	Formamide	58.2	35.1	1.6	21.5
	Thiodilycol	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
	Dipropyleneglycol	33.9	29.4	0	4.5

γ_L is the surface tension of liquid; γ_L^a is the nonpolar dispersion force; γ_L^b is the dipole force; and γ_L^c is the hydrogen bonding force.

Table II Surface Tensions ($\times 10^{-5}$ N cm^{-1}) of PET Film Treated with Low-Temperature Plasma

Plasma Treatment	Nonpolar Dispersion Force (γ_S^a)	Dipole Force (γ_S^b)	Hydrogen Bonding Force (γ_S^c)	Solid Surface Tension (γ_S)	Critical Surface Tension (γ_c)
Blank	36.3	1.6	4.3	42.2	42.0
O_2	14.3	2.7	40.1	57.1	57.5
N_2	17.6	1.0	38.4	57.0	57.0
He	16.8	1.1	37.2	55.1	56.0
Ar	17.6	1.2	37.2	56.0	56.0
H_2	33.0	0.9	15.4	49.3	50.0
CH_4	27.4	9.8	2.0	39.2	39.0

Schematic representation of the plasma reactor system is shown in Figure 1. Glow discharge was generated by a Yamato Plasma Generator PR501A (made in Japan), which is a capacitively coupled reactor with an internal electrode; the volume of the plasma chamber is 215 (inside diameter) $\times$ 275 mm (length). The conditions of low-temperature plasma reaction were as follows: the gas sources were O_2, N_2, He, Ar, H_2, and CH_4; the frequency was 13.56 MHz; the irradiating time was 3 min; the power was 300 W; and the pressures in the reaction chamber was 100 Pa. The plasma-treated samples were put in a desiccator 24 h later, and the surface properties were measured.

The contact angle was measured according to the method of drop with an apparatus FACE CA-A (Kyowa Kaimenkagaku Co. made in Japan). The measurement was carried out at a temperature of 20 $\pm$ 1°C and at a humidity of 45 $\pm$ 5% RH. The liquids used in measuring the contact angle of the PET film are shown in Table I. According to Kitazaki and Hata,[6] the liquids of series A, B, C, and D are characterized as follows. The liquids of series A consist of saturated hydrocarbons (a type of $\gamma_L = \gamma_L^a$). The liquids of series B consist of ester of halogenated acid (a type of $\gamma_L = \gamma_L^a + \gamma_L^b$). The liquids of series C (a type of $\gamma_L = \gamma_L^a + \gamma_L^b + \gamma_L^c$) and the liquids of series D (a type of $\gamma_L = \gamma_L^a + \gamma_L^c$) consist of water, alcohol, and formamide, which are water-soluble or have low interficial tension to water $\gamma_{SL} < 30 \times 10^{-5}$ N $\cdot$ cm^{-1} and contain a hydrogen bond. All liquids are at the level of analytical reagent (AR).

The critical surface tension γ_c was extrapolation of the linear cos θ versus γ_L plot to cos $\theta = 1$, which gives the surface tension γ_L of a liquid as γ_c of the sample.[7]

The Fowkes equation was extended by Kitazaki and Hata[2] according to Zisman's theory of critical surface tension γ_c.

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

The corresponding three components, nonpolar dispersion force γ_S^a, dipole force γ_S^b, and hydrogen bonding force γ_S^c of the samples were evaluated by the eq. (1), so the surface tension γ_S of the PET film can be obtained by the following equation:

$$\gamma_S = \gamma_S^a + \gamma_S^b + \gamma_S^c \quad (2)$$

The ESCA measurements (Shimazu ESCA 750, made in Japan) were made for characteriza-

Table III Contact Angles to Water (θ_{H_2O}) and ESCA Intensity of Surface Element of PET Film Treated with Low-Temperature Plasma

Plasma Treatment	Blank	O_2	N_2	He	Ar	H_2	CH_4
θ (°)	70.0	24.4	25.0	28.0	28.0	47.2	74.0
C (%)	73.11	64.32	67.91	68.97	68.14	77.70	92.37
O (%)	26.89	34.29	29.69	30.02	31.68	22.30	7.63
N (%)	0.00	1.39	2.40	1.01	0.00	0.00	0.00
(O + N)/C	36.78	55.47	47.25	44.99	46.75	28.71	8.26

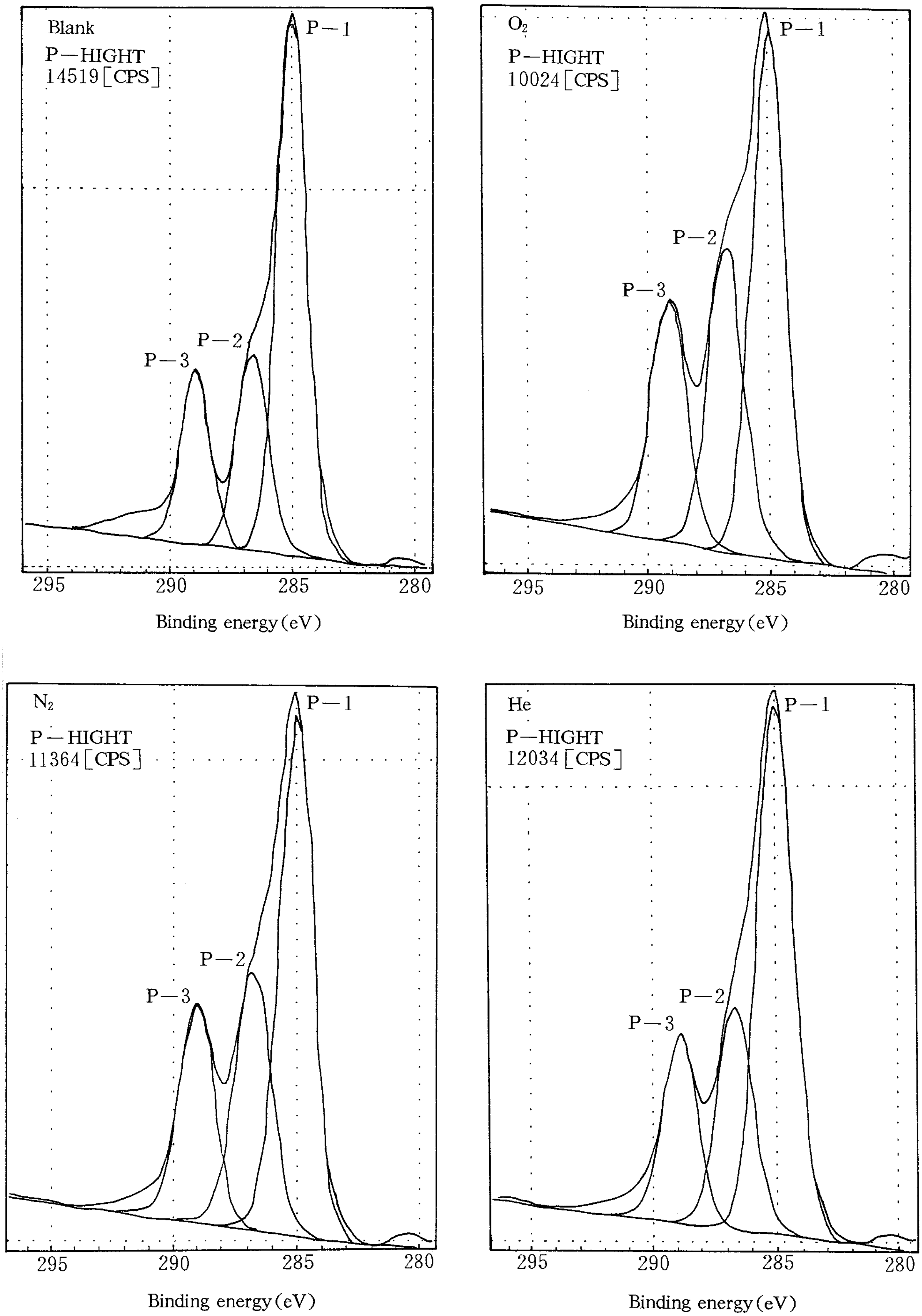

Figure 2 Effect of wave analysis on C_1s spectrum of the PET film treated with low-temperature plasma: P-1, —CH—: P-2, —CO—; P-3; —COO—.

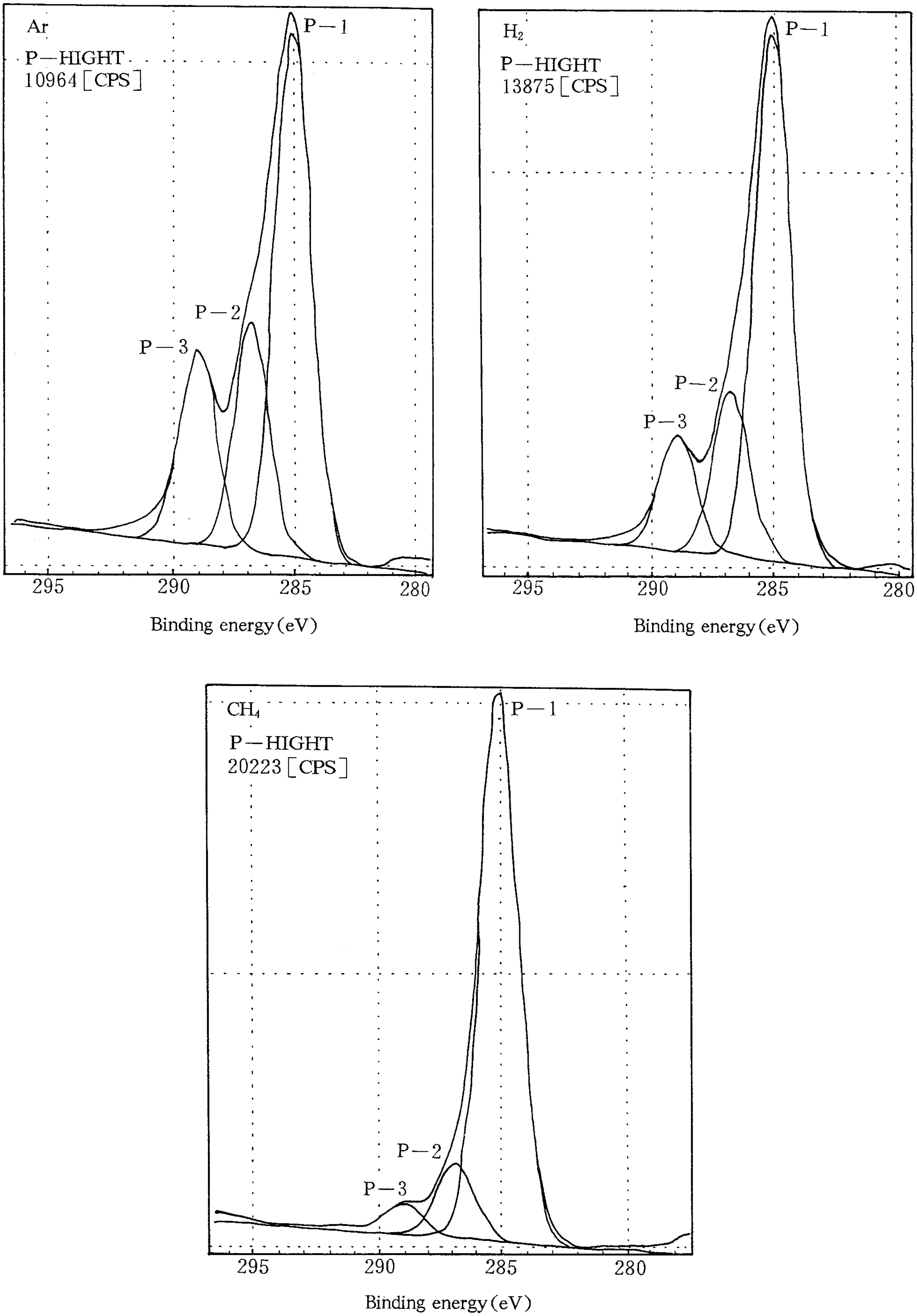

Figure 2 (*Continued from the previous page*)

tion of chemical species of surface layers of the PET film. Mg–K$\alpha_{1\cdot 2}$ X-ray was used as the source. Operating parameters were 8 kV and 30 mA.

RESULTS AND DISCUSSION

The PET films were treated with plasma in six kinds of gases (O_2, N_2, He, Ar, H_2, and CH_4). The results of the surface tension γ_S and three components, γ_S^a, γ_S^b, and γ_S^c, and the critical surface tension γ_C of the PET film are summarized in Table II.

From the data in Table II, it is evident that the value of the surface tension γ_S of PET film obtained by the extended Fowkes equation is corresponds highly to γ_c of Zisman's plots, which coincides with the theory of Kitazaki and Hata.[6] The surface tensions of PET films treated with O_2, N_2, He, and Ar plasma for a short time (3 min) are all highly increased to $56 \sim 57.5 \times 10^{-5}$ N cm^{-1}, the surface of the film is in a high energy state, and its hydrophilicity is improved. The surface tension of PET treated with CH_4 plasma is decreased to 39×10^{-5} N cm^{-1}, and the surface-free energy is also decreased. According to the surface tension γ_S and its three components, γ_S^a, γ_S^b, and γ_S^c, of the PET film, we can conclude that the nonpolar dispersion force γ_S^a is decreased by 50–60%, but the hydrogen bonding force γ_S^c is increased by nine times, and the surface-free energy is increased markedly by the plasma treatments with O_2, N_2, He, and Ar, as compared with the untreated sample. The wettability of PET is increased because of the interaction between the hydrogen bond and dipole–interdipole in the vertical direction of the interface.[8] The nonpolar dispersion force γ_S^a keeps unchanging, but the hydrogen bonding force γ_S^c is increased by 3.6 times in the H_2 plasma treatment, so the surface-free energy is also increased. The hydrogen bonding force γ_S^c of CH_4 plasma-treated PET is decreased to 2.0×10^{-5} N cm^{-1}; thus, the surface is in a low-energy state. Therefore, it is apparent that the increase in surface-free energy and wettability by these plasmas is due to the increase in the hydrogen bonding force γ_S^c, which corresponds to the previous article.[9]

The wettability of the sample is tightly related to the presence of a particular functional group that resides in the outermost surface layer.[10] The study showed that an acting force was produced in the vertical direction of the interface by introducing oxygen or nitrogen polar functional groups into the surface layer of fibregenic superpolymer, which can improve the wettability of polymer. The relationship between the surface chemical structure and surface wettability of plasma-treated PET was characterized by ESCA. The contact angle to water θ_{H_2O} and the relative content of the surface elements on the PET film treated with plasma in six kinds of gases are listed in Table III. It is evident in Table III that the surface wettability of PET treated with plasma in O_2, N_2, He, and Ar is improved greatly, and the contact angle to water is decreased to 24–28°. The surface wettability of H_2 plasma-treated PET is improved slightly, and the contact angle to water is decreased to 47°. The surface wettability of CH_4 plasma-treated PET is dropped, and the contact angle to water is increased to 74°. From the element content in the surface of PET shown in Table III, it is apparent that the O_2, N_2, He, and Ar plasma treatments lead to an increase in oxygen intensity and a decrease in carbon intensity. In addition, a small amount of nitrogen is introduced into the surface layer of the O_2, N_2, and He plasma-treated PET. The ratios of (O + N)/C for the O_2, N_2, He, and Ar plasma-treated PET are increased to 55.47, 47.25, 44.99, and 46.75, respectively, while the untreated sample is 36.78. The H_2 plasma treatment leads to a decrease in oxygen intensity and an increase in carbon intensity. Whereas the oxygen intensity is decreased greatly, and the carbon intensity is increased markedly by CH_4 plasma treatment and the ratio of (O + N)/C is only 8.26.

ESCA spectra for C_1s of plasma treatments in six kinds of gases are shown in Figure 2; the C_1s spectrum of the untreated sample is also shown in the same figure as a comparison. The intensity of —CH— at about 285.0 eV is decreased, but those of the —CO— and —COO— at 286.0–289.0 eV are increased by O_2, N_2, He, and Ar plasma treatment. The results obtained by ESCA indicate that the contents of oxygen and nitrogen elements in the O_2, N_2, He, and Ar plasma-treated PET surface are increased. A large amount of oxygen and nitrogen polar functional groups are introduced into the PET surface; thus, the contribution of the hydrogen bonding force γ_S^c of O_2, N_2, He, and Ar plasma-treated samples increase markedly. The surface wettability of PET can be improved effectively by the interaction between the hydrogen bond and dipole–interdipole in the vertical direction of the interface. It is evident from the C_1s spectrum in Figure 2 that the intensity of —CH—

Table IV Changes in Relative Peak Areas of C_1s Spectra of the PET Film Treated with Low-Temperature Plasma

Peak	Chemical Component	Binding Energy (eV)	Relative Peak Area (%)						
				Plasma Treatment					
			Blank	O_2	N_2	He	Ar	H_2	CH_4
P-1	—CH—	285.0	58.64	46.45	50.43	56.56	54.37	64.77	83.49
P-2	—CO—	286.6	22.52	29.86	27.24	23.76	24.23	20.81	11.55
P-3	—COO—	288.9	18.84	23.69	22.33	19.68	21.40	14.42	4.96

group increases slightly, and those of —CO— and —COO— groups decrease when PET film has been subjected to H_2 plasma. This phenomenon indicates that the hydrocarbon compounds are produced, the oxygen functional groups are reduced after being treated with H_2 plasma, and the hydrogen bonding force of PET surface increases because of the effect of the oxygen polar groups. As a result, the surface-free energy and wettability of PET can still be improved by H_2 plasma treatment. It is known from Figure 2 that the intensities of —CO— and —COO— groups at 286.0–289.0 eV obviously drop, but that of the —CH— group at 285.0 eV increases greatly by CH_4 plasma treatment. It can be concluded that a large amount of hydrocarbon were produced in the surface of PET when exposed to CH_4 plasma. The great decrease in oxygen content and carbon content in the PET surface lead to the hydrogen bonding force; the surface free energy and the surface wettability are all reduced. The relative peak areas of C_1s spectra of the PET film treated with low-temperature plasma in six kinds of gases are shown in Table IV.

CONCLUSIONS

The surface wettability of PET can be improved by low-temperature plasma, and the degree of the modification is mainly due to the kind of the gas. The surface tension of PET treated with O_2, N_2, He, and Ar plasma for a short time increase sharply from 42.0×10^{-5} N cm^{-1} to 56.0–57.5 $\times 10^{-5}$ N cm^{-1}. The nonpolar dispersion force γ_S^a obtained by the extended Fowkes equation decreases by 50–60%, while the hydrogen bonding force γ_S^c increases by 9 times. The information from the ESCA experiment indicates that the carbon content decreases and the oxygen content increases in the surface of PET, and a large amount of oxygen polar functional groups are introduced into the surface of plasma-treated PET, which strengthen the interaction between the hydrogen bond and the dipole–interdipole in the vertical direction of the interface. This is the important reason for improving the wettability of PET. The surface wettability of PET is also improved by H_2 plasma treatment. But the CH_4 plasma treatment does not improve the wettability of PET and leads to the decrease of the hydrogen bonding force and the surface-free energy; this is due chiefly to the decrease of oxygen polar functional groups and the increase of hydrocarbon on the PET surface.

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