

An XPS Investigation of Polymer Surface Dynamics. I. A Study of Surfaces Modified by CF₄ and CF₄/CH₄ Plasmas

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SYNOPSIS

For making the surface hydrophobic, poly(ethylene terephthalate) (PET) films were subjected to treatment by CF₄ and CF₄/CH₄ plasmas, and the PET fabrics, to impregnation (padding) with Oleophobol S for comparison. The electronic structure of the modified surface was differentiated by XPS (ESCA). The surface dynamics upon heating and dipping into water was investigated by the angle-dependent XPS technique. Application of the XPS technique to these topics gave a wealth of information. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most widely used polymers in industry. Detailed knowledge of the surface dynamics of the modified PET surface is important when it is used either by itself or as a substrate.

It has been well known for years, that unlike the more rigid metals and ceramics, the macromolecules may orient themselves at the surface in a way that is significantly different from that in the bulk of polymers and that the plasma technique is available for the surface modification of polymers. Also, the past two decades have witnessed the growing awareness of the great potential of XPS (or ESCA) as a sensitive tool for probing the surface of polymers. A great volume of literature, therefore, has been published in recent years to study the interaction of plasma with the polymer surface and the dynamic behavior of the treated surface by the XPS technique.

An attempt has been made in the present article to determine if such observations could help determine whether the surface modified by plasma under various experimental conditions and the dynamic

behavior in further detail can be characterized and differentiated by XPS. In this article, the surface dynamics of polymers denotes time-dependent (e.g., the aging effect upon contacting with water) and temperature-dependent (e.g., upon heating) processes.

EXPERIMENTAL

- A. The XP spectra (MgK α) were recorded on a PHI 5300 ESCA System (Perkin-Elmer) instrument at 250 W (12.5 kV \times 20 mA) by assuming a binding energy (BE) of adventitious carbon equal to 284.6 eV. The vacuum system was kept higher than 1.5×10^{-6} Pa. Data massage (e.g., X-ray satellite subtraction, background subtraction, normalization, curve-fitting, etc.) was performed on a PE 7500 professional computer. The samples in film form were clamped onto the sample holder.
- B. The plasma processor used was supplied by Plasma Electronic. The plasma was generated capacitively and operated at frequency of 100 kHz. The volume of the vacuum chamber was $0.5 M^3$. Plasma was restricted to a volume of $20 \times 20 \times 50 \text{ cm}^3$. The samples were treated with a power of 350 W for CH₄ plasma and of 250 W for CF₄ plasma, mass flow rates of 5–90 sccm, pressure of 0.05–1.00 mbar, and elec-

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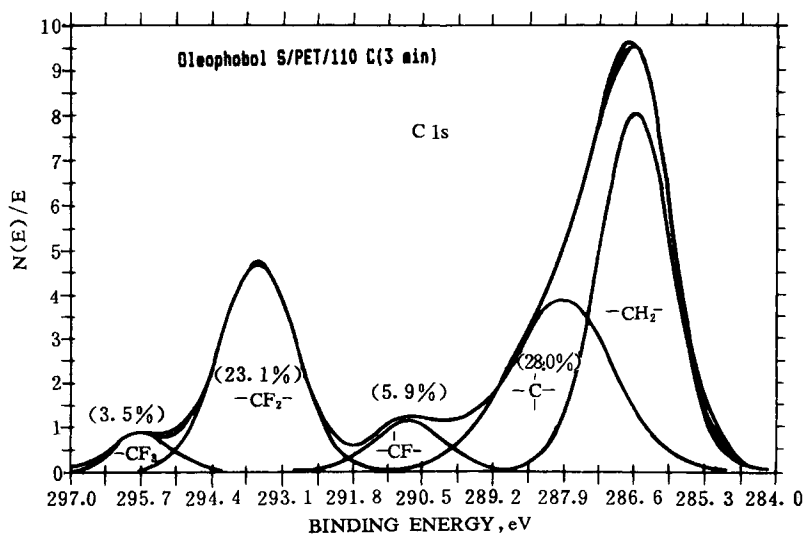


Figure 1 C1s spectra of the PET fabric surface (without charge corrected) (padding with Oleophobol S/heating at 110°C, 3 min.).

trode separation of 20 mm. Samples were transported through the plasma region with a speed of 0.1 m/min. Exposure time to plasma was preset at 2.1 min.

The precursor gases, CF_4 and CH_4 , were commercially purchased from Carbongas and Merck, respectively, without further purification. The flow rate of each reaction gas was determined by a mass flowmeter in such a way that the composite parameter W/FM was kept at a constant value of $0.2 \times 10^9 \text{ J kg}^{-1}$.

- C. Commercially available 50 micron poly(ethylene terephthalate) (PET) foils were used. The foils were cleaned in methanol followed by acetone and deionized water at room temperature. The PET fabrics used were washed, scoured, and fixed Diolen pile fabrics, 67 g/sq m. Both PET foils and fabrics were used and were exposed to the XPS analysis. Foils were then used without further treatment for XPS studies. Fabrics were, additionally, finished (padded) with a conventional, fluorinated polyacrylate resin (Oleophobol S), supplied by Chemische Fabrik Pfersee, prior to the XPS analysis.

RESULTS AND DISCUSSION

A. Comparison Surface Modification with Oleophobol S and Plasmas

Before recording, the multiplex spectra of C1s and F1s, at all events, were performed. The survey spec-

tra showed the presence of carbon, fluorine, and a small amount of oxygen. In understanding of the dynamics of surfaces with a hydrophobic nature, the overwhelming role of fluorine and carbon coming into play has been well recognized. The secondary effect of oxygen can be less important in the assignment of the multiplex spectra and, therefore, it can be dealt together with fluorine as shown in the figures. As the first example for comparison, we show here the C1s spectrum of the PET fabric treated with Oleophobol S (see Fig. 1). With the aid of the assignment of the fluorine-containing peaks reported in the literature¹ and the procedure of curve-fitting, the C1s spectra can be well determined into five components as expressed in Figure 1[†] (the same below). It is evident that the $-\text{CF}_2-$ and $-\text{CF}_3$ groups should obviously stem from the perfluoro functional groups involved in Oleophobol S, and the appearance of $-\text{CF}$ and $-\text{C}-$ groups should be reasonably ascribed to the cross-linking between the main polymeric chains.¹ Apparently, the CF_2 component dominates the surface among the three F-containing peaks.

Of considerable importance is the surface modification by plasmas. Instead of fabric specimens, the PET films were employed here for obtaining better spectra.

Unlike the C1s spectra of PET fabrics treated with Oleophobol S as mentioned above, the CF_4

[†] Peak $-\text{CF}_3$ may contain some of $-\text{CF}_2\text{O}-$; peak $-\text{CF}_2-$ may contain some of $-\text{CFO}-$; peak $-\text{CF}$ may contain some of C=O ; and peak $-\text{C}-$, $-\text{CH}_2-$ may contain some of $\text{C-O}-$.

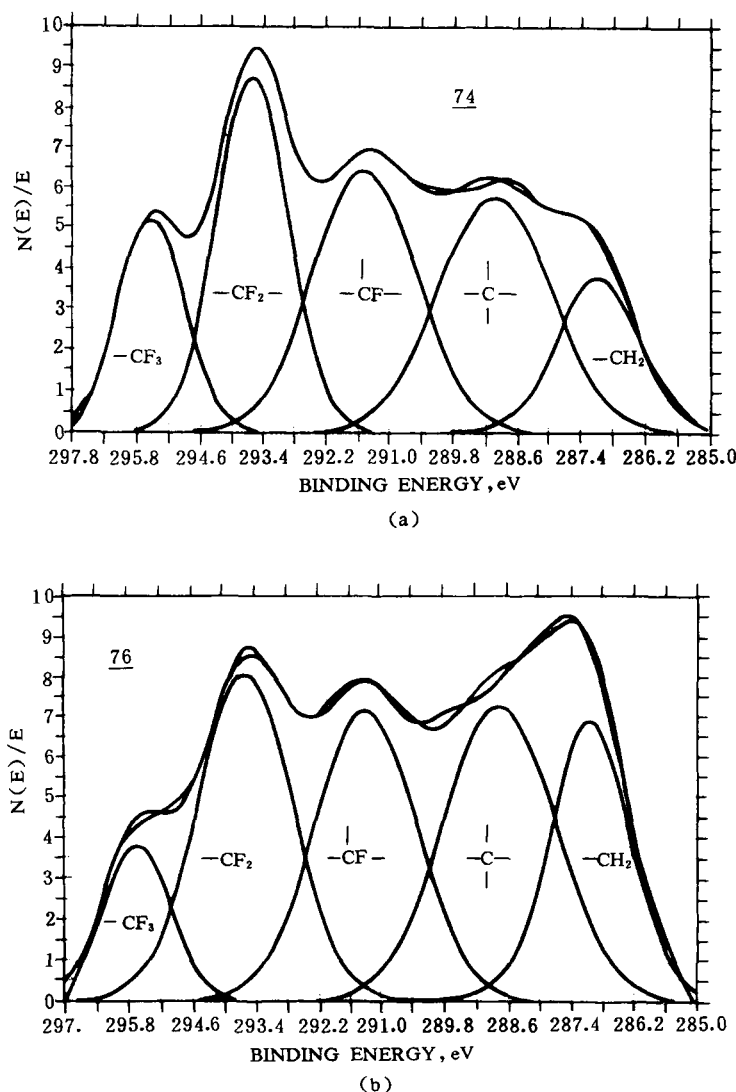
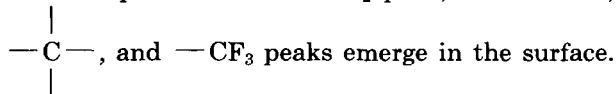


Figure 2 C1s spectra of CF_4 plasma-modified PET surfaces (without charge corrected): (a) specimen 74: (1) CH_4 plasma, (2) CF_4 plasma; (b) specimen 76: (1) Ar plasma; (2) CF_4 plasma.

plasma-modified surface of PET films displays much involved characteristic envelopes (see Fig. 2). In contrast to those as shown in Figure 1, a considerable change in intensities of the fluorine-containing peaks can be found quantitatively, revealing that, at the expense of the $-\text{CF}_2-$ peak, more $-\text{CF}$,



The emergence of the peak ($-\text{CF}$, $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$) indicates a highly cross-linked network, and the latter ($-\text{CF}_3$) may imply the appearance of the end

groups of oligomers to some extent and so do the weak links.

It is obvious that, not like the PET surface treated with Oleophobol S, the plasma-treated surfaces of PET films can hardly keep the surfaces intact to the same extent as does Oleophobol S as a consequence of the strong impact in plasma.

The addition of CH_4 to a saturated fluorocarbon CF_4 causes a remarkable change in the C1s spectra. Figure 3(a)–(c) shows the C1s spectra of PET surfaces modified by $(\text{CF}_4 + \text{CH}_4)$ plasma at molar ratios CF_4/CH_4 of 3 : 1, 2 : 1, and 1 : 1, respectively.

As shown in Figure 3, as long as the CH_4 (a kind of hydrogen source) is introduced into CF_4 gas, there

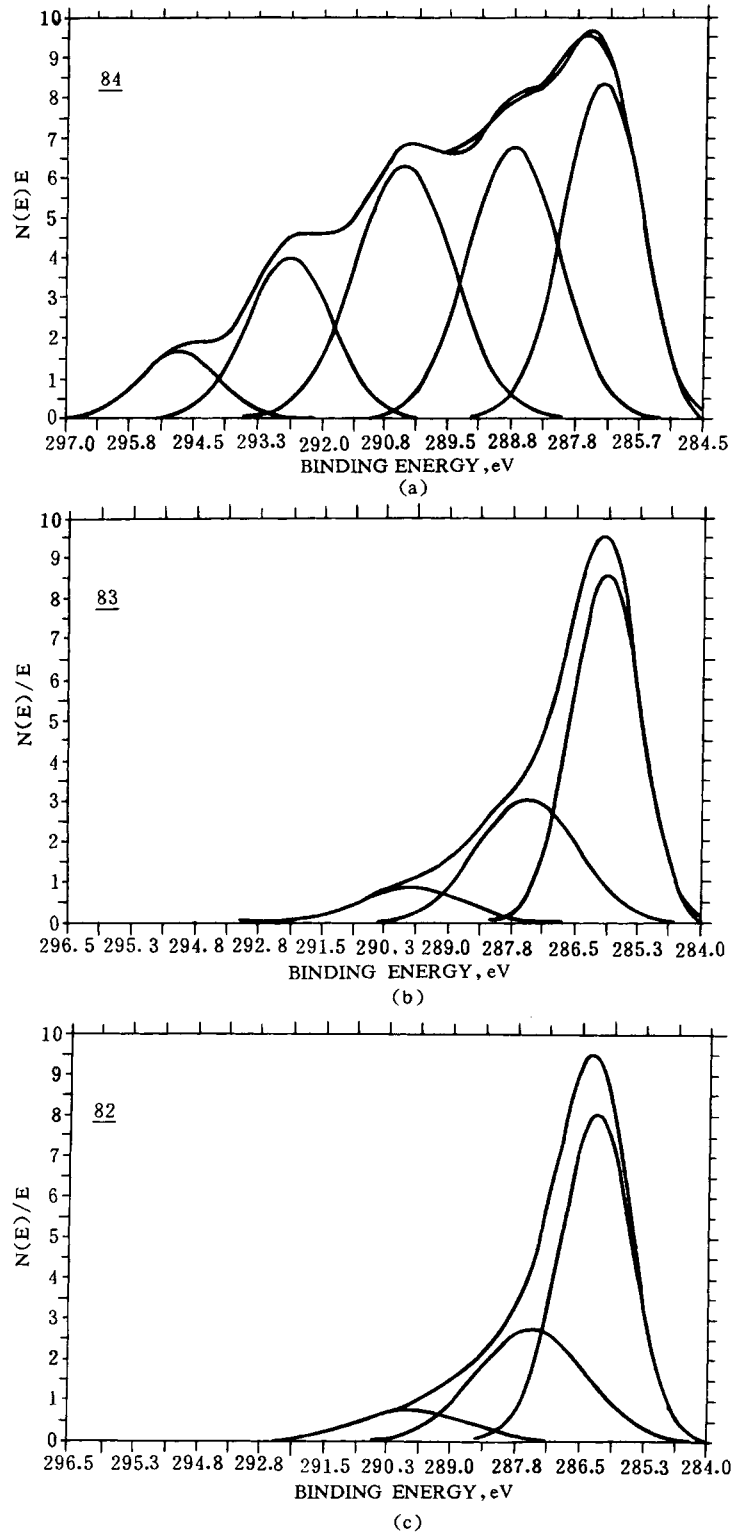


Figure 3 C1s spectra of PET surfaces modified by $(\text{CF}_4 + \text{CH}_4)$ plasma under different molar ratios of CF_4/CH_4 (without charge corrected): (a) 3 : 1; (b) 2 : 1; (c) 1 : 1.

Table I XPS Data Collection

Condition	Model Polymer PTFE	Specimen No.											
		74		76		84		83		82			
		(1) CH ₄ Plasma (2) CF ₄ Plasma	(1) Ar Plasma (2) CF ₄ Plasma	Molar Ratio CF ₄ /CH ₄ 3 : 1	Molar Ratio CF ₄ /CH ₄ 2 : 1	Molar Ratio CF ₄ /CH ₄ 1 : 1							
F/C ratio	2.00	1.45	1.24	0.72	0.09	0.09							
O/C ratio	—	0.03	0.10	0.15	2.10	1.76							
F1s, eV	689.0	688.2	688.3	688.0	686.9	686.8							
F(KVV)													
Auger parameter α^*	1341.2 ^a	1341.3	1341.2	1341.8	1342.8	1342.2							
$\Delta\alpha^*$	0.0	0.0	0.0	0.6	1.6	1.0							

C1s	BE		A.C.		BE		A.C.		BE		A.C.	
	(eV)	(%) ^b	(eV)	(%) ^b	(eV)	(%) ^b	(eV)	(%) ^b	(eV)	(%) ^b	(eV)	(%) ^b
—CH ₂ —	—	—	284.6	12.2	284.6	18.4	284.6	27.3	284.6	59.5	284.6	59.9
—C—	—	—	286.5	24.6	286.3	25.7	286.3	25.8	286.1	30.6	285.8	31.3
—CF—	—	—	289.0	25.3	288.9	23.3	288.5	26.6	288.4	9.9	288.2	8.8
—CF ₂ —	291.8	100.0	291.1	24.6	291.2	24.5	290.7	14.3	—	—	—	—
—CF ₃	—	—	293.0	13.3	293.2	8.1	292.9	6.0	—	—	—	—

^a Ref. 2.^b Atomic concentration.

is a ready decrease in the ratio of F/C, leading to a higher extent of cross-linking as indicated by the

increase in the $\begin{array}{c} | \\ \text{—C—} \\ | \end{array}$ component.

B. Characterization of the Surfaces Treated by Plasmas

To obtain a better understanding of the dynamic behavior of the surface, some parameters must be first looked at for the characterization. All the data, such as ratios of F/C, O/C, binding energies of F1s, and Auger parameter[§] α^* of F(KVV) electrons, can be derived from C1s (Figs. 3 and 4) and F1s and O1s (the latter two not shown for simplicity), as listed in Table 1. For comparison, the model polymer, polytetrafluoroethylene (PTFE) is also referenced in the second column of Table I. Some conclusions can be drawn as follows:

1. From the left to the right side of the table appear some regular trends, e.g., the F/C ratio is decreasing in parallel with the decreasing binding energies of F1s peaks, denoting that the structures of the modified surfaces manifest themselves to be very different from the model polymer PTFE as evidenced by the ca. a 1–1.6 eV difference of the Auger parameter $\Delta\alpha^*$ of the F(KVV) electron. This becomes clearer as the CH₄ gas is gradually added into the saturated CF₄. By the definition of α^* , it implies that the relaxation energy of the F atom embedded in the carbon matrix is increasing while CH₄ is mixed in the plasma.

As can be seen from Figures 2 and 3, there is a remarkable change in the shape of the envelopes. The quantitative data derived from the C1s spectra of all the specimens were collected in Table I as well.

It is noted in Table I that there is a borderline separating the six specimens into two groups, i.e., the first group characteristic of the dominated —CF₂ in the surface in-

[§] $\alpha^* = \text{KE}(\text{Auger electron}) + \text{BE}(\text{photoelectron})$.

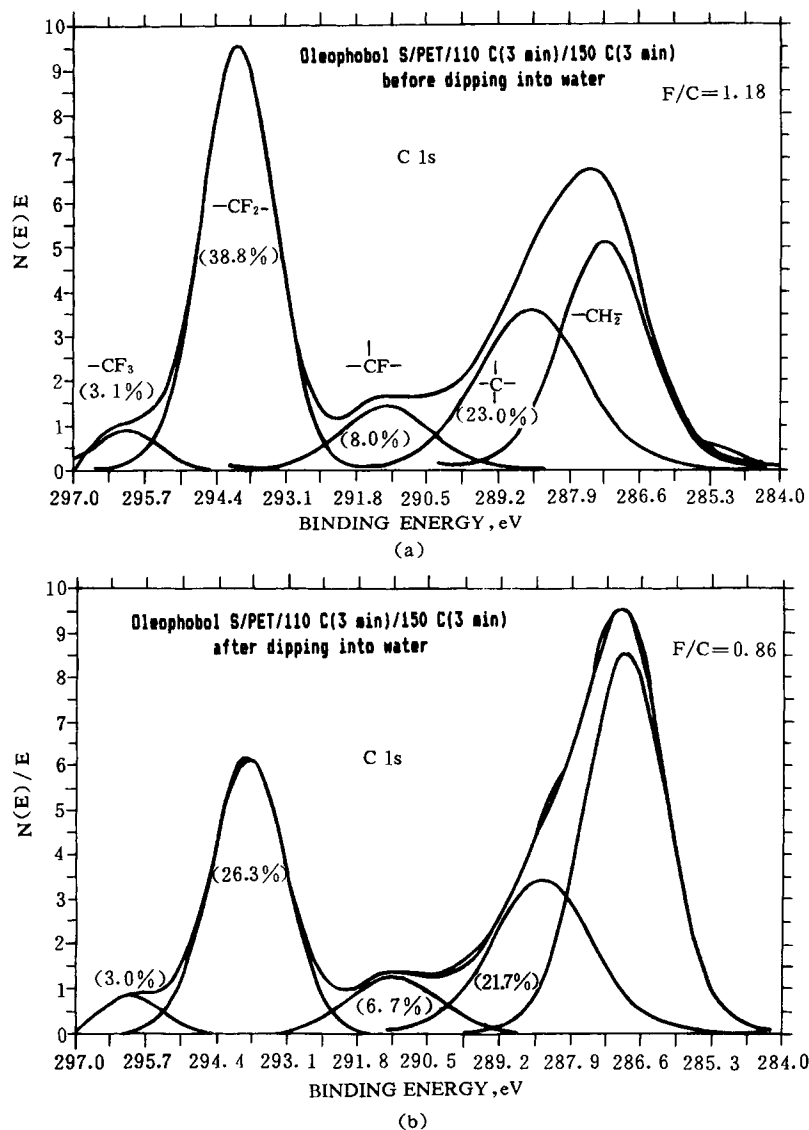


Figure 4 C1s spectra of PET fabrics (without charge corrected). Dynamic behavior of Oleophobol S-treated surface: (a) before dipping into water; (b) after dipping into water; (c) on heating at 110°C for 1 h; (d) on heating at 150°C for 0.5 h.

cludes PTFE, 74 and 76, and specimens 84, 83, and 82 belong to the second group with features of less $-CF_2$ contained and are

dominated by the presence of the $-C-$

and $-CF$. In other words, the depression of the functional group $-CF_2$ in the surfaces should originate from the addition of CH_4 . This fact is consistent with the change of α^* , as it is well recognized³ that an increment of α^* (e.g., from 1341.2 eV of PTFE to 1342.2 eV of 82) indicates a larger relax-

ation energy around the fluorine atom by carbon atoms attached to it, resulting in a more stable chemical environment.

2. The distinct feature designated to both groups leads to the conclusion that the formation of these characteristic surfaces should invoke a different mechanistic explanation.

Yasuda et al.,^{4,5} reported that the addition of CH_4 or other hydrocarbons enhanced the plasma polymerization (a deposition process) of saturated fluorocarbon (say CF_4) because the hydrocarbon acts as a source of

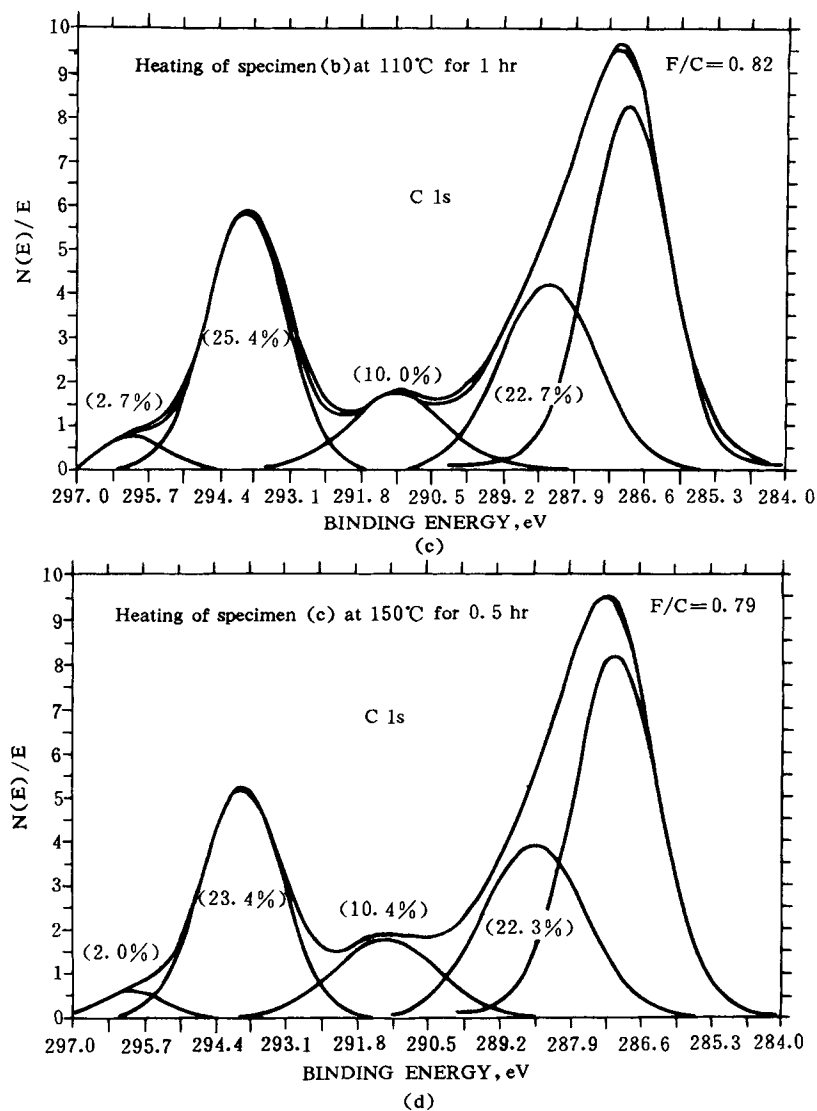
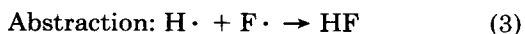
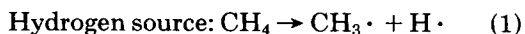


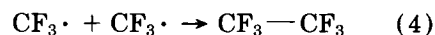
Figure 4 (Continued from the previous page)

hydrogen in the plasma. The major premise for forming a polymeric structure, or the so-called plasma-polymerized structure, requires the breaking of C—F bonds. The resulting structure through deposition (or plasma polymerization) depends on the reduction of etching (or ablation) caused by the active fluorine-based species F, i.e.,



The scavenging action (3) of hydrogen can be easily visualized by comparing the

bonding energies of F—F (153 kJ mol^{-1}) and H—F (558 kJ mol^{-1}). The polymerization can be realized as (4)



It is clear from the above discussion that there is no way for reaction (4) to occur in the case of pure CF_4 . In other words, the CF_4 plasma is nonpolymerizable and should result in a different structure of the modified surface. Actually, the overwhelming amount of — CF_2 functional groups incorporated into the surfaces with much higher F/C ratios was verified by the C1s spectra of specimens 74 and 76 (cf. Fig. 2 and Table I),

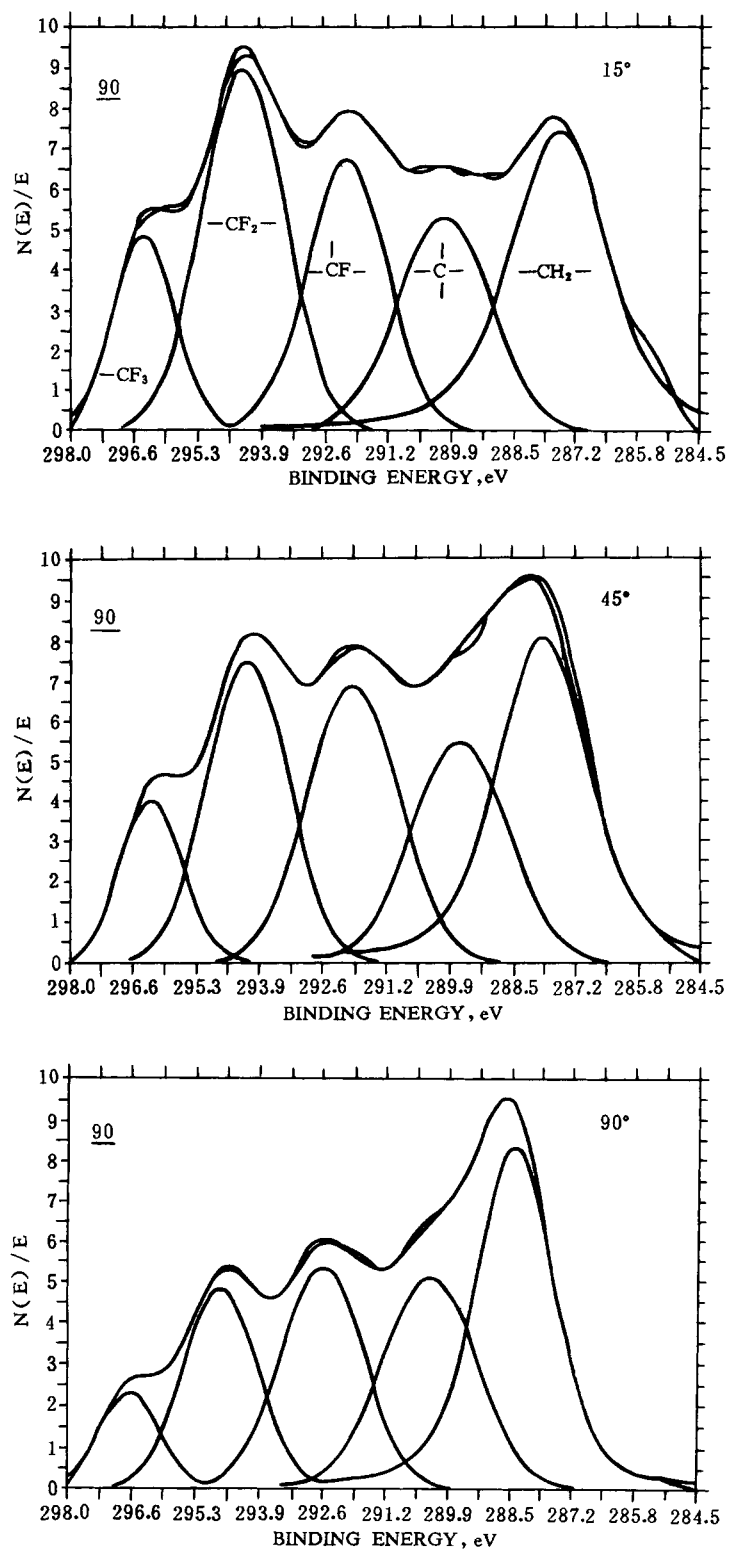


Figure 5 C1s spectra of 90 (before dipping into water) by angle-dependent XPS (without charge corrected).

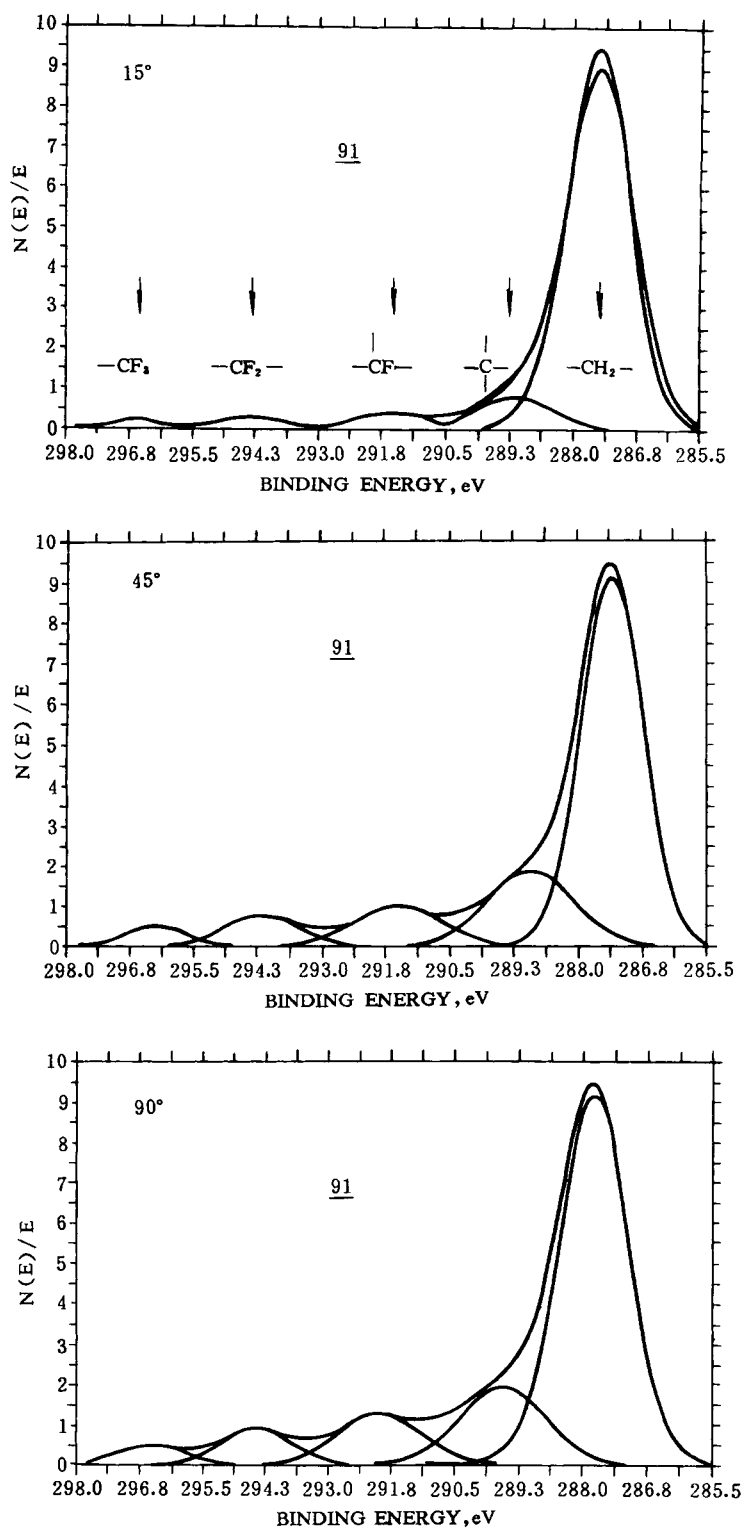
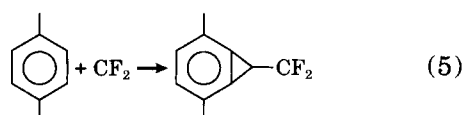


Figure 6 Cls spectra of 91 (after dipping into water for 1 h) by angle-dependent XPS (without charge corrected).

whatever the prior treatment to the PET surface was done by CH₄ or Ar plasma. To describe this, one would usually prefer to use the terminology "implantation"^{4,5} or "fluorination."^{6,7}

3. It can be noted from Table I that specimen 74 is the one with the highest F/C ratio, of ca. 1.5, that was prepared using two plasmas one after another. The first treatment by CH₄ plasma resulted in a polymeric carbon film (or a —C : H film, the so-called diamondlike film) possessing a graphitelike structure.⁸ The latter is, in fact, a structure with double bonds that is subject to being attracted to active fluorocarbene (—CF₂—) behaving with both radical (CF₂, S₁, and T₁) and acid-base properties (fundamental CF₂, S₀) in the plasma phase.⁹ It may react by the following mechanism:



The reason for predepositing a polymeric carbon film onto the PET surface is threefold:

1. To enhance the adhesion with the underlying polymers.
2. To offer a surface allowing for better wetting with the fluorine-containing structure of the resulting CF₄ plasma.
3. To prepare a highly cross-linked surface that may improve the time-dependent surface dynamics.
4. Usually, the Ar plasma is often employed as an activated agent and a source of free rad-

icals at the surface.¹⁰ It provides active sites to which the fluorine radical CF_x can be grafted. Therefore, specimen 76 can have a F/C ratio of 1.24, a little higher than the treatment without Ar plasma.

C. Surface Dynamics Studies

The dynamic behavior of PET fabrics treated with Oleophobol S upon heating in air and/or dipping into water are shown in Figure 4(a)–(d). It was found that the intensity of the main peak, —CF₂, in the C1s spectrum decreases from 38.8% (a) to 26.3% (b) after dipping the sample (a) into water. Upon heating of the sample (b) at 110°C for 1 h [see (c)], the intensity of the —CF₂ peak no longer increases as normally expected, even on further heating at 150°C (d). It is seen that on heating the ratio of F/C decreases from 0.86 (b) to 0.82 (c) and then to 0.79 (d), which can hardly reverse to the original level of 1.18 as indicated in (a). This interesting result enables us to speculate this fact in terms of a model of highly cross-linked density, which should be of paramount importance among factors hampering the mobility of the —CF₂ group reversibly in the surface region. In addition, the formation of a higher cross-linked network can be confirmed as well by the increment of the —CF peak as observed from 6.7% (b) to 10.0% (c), and then to 10.4 (d). To gain further insight, needed is the angle-dependent XPS, which turns out to be a powerful tool for nondestructive depth profiling of polymeric films, i.e., by tilting the take-off angle and taking 76 as a test specimen before and after dipping into water for 1 h, i.e., 90 and 91 (see Figs. 5 and 6). (For the use of angle-dependent XPS, a polymeric film must be employed instead of, e.g., a pow-

Table II Dynamic Data of Angle-dependent XPS

Condition	No.											
	90		91		97		98		99		100	
	Virgin	Dipping into Water, 1 h	Virgin	Dipping into Water, 3 min	Virgin	Dipping into Water, 12 s	Virgin	Dipping into Water, 3 min	Virgin	Dipping into Water, 12 s	Virgin	Dipping into Water, 12 s
Take-off Angle	Atomic Ratio											
	F/C	O/C	F/C	O/C	F/C	O/C	F/C	O/C	F/C	O/C	F/C	O/C
15°	1.18	0.094	0.24	0.46	1.01	0.11	0.30	0.46	1.10	0.10	0.49	0.28
45°	1.16	0.089	0.34	0.38	1.07	0.11	0.43	0.35	1.00	0.11	0.56	0.25
90°	1.06	0.12	0.36	0.33	0.94	0.14	0.47	0.33	1.00	0.13	0.56	0.27

Table III Decay Rate Parameter, k

	Take-off angle θ		
	15°	45°	90°
	Depth, Å, $3\lambda \sin\theta$		
	20	55	78
k	0.33	0.18	0.12

λ : inelastic scattering free path of electrons; θ : take-off angle.

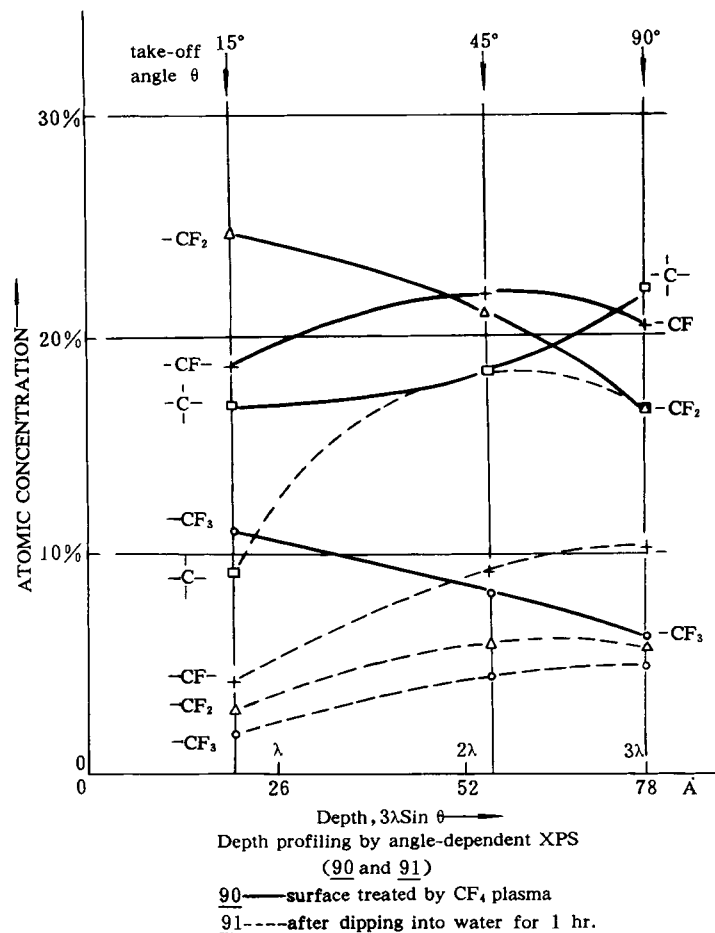
der sample.) The dynamic data from angle-dependent XPS for dipping times of 1 h (90, 91), 3 min (97, 98), and 12 s (99, 100) are all shown in Table II, where 90, 97, and 99 are the same as 76 before dipping into water; 91, 98, and 100 represent specimens of 76 after dipping into water for 1 h, 3 min, and 12 s, respectively.

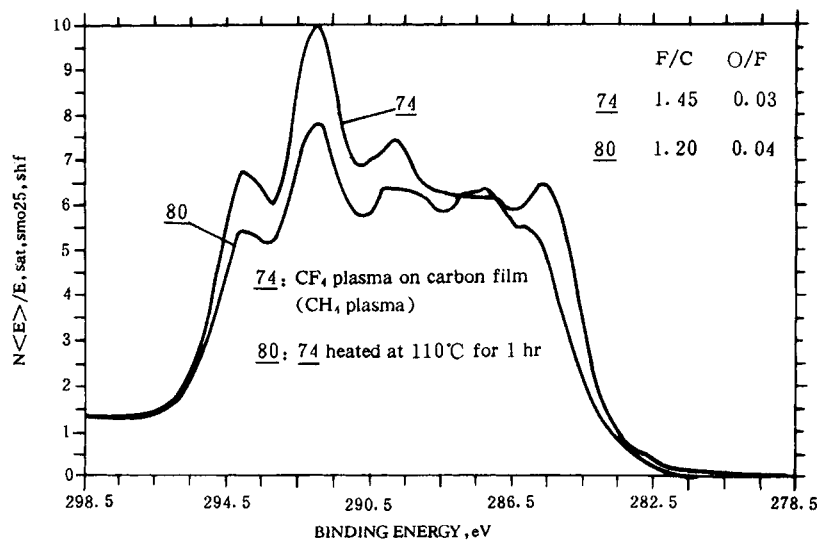
Based on the decay equation, $A_t = A_0 t^{-k}$ (where A_t is the F/C ratio at time t ; A_0 , the F/C ratio at

time $t = 0$; and k , the decay rate constant), the k value can be calculated using the data of Table II as seen in Table III. It is interesting to find that on the top layers of the surface region, e.g., at the depth of 20 Å, the decay rate constant k shows a value almost three times that at the depth of ~ 80 Å. The k will decrease to a constant at a depth larger than 3λ (see footnote to Table III).

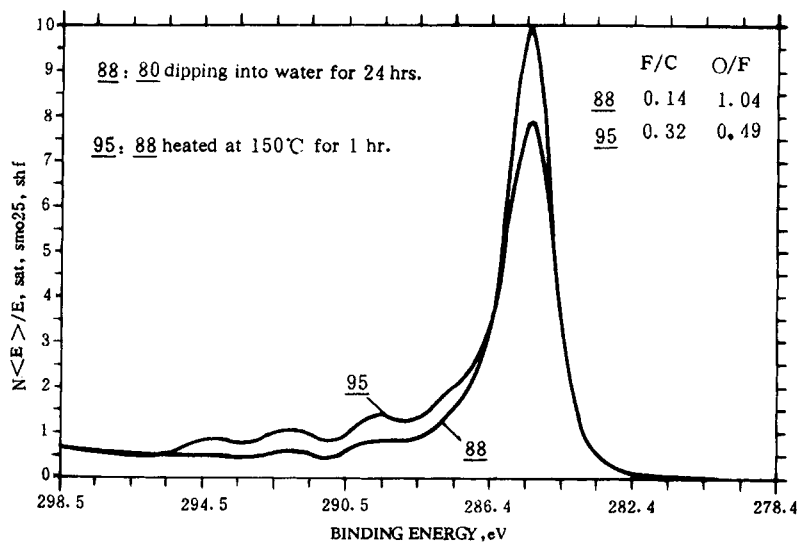
Obviously, the data from the angle-dependent XPS technique can be easily used for the study of the surface dynamics in terms of the layered structure in depth, if compared with the data obtained from the contact angle method.

To quantitatively and intuitively understand the surface dynamics of a polymer, a simplified expression of the depth profile can also be drawn as the one in Figure 7 with the aid of the angle-dependent XPS and the curve-fitting procedure. One can see from Figure 7 the distribution of CF_x ($x = 0, 1, 2, 3$) components along with depth before and after specimen 76 was dipped into water (see 90 and 91 in Fig. 7). The meaningful patterns in Figure 7 sup-

**Figure 7** Depth profiling by angle-dependent XPS.



(a)



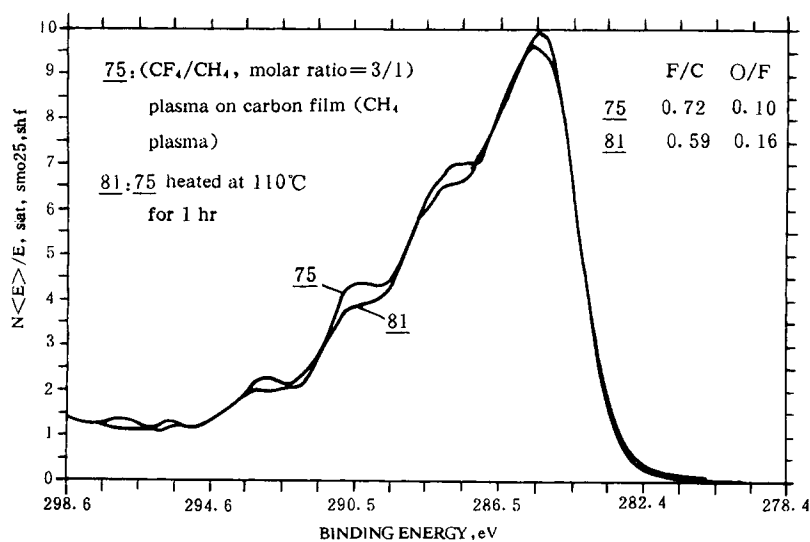
(b)

Figure 8 Dynamic behavior of 74 upon (a) heating and (b) dipping into water (with charge corrected for C1s spectra).

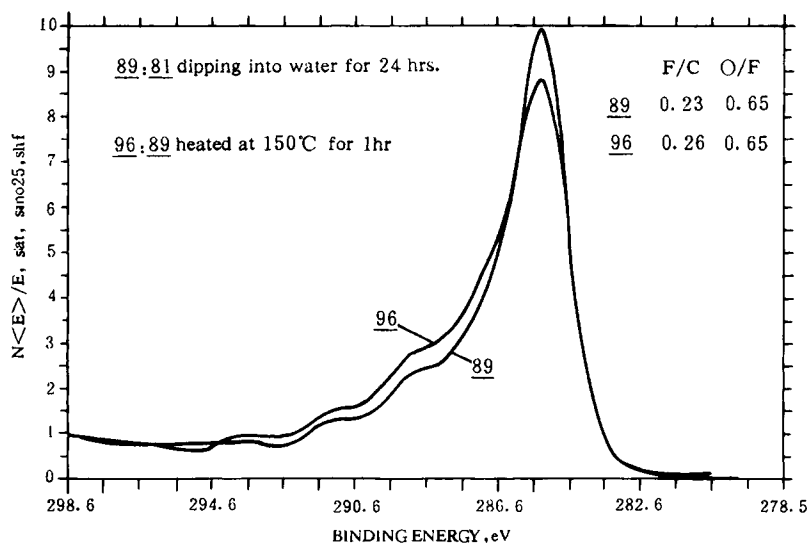
port the point of view intuitively that all the fluorine-based functional groups (CF_x, $x = 0, 1, 2, 3$) in the surface region migrate mainly toward the bulk from the surface when contacting with water rather than escaping on the way out of the surface.

We are now in a place to discuss some interesting features involved in the plasma-modified surfaces. To begin with, the PET fabric treated with Oleo-

phobol S was chosen. We have shown in the text that the fluorine-based functional groups in the surface of the PET fabric migrated toward the air-facing surface upon heating [see Figs. 1 and 4 (a)]. Unlike this, the plasma-treated specimens 74 (CF₄ plasma-modified PET) and 75 (CF₄/CH₄ = 3 : 1 plasma-modified PET) gave rise to an abnormal depression of both the ratio of F/C and —CF₂%. One of the



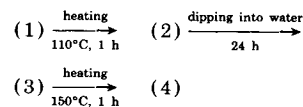
(a)



(b)

Figure 9 Dynamic behavior of 75 upon (a) heating and (b) dipping into water (with charge corrected for C1s spectra).

reasons for that may come from the transportation of weak-linked oligomers (generated under the strong impact of plasma) on the way out of the surface¹¹ [cf. Figs. 8(a) and 9(a)]. For comparison purposes, *in situ* treatment was performed in the following sequence and the data are collected in Table IV:



As far as the treatment from (3) to (4) is concerned, nothing special was recorded but a normal increase in intensities of fluorine-containing peaks

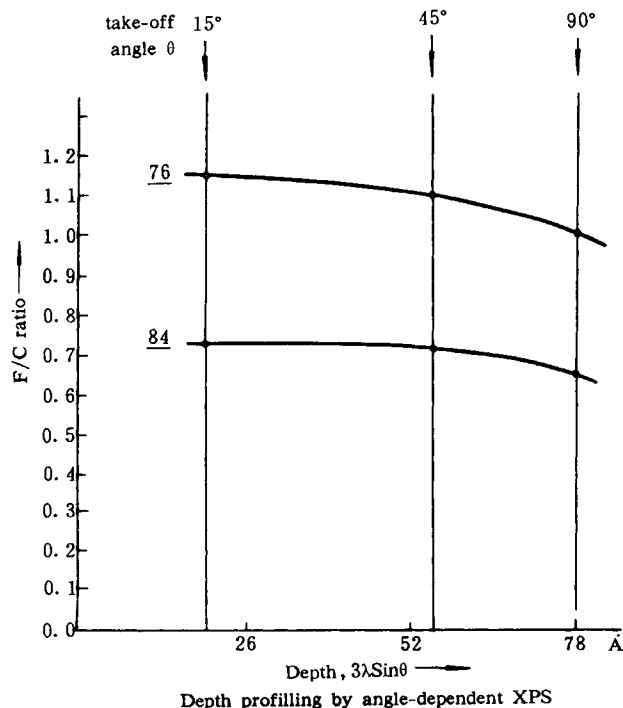
Table IV Dynamic Data of 74 and 75

	Sequence of Treatment			
	(1)	(2)	(3)	(4)
	(1) → (2) → (3) → (4)			
	No. of specimen			
	74	80	88	95
F/C	1.45	1.20	0.14	0.32
—CF ₂ %	22.30	19.40	1.00	5.00
	No. of Specimen			
	75	81	89	96
F/C	0.72	0.59	0.23	0.26
—CF ₂ %	10.50	9.50	4.20	4.80

by a very small amount, meaning that it can never return again to the original level owing to the highly irreversible cross-linked network formed by plasma and heating.

Another feature that should be emphasized here is the homogeneity of the surface layers. Using the data of angular-dependent XPS (cf. Table II), the

depth profiling (F/C vs. depth) can be depicted as shown in Figure 10 for specimens 76 and 84 (for simplicity, not shown were the F1s spectra). The change of F/C ratio as a function of the depth apart from the utmost layers of the surface for both 76 and 84 was plotted simultaneously in Figure 10. It is worth noting that the curve for 84 looks fairly flatter and positioned at a lower level than that for 76. It means that much more uniform layers can be expected via plasma polymerization, at least in the thickness of the first 50 Å, than via implantation. More details will be published elsewhere.¹²

**Figure 10** F/C vs. depth.

CONCLUSIONS

1. In the present paper, the surfaces of PET modified with CF₄ and CF₄/CH₄ plasmas were examined by XPS to differentiate the mechanisms available for the rationalization. The structure of surfaces modified by CF₄ plasma (via implantation) can be visualized by looking at the XPS data, characteristic of a higher F/C of 1.2–1.5, higher —CF₂%, higher binding energy of F1s, lower O/F of less than 0.1, and a lower Auger parameter α^* . Whereas the essential features of the surfaces formed by (CF₄ + CH₄) plasma (via plasma polymerization) are just in the opposite direction, i.e., a lower F/C within 0.1–0.7 depending on the amount of CH₄ added into the plasma, i.e., CF₄/CH₄ = 3 : 1, 2 : 1, and 1 : 1, lower

- CF₂%, lower binding energy of F1s, higher O/F of ca. 0.15–2.0, and higher α^* .
- Using angle-dependent XPS, a nondestructive depth profiling of the F/C ratio as a function of the depth has been found very useful for the study of surface dynamics. A uniform film can be easily formed by (CF₄ + CH₄) plasma (via plasma polymerization) as demonstrated by the lower curve shown in Figure 10. On the contrary, a nonuniform film as presented by the upper curve in Figure 10 could usually be ascribed to the implantation (sputtering or fluorination).
 - The distribution pattern of fluorine-based functional groups along with the depth was also obtained. It is interesting to find that on the top layers in the surface region, e.g., at the depth of 20 Å, the decay rate constant k shows a value almost three times of that at the depth of ca. 80 Å. k inclines to a constant value at some depth larger than 3λ (~ 80 Å), leading to a layered structure upon which surface dynamics can be intuitively rationalized.
 - The meaningful patterns do support experimentally the point of view intuitively that all the fluorine-based functional groups in the surface region migrate mainly toward the bulk from the surface when dipping into water rather than escaping on the way out of the surface.
 - Unlike the PET surface treated with Oleophobic S, upon heating, an abnormal depression of both the F/C ratio and —CF₂% in the surface modified by plasma can occur. It may come from the transpor-

tation of weak-linked oligomers under the strong impact of plasma moving toward the interface between air and the polymeric surface from the bulk.

REFERENCES

- T. W. Wydeven, M. A. Golub, and N. R. Lerner, *J. Appl. Polym. Sci.*, **37**, 3343 (1989).
- C. D. Wagner et al., *Handbook of X-ray Photoelectron Spectroscopy*, PE Corp., Eden Prairie, MN, 1979.
- C. D. Wagner, *J. Elect. Spectrosc. Rel. Phenom.*, **47**, 283 (1988).
- T. Yasuda, T. Okuno, and K. Yoshida, *J. Polym. Sci. Part B Polym. Phys.*, **26**, 1781 (1988).
- T. Yasuda, K. Yoshida, and T. Okuno, *J. Polym. Sci. Part B Polym. Phys.*, **26**, 2061 (1988).
- M. Strobel, S. Corn, C. S. Lyons, and G. A. Korba, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1125 (1985).
- P. M. Scott, L. J. Matienzo, and S. V. Babu, *J. Vac. Sci. Technol. A*, **8**(3), 2382 (1990).
- A. K. Sharma and H. Yasuda, *J. Appl. Polym. Sci.*, **38**, 741 (1989).
- S. Mournet, F. Arefi, M. Goldman, and J. Amouroux, in *Proceedings of International Symposium on Plasma Chemistry*, R. d'Agostino, Ed., IUPAC, Pugnochiuso, Italy, Sept. 4–8, 1989, Vol. 11, p. 1167.
- S. Mournet, F. Arefi, M. Goldman, and J. Amouroux, in *The Fourth Annual International Conference of Plasma Chemistry and Technology*, Herman V. Boenig, Ed., 1989, p. 9.
- D. R. Wheeler and S. V. Pepper, *J. Vac. Sci. Technol. A*, **8**(6), 4046 (1990).
- J. Q. Wang, W. Xiang, and X. D. Chen, to appear.

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