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A Study of Surface Dynamics of Polymers.

III. Surface Dynamic Stabilization by Plasma Polymerization

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Synopsis

As demonstrated in Part II of this series of studies, the hydrophobic character of CF_4 plasma-treated Nylon 6 and poly(ethylene terephthalate) (PET) decay with time of water immersion, and the rate of decay can be used as a measure for the surface mobility of (substrate) polymers. The same method of using fluorine-containing moieties introduced by CF_4 plasma treatment as surface labeling is applied to investigate the influence of a thin layer of plasma polymer of methane applied onto the surface of those polymers. An ultrathin layer of plasma polymer provides a barrier to the rotational and diffusional migration of the introduced chemical moieties from the surface into the bulk of the film. The influence of operational parameters of plasma polymerization on the surface dynamic stability are examined by measuring the decay rate constants for (subsequently) CF_4 plasma-treated samples. The rate constant was found to decrease sharply with increasing value of plasma energy input manifested by J/kg monomer, and no decay was observed as the energy input reached a threshold value (about 6.5 GJ/kg for PET, about 7.0 GJ/kg for Nylon 6), indicating that unperturbable surfaces can be created by means of plasma polymerization.

INTRODUCTION

In Part II¹ of this series of studies, using the surface-labeling technique by CF_4 plasma, the decay characteristics of hydrophobic character of CF_4 plasma-treated Nylon 6 and PET, when those films were immersed in water, were investigated. It was shown that the mobility of macromolecules at and in the vicinity of the surface, which is responsible for the decay phenomenon, may be semiquantitatively expressed by the decay rate parameter k , which is given by the equation; $A_t = A_0 t^{-k}$, in which A_0 is the value of the parameter that describes surface character, such as contact angle of water or ESCA F_{1s} peak intensity, of the original sample; and A_t is the corresponding value of the parameter for a sample immersed in water for time t .

Apparent loss of hydrophobic characteristics of CF_4 plasma-treated Nylon 6 and PET films upon immersion in water is primarily due to the rotational and the diffusional migration of the fluorine-containing moieties from the water/polymer interface into the bulk phase of film. This interpretation of decay phenomena was strongly supported by the fact that the loss of hydrophobicity upon water immersion is recoverable when the samples are heat treated at elevated temperatures. Upon heat treatment, the contact angle of water as well as the ESCA F_{1s} peak increase toward the original values.

The decay rate and the total extent of decay are found to be functions of the crystallinity of the polymer sample, as anticipated. On the other hand, the value of k s indicated that the surface mobility of PET is significantly greater than that of Nylon 6, despite its bulkier and stiffer macromolecule.

In Part I,² dealing with the decay of hydrophilicity of oxygen plasma-treated polymer surfaces in air, it was demonstrated that an ultrathin layer of plasma polymer of methane, placed prior to oxygen plasma treatment, significantly reduced the decay. These two phenomena, i.e., the loss of hydrophilic character in a dry atmosphere and the loss of hydrophobicity under wet conditions, of surface-treated polymers are demonstrations of the same principle: that surface configuration changes according to the surrounding medium.

In this paper, additional evidence is presented to demonstrate the basic principle described above by showing that the barrier effect of the plasma polymer of methane can also be utilized to reduce the decay of hydrophobic characteristics under wet conditions. We further intended to prove that surface dynamic change, rather than other failure mechanisms such as chemical reactions, surface contamination, and the lack of adherence of the modified layer to the substrate, is primarily responsible for many decay phenomena observed with surface-modified polymers.

EXPERIMENTAL

Polymer Samples

In this study, films are used as substrate materials to support plasma polymer of methane, and no effort was made to evaluate detailed characteristics of the substrate polymers (Part II covered some of these factors). Polymer samples used in this study are commercially available polymers specially prepared for this study.

Nylon 6 Films

A special batch of unoriented film without any surface treatment (thickness 75 μm) was provided by courtesy of Toyo Synthetic Films Co., Japan. The surfaces of the films were cleaned by a nonionic detergent solution (2 g/L) and sodium phosphate solution (2 g/L). The samples were rinsed well with distilled water and dried in air overnight.

PET Films

These films are a special batch of biaxially oriented film without any surface treatment (thickness 50 μm). Films were cleaned by the above-mentioned procedure. The cleaned films were stored in a desiccator with silica gel.

Plasma Treatment of Films

Application of Plasma Polymer of Methane (Pretreatment of Films)

Approximately 4 \times 4 in. films were cut and placed on an aluminum disc, held by metal clamps at the four corners of the sample. The aluminum disc was placed between the two electrodes of the plasma polymerization reactor

TABLE I
Conditions of Plasma Polymerization of CH₄ Applied on Nylon 6 Films

Sample	Wattage	Flow rate (SCCM)	P_0 (mtorr)	P_g (mtorr)	Thickness on TM (nm)	W/FM (GJ/kg)
Nylon 6/ M-1	75	6.30	56.1	65.1	60	1.0
Nylon 6/ M-2	75	2.52	31.0	34.7	60	2.5
Nylon 6/ M-3	75	1.58	24.0	29.6	60	4.0
Nylon 6/ M-4	75	1.15	18.5	23.5	60	5.5
Nylon 6/ M-5	75	0.90	15.4	20.2	60	7.0

and was rotated at a constant speed during plasma polymerization in order to coat the substrate uniformly; i.e., the substrate films rotated repeatedly in and out of the glow discharge. The plasma polymerization was carried out in a bell-jar reactor using a magnetron glow discharge at 10 kHz, details of which were described previously.^{3,4}

Deposition of the polymer was monitored by means of a quartz crystal thickness monitor placed in the glow zone. The coating thickness was controlled according to the experimentally determined calibration curve which correlates the thickness monitor reading under a set of plasma polymerization conditions (obtained by the stationary sensor head) to the deposition thickness of polymer onto the continuously rotating substrate films. The actual thickness of the coating is about 30% of the thickness monitor reading; however, the correlation factor varies depending on the conditions of plasma polymerization.⁵ Samples with an estimated coating thickness of 20 and 40 nm were prepared under various conditions of plasma polymerization summarized in Tables I (Nylon 6) and II (PET). The thickness monitor reading (TM) is listed in the tables and referred to as the thickness of coating in the following text. This process of depositing a plasma polymer of methane on the surface of a film is referred to as "pretreatment" in the following sections of this paper.

CF₄ Plasma Treatment

A plasma reactor, IPC-1001-148 AN (International Plasma), with capacitive coupling of rf (13.56 MHz) by external electrodes, was used to treat the surfaces of films (with or without the pretreatment). CF₄ (without carrier gas)

TABLE II
Conditions of Plasma Polymerization of CH₄ Applied on Pet Films

Sample	Wattage	Flow rate (SCCM)	P_0 (mtorr)	P_g (mtorr)	Thickness on TM (nm)	W/FM (GJ/kg)
PET/M-1	85.17	4.36	43.6	46.3	120	1.6
PET/M-2	85.74	1.47	20.4	18.7	120	4.9
PET/M-3	84.15	0.48	9.22	7.2	120	14.7
PET/M-4	85.16	4.43	43.3	45.8	60	1.6
PET/M-5	85.78	1.42	20.2	19.0	60	5.1
PET/M-6	84.15	0.48	9.63	7.5	60	14.7

was used at a fixed flow rate of 50 cc(STP)/min. The treatment was carried out at a pressure of 1.5 torr with applied wattage of 150 W for 5 min. The term "treatment" in the following text refers to the CF_4 plasma treatment described here.

Contact Angle Measurement

The advancing contact angle of water was measured by the following procedure. First, a droplet of water ($2.7 \mu\text{L}$) was placed on the center part of a film, and a photograph of the profile of the water droplet on the surface was taken. Every 20 sec additional water ($2.7 \mu\text{L}$) was added to the water droplet, and a photograph was taken immediately. The procedure was repeated five times. By measuring the contact angles of the water droplets as shown on the photographic prints, the advancing contact angle of water on the sample was determined.

ESCA Measurement

A Shimadzu ESCA 750 with a data analysis system was used for the measurements of C_{1s} , F_{1s} , O_{1s} , and N_{1s} peaks, using an aluminum foil-filtered MgK_α x-ray (8 kV, 30 mA). The major emphasis of ESCA analysis in this study was on the accurate estimate of the number of fluorine atoms at the surface and, to a lesser extent, on the confirmation of types of fluorine-containing carbons.

Since the absolute intensity of F_{1s} peaks may change, owing to factors involved with the equipment, the reliability of the absolute value of the peak intensity is questionable. Efforts to normalize the peak intensity by taking the ratio of F/C or the atomic percent at the surface, on the other hand, involve similar ambiguities when surface modifications, which introduce atoms that were not present in the original sample, are employed. Because the CF_4 plasma treatment introduces additional C, F, and O atoms onto the surface of the substrate film, it was decided to use the peak intensity measurement to describe the total number of fluorine atoms. In order to minimize the effect of sensitivity drift of the equipment, the following procedure was adopted.

On each set of measurements, the C_{1s} spectrum of a reference sample of PET film was taken, and the intensity of the C_{1s} peak at 285 eV was compared with that measured in the previous run. The calibration factor was computed from the ratio of the peak intensities in order to compensate for the decrease in sensitivity of ESCA due to contamination of the anode. If a significant decrease in sensitivity was noticed, the equipment was readjusted following the baking procedure. By this procedure, the variation of F_{1s} peak intensity (due to surface dynamic change) could be examined with reasonable accuracy, although the absolute values might not be directly compared with data taken with other equipment. The C_{1s} peak at 285 eV was taken as the reference to compensate the charge effect.

Preparation of Water-immersed Samples

Water immersion of plasma-treated samples was carried out at room temperature immediately after the plasma treatment. After a preset immersion

TABLE III
Effects of CH₄ Plasma Polymerization on Contact Angle of Water
On CF₄ Plasma-treated Nylon 6 Films Immersed in Water

Submerged time (min)	Contact angle (degrees)					
	Nylon 6 no pretreatment	Nylon 6/ M-1	Nylon 6/ M-2	Nylon 6/ M-3	Nylon 6/ M-4	Nylon 6/ M-5
0	115.0	115.0	114.9	113.0	112.0	111.5
5	102.0	100.5	102.5	104.5	107.0	115.5
						(10 min 118.3)
						(15 min 116.5)
30	95.0	97.9	98.5	100.1	102.5	114.3
60	92.0	93.1	94.7	95.5	100.3	111.3
90	91.5	92.6	95.1	94.4	96.0	109.3
120	89.6	90.8	93.6	93.0	94.0	111.3
No CF ₄ treatment	63.5	72.8	71.5	71.4	69.6	68.0

time (5, 30, 60, 90, and 120 min), a sample was picked out of water and placed immediately into liquid nitrogen and was allowed to freeze for 15 min. The frozen samples were freeze-dried at -113°C in order to preserve the surface configuration (specific arrangement of chemical moieties and atoms at the surface) at the end of each predetermined period of water immersion. The freeze-dried samples were used for the measurements of contact angles of water and ESCA peaks.

RESULTS AND DISCUSSION

Nylon 6 Films

The effect of pretreatment is investigated by measurement of contact angles of water and of ESCA F_{1s} peaks for the subsequently treated samples. The conditions of the pretreatment are manifested by the composite plasma polymerization parameter W/FM , where W is the discharge wattage in watts, F is the volume flow rate, and M is the molecular weight of monomer. The SI units of this parameter are J/kg, which represents the energy input per unit

TABLE IV
Intensities of ESCA F_{1s} peaks of CF₄ Plasma-treated Nylon 6 Films Immersed in Water

Submerged time (min)	ESCA F_{1s} Intensity (cps $\times 10^4$)					
	Nylon 6 no pretreatment	Nylon 6/ M-1	Nylon 6/ M-2	Nylon 6/ M-3	Nylon 6/ M-4	Nylon 6/ M-5
0	8.16	8.08	8.01	7.96	7.75	6.53
5	7.09	6.96	7.24	7.42	7.33	6.90
						(10 min 6.93)
						(15 min 6.92)
30	6.47	6.50	6.83	7.10	6.88	6.68
60	6.20	6.37	6.72	7.01	6.42	6.65
90	6.59	6.19	6.25	7.01	7.23	6.69
120	6.05	6.27	6.57	6.95	7.20	6.57

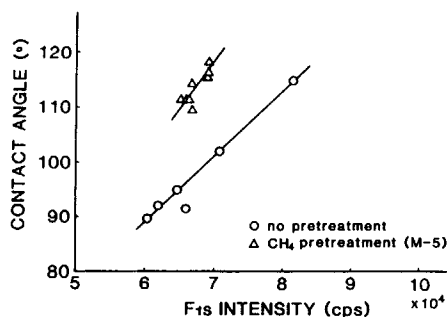


Fig. 1. The correlation between contact angle of water and ESCA F_{1s} peak intensity for Nylon 6/M-5.

mass of monomer (CH_4). Contact angles of water on various samples after they are immersed in water for various periods of time are shown in Table III. The decay of hydrophobicity due to water immersion is less for samples prepared with pretreatment, and its reduction is dependent on the condition of plasma polymerization of methane; i.e., the higher the W/FM value, the lower the decay.

Results of ESCA also follow trends similar to those observed for the contact angles of water described above. Intensities of ESCA F_{1s} peaks are summarized in Table IV. The changes due to water immersion observed by ESCA are considerably less than those observed by measuring the contact angle of water. These trends may reflect the difference in nature of these two measure-

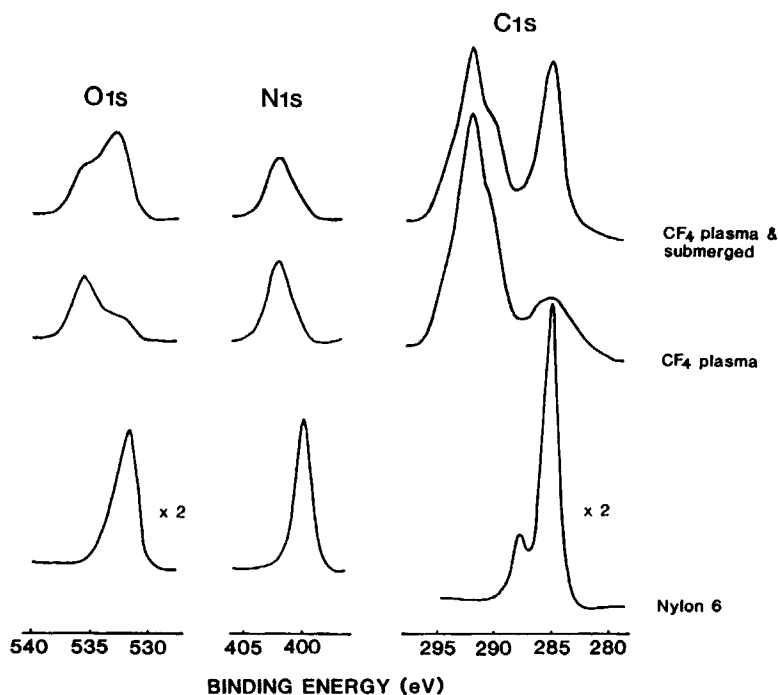


Fig. 2. Changes in ESCA signals of Nylon 6 film on CF_4 plasma treatment and subsequent water immersion (120 min).

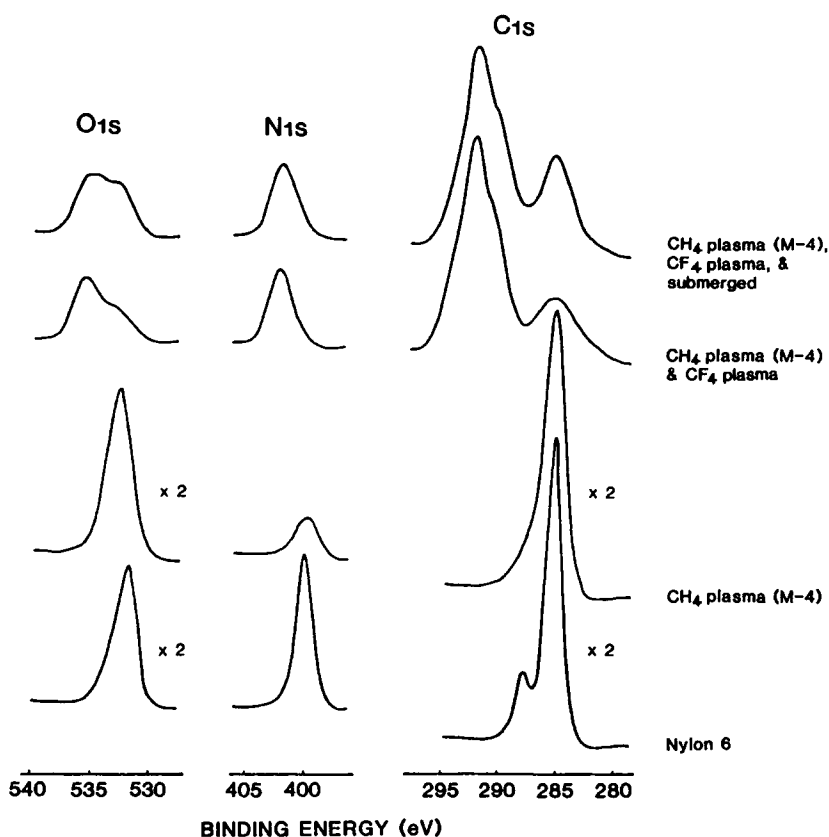


Fig. 3. Changes in ESCA signals of Nylon 6 film on CH_4 plasma pretreatment, CF_4 plasma treatment, and water immersion (120 min); W/FM for the pretreatment = 5.5 GJ/kg.

ments. ESCA observation is not strictly restricted to the top surface (i.e., the depth of electron escape is on order of 2.5–5.0 nm), whereas the contact angle tends to show the character of the top surface. Consequently, the correlation between advancing contact angle of water and ESCA F_{1s} peak intensity is dependent on the substrate polymer when CF_4 plasma treatment is applied onto polymer films without pretreatment, as shown in Part II. In other words, although there is a clear correlation between contact angle of water and ESCA F_{1s} peak intensity, two separate correlation lines can be drawn for Nylon 6 and PET.

The surface characteristics of Nylon 6 treated with CH_4 plasma are obviously different from those for untreated Nylon 6. When the combined character of thickness and mobility (tightness of structure) of plasma polymer of methane reaches a certain level, it is anticipated that the CF_4 plasma treatment of such a surface would have surface dynamic characteristics significantly different from that of Nylon 6. Figure 1 shows correlations between advancing contact angle of water and ESCA F_{1s} peak intensity for Nylon 6 and for Nylon 6/M-5.

Changes in profiles of ESCA signals due to water immersion are shown in Figure 2 for CF_4 plasma-treated film without pretreatment, and Figures 3 and 4 contain the same information for CF_4 plasma-treated films with CH_4 plasma

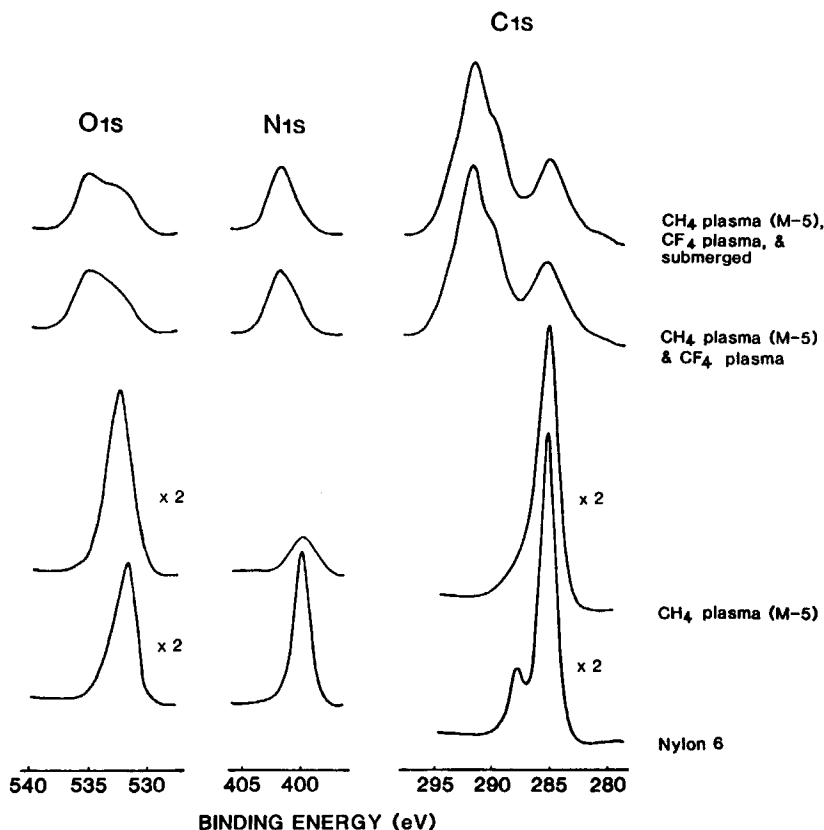


Fig. 4. Changes in ESCA signals of Nylon 6 film on CH_4 plasma pretreatment, CF_4 plasma treatment, and water immersion. W/FM for the pretreatment = 7.0 GJ/kg.

pretreatment at different levels of W/FM . As discussed in Part II,¹ the main effect of CF_4 plasma treatment may best be described as the surface implantation of fluorine-containing moieties (surface labeling) rather than the deposition of plasma polymer of CF_4 . It is known that CF_4 does not form polymer in plasma unless hydrogen atoms are present.⁵ The influence of water immersion is seen in the decrease of the C_{1s} peak at 293 eV and the increase of the C_{1s} peak at 285 eV and the increase of the lower binding energy O_{1s} peak (original peak in Nylon 6). Figures 2 and 3 show that (1) the pretreatment by CH_4 plasma (polymerization) covers most of the surface and (2) the changes caused by water immersion described above are reduced remarkably, indicating the presence of a barrier layer, consisting of the plasma polymer, to the rotational and diffusional migration of surface-implanted fluorine-containing groups.

PET Films

In order to investigate the effect of the thickness of plasma polymer of CH_4 (pretreatment), ultrathin films of different thicknesses were applied to PET films. Results of the measurement of contact angles of water are summarized in Table V. Results of ESCA analysis are summarized in Table VI. The trend in the decrease of water contact angle on immersion seen for PET is similar to

TABLE V
Contact Angles of Water on CF₄ Plasma-treated PET Films Immersed in Water

Submerged time (min)	Contact angle (degrees)						
	PET no pretreatment	Thickness 120 nm			Thickness 60 nm		
		PET/ M-1	PET/ M-2	PET/ M-3	PET/ M-4	PET/ M - 5	PET/ M-6
0	97.0	98.5	94.3	54.5	97.2	102.7	87.0
5	76.0	81.0	89.5	82.0	80.5	98.3	103.5
15	—	77.0	88.5	84.0	78.5	97.5	105.0
30	72.3	79.5	89.5	80.5	76.5	99.0	94.0
60	72.0	78.0	88.0	80.0	74.5	96.3	86.0
90	71.5	76.5	89.0	80.5	75.5	98.5	89.0
120	71.5	75.8	87.8	80.0	73.8	98.0	90.0
No CF ₄ treatment	69.0	69.5	74.0	75.0	72.5	73.8	74.5

TABLE VI
Intensities of ESCA F_{1s} Peaks of CF₄ Plasma-treated PET Films Immersed in Water

Submerged time (min)	ESCA F _{1s} Intensity (cps × 10 ⁴)						
	PET no pretreatment	Thickness 120 nm			Thickness 60 nm		
		PET/ M-1	PET/ M-2	PET/ M-3	PET/ M-4	PET/ M-5	PET/ M-6
0	9.31	9.13	8.24	3.45	9.17	8.09	5.31
5	6.98	6.88	6.97	6.87	7.42	6.64	6.22
15	—	7.11	7.16	6.73	7.01	7.04	5.91
30	5.24	6.81	6.00	6.13	6.47	6.06	6.07
60	6.00	6.09	6.07	5.03	6.12	5.80	5.80
90	5.32	6.00	6.04	5.14	6.58	5.71	5.76
120	5.76	5.82	6.06	5.16	6.47	5.77	5.49

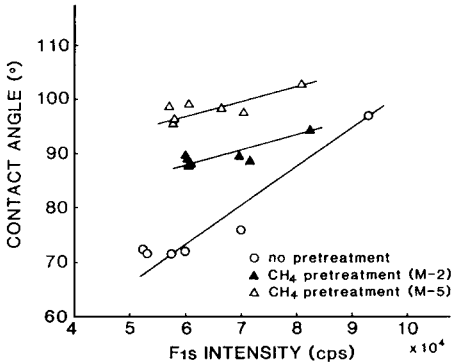


Fig. 5. The correlation between contact angle of water and ESCA F_{1s} peak intensity for PET, PET/M-2, and PET/M-5.

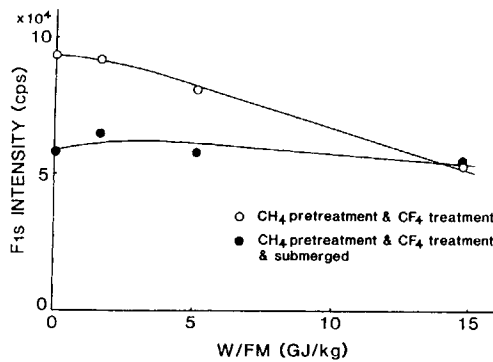


Fig. 6. ESCA F_{1s} peak intensities for unimmersed and water-immersed CF_4 plasma-treated PET films as functions of W/FM values of CH_4 plasma pretreatment thickness of plasma polymer of methane TM = 60 nm.

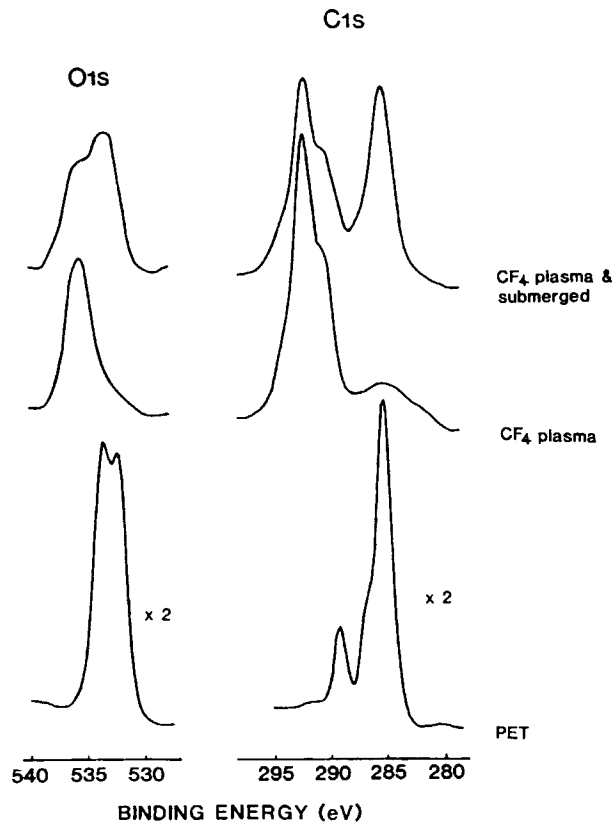


Fig. 7. Changes in ESCA signals of PET films due to the treatments (without pretreatment); water immersion: 120 min.

that seen for Nylon 6. The effect of thickness of plasma polymer of methane, although relatively small, can be seen in the correlation between advancing contact angle and ESCA F_{1s} peak intensity, as shown in Figure 5. The correlation lines for pretreated films deviate from that for PET (without pretreatment), and the contact angle of water becomes less sensitive to ESCA F_{1s} peak intensity, depending on the thickness of plasma polymer of methane. A layer too thick tends to lose its effectiveness.

The general trend observed for samples prepared without pretreatment (shown in Part 2) is also seen for samples prepared with pretreatment; namely, changes of ESCA F_{1s} signal intensity as a function of water immersion time indicate that ESCA F_{1s} peak intensities also follow similar changes observed for contact angles of water. On the other hand, plots of ESCA F_{1s} peak intensities for unimmersed films and for water-immersed films, as functions of W/FM values of the plasma pretreatment, as given in Figure 6, show that the ESCA F_{1s} peak intensity decreases with increasing value of W/FM ,

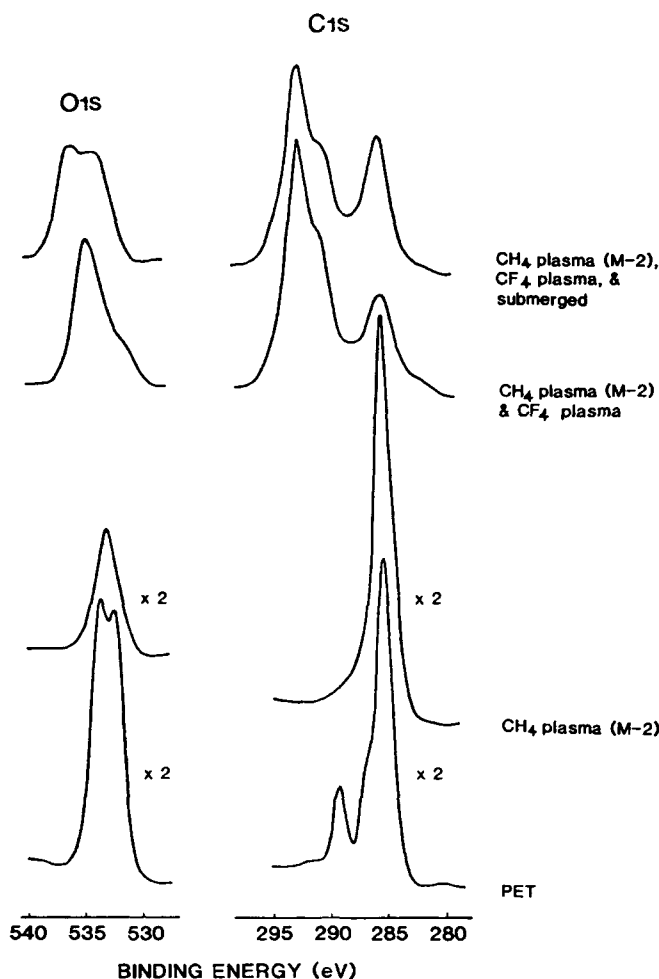


Fig. 8. Changes in ESCA signals of PET films due to the treatments; pretreatment conditions: $W/FM = 5.0$ GJ/kg, $TM = 120$ nm; water immersion = 120 min.

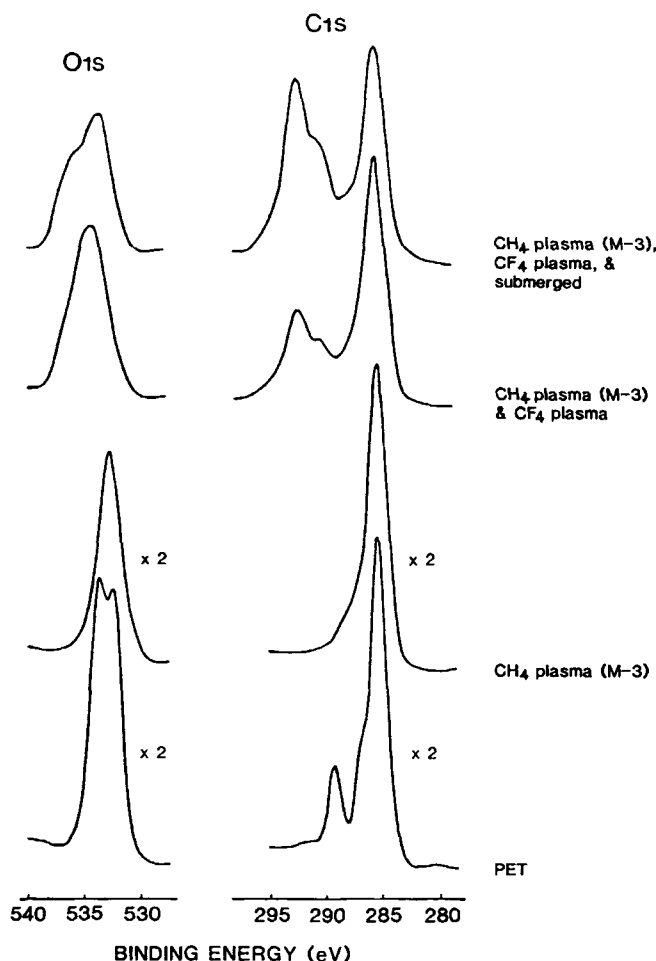


Fig. 9. Changes in ESCA signals of PET films due to the treatments; pretreatment conditions: $W/FM = 15$ GJ/kg, $TM = 120$ nm; water immersion = 90 min.

which indicates that the surface implantation of fluorine-containing moieties by CF_4 plasma becomes progressively more difficult with increasing value of W/FM . This observation is in accordance with the concept that the CF_4 plasma treatment is the surface implantation of fluorine-containing moieties which proceeds via elimination of HF .⁵ The presence of hydrogen atoms on the surface is a key factor for such a reaction. Results indicate that the high W/FM conditions of plasma polymerization of methane, which forms a tighter network, decreases the number of hydrogen atoms on the surface. Changes in profiles of ESCA signals of PET films are shown in Figures 7 through 9.

Effect of Conditions of Plasma Polymerization of Methane (Pretreatment) on Surface Mobility

The physical properties of plasma polymers are highly dependent on conditions of plasma polymerization. The energy input of glow discharge mani-

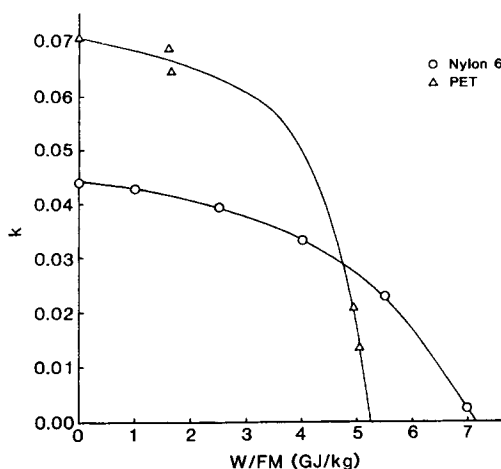


Fig. 10. Effect of the pretreatment condition on the decay rate constant, k , for Nylon 6 and PET films subsequently treated by CF_4 plasma.

fed by W/FM (energy per unit mass of monomer) seems to influence most strongly the physical properties of the polymer deposited. Consequently, the surface dynamic characteristics of CF_4 plasma-treated films discussed above are also influenced by the energy input levels of methane plasma pretreatment. Figure 10 depicts the influence of conditions of plasma polymerization of methane on the decay rate constant, k s in the relationship given by

$$A_t = A_0 t^{-k}.$$

The values of k s are calculated from the slopes of initial linear portions of $\log(\text{contact angle})$ versus $\log(\text{water immersion time in minutes})$. Plots (not shown) are described in Part II.¹ Results clearly show that the higher the value of W/FM in pretreatment, the higher the barrier characteristics of the layers. The trends shown in the figure seem to suggest that there exists a critical level of energy input which transforms the network of plasma polymer of methane to a highly unperturbable state. Plasma polymers of methane formed with energy input level below the critical value are not tight enough to prevent dynamic changes of the subsequently CF_4 plasma-treated surfaces.

CONCLUDING REMARKS

The rotational and diffusional migration of fluorine-containing moieties introduced on the face of polymer films by CF_4 plasma treatment are largely responsible for the change of surface characteristics occurring on the immersion of samples in water (as discussed in Part II). Such surface dynamic changes are related to the mobility of macromolecular segments which receive the fluorine-containing moieties. These surface dynamic changes can be minimized by placing a thin layer of plasma polymer of methane before CF_4 plasma treatment (surface labeling). Although a very tight film of plasma polymer of methane makes the surface implantation of fluorine-containing moieties more difficult (due to the reduced number of hydrogen atoms available for the reaction), the implanted moieties remain on the surface upon water immersion.

The data on the surface mobility parameters presented in this paper indicate that the often cited "tight network of plasma polymer" cannot be intuitively assumed but can be obtained only under certain conditions, indicating the importance of the system-dependent aspect of plasma polymerization. The role of the barrier presented in this paper seems to support the concept that the rotational and diffusional migrations of the surface moieties into the bulk phase of the polymer are responsible for the changes in surface properties which occur when the surrounding environment or conditions are changed. Tight networks of plasma polymers provide dynamically stable (environmentally imperturbable) surfaces, which seem to be important in many applications of polymers.

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