

Characterization of Surface Properties of Plasma-Polymerized Fluorinated Hydrocarbon Layers: Surface Stability as a Requirement for Permanent Water Repellency

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SYNOPSIS

Plasma polymers were deposited on poly(ethylene terephthalate) (PET) substrates using fluorocarbons such as CF₄, C₂F₆, C₃F₆, C₄F₈, and mixtures thereof with CH₄. The fluorocarbons selected were of saturated structure (CF₄, C₂F₆), unsaturated structure (C₃F₆), and cyclic structure (C₄F₈). The addition of CH₄ to any of the fluorocarbons caused a deposition of plasma polymers. However, the deposition rate strongly depended on the amount of CH₄ added. A fluorocarbon-dominated feed, i.e., fluorocarbons with 17 mol % CH₄, was found to lead to an effective deposition of plasma polymers, whereas a CH₄-rich feed, i.e., fluorocarbons with 67 mol % CH₄, led to an ineffective polymer deposition. For the same molar composition of fluorocarbon/CH₄, polymer deposition depended on the fluorocarbon structure. It decreases in the order C₃F₆ > C₄F₈ > C₂F₆ > CF₄. Elemental analysis showed an atomic ratio F/C of 2.2 and 2.3 for C₃F₆ and C₄F₈ plasma polymer powder, respectively, whereas the corresponding values obtained from X-ray photoelectron spectra (XPS) surface analysis of films showed 1.5 and 1.6, respectively. An explanation could lie in bulk and surface differences of the deposited layers. Contact-angle measurements revealed that among the monomers employed only C₃F₆ with 17 mol % CH₄ resulted in a relatively stable, hydrophobic surface. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The dynamics and mobility of polymer surfaces and interfaces is a subject of theoretical and practical interest.^{1,2} It was recognized years ago that polymer surfaces and interfaces are mobile and will rearrange or reorient in response to the surrounding environment.^{3,4} The low-temperature plasma technique provides a powerful tool for producing a stable polymer surface and has been widely employed.⁵⁻⁸ Since many fabrication parameters have been found to affect the formation of plasma polymers and, thus, the dynamic behavior of plasma polymer surfaces,

it is essential to investigate the main influencing parameters. Our particular interest was to produce durable, hydrophobic surfaces by means of plasma polymerization. This subject is of great technical importance for water-repellent textile finishes, which lose part of their hydrophobic properties after several wash cycles. In the present study, we investigated diverse perfluorocarbons such as CF₄, C₂F₆, C₃F₆ (perfluoropropene), and C₄F₈ (perfluorocyclobutane), either as pure fluorocarbon gases or as mixtures with various amounts of CH₄. The plasma-polymerized surfaces were characterized using contact-angle measurements, elemental analysis, IR spectroscopy, and XPS.

EXPERIMENTAL

The pilot scale plasma processor was supplied by Plasma Electronic GmbH. Glow discharge was generated capacitively, operating at 13.56 MHz with a

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continuously variable output power from 0 to 1000 W. The volume of the vacuum chamber is 0.5 m^3 . Plasmas were restricted to a volume of $20 \times 20 \times 50 \text{ cm}^3$. Gaseous monomers were fed to the chamber through a regulator and a needle valve. The flow rate of the gas was measured with a mass flowmeter and the pressure in the chamber was controlled by a Balzers pressure gauge, Model TPG 300. Plasma polymer layers were deposited on a 50 micron PET sheet ($80 \times 20 \text{ mm}$), which was mounted on the grounded electrode. CH_4 (Carbon Gas Ltd.), CF_4 , C_2F_6 (Merck Ltd.), C_3F_6 (Fluka Ltd.), and C_4F_8 (Fluorochem. Ltd.) were all supplied in a purity of more than 99% and used without further purification. The reaction system was pumped down to $1.33 \times 10^{-2} \text{ Pa}$ or lower using a rotatory pump. The pump was installed with WF-alumina cartridge. Monomer gases, adjusted to a desired flow rate, were introduced into the chamber. Fluorocarbons and CH_4 gas were fed to the chamber separately through an inlet inside and outside the plasma region. Once the preset pressure (typical 1–100 Pa) was reached and remained constant, the glow was initiated and set at the desired level. The glow continued for a predetermined period of time. After plasma treatment, the vacuum chamber simply vents to the atmosphere; samples were carefully handled to avoid surface contamination of the films.

CHARACTERIZATION OF PLASMA POLYMERS

Elemental analysis of plasma polymers, scratched from the reaction chamber walls and collected as powders, was performed using a LECO CHN-Analyzer. IR spectra of plasma polymer films and powders were recorded on a Bruker IFS-88 equipped with a nitrogen-cooled MCT-detector using the ATR technique and KBr-disc transmission mode, respectively. XP-spectra ($\text{MgK}\alpha$) of films were recorded on a PHI 5300 ESCA system (Perkin-Elmer) at 250 W ($1.25 \text{ kV} \times 20 \text{ mA}$) by assuming the adventitious carbon having a binding energy equal to 285.0 eV. The vacuum system was kept at $1.33 \times 10^{-6} \text{ Pa}$. Data processing, such as X-ray satellite subtraction, background subtraction, normalization, and curve fitting were done on a PE 7500 personal computer.

CHARACTERIZATION OF PLASMA POLYMER SURFACES

The surface topography of the films was determined using scanning electron microscopy. Ellipsometry

was employed to measure thicknesses of the films with a Moss Ellipsometer (Model EL4). Light from the Xe arc lamp was incident on a $2 \times 3 \text{ mm}^2$ area of the film surface. Contact angles of water, formamide, diiodomethane, glycol, 1-bromonaphthalene, nitromethane, and toluene on the films deposited on PET sheets were measured with a Rame-Hard Inc. Model A-100 goniometer using the sessile drop technique and recorded within 30 s from the time of application of the drop. Each value of contact angle was the average of at least four determinations. The variation between determinations for a single system was generally $\pm 3^\circ$. Surface free energy was estimated using the Fowkes method.^{9–12} Wettability measurements were performed by determining the advancing and receding water-contact angles.¹³

RESULTS AND DISCUSSION

Plasma polymers were formed using different ratios of fluorocarbons and methane. Figures 1 and 2 show the IR spectra of polymers prepared from CF_4/CH_4 and $\text{C}_3\text{F}_6/\text{CH}_4$ plasma. The IR spectra from $\text{C}_2\text{F}_6/\text{CH}_4$ and $\text{C}_4\text{F}_8/\text{CH}_4$ plasma polymers largely resemble those of CF_4/CH_4 and $\text{C}_3\text{F}_6/\text{CH}_4$ polymers and are not shown explicitly. IR spectra of the polymers feature mainly four characteristic bands. Comparing the spectra of polymers prepared from the different monomers, the following conclusions may be drawn: The IR spectra of C_3F_6 and C_4F_8 plasma polymers exhibit only a small band at 2930 cm^{-1} due to the nonexistence of CH groups in the polymers. As CH_4 is introduced into a fluorocarbon discharge, an absorption peak in the IR spectra of the resultant polymers appears. Consequently, the band in the region $980\text{--}1350 \text{ cm}^{-1}$ declines upon increasing addition of CH_4 . The dependence of the structure of plasma polymers on the type of fluorocarbon employed in the discharge can be clearly seen by comparing the bands in the region $980\text{--}1350 \text{ cm}^{-1}$. The band for $\text{C}_3\text{F}_6/\text{CH}_4$ and $\text{C}_4\text{F}_8/\text{CH}_4$ plasma polymers is basically a single and broad peak, whereas those for CF_4 and $\text{C}_2\text{F}_6\text{--}50 \text{ mol } \% \text{ CH}_4$ and $\text{--}33 \text{ mol } \% \text{ CH}_4$ plasma polymers appear to be no longer a single band, but a combination of several overlapping peaks. The results suggest that when fluorocarbons, fed with various amounts of CH_4 , were used for plasma polymerization, all the resulting polymers contained hydrogen. For the same molar composition of fluorocarbons/ CH_4 , C_3F_6 , and C_4F_8 resulted in fewer hydrogen-containing polymers as indicated by the signals of the CH_n groups of the IR spectra.

Table I presents the elemental composition of C,

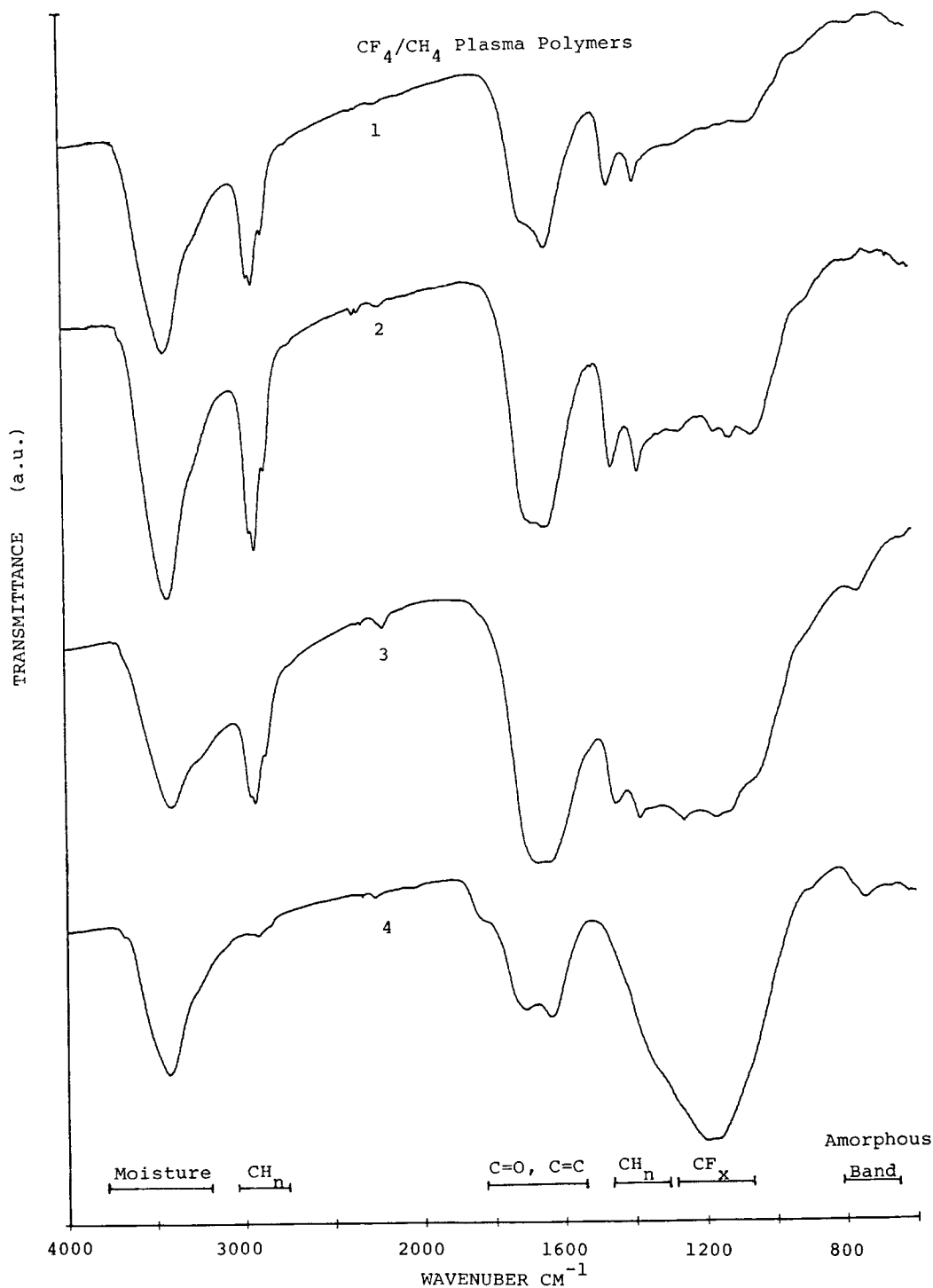


Figure 1 IR spectra of plasma polymers deposited from (1) CF_4 -67% CH_4 , (2) CF_4 -50% CH_4 , (3) CF_4 -33% CH_4 , and (4) CF_4 -17% CH_4 plasmas. IR spectra of $\text{C}_2\text{F}_6/\text{CH}_4$ plasma polymers show similar results.

H, and N and the atomic ratio F/C of the plasma polymers. The F and O content of the plasma polymers are plotted, respectively, in Figure 3(a) and

(b) as a function of the molar composition of the monomers. It should be pointed out that within the limits of the analytical technique the elemental

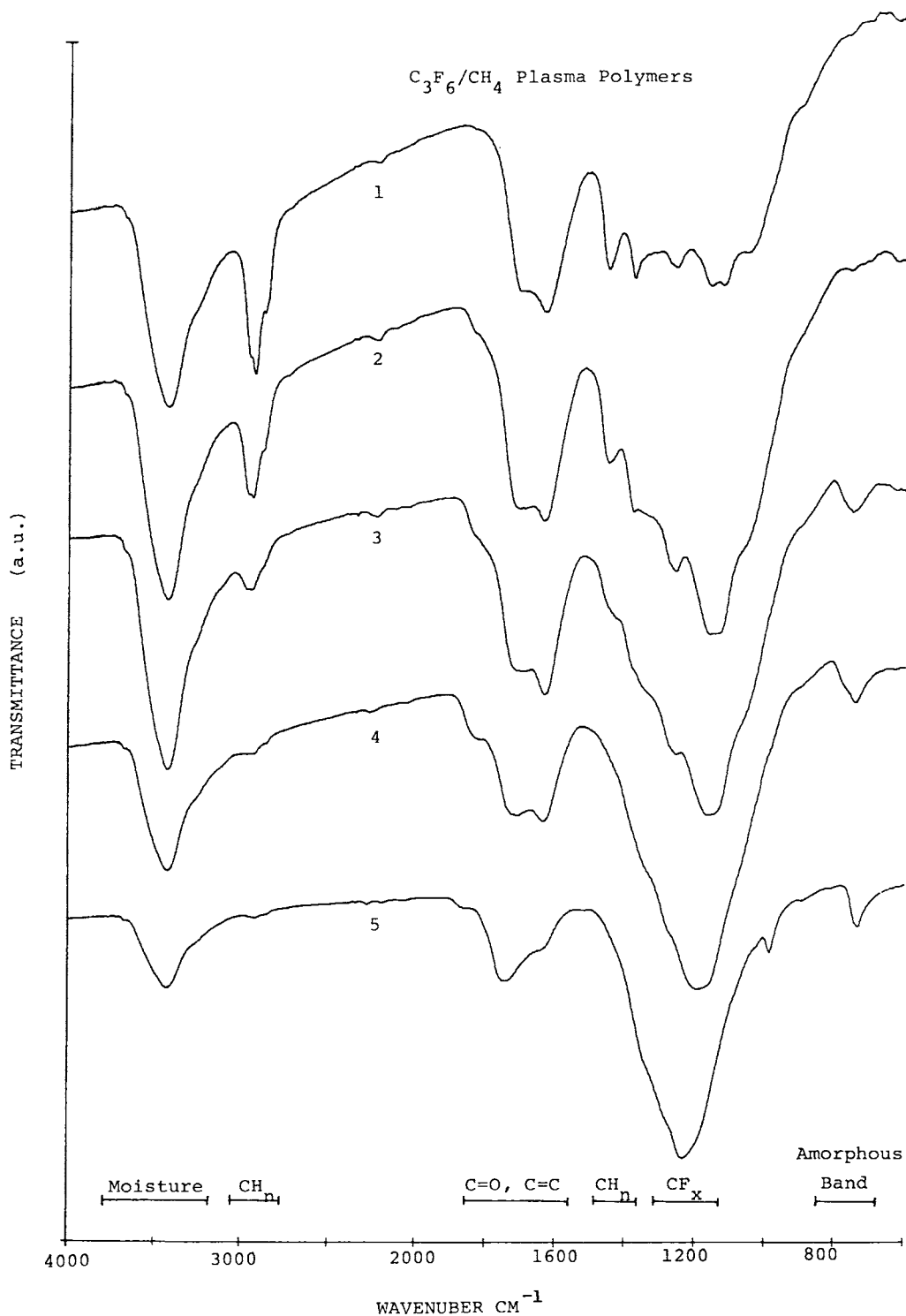


Figure 2 IR spectra of plasma polymers deposited from (1) C_3F_6 -67% CH_4 , (2) C_3F_6 -50% CH_4 , (3) C_3F_6 -33% CH_4 , (4) C_3F_6 -17% CH_4 , and (5) C_3F_6 plasmas. IR spectra of C_4F_8/CH_4 plasma polymers show similar results.

composition of C, H, N, and F were merely given and that the O content of polymers was estimated. From the results, two general observations may be

made: (1) The polymers contain not only oxygen but also nitrogen even though these elements are absent in the monomers. (2) The F and N contents

Table I Results of Elemental Analysis and Atomic Ratio of Plasma Polymers

Monomer Composition	Elemental Composition (%)					Atomic Ratio	
	C	H	N	O	F	F/C	F/C ^a
CF ₄ -mol % CH ₄							
50	59.61	5.89	4.64	24.21	5.65	0.09	
33	52.10	4.81	6.23	26.17	10.69	0.21	
17	36.28	1.34	7.36	15.62	39.40	1.09	0.5
C ₂ F ₆ -							
50	54.45	5.20	4.70	26.95	8.50	0.16	
33	53.44	4.06	5.61	17.46	19.43	0.36	
17	37.18	1.17	5.56	11.84	44.25	1.19	0.4
C ₃ F ₆ -							
50	46.72	3.47	2.88	31.59	15.85	0.34	
33	44.85	2.75	3.78	22.82	25.80	0.58	
17	37.28	1.31	4.51	17.75	39.05	1.05	0.6
0	25.94	0.33	6.77	10.11	56.86	2.19	1.5
C ₄ F ₈ -							
50	57.06	4.56	4.69	19.74	13.95	0.24	
33	51.34	3.06	5.22	13.21	27.18	0.53	
17	36.93	0.87	5.39	6.64	50.17	1.36	0.4
0	25.56	—	7.26	8.22	59.26	2.32	1.6

^a Atomic ratio F/C as derived from ESCA analysis.

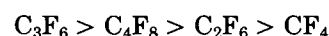
of the polymers increase and the C, H, and O contents decrease with increasing fluorocarbon concentration.

Oxygen incorporation is most probably due to (a) reactions with trace amounts of oxidizing contaminants, water, or dissolved oxygen in the monomers also being present in the process chamber during treatment or (b) postreaction of long-lived free radicals, formed during plasma treatment and trapped in the deposits, with atmospheric oxygen or water vapor after removal of the polymers from the vacuum chamber.¹⁴ It is hard to explain nitrogen incorporation, but it might be attributed to air leakage into the vacuum chamber during plasma processing, which, no doubt, also prompts oxygen incorporation. Another explanation might be nitrogen impurities in the monomers. As shown in Table I, the atomic ratio F/C of plasma polymer powders calculated on the basis of elemental analysis data is higher than that of the corresponding plasma polymer films obtained from XPS analysis. A proposed explanation is that CF_x groups at the upmost layers of plasma polymer films, on the one hand, undergo more bond breaking of C—F from exposure to UV radiation and ion bombardments than those in the bulk and, on the other hand, the surface of plasma polymer film suffers considerably from ablation and etching during long plasma treatment times, resulting in a

relatively less fluorinated upmost layer seen by ESCA analysis.

From Figure 3(a) and (b), it is clearly demonstrated that a fluorocarbon, or a fluorocarbon-dominated feed (fluorocarbons with 17 mol % CH₄), results in higher F contents and lower O contents. This is in good accordance with the results of the IR spectra and XPS analysis. From these results, one should predict a significant difference in wettability of these film samples.

The deposition rate is given in Figure 4 as a function of molar composition of the feed. It is found that pure fluorocarbon plasmas, such as C₃F₆ and C₄F₈, exhibit low deposition rates; the addition of small amounts of CH₄ to any of the fluorocarbon monomers leads generally to a significant rise in the deposition rate. Upon further addition of CH₄, the deposition rate of plasma polymers is reduced again. For the same molar composition of fluorocarbons/CH₄, the deposition rate depends on the fluorocarbon monomer. The following ranking was found:



It is assumed that the characteristic plasma particles are responsible for the different deposition rates. CF₄ plasmas are characterized by a high concentration of F atoms and relatively low concentration of CF_x

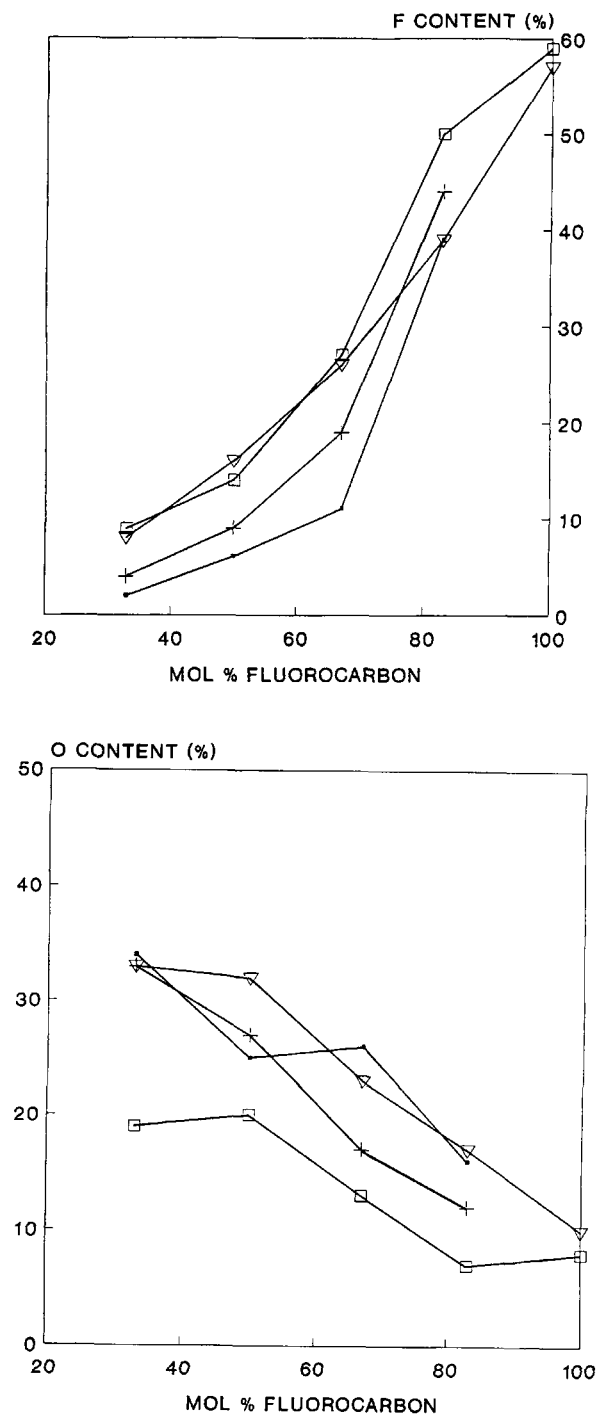
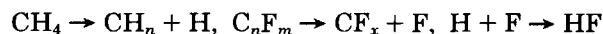


Figure 3 (a) F content of plasma polymers as a function of molar composition of monomers. F content derived from elemental analysis. The plasma polymers were prepared from (\blacksquare) CF_4/CH_4 , ($+$) $\text{C}_2\text{F}_6/\text{CH}_4$, (\triangleleft) $\text{C}_3\text{F}_6/\text{CH}_4$, and (\square) $\text{C}_4\text{F}_8/\text{CH}_4$ plasmas. (b) O content of plasma polymers as a function of molar composition of monomers. O content derived from elemental analysis. The plasma polymers were prepared from (\blacksquare) CF_4/CH_4 , ($+$) $\text{C}_2\text{F}_6/\text{CH}_4$, (\triangleleft) $\text{C}_3\text{F}_6/\text{CH}_4$, and (\square) $\text{C}_4\text{F}_8/\text{CH}_4$ plasmas.

radical species, whereas C_2F_6 plasmas are characterized by high concentrations of CF_x and low numbers of F atoms.^{15,16} The CF_x/F ratio in a CF_4 plasma is too low to form plasma polymers. For C_2F_6 plasmas having a fairly high CF_x/F ratio, this lack of polymer formation is attributed to competitive ablation and polymerization (CAP)¹⁷ and to ion-assisted etching.¹⁸ C_3F_6 and C_4F_8 , respectively, unsaturated and cyclic, saturated fluorocarbon were found in this study to be able to polymerize under the plasma conditions employed. This might be due to plasma polymerization from the CF_x species being predominant over plasma ablation by the F atoms in their discharges. The addition of a small amount of CH_4 to a fluorocarbon feed, resulting in considerable amounts of plasma polymers, is supposed to be capable of supplying the resulting plasmas with a much higher density of CF_x species, because in the plasmas, the following reactions can take place:



Although all the CH_4 -mixed fluorocarbon discharges lead to a distinct deposition of plasma polymers, their deposition rate differs substantially. The lower deposition rates for CF_4/CH_4 and $\text{C}_2\text{F}_6/\text{CH}_4$ plasmas are reasonably attributed to that these plasmas have a lower capacity to produce polymerizing species. $\text{C}_3\text{F}_6/\text{CH}_4$ plasmas produced more deposits than did $\text{C}_4\text{F}_8/\text{CH}_4$ plasmas. It is presumed to result from the coexistence of plasma-state polymerization and plasma-induced polymerization for $\text{C}_3\text{F}_6/\text{CH}_4$, and for $\text{C}_4\text{F}_8/\text{CH}_4$ only is plasma-state polymerization available.¹⁹ As outlined in Figure 4, increasing amounts of CH_4 reduced the deposition rates of plasma polymers. The results suggest that there might exist a twofold effect of CH_4 , i.e., hydrogen atoms in the plasmas. As mentioned above, hydrogen, on one hand, can capture F atoms and reduce recombination processes " $m\text{F} + n\text{CF}_x \rightarrow \text{C}_n\text{F}_m$," thus increasing CF_x density and raising the deposition rate of plasma polymers. Hydrogen, on the other hand, is able to react with CF_x species and deplete CF_x species, forming unreactive HF and thus decreasing plasma polymer deposition. At a fluorocarbon dominated feed, the former effect of H is considered to play a leading role in plasma polymer deposition, whereas at a CH_4 -rich fluorocarbon feed, the latter is supposed to be mainly responsible for the formation of plasma polymers.²⁰

Plasma polymer layers varied in thickness from approximately 0.5 to 2 microns, depending on

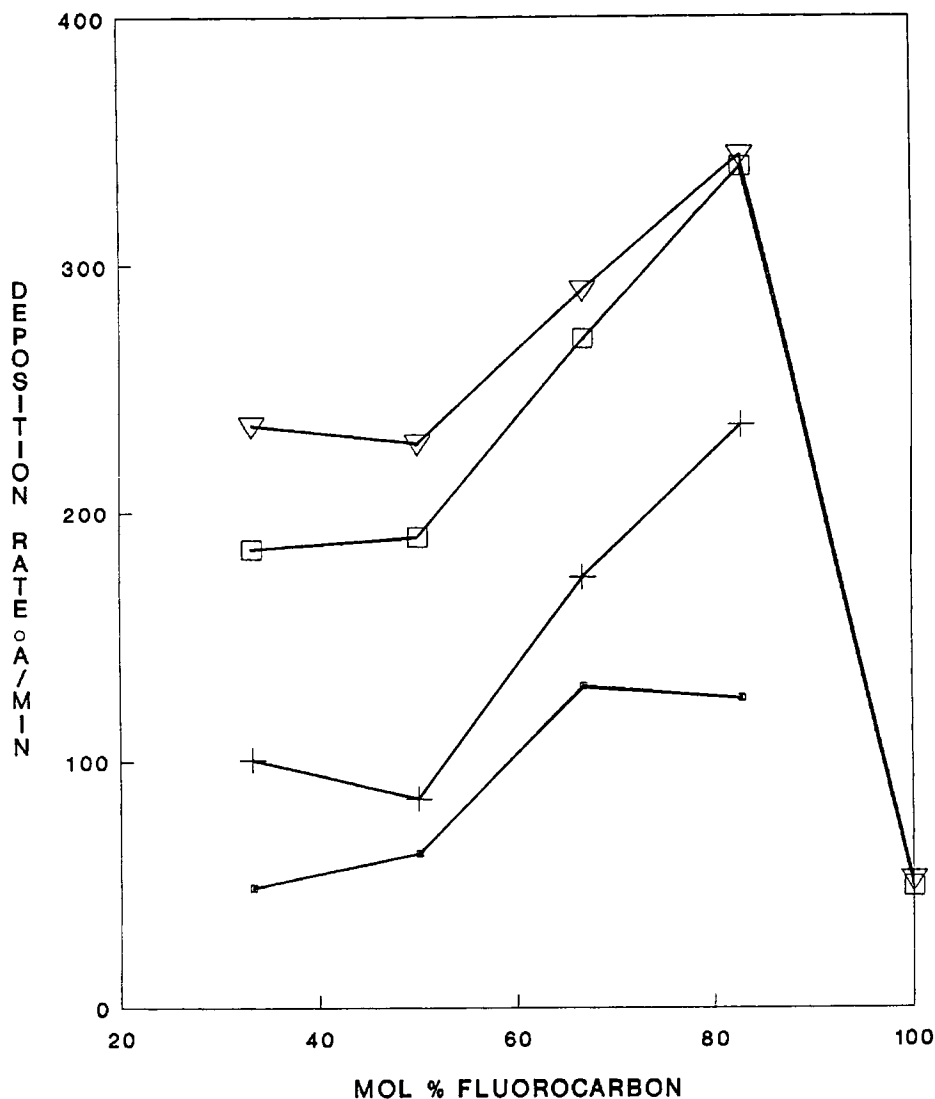


Figure 4 Deposition rate of plasma polymers as a function of molar composition of monomers. The plasma polymers were prepared from (■) CF₄/CH₄, (+) C₂F₆/CH₄, (◁) C₃F₆/CH₄, and (□) C₄F₈/CH₄ plasmas.

plasma conditions employed. Though the films cover a wide range of thickness, they show very similar surface topography. Surface topographical variation was below 0.1 micron, as determined by scanning electron microscopy. Accordingly, it was supposed that all changes in contact angle can be solely attributed to chemical modifications of the surface.^{21,22} Measurements of the contact angle of water and other liquids of differing polarity were performed and the surface free energy was estimated using the Fowkes method.⁹⁻¹² Surface energies of plasma polymers, prepared from the fluorocarbons/CH₄ mixtures, were examined as a function of molar

composition of the feed. The results are presented in Table II. As shown in the table, a significant change in surface free energy is reached with a pure fluorocarbon or a fluorocarbon-dominated feed of 17 mol % CH₄. It is also found that the tendency of surface free energy varying with feed composition is well in accord with the oxygen content of samples [see Fig. 3(b)], but the correlation of results from surface energy analysis with those from elemental analysis (bulk analysis) needs to be very carefully dealt with. Samples with higher oxygen content, produced by more CH₄-containing feed, led to a surface with higher surface energy.

Table II Surface Free Energy of Plasma Polymer Films and Plasma Operational Parameters

Monomer Composition	Surface Energy (mJ/m)			Flow Rate (SCCM)	Time (min)
	r_s^d	r_s^p	r_s		
CF ₄ -mol % CH ₄					
50	29.2	9.0	38.2	28	105
33	28.6	9.3	37.9	28	72
17	25.5	3.6	29.1	28	50
0	17.6	2.6	20.2	20	2
C ₂ F ₆ -					
50	28.1	8.1	36.2	28	60
33	28.1	6.8	34.9	28	75
17	22.6	3.4	26.0	28	60
0	14.8	2.1	16.9	20	2
C ₃ F ₆ -					
50	26.6	8.1	34.7	28	60
33	28.1	4.4	32.5	28	52
1	22.6	3.6	26.2	28	60
0	13.7	1.8	15.5	20	20
C ₄ F ₈ -					
50	27.0	8.4	35.5	28	45
33	27.6	3.6	31.2	28	45
17	19.8	2.4	22.2	28	60
0	14.1	1.7	15.8	20	20

Plasma parameters: 13.56 MHz, 13.3 Pa, and 160 W for all experiments. $r_s = r_s^d + r_s^p$, where r_s is surface free energy and r_s^d and r_s^p are dispersive and polar components of surface energy, respectively.

The dynamic behavior of surfaces produced by pure fluorocarbon or fluorocarbons/CH₄ plasmas was studied by determining their wetting properties. From measurements of wettability, it is concluded that only pure fluorocarbon and fluorocarbon-dominated (17 mol % CH₄) plasmas might lead to permanent hydrophobic surfaces of the polymers. Figure 5 shows a plot of the advancing and receding water-contact angles (as determined by values of cosine of the contact angles of C₂F₆ plasma-treated and the C₃F₆ plasma-polymerized layer as a function of the drop volume¹³). From Figure 5 it can be seen that values of cosine θ for the treated samples equal -0.19 and -0.29, corresponding to contact angles of 101° and 107°. Although these samples have different advancing contact-angle values, they are predominantly hydrophobic in contact with air. The receding contact angle for both films sharply decreased when water was successively withdrawn; however, a plateau was reached for the C₃F₆ plasma-polymerized film. It is known that for surfaces treated with C₂F₆ plasmas the hydrophobicity results from fluorinated molecular chains of polymers on the substrate.

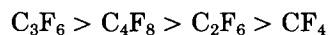
For C₃F₆ plasma-polymerized layers, the hydrophobicity is due to formation of the highly fluorinated and cross-linked plasma polymer layers on the substrate's surface. After exposure to water, the less cross-linked, hydrophobic segments of polymer molecules (from C₂F₆ plasma-treated samples) are liable to turn away from the water interface into the bulk. On the contrary, the rotational and diffusional migrations of the fluorine-containing moieties of plasma polymers (from C₃F₆ plasma polymerization) do not so easily respond to the new environment.²³⁻²⁵ As a result, a higher degree of hysteresis in water-contact angles (the difference between advancing and receding contact angles) must be observed for the C₂F₆ plasma-treated sample. A comparison between the time dependence of the hysteresis effect for C₂F₆, C₃F₆, C₄F₈, and C₃F₆-17 mol % CH₄ plasma-treated samples is given in Figure 6. It shows that the slope of the straight line (83 mol % C₃F₆ plasma-polymerized sample), hence, the time dependence, is the smallest among the samples. At the same time, our results of wettability measurements within all plasma-treated species also show that only from the C₃F₆-17 mol % CH₄ plasma

were polymers with a relatively stable, hydrophobic surface formed.

CONCLUSIONS

Pure fluorocarbon monomers (CF_4 , C_2F_6 , C_3F_6 , C_4F_8) and their mixtures with various amounts of CH_4 added were subjected to plasma polymerization to investigate influence of molecular structure and composition of fluorocarbons on both surface properties and deposition processes of the resulting polymers.

The addition of CH_4 to a fluorocarbon feed generally leads to plasma polymers of lower F content. The addition of small amounts of CH_4 to a feed of the fluorocarbons (e.g., 17 mol % CH_4) causes a significant increase in the deposition of plasma polymers and, moreover, further addition of CH_4 will decrease plasma polymer deposition. When the same molar composition of feed was employed, the deposition of polymers depended on molecular structure of the fluorocarbon in the feed. The following ranking in deposition rates was observed:



Wettability measurements suggest that only from pure fluorocarbon plasmas and fluorocarbon-domi-

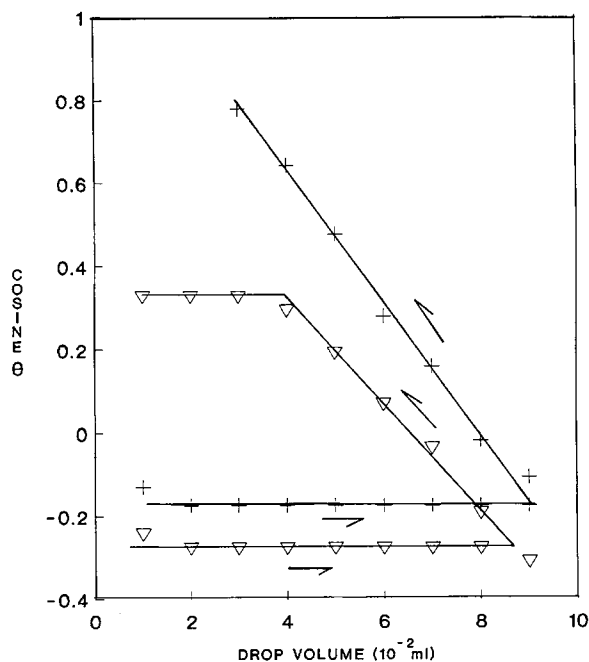


Figure 5 Advancing and receding water-contact angles of (+) C_2F_6 and (<) C_3F_6 plasma-treated PET films.

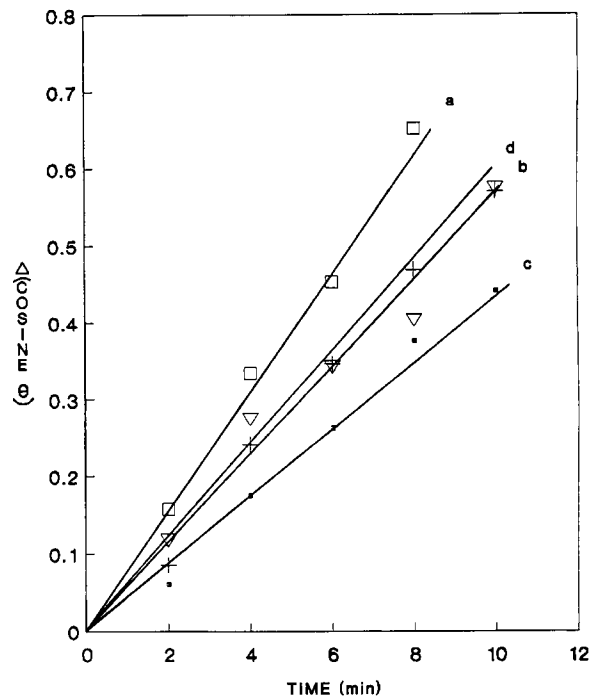


Figure 6 Time dependence of hysteresis effect for (a) C_2F_6 , (b) C_3F_6 , (c) C_3F_6 -17 mol % CH_4 , and (d) C_4F_8 plasma-treated PET foils.

nated (83 mol % fluorocarbons -17 mol % CH_4) plasmas can hydrophobic surfaces of polymers be achieved. F/C ratios of those polymers from bulk analysis were found to be in the range of 1.1-2.3, whereas those at the surface were from about 0.5 to 1.5. From all monomers used in this study, the mixture C_3F_6 -17 mol % CH_4 is the only one that gives a relatively stable and hydrophobic surface, as determined by contact-angle measurements.

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