

Grafting Fluorocarbons to Polyethylene in Glow Discharge

TOSHIHARU YAGI, ATTILA E. PAVLATH, and ALLEN G. PITTMAN,
*Western Regional Research Center, U.S. Department of Agriculture,
Berkeley, California 94710, and Daikin Kogyo Co., Ltd., Osaka, Japan*

Synopsis

A systematic surface fluorination of high-density polyethylene was carried out using CF_4 , CF_3H , CF_3Cl , and CF_3Br , in a radio-frequency glow discharge. Based on ESCA and wettability measurements, all of these compounds provided a fluorocarbon layer on high-density polyethylene surface, but the fluorine to carbon ratio and extractability of the films were strongly dependent on the starting materials and the location of the sample specimen in the reactor chamber as well as the duration of the reaction. The results with vertically held, CF_3H -treated samples showed a high level of nonextractable surface fluorination and very little change in wetting properties before and after extraction with $\text{CF}_2\text{ClCFCl}_2$.

INTRODUCTION

The surface fluorination of organic materials is an important process, since it can provide poly(tetrafluoroethylene)-like surface properties on economical materials. Glow discharge or plasma treatment is one of the best methods for obtaining such a surface. Most studied in the past have involved unsaturated fluorocarbons, such as tetrafluoroethylene and hexafluoropropylene. Such compounds polymerize easily in a glow discharge and produce a pinhole free thin film on the substrate.¹ In these cases, the adhesion between the plasma polymerized product and the substrate was not strong, and the polymer layer was easily removed from the surface with a fluorinated solvent.² There appeared to be little or no chemical bonding between the polymer and the substrate. The important requirement in creating a fluorinated surface is to obtain a layer of fluorocarbon grafted to the surface of the substrate. For this purpose, the use of saturated fluorocarbons appears to be more desirable, since the forming radicals would not polymerize easily in the gas phase, leaving more opportunity for surface reactions. In this study, the surface fluorination of high-density polyethylene (HDPE) was investigated by the use of CF_4 , CF_3H , CF_3Cl , and CF_3Br as starting materials.

EXPERIMENTAL

The experimental system was practically identical to the one described in a previous paper.³ A 13.56-MHz generator was used at 25 W. The duration of the reaction varied between 1 and 5 min. Gases were introduced through micrometer valves, and the pressure was maintained at 0.2–0.5 torr. Fluorocarbons were commercial materials. The substrate was high-density polyethylene

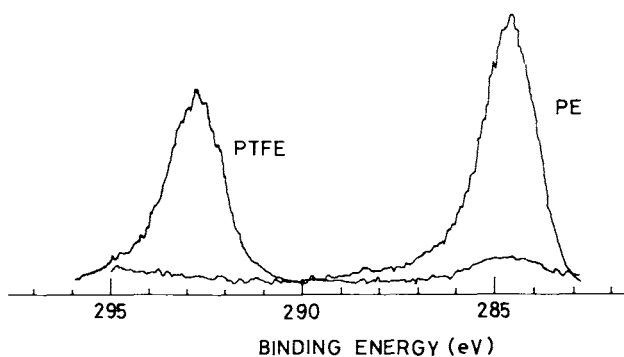


Fig. 1. ESCA carbon 1s spectra of polytetrafluoroethylene (PTFE) and high-density polyethylene (HDPE).

(HDPE) film cleaned in an ultrasonic cleaner using $\text{CF}_2\text{ClCFCl}_2$. Substrate samples (20 mm \times 20 mm) were placed both horizontally and vertically in the center of the reactor chamber on a glass plate. In this study, capacitive cylindrical electrodes were used. Analysis of the surface was made by X-ray photoelectron spectroscopy (ESCA) using a DuPont 650 Electron Spectrometer. ESCA can provide surface information to depths of 50–100 Å. The ESCA analysis involved the determination of carbon, fluorine, and oxygen. Where applicable, chlorine and bromine were also measured. The carbon spectrum is the most important since it contains chemical structural information.

Figure 1 shows the carbon 1s spectra of poly(tetrafluoroethylene) (PTFE) and HDPE used in this study. In the HDPE spectrum, one sharp peak is observed at 284.7 eV, characteristic of the CH_2 group. One sharp peak is also observed at 293.0 eV for PTFE spectrum, characteristic of the CF_2 group. The distance between the two peaks is about 8 eV. The spectrum of fluorinated HDPE, prepared by glow discharge, is expected to be diffuse in this range. A surface similar to PTFE is the final goal of the surface fluorination of HDPE.

Figure 2 shows a typical example of an ESCA carbon 1s spectrum of fluorinated HDPE prepared by glow discharge using CF_4 as the fluorinating agent. The peak shape is broad and complex, and binding energy ranged from 296 to 283 eV exhibiting overlapping of each peak. The quantitative evaluation of the ESCA data was carried out by deconvolution of the carbon 1s spectrum using a nonlinear least square curve fitting program.⁴ The existence of only the five major characteristic carbon components, CF_3 (293–294 eV), CF_2 (291–292 eV), CF

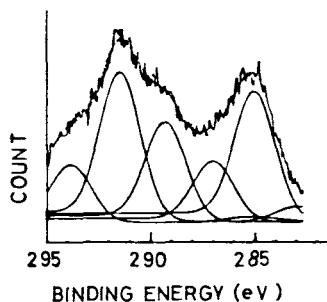


Fig. 2. ESCA carbon 1s spectrum of fluorinated high-density polyethylene, prepared by glow discharge using CF_4 as starting material (horizontal placement).

(288.5–289.5 eV), CO (286.4–287.5 eV), and CH₂ (284.5–285.0 eV), was assumed in the deconvolution process. C—Cl and C—Br groups are assumed to appear in the range of the CO group. Even though the treatment is carried out under the exclusion of oxygen, using argon gas as carrier, some CO-type groups are always present. Such groups can be detected on the surface of HDPE samples treated in glow discharge under argon atmosphere, even when the sample was kept under argon for 24 h after the treatment. It may be presumed that stable free radicals form under the glow discharge treatment which react with oxygen as soon as the sample is exposed to air.

Surface wettability studies were carried out using the normal alkanes (decane, dodecane, tetradecane and hexadecane) as test liquids. After the advancing contact angle (θ) was measured, $\cos \theta$ was plotted against the surface tension. The critical surface tension (CST) was then obtained by extrapolating this line to $\cos \theta = 1$ after the procedure described by Zisman.⁵

RESULTS AND DISCUSSION

Horizontal Placement of Sample Specimens in Chamber

Figure 3 shows typical ESCA carbon 1s spectra for polymer deposition or grafting on a horizontal HDPE surface obtained by glow discharge using CF₄, CF₃H, CF₃Cl, and CF₃Br as starting materials. The spectra are shown for both extracted (with CF₂ClCFCl₂) and nonextracted specimens. Since the sample was placed flat on a glass surface during the reaction, only the upper surface was

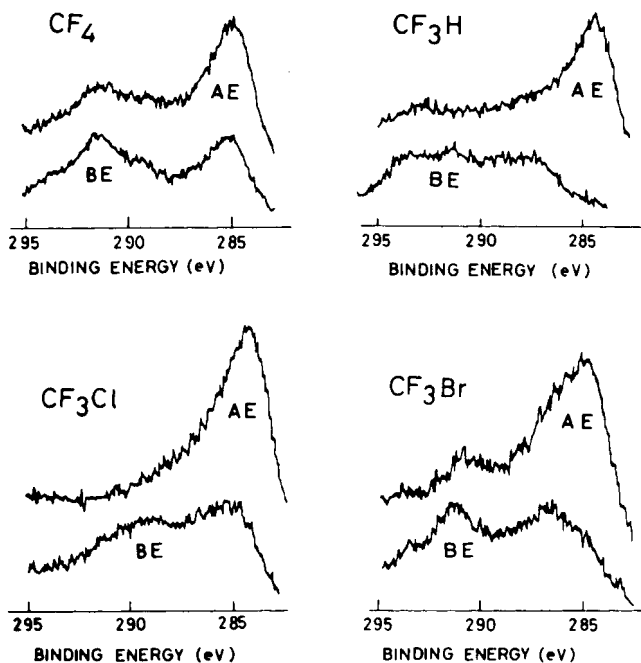


Fig. 3. ESCA carbon 1s spectra for polymer deposition or grafting on high-density polyethylene surface prepared by glow discharge using CF₄, CF₃H, CF₃Cl, and CF₃Br as starting material (horizontal placement). (BE = before extraction with CF₂ClCFCl₂, and AE = after extraction.)

TABLE I
Percentage Contribution of Each Carbon Group to Total Amount of Carbon on Horizontally Placed and Plasma-Treated HDPE Surface^a

Starting material	CF ₃		CF ₂		CF		CO, CCl, CBr		CH ₂	
	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE
CF ₄	11.6	3.0	30.0	15.7	20.1	12.9	11.2	13.2	26.1	55.3
CF ₃ H	18.9	7.3	21.7	7.1	21.2	8.2	26.6	17.3	11.3	60.0
CF ₃ Cl	0	0	12.2	0	20.4	5.9	26.7	20.3	40.6	73.7
CF ₃ Br	9.7	2.4	25.9	14.1	15.1	13.1	26.0	24.1	22.6	46.3

^a These data are based on the deconvolution of ESCA carbon 1s spectra. BE = before extraction with CF₂ClCFCl₂, and AE = after extraction.

analyzed. Deconvolution of these carbon 1s spectra showed the presence of all five components before extraction regardless of the starting materials (Table I). In case of CF₃Cl, neither CF₃ nor CF₂ was present after extraction. The atomic ratios calculated from ESCA measurements are summarized in Table II. Figure 4 illustrates the results of wettability measurements on the plasma-modified HDPE samples.

In the case of CF₄, the ESCA spectra were not very different before and after extraction. Two characteristic peaks were observed in both spectra at 291.5 and 285.0 eV. The former peak was in the range of the CF₂ group, while the latter appeared where CH₂ should be. Deconvolution indicated 11.6 mol % CF₃ group for the sample before extraction and the 3.0 mol % CF₃ group for the extracted sample (Table I). Radicals of F and CF₃ would be expected to predominate and to react with the HDPE surface in a CF₄ discharge. Formation of CF₃ groups on the surface of HDPE would be expected by the direct reaction of CF₃· radicals, since there are no CH₃ group in HDPE, where direct substitution of an F· radical for H· could occur. The F/C ratio was 1.50 before and 1.05 after extraction, indicating approximately 30% loss of fluorine. These ratios are less than the 2.00 of pure PTFE, but the result is encouraging. CST values of samples were 20.8 and 23.1 dyn/cm before and after extraction, respectively. The reported value for PTFE is 18.5 dyn/cm.

The spectral features of carbon 1s obtained with CF₄ were very similar to those of CF₃CF₃ treatment, shown in Figure 5. This indicates that the CF₄ glow creates almost the same reactive species as a CF₃CF₃ glow, where the CF₃· radical dominates. According to Truesdale and Smolinsky,⁶ a CF₄ discharge provides F, F₂, and mainly CF₃CF₃ which further suggests the formation of CF₃· radicals.

TABLE II
Atomic Ratios of Plasma-Treated HDPE (Horizontal Placement)^a

Starting material	F/C		O/C		Cl/C		Br/C	
	BE	AE	BE	AE	BE	AE	BE	AE
CF ₄	1.50	1.05	0.06	0.10				
CF ₃ H	1.69	0.87	0.09	0.12				
CF ₃ Cl	0.81	0.18	0.07	0.09	0.68	0.48		
CF ₃ Br	1.00	0.50	0.05	0.13			0.26	0.22

^a Ratios are calculated from ESCA data. BE = before extraction with CF₂ClCFCl₂, and AE = after extraction.

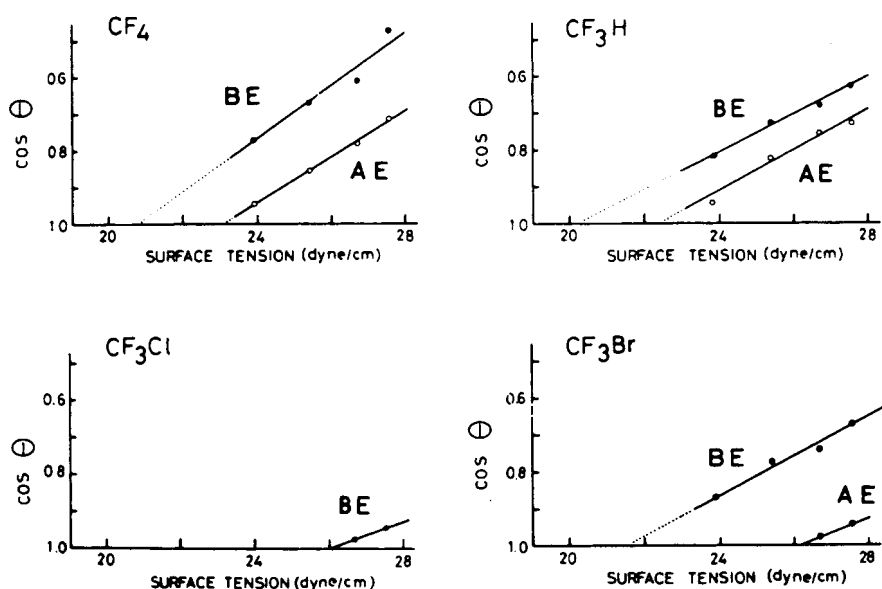


Fig. 4. Wettability results of fluorinated high-density polyethylene surface prepared by glow discharge using CF_4 , CF_3H , CF_3Cl , and CF_3Br as starting materials (horizontal placement). (BE = before extraction with $\text{CF}_2\text{ClCFCl}_2$, and AE = after extraction.)

With CF_3H , one could expect the formation of $\text{CF}_3\cdot$ and $\text{H}\cdot$ radicals in the first step. The homolytic fission of a C—F bond requires 20 kcal/mol more energy, but this is still within the range of the energy available in a glow discharge; therefore, the formation of $\text{CF}_2\text{H}\cdot$ radical is also likely. These monoradicals could be further dissociated into $\text{CF}_2\cdot$ biradicals, but it would require additional energies. Statistically, the presence of $\text{CF}_2\cdot$ is not very likely. The shape of the carbon 1s spectrum before extraction was very broad, and there was no characteristic peak. After extraction there was a marked change in the ESCA spectrum, with one major peak at 285 eV (in the range of the CH_2 group). Deconvolution of this spectrum indicated 7.3 mol % CF_3 group, 7.1 mol % CF_2 group, and 8.2 mol % CF group. The F/C ratio was very high before extraction (1.69), but approximately 50% was lost after extraction. The ESCA spectra did not exhibit

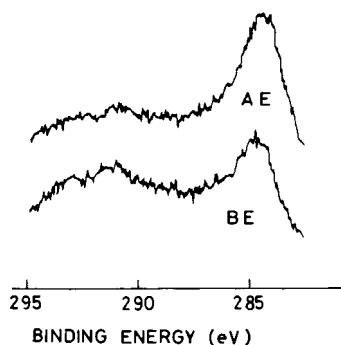


Fig. 5. ESCA carbon 1s spectra of fluorinated high-density polyethylene, prepared by glow discharge using CF_3CF_3 as starting material (horizontal placement). (BE = before extraction with $\text{CF}_2\text{ClCFCl}_2$, and AE = after extraction.)

the characteristic CF_2 peak observed with CF_4 ; nevertheless, the CST values were comparable: 20.3 and 22.5 dyn/cm before and after extraction, respectively.

Using CF_3Cl in the glow discharge, not only the lowest F/C values were observed both before and after extraction among the four starting materials, but also the largest percentage of fluorine was lost during extraction. The carbon 1s spectrum of a treated HDPE sample before extraction is broad and complex, compared to the spectra of untreated HDPE and PTFE. Two broad peaks were observed (289.9 and 285.0 eV) for a treated sample before extraction. After extraction only the 285.0 eV peak remained. Table I shows that the surface of the treated sample before extraction contained 12.2 mol % CF_2 and 20.4 mol % CF. Extraction completely eliminated the CF_2 peak, and only the CF group remained on the surface at a level of 5.9 mol %. Table II shows that the C/F ratio was 0.81 before extraction and 0.18 after extraction. Evidently, approximately 78% of the fluorine was extracted with $\text{CF}_2\text{ClCFCl}_2$. On the other hand, the Cl/C ratio before and after extraction was 0.68 and 0.48, respectively, indicating only a 39% loss of chlorine. Apparently, the chlorine-containing groups were more permanently bound to the surface of the substrate than the ones with fluorine.

Figure 4 illustrates the results of wettability measurement based on advancing contact angle measurements. The CST was 26.0 dyn/cm before extraction, but could not be determined after extraction, since all of the test liquids completely wetted the surface. The F/C ratio of a sample before extraction (CF_3Cl glow) is 0.81. This value is almost the same as the 0.83 value obtained for the extracted sample after CF_3H treatment. Nevertheless, the CST value of a sample before extraction after CF_3Cl treatment is 26.0 dyn/cm, compared to 22.5 dyn/cm obtained for an extracted sample following CF_3H treatment. The higher CST value after CF_3Cl treatment is evidently due to bound chlorine, which Zisman has previously shown to increase the CST.⁵ It appears, therefore, that, for low CST values, chlorine-containing compounds should be avoided for surface fluorination with a glow discharge.

The results of surface fluorination with CF_3Br was more promising. Two characteristic peaks were observed at 291.2 and 285.0 eV in the sample prior to extraction. The peaks were in the range of CF_2 and CH_2 groups, respectively. There were two peaks, a large one at 285.0 eV and a small one at 291.2 eV in the extracted sample. The difference between the two spectra (extracted vs. nonextracted) is not large compared to that of the CF_3Cl treatment. It can be seen in Table I that 2.4 mol % CF_3 group, 14.1 mol % CF_2 group, and 13.1 mol % CF group have remained on the surface after $\text{CF}_2\text{ClCFCl}_2$ extraction of the CF_3Br -treated sample. The reactivity of CF_3Br to HDPE in glow discharge appears to be quite different from that of CF_3Cl . This difference might be related to the weak bond energy of C—Br (54.0 kcal/mol), compared to that of C—Cl (66.5 kcal/mol) and C—F (107.0 kcal/mol). The formation of Br radicals in the glow would be expected to predominate, and these radicals apparently tend to recombine forming Br_2 or HBr from liberated hydrogen radicals, rather than brominating the HDPE surface. The wettability data for CF_3Br -treated samples both before and after extraction also indicate a higher level of bound fluorine than when CF_3Cl was used. The value of CST was 21.5 dyn/cm before and 26.2 dyn/cm after extraction. The presence of bromine in the starting material is less troublesome than that of chlorine, since only a small amount of bromine

seems to graft to the surface. It might be even beneficial to use this type of compound since an $R_f\text{---Br}$ compound could more easily provide the $R_f\cdot$ radical than a perfluoro- compound.

Vertical Placement of Sample Specimen in Chamber

In the experiments described above, the sample specimens were placed horizontally in the reactor chamber. We subsequently noted some variation in grafting levels when the HDPE samples were held vertically in the reactor center. As shown in Figure 6, the CF_3H treatment with samples in a vertical position showed quite different results from those obtained in a horizontal placement. In the carbon 1s spectra (before extraction), there were no characteristic peaks, and the shape of these two spectra was very similar. As shown in Table III, samples treated with CF_3H both before and after extraction contain almost the same amount of each of the possible fluorinated groups. A comparison of the F/C ratios after extraction of the samples held horizontally (Table II) or vertically (Table IV) shows that less grafting occurred on vertically held samples using CF_3Cl and CF_4 , and more grafting occurred using CF_3Br and CF_3H .

The results are promising, especially in the case of the CF_3H treatment. The F/C ratio of a sample before extraction was 1.66 and that of extracted sample was 1.58, indicating a high level of grafting. These values approach the F/C ratio in PTFE (i.e., 2.0). Figure 7 shows the wettability data of the sample placed vertically in the reactor chamber. For the CF_3H treatment, the CST value of

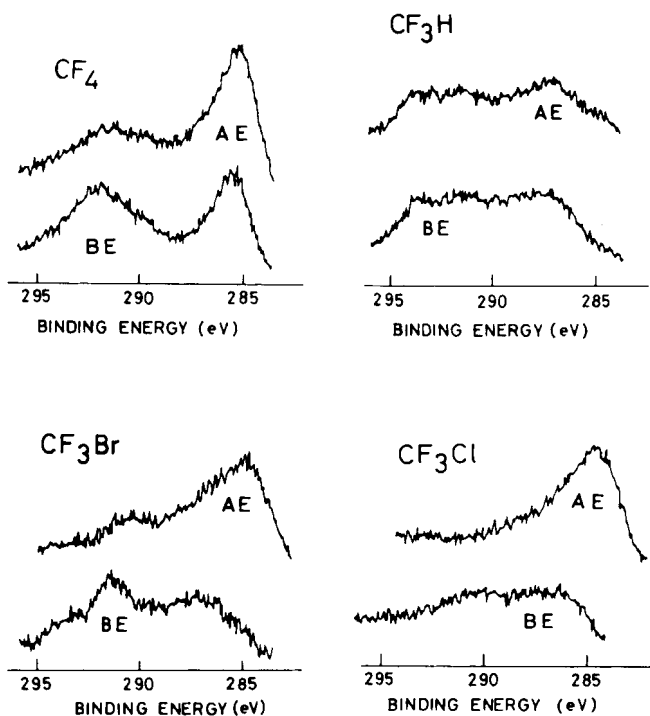


Fig. 6. ESCA carbon 1s spectra for polymer deposition or grafting on high-density polyethylene surface prepared by glow discharge using CF_4 , CF_3H , CF_3Cl and CF_3Br as starting materials (horizontal placement). (BE = before extraction with $\text{CF}_2\text{ClCFCl}_2$, and AE = after extraction.)

TABLE III
Percentage Contribution of Each Carbon Group to Total Amount of Carbon on Vertically Placed and Plasma-Treated HDPE Surface^a

Starting material	CF ₃		CF ₂		CF		CO, CCl, CBr		CH ₂	
	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE
CF ₄	7.8	5.3	29.7	19.3	18.8	14.9	11.8	13.4	31.9	47.1
CF ₃ H	20.0	18.9	24.2	22.5	21.0	20.5	25.7	25.6	9.0	12.5
CF ₃ Cl	20.0	0	14.2	0	21.4	6.0	29.0	22.1	33.5	71.8
CF ₃ Br	11.8	2.0	25.2	10.1	18.9	8.5	26.4	22.0	17.5	57.3

^a These data are based on the deconvolution of ESCA carbon 1s spectra. BE = before extraction with CF₂ClCFCl₂, and AE = after extraction.

the sample before extraction was 21.3 dyn/cm, and that of extracted sample is 22.7 dyn/cm. There was very little change in the wettability property of both samples. These ESCA and wettability results show that the HDPE surface obtained from CF₃H (held vertically in the reactor chamber) approaches the PTFE surface in wettability and surface constitution.

In an effort to learn more about the factors involved in grafting to HDPE in vertical placement, the time dependence of CF₃H treatment was examined. In Figure 8 the spectra on the left side are from samples before extraction and on the right side are from extracted samples. The peak shape of those before extraction are almost the same. On the other hand, in the case of extracted samples, the large CH₂ peak observed at 1–3 min residence time became gradually smaller, shifting to a higher energy field at 4 min, and completely disappearing at 5 min. The results of the treatments at 5- and 10-min residence times are practically the same within the limits of experimental error.

Figure 9 shows the time dependence of the F/C ratio. The ratio before extraction was fairly constant over the 1–5-min residence time period. It can be seen from the extracted sample that a considerable portion of fluorocarbon was removed by CF₂ClCFCl₂ extraction until the residence time was at least 5 min. It seems that during the glow discharge charge, crosslinking reaction occurs between the accumulated polymer layer and the grafting layer and/or substrate the HDPE. Hydrogen, both in HDPE and the deposit layer, seems to be the starting point for the crosslinking reaction, since fluorinated polymethylenes, such as poly(vinylfluoride), poly(vinylidene fluoride), or poly(trifluoroethylene), tend to crosslink under the high energy field, while poly(tetrafluoroethylene) undergoes depolymerization under the same conditions.⁷

The surprisingly high fluorine-containing and extraction-resistant surface

TABLE IV
Atomic Ratio of Plasma-Treated HDPE (Vertical Placement)^a

Starting material	F/C		O/C		Cl/C		Br/C	
	BE	AE	BE	AE	BE	AE	BE	AE
CF ₄	1.40	0.84	0.13	0.15				
CF ₃ H	1.66	1.58	0.10	0.09				
CF ₃ Cl	0.48	0.07	0.11	0.14	0.69	0.51		
CF ₃ Br	1.43	0.89	0.12	0.16			0.34	0.29

^a Ratios are calculated from ESCA data. BE = before extraction with CF₂ClCFCl₂, and AE = after extraction.

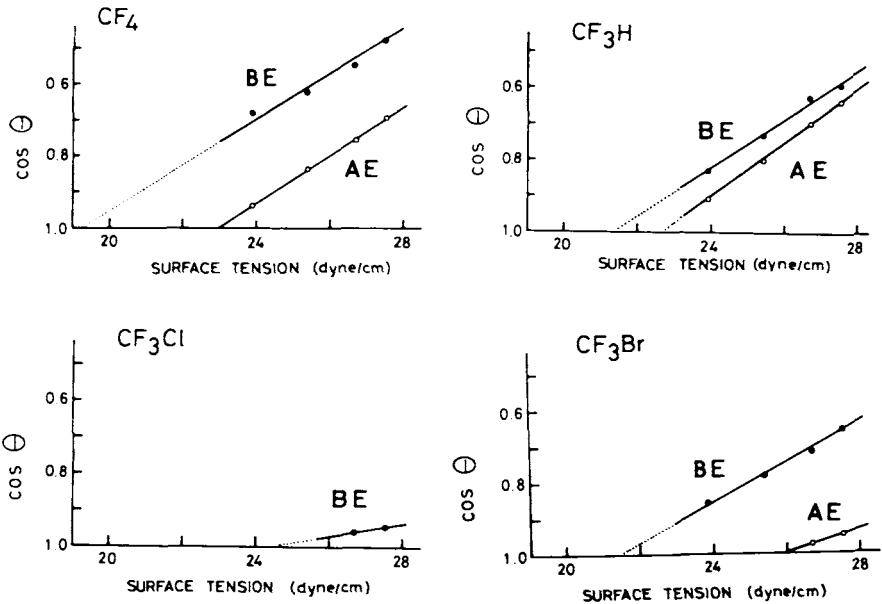


Fig. 7. Wettability results of fluorinated high-density polyethylene prepared by glow discharge using CF_4 , CF_3H , CF_3Cl , and CF_3Br as starting materials (vertical placement). (BE = before extraction with CF_2CFCl_2 , and AE = after extraction.)

obtained on a HDPE sample in vertical position cannot be explained, but certain hypotheses may be presented for consideration. In a high-frequency discharge created with capacitive cylindrical electrodes, the electron density is quite uniform in the center where both the horizontal and vertical samples were located. One possible explanation of the difference in the results is gravitational effect. The forming fluorocarbon radicals may react not only with the HDPE surface, but also with each other. The latter reaction produces larger molecules. Repeated combination may reach such size that the molecule can no longer remain in vapor phase. This may result in the deposition of such large molecules on horizontal surfaces without grafting. Such deposition would compete with the original surface for the reaction with additional fluorocarbon radicals. Obviously, such ungrafted deposit would be easily eliminated through extraction. However,

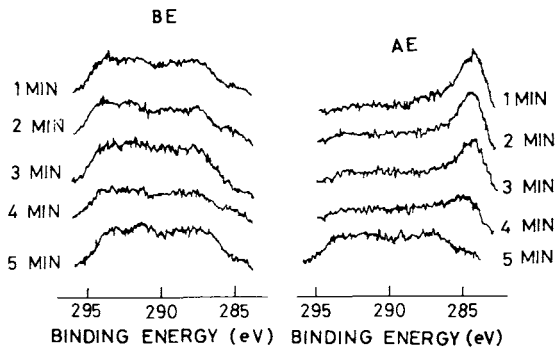


Fig. 8. Change of ESCA carbon 1s spectra with plasma residence time. Sample were prepared by CF_3H glow discharge with vertical sample placement in reactor chamber. (BE = before extraction with CF_2CFCl_2 , and AE = after extraction.)

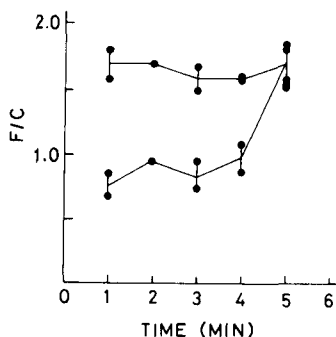


Fig. 9. Plasma residence time dependence of fluorine to carbon ratio (F/C) of fluorinated high-density polyethylene prepared by CF_3H glow discharge (vertical placement).

this still does not explain why only the CF_3H provides extraction resistant grafting in vertical position. Glow discharge chemistry of multiatomic molecules are still too complex to explain this unexpected behavior; nevertheless, it is an excellent method to obtain extraction resistant fluorocarbon surfaces.

CONCLUSIONS

It was found that extraction-resistant fluorocarbon surfaces can be obtained in an electric glow discharge using simple saturated fluorocarbons as starting materials. The presence of chlorine and bromine in the starting materials appears to be undesirable, since the grafting is not limited to fluorocarbon radicals, although more readily available fluorobromocarbons might be useful, since only a small amount of bromine is grafted to the surface. The starting materials do not necessarily have to be perhalogenated compounds, although high fluorine content is desirable. The success with CF_3H indicates that the presence of one hydrogen at the end of the fluorocarbon chain might be beneficial. It is further evident that care should be used to decide the location of the sample in the glow discharge and residence time in the glow is an important factor.

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