GRAFTING FLUOROCARBONS TO POLYETHYLENE IN GLOW DISCHARGE

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ABSTRACT

A systematic surface fluorination of polyethylene was carried out using CF_3Cl, CF_3Br, CF_4 and CF_3H in a radiofrequency glow discharge. Based on ESCA and wettability measurements,all of these compounds deposit higher molecular weight fluorocarbons, but the fluorine to carbon ratio and the extractability of the films using $CF_2ClCFCl_2$ is strongly dependent on the starting material. Best results were obtained with CF_3H.

1. INTRODUCTION

The surface fluorination of organic materials is an important process, since it can provide poly-(tetrafluoroethylene)-like surface properties on conventional materials. Glow discharge is one of the best methods for obtaining such a surface. Most studies 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 appeared 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_3Cl, CF_3Br, CF_4 and CF_3H as starting materials.

2. EXPERIMENTAL

The experimental system was practically identical to one described in a previous paper (3). A 13.45 MHz generator was used at 25W. The residence time varied between 1 to 5 minutes. 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 (HDPE) which was cleaned in an ultrasonic cleaner using $CF_2ClCFCl_2$. Substrate samples (20x20 mm^2) were placed both horizontally and vertically in the reactor chamber. Analysis of the surface was made using X-ray photoelectron spectroscopy (ESCA) and surface wettability by measuring the advancing liquid contact angle of nonhydrogen bonding liquids (decane, dodecane, tetradecane and hexadecane) (4). The deconvolution of carbon 1s spectra was carried out by a nonlinear least square curve fitting program (5). The existence of only the major five characteristic carbon components, CF_3 (293.5-294.0 eV), CF_2 (291.5 eV), CF (289.0 eV), C-O (& C-Cl or C-Br)(287.0 eV) and CH_2 (285.0 eV) was assumed in the deconvolution process.

3. RESULTS AND DISCUSSION

The atomic ratios calculated from the ESCA measurements and the surface wettability based on contact angle measurements are summarized in Table I. These data were obtained from the experiments when the substrate samples were placed horizontally in the reactor chamber. Typical carbon 1s spectra are shown for the polymer depositions obtained from the four starting materials in Fig. 1. The spectra are shown for both before and after extraction with $CF_2ClCFCl_2$. Deconvolution of the spectra indicated the presence of all five components regardless of the starting materials. After extraction, however, the CF_3 and CF_2 components generally decreased more than the CF group. Fig. 2 shows a characteristic deconvoluted carbon 1s spectra before and after extraction. Fig. 3 illustrates the results of the wettability measurement.

In the case of CF_3Cl, the ESCA spectra were considerably different before and after extraction. The F/C ratio was 0.81 before extraction, in contrast to the 0.18 value obtained after extraction. This indicates that 78% of the fluorine content was extractable by $CF_2ClCFCl_2$. At the same time, the Cl/C ratio before and after extraction was 0.68 and 0.48 respectively, indicating only a 39% loss of the chlorine content. Apparently, the chlorine containing species are more readily bound to the surface of the substrate. The F/Cl ratio is 0.36 on the surface after extraction, even though the starting material, CF_3Cl, has a 3:1 ratio. The critical surface tension (CST) was 26.0 dyne/cm before extraction, but could not be determined after extraction, since all test liquids wetted the surface.

The result of the surface fluorination was somewhat better with CF_3Br. The F/C ratio before and after extraction was 1.00 and 0.50 respectively, indicating almost 50% retention. Approximately, 85% of the bromine was retained after extraction, but the total amount was quite small (0.22). The F/Br ratio is greater than 3:1. The reactivity of CF_3Br to HDPE in glow discharge appears to be quite different from that of CF_3Cl. Such a 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 $CF_3^{\bullet}$ and $Br^{\bullet}$ radicals in the glow would be expected to predominate and the $Br^{\bullet}$ radicals apparently tend to recombine froming Br_2 or HBr from liberated hydrogen radicals, rather than brominate the surface of the polyethylene. The results of these experiments are very similar to those of CF_3-CF_3, where $CF_3^{\bullet}$ radicals are the dominant species in glow discharge (6). The wettability data before and after extraction also indicates a higher level of bound fluorine than when CF_3Cl was used. The value of CST was 21.5 dyne/cm before and 26.2 dyne/cm after extraction.

In comparison with CF_3Cl and CF_3Br treatments, the fluorinated surface obtained with CF_4 was more resistant to the extraction process. The F/C ratio was 1.50 before and 1.05 after extraction, indicating approximately 30% loss. This ratio is less than the 2:1 value of pure poly-(tetrafluoroethylene), but the result is promising. The CST values were 20.8 and 23.1 dyne/cm before and after extraction. This value approaches the 18.5 dyne/cm value reported for poly-(tetrafluoroethylene). The ESCA spectra exhibited mostly two peaks both before and after extraction : 291.3 and 285.0 eV. The former is in the range of the CF_2-group, while the latter appears where CH_2 should be. The deconvolution of the spectra show other components too, but these two appear to dominate.

In the case of CF_3H, one could expect the formation of $CF_3^{\cdot}$ and $H^{\cdot}$ radicals, but the bond energy of C-H (87.0 Kcal/mol) is quite close to that of C-F bond. Therefore, the appearance of $CF_2H^{\cdot}$ radical is also likely. The F/C ratio was very high before extraction, even higher than with CF_4 : 1.69, but approximately 50% of it was lost during extraction. The ESCA spectra did not exhibit the characteristic CF_2 and CH_2 peaks observed with CF_4, nevertheless the CST values were comparable : 20.3 and 22.5 dyne/cm before and after extraction respectively.

In the experiments described above, the substrate samples were placed horizontally in the reactor chamber. We subsequently noted some variation in grafting levels when the HDPE samples were held vertically in the reaction chamber. A comparison of the F/C ratios after extraction of samples held horizontally (Table I) or vertically (Table II) shows that less grafting occurred on vertically held samples using CF_3Cl or CF_4 and more grafting occurred using CF_3Br and CF_3H. The results with vertically held CF_3H treated samples showed a high level of non-extractable surface fluori nation (Fig. 4) and very little change in wetting properties before and after extraction. As would be expected, residence time in the reactor also effects the level of surface modification. Fig. 5 shows that the F/C ratio (using CF_3H) before extraction is fairly constant over a 1-5 minutes residence time. It can be seen that a considerable portion of fluorocarbon was removed by extraction until the residence time was at least 5 minutes. Increased time of exposure in the plasma may result in surface crosslinking of deposited fluorocarbon, and/or anchoring of the deposited material to the surface of the substrate.

4. CONCLUSION

It was found that extraction resistant fluorocarbon surfaces can be obtained in electric glow discharge using simple saturated fluoro-carbons 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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TABLE I

Surface properties of plasma-treated HDPE (horizontal placement)
(5 minute residence time)

	Starting material	F/C	Cl/C	Br/C	O/C	CST* dyne/cm	Contact angle in H_2O
Before extraction	CF_3Cl	0.81	0.68	--	0.07	26.0	101
	CF_3Br	1.00	--	0.26	0.05	21.5	106
	CF_4	1.50	--	--	0.06	20.8	116
	CF_3H	1.69	--	--	0.07	20.3	105
After extraction	CF_3Cl	0.18	0.48	--	0.09	wet	91
	CF_3Br	0.50	--	0.22	0.13	26.2	98
	CF_4	1.05	--	--	0.10	23.1	107
	CF_3H	0.83	--	--	0.15	22.5	104

*CST = Critical Surface Tension

TABLE II

Surface properties of plasma-treated HDPE (vertical placement)
(5 minute residence time)

	Starting material	F/C	Cl/C	Br/C	O/C	CST* dyne/cm	Contact angle in H_2O
Before extraction	CF_3Cl	0.48	0.68	--	0.16	24.4	98
	CF_3Br	1.43	--	0.28	0.07	21.6	103
	CF_4	1.40	--	--	0.08	19.3	110
	CF_3H	1.66	--	--	0.11	21.3	108
After extraction	CF_3Cl	0.07	0.48	--	0.09	wet	90
	CF_3Br	0.89	--	0.28	0.07	26.0	96
	CF_4	0.84	--	--	0.09	22.5	104
	CF_3H	1.58	--	--	0.09	22.7	108

* CST = Critical Surface Tension

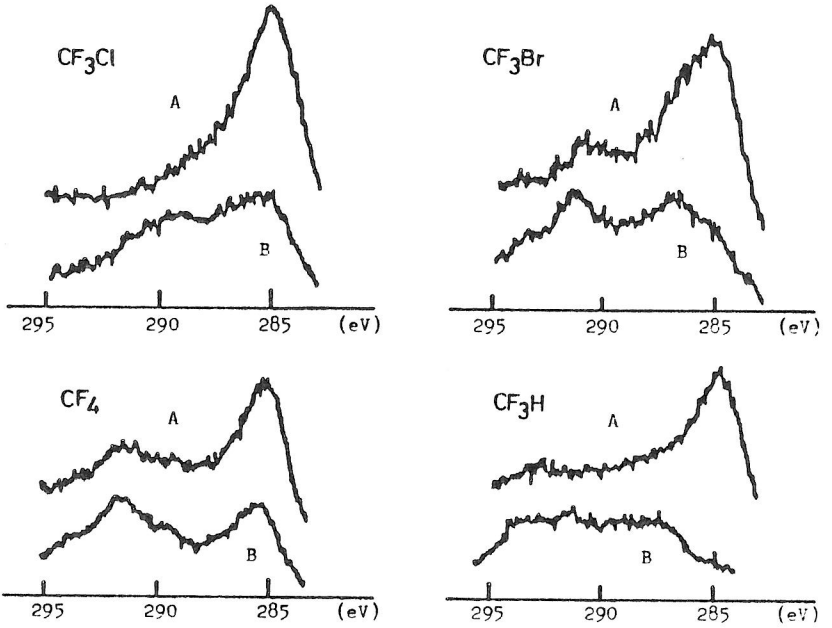

Figure 1. ESCA spectra of HDPE surface treated by CF_3Cl, CF_3Br, CF_4 and CF_3H plasma. Symbol B means before, symbol A means after extraction with $CF_2ClCFCl_2$.

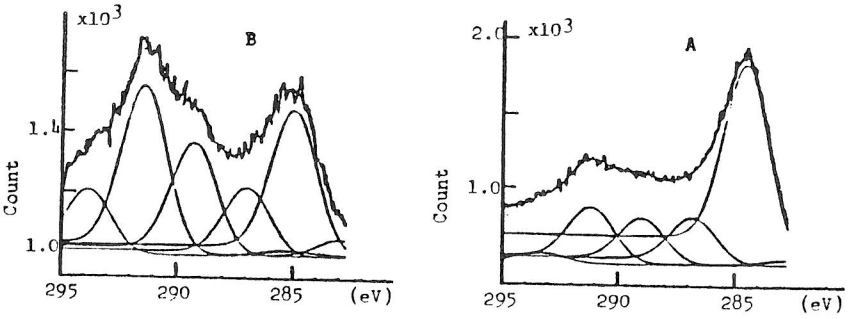

Figure 2. Characteristic deconvoluted carbon 1s spectra of CF_4 plasma system. Substrate HDPE was set holizontally in chamber. Symbol B means before, symbol A means after extraction with $CF_2ClCFCl_2$.

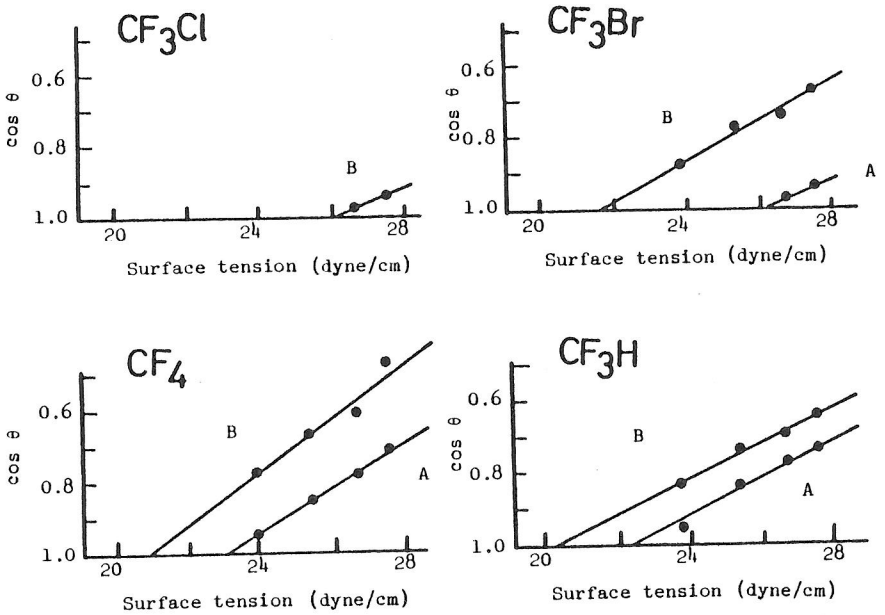

Figure 3. Wettability of HDPE surface treated by CF_3Cl, CF_3Br, CF_4 and CF_3H plasma. Symbol B means before, symbol A means after extraction with $CF_2ClCFCl_2$.

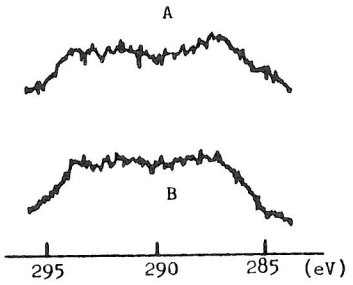

Figure 4. ESCA spectra of CF_3H plasma system. Substrate HDPE was set vertically in chamber.

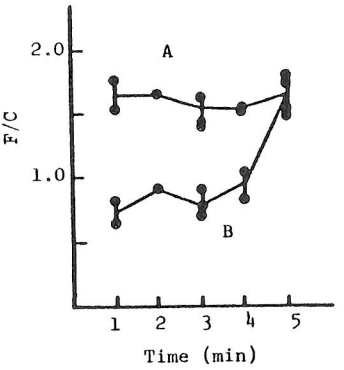

Figure 5. Change of fluorine to carbon ratio (F/C) with plasma exposure time in CF_3H plasma system. Symbol B means before, symbol A means after extraction with $CF_2ClCFCl_2$.