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### Surface Analysis of Plasma-Polymerized Fluorocarbon Films by X-Ray Photoelectron Spectrometry

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## Surface Analysis of Plasma-Polymerized Fluorocarbon Films by X-Ray Photoelectron Spectrometry

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### ABSTRACT

The surface of films deposited from hexafluoroethane and tetrafluoroethylene on plastic and wool textile substrates was analyzed by x-ray photoelectron spectroscopy. The carbon 1s spectra obtained from the fluorocarbon surfaces could be resolved into five lines. The three highest binding energy lines were assigned to carbons containing one, two, and three fluorine atoms, respectively. Surface oxidization was detected by the presence of two oxygen 1s lines on the surface of the films. Two fluorine 1s electron lines were observed on the surface of the films formed from hexafluoroethane on wool. These lines were assigned to fluorine covalently bound to carbon and ionic fluoride. The surface oxygen-fluorine atom ratio was found to vary considerably among the various surfaces analyzed. Fluorocarbon films obtained from plasma polymerization of tetrafluoroethylene contained a significant amount of trifluoromethyl and fluoromethyl groups on the surface, indicating extensive monomer

breakdown in the plasma. The degree of substrate coverage and the chemical structure of the deposited film could be determined from this x-ray photoelectron spectroscopic study.

A low-temperature plasma is a unique gas-phase method for polymerizing organic monomers onto a variety of substrates [1]. We [2], as well as others [1], have utilized this process to polymerize fluorocarbon monomers onto a variety of surfaces. Fluorocarbon films have been utilized as protective coatings to impart oil and water repellency to surfaces and soil resistance to fabrics [3, 4].

In this paper we present the results of the surface analysis of plasma-polymerized hexafluoroethane and tetrafluoroethylene films on polymer and wool textiles by x-ray photoelectron spectroscopy (XPS). This technique is particularly applicable to the surface analysis of plasma-polymerized films and especially fluorocarbon films. Photoejected electrons escape from the region of approximately 25 Å from the surface and, therefore, only the surface is analyzed. Plasma-polymerized films are known to undergo rapid surface oxidation when exposed to the atmosphere, and XPS is capable of detecting this oxidation [1]. Fluorine atoms are capable of shifting the binding energy of carbon to a sufficient extent that one is able to distinguish between  $CF_3$ ,  $CF_2R$ , and  $CFR_2$  functional groups on the surface due to the difference in core electron binding energies of carbon [5]. Utilizing surface atom core electron binding energy line intensities, one is able to estimate the relative atom ratio on the surface [6].

Data are presented from plasma-polymerized fluorocarbon films on polystyrene, polypropylene, and wool textiles. The plastic substrates represent the case of a more smooth and inert surface, while wool textile is an example of an extremely uneven surface containing various reactive functional groups. It has been generally observed that core electron line shapes are related to the smoothness and regularity of the surface [7]. As anticipated, electron line widths were found to be more uniform from films deposited on polystyrene and polypropylene. We find that the fluorocarbon character of the surfaces studied varied considerably depending on the extent of surface coverage and surface oxidation.

## EXPERIMENTAL SECTION

### Chemicals

Research grade hexafluoroethane and tetrafluoroethylene were obtained from the Matheson Company, East Rutherford, New Jersey, and used as received.

### Plasma Polymerization

Fluorocarbon coatings were polymerized onto the polymer and wool fabric substrates using an apparatus and procedure previously described in the literature [2]. The substrate was surrounded by the external electrodes used to excite the plasma. The conditions employed to obtain the plasma-polymerized films are given in Table 1.

### Surface Analysis

X-ray photoelectron spectra were measured using a Varian IEE-15 spectrometer with a  $MgK_{\alpha}$  target. The application of this technique for the surface analysis of textiles has been described in considerable detail elsewhere [9, 10].

### Curve Fitting

The core electron spectra were fitted to Lorentzian or Gaussian peak shapes by a nonlinear least squares computer

TABLE 1. Plasma Parameters for Deposition of Fluorocarbons on Plastic and Wool Substrates

Substrate	Gas	Power (W) net coupled into gas	Pressure (Torr) (in plasma)	Time (min) film deposition
Polypropylene	$C_2F_6$	50	1	5
Polystyrene	$C_2F_6$	50	1	5
Wool 31B	$C_2F_6$	25	1	2.5
31C	$C_2F_6$	25	1	5
31E	$C_2F_6$	75	1	1
Polypropylene	$C_2F_4$	50	1	7
Polypropylene <sup>a</sup>	$C_2F_4$	50	1	5
30B	$C_2F_4$	25	1	2.5
30E	$C_2F_4$	75	1	1

<sup>a</sup>No argon carrier gas.

fitting program [8]. Each function is described by four independent parameters. These parameters are the width, the position, an intensity factor, and a tail height to peak height ratio. A leading constant or exponential tail can be used. In order to compare results, the combination of parameters giving the most consistent fit of all the data in a series was used. Carbon and oxygen spectra were fitted with Lorentzian functions with a leading constant tail. Fluorine electron spectra were best fitted using Gaussian functions with a leading constant tail. Core electron line widths were found to vary considerably when measured on textile surfaces. Fluorocarbon films deposited on smooth polymer substrate gave electron spectra whose lines were fairly constant. Using routine operating conditions, electron lines measured on the Varian instrument obtained from pure organic compounds on tape were around 2.6 eV wide. In order to obtain physically realistic fits, electron line widths were fixed at 2.6 eV when oxygen and fluorine electron spectra were deconvoluted. Line width for carbon spectra are those selected by the computer program that led to convergence.

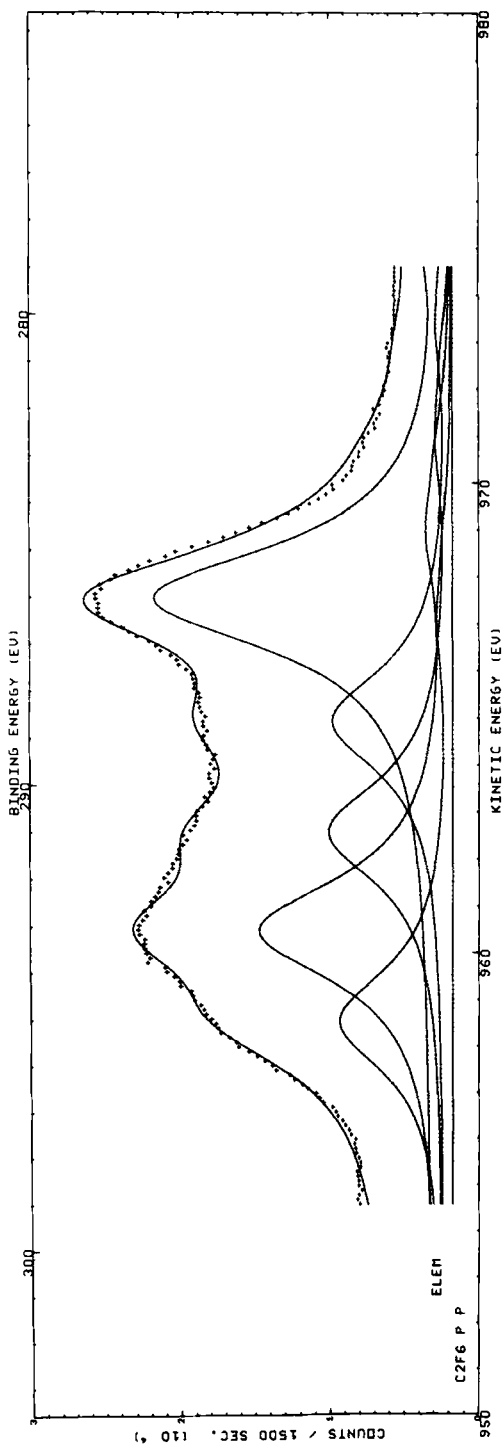
## RESULTS AND DISCUSSION

The plasma parameters employed for the polymerization of the fluorocarbon monomers on polypropylene, polystyrene, and wool fabric are given in Table 1. Typical properties common to plasma-polymerized films have been discussed extensively in a recent review [1]. Previous studies on the deposition of fluorocarbon films in the plasma system employed indicated that deposition rates between 250 and 450 Å/min are typical for the plasma polymerization conditions employed in this work [2]. Films from hexafluoroethane and tetrafluoroethylene were first deposited on polypropylene and polystyrene surfaces. These plastic substrate surfaces were fairly uniform, and the films deposited on them were used to test the ability of the curve fitting procedure to deconvolute the data.

### ELECTRON SPECTRA FROM FLUOROCARBON FILMS ON POLYPROPYLENE AND POLYSTYRENE

#### Carbon 1s Electron Spectra

Typical carbon 1s electron spectra obtained from plasma-polymerized hexafluoroethane and tetrafluoroethylene on polymer substrate are presented in Figs. 1a and 2a. The data calculated



(a)

FIG. 1a. XPS spectra from plasma-polymerized hexafluoroethylene films. Carbon 1s spectrum from film deposited on polyethylene.

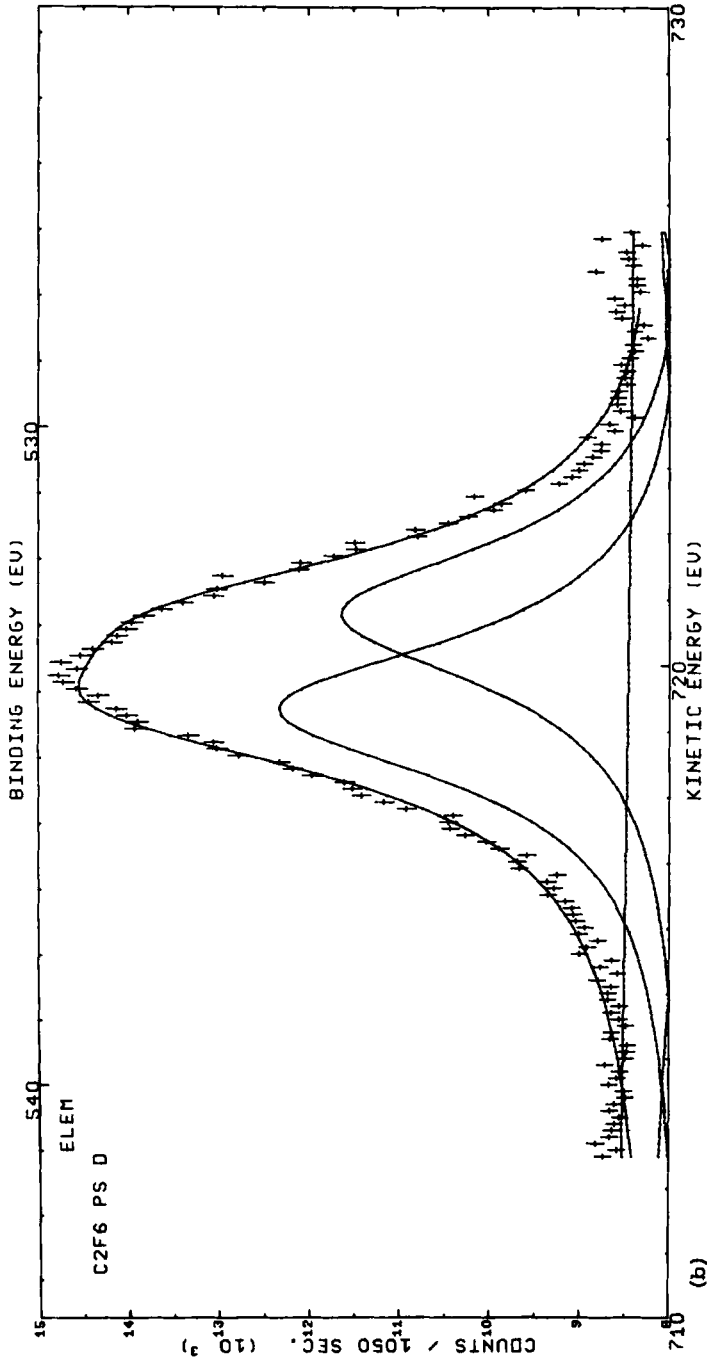


FIG. 1b. XPS spectra from plasma-polymerized hexafluoroethylene films. Oxygen 1s spectrum from film deposited on polystyrene.

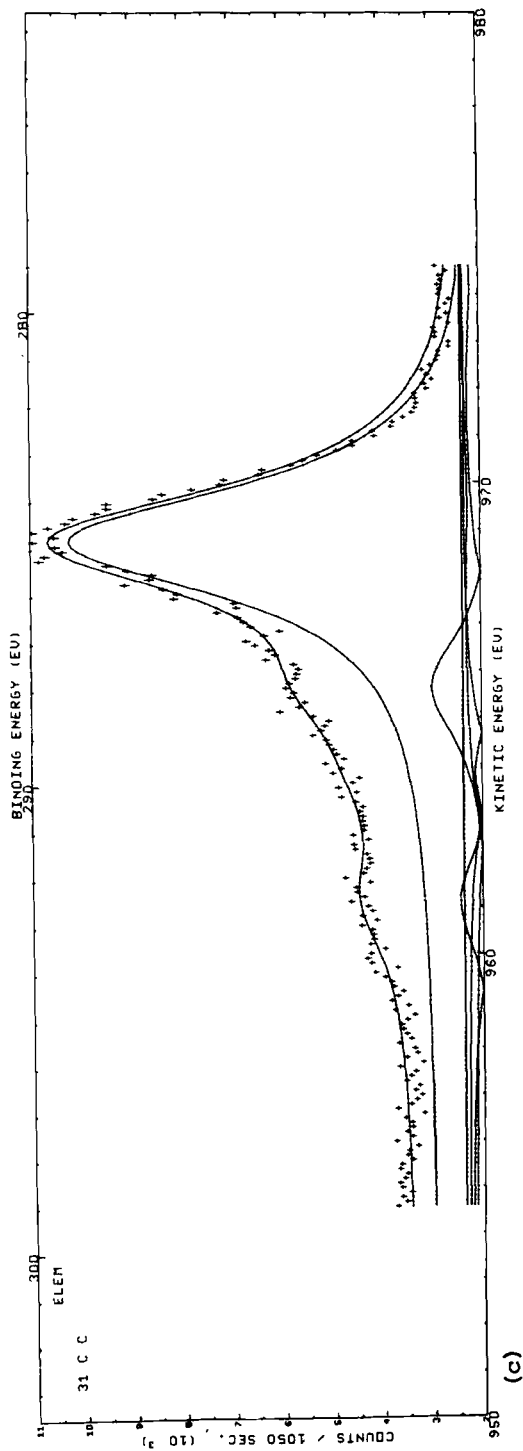


FIG. 1c. XPS spectra from plasma-polymerized hexafluoroethylene films. Carbon 1s spectrum from film deposited on wool fiber (sample 31C).



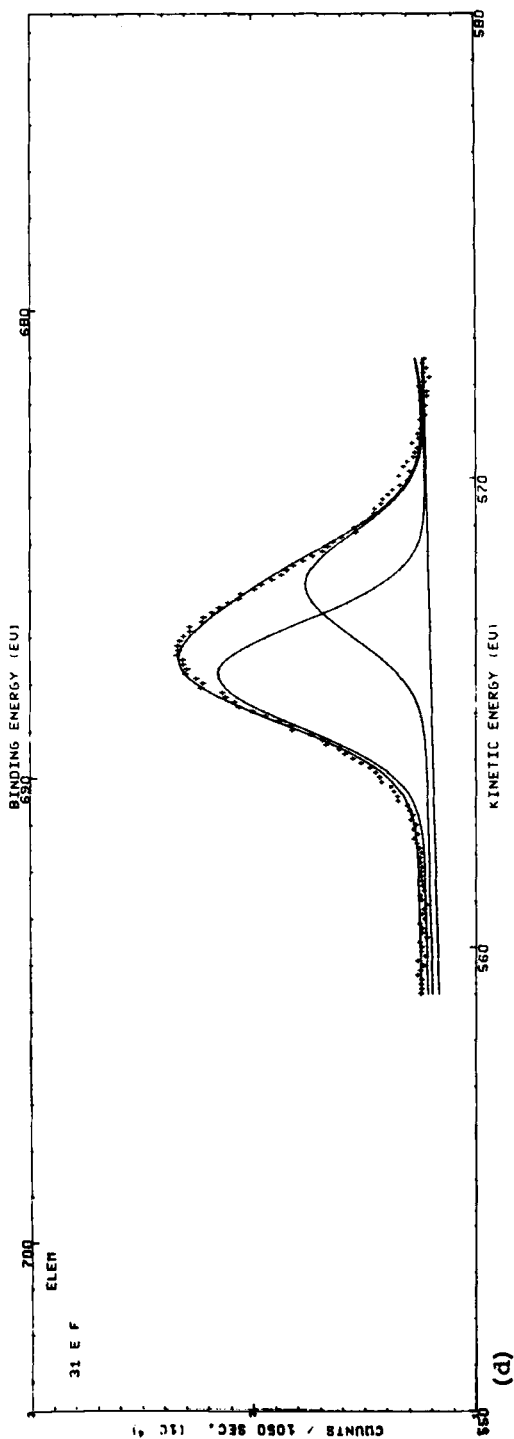


FIG. 1d. XPS spectra from plasma-polymerized hexafluoroethylene films. Fluorine 1s spectrum from film deposited on wool fiber (sample 31E).

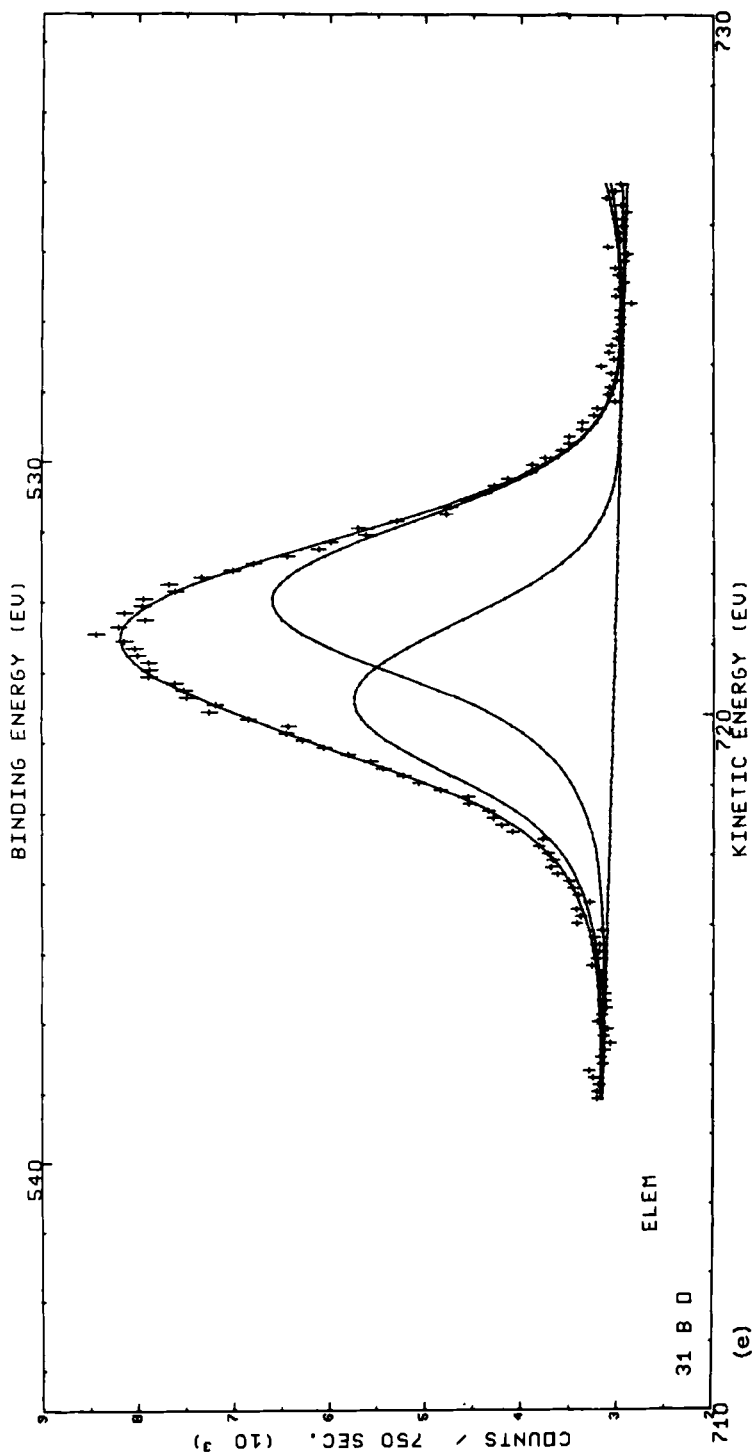


FIG. 1e. XPS spectra from plasma-polymerized hexafluoroethylene films. Oxygen 1s spectrum from film deposited on wool fiber (sample 31B).

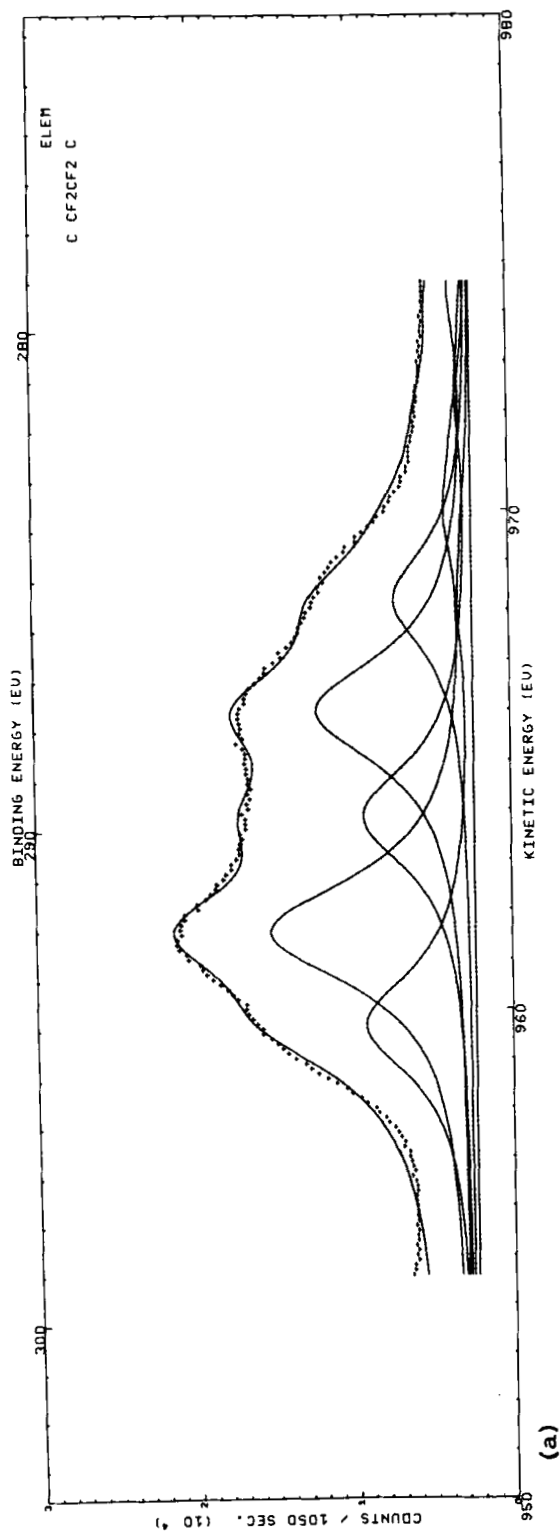


FIG. 2a. XPS spectra from plasma-polymerized tetrafluoroethylene films. Carbon 1s spectrum from film deposited on polypropylene.

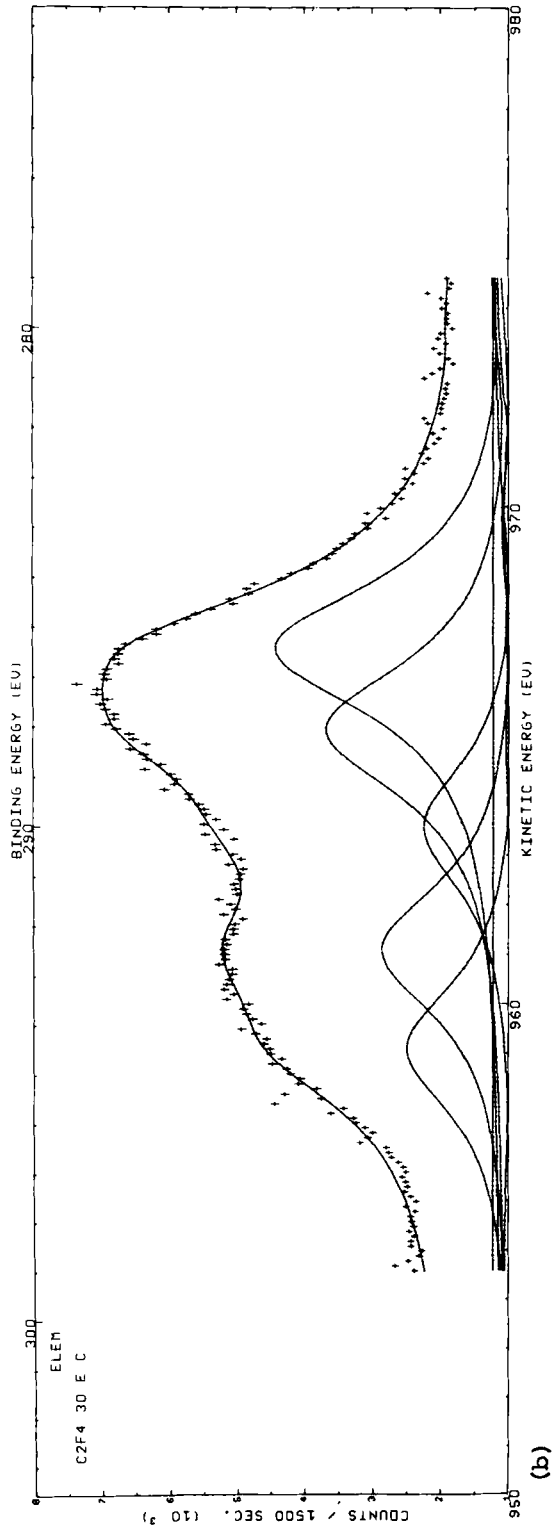


FIG. 2b. XPS spectra from plasma-polymerized tetrafluoroethylene films. Carbon 1s spectrum from film deposited on wool fiber (sample 30E).

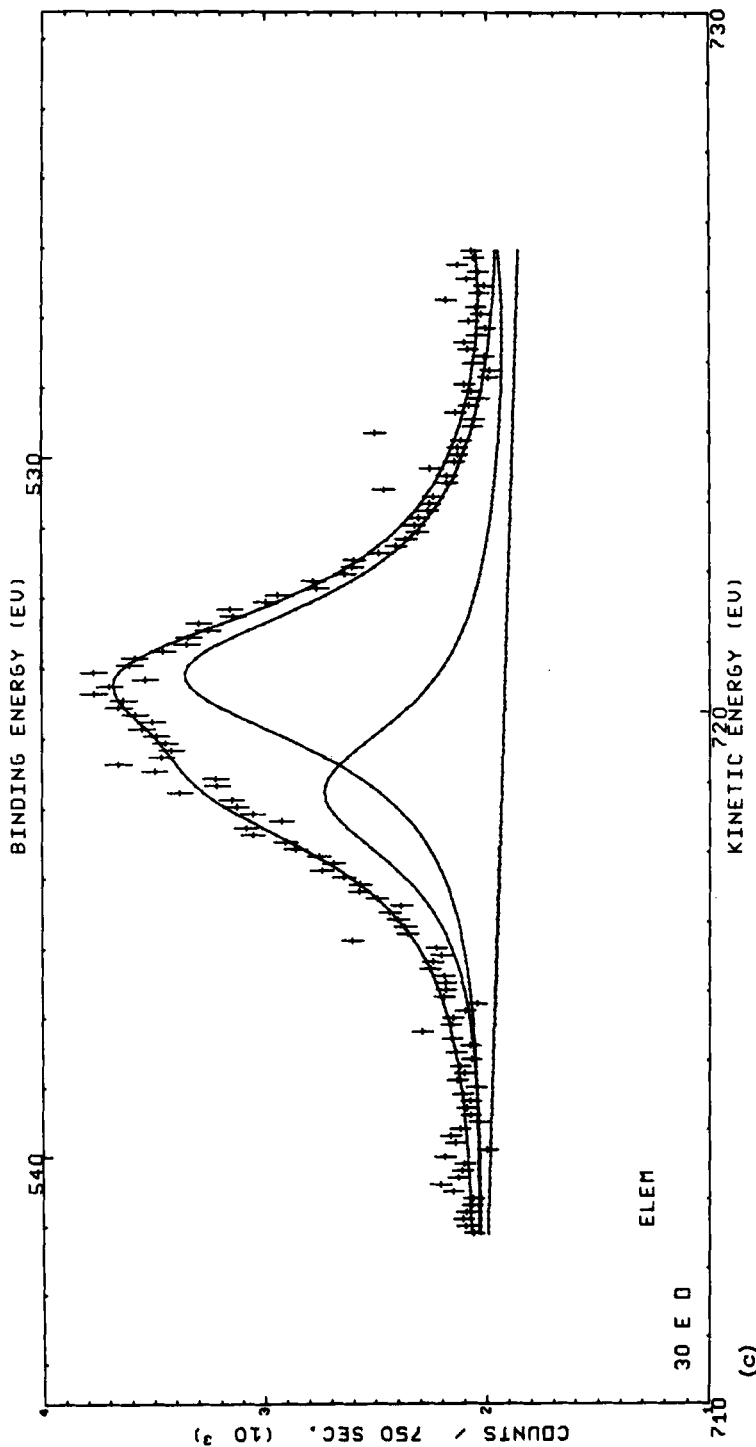


FIG. 2c. XPS spectra from plasma-polymerized tetrafluoroethylene films. Oxygen 1s spectrum from film deposited on wool fiber (sample 30E).

from the spectra such as line position, half width, and relative intensities are given in Table 2. The spectra were fitted using five lines. The rationale for a five-line model is the following. The binding energies of carbon in fluorocarbon polymers containing  $\text{CF}_3$ ,  $\text{CF}_2\text{R}$ , and  $\text{CFR}_2$  groups, where R is hydrogen or alkyl, have been reported. The carbon 1s binding energy in the  $\text{CF}_3$  group is around 294 eV and the  $\text{CF}_2$  carbon is 292 in tetrafluoroethylene [5]. Polymers containing  $\text{CFR}_2$  groups yield binding energies between 289.4 and 290.9 eV depending on the electronegativity of the R group [5, 11]. The line at lowest binding energy is assumed to arise from aliphatic carbon and is used as a reference at 285.0. There are several functional groups containing carbon that give rise to binding energies between 285 and 290 eV. Carbon containing a single bond to oxygen, such as alcohols or ethers, occurs around 286.5 to 286.8 eV [12]. Carbon in ketones is around 288.1 eV, while carbonyl carbon in acids or esters occurs around 289.5 [12]. The binding energy of carbon is shifted to higher energies when fluorocarbon groups are attached and carbon adjacent to carbon bonded to fluorine occurs in this range [5].

The spectra were fitted with a fifth line whose position ranged between 287.2 and 287.8 eV. There is little doubt that the carbon electron lines in the region of 294 and 292 eV are due to  $\text{CF}_3$  and  $\text{CF}_2\text{R}$  carbons. The carbon electron line around 290 eV is probably a combination of lines arising from carbonyl carbon and carbon containing one fluorine. The line in the region of 287.5 eV is probably a composite of lines due to carbon singly bonded to oxygen and carbon attached to carbon bonded to fluorine atoms. The position of the two lines above 285.0 eV are probably least certain; however, a reasonably consistent fit of the spectra was obtained. Line widths ranged from 2.43 to 2.69 eV for the fluorocarbon films deposited onto polymer substrates.

### Oxygen 1s Electron Spectra

Polymers formed in plasmas are readily oxidized on the surface after exposure of the film to the atmosphere [1]. We have previously reported that fluorocarbon polymers obtained by plasma polymerization of perfluorobutene-2 contain a high concentration of unpaired spins, and these radicals probably react with oxygen yielding oxygen-containing species on the surface [2]. The assignment of carbon electron lines in the region between 286 and 290 eV to carbon functional groups containing oxygen is also supported by the detection of oxygen on the surface of these films.

An example of the oxygen 1s electron spectra obtained from the fluorocarbon films on polymer substrate is given in Fig. 1b.

Oxygen 1s electron line parameters obtained from the spectra are presented in Table 2. The oxygen 1s electron line spectra were deconvoluted into two lines for all spectra other than the spectra obtained from tetrafluoroethylene films on polymer substrate. The oxygen 1s electron spectra consisted of two lines at 532.0 and 533.4 eV for  $C_2F_4$  polymer on polystyrene and 532.4 and 534.5 eV for  $C_2F_6$  polymer on polypropylene. The oxygen 1s electron binding energy in most organic functional groups occurs around 532 eV [13]. This includes oxygen in alcohols, ethers, ketones, and carboxylic acids. The oxygen 1s line at higher binding energy is above that observed for most organic compounds. The oxygen 1s line at higher binding energies was only observed on films containing fluorine. We suggest that the higher binding energy oxygen 1s line arises when oxygen is bonded to carbon atoms containing fluorine such as  $CF_3-O-CF_2-$ . The electron-withdrawing fluorocarbon groups could increase the binding energy of the oxygen atom.

### Fluorine 1s Electron Spectra

The fluorine 1s electron line appeared to be symmetrical for the fluorocarbon films on polypropylene and polystyrene. The fluorine 1s electron line from fluorocarbon films polymerized from hexafluoroethane had a width of 2.75 eV. The width of the fluorine lines obtained from films from polymerized tetrafluoroethylene ranged in width from 3.0 to 3.3 eV. In general, the fluorine electron line was quite intense from these films and ranged in intensity from 96 to 160 thousand counts per second.

## ELECTRON SPECTRA FROM FLUOROCARBON FILMS ON WOOL TEXTILE

### Carbon 1s Electron Spectra

Using plasma polymerization conditions similar to those employed to polymerize films on polymer substrate, the fluorocarbon film thickness and density of coverage were much lower when the substrate was wool textile. The low level of fluorocarbon film coverage was indicated by much lower fluorine electron line intensities and weaker carbon electron lines at higher binding energies. The carbon electron lines were shifted about 1 eV lower than measured on fluorocarbon films on polymer substrate. The binding energy of carbon bonded to fluorine not adjacent to other fluorocarbon groups is lower than when the adjacent carbon is also fluorinated. Clark et al. [5] have studied

TABLE 2. X-ray Photoelectron Spectral Data Obtained from Plasma-Polymerized Fluorocarbon Surfaces

Sample	C 1s Intensity		Carbon 1s B.E. eV (ratio)		FWHM (eV)	O 1s Intensity (counts/sec)		
	1000 (counts/sec)							
1. C <sub>2</sub> F <sub>6</sub> on polypropylene	8.0	285.0 (1)	287.6 (0.402)	290.0 (0.415)	292.1 (0.648)	294.0 (0.380)	2.69	2,373
2. C <sub>2</sub> F <sub>6</sub> on polystyrene	7.82	285.0 (1)	287.6 (0.426)	289.8 (0.336)	292.1 (0.508)	294.1 (0.316)	2.72	3,730
3. C <sub>2</sub> F <sub>6</sub> on wool 31C	4.779	285.0 (1)	286.0 (0.37)	288.3 (0.22)	290.1 (0.105)	292.9 (0.124)	2.26	7,230
4. C <sub>2</sub> F <sub>6</sub> on wool 31B	4.124	285.0 (1)	286.4 (2.5)	287.7 (0.0008)	289.0 (0.505)	290.4 (0.0008)	1.7	4,467
5. C <sub>2</sub> F <sub>6</sub> on wool 31E		285.0 (1)	285.9 (1.28)	287.7 (2.7)	289.7 (4.7)	291.7 (0.00005)	2.12	
6. C <sub>2</sub> F <sub>4</sub> on polypropylene with argon, C	18.231	285.0 (1)	287.2 (2.2)	289.3 (1.42)	291.6 (2.62)	293.5 (1.41)	2.66	4,905
7. C <sub>2</sub> F <sub>4</sub> polypropylene no argon, D	14.7	285.0 (1)	287.8 (0.58)	289.8 (0.37)	292.3 (0.61)	294.3 (0.43)	2.43	6,450
8. C <sub>2</sub> F <sub>4</sub> on wool 30B	2.06	285.0 (1)	286.8 (0.85)	289.7 (0.40)	291.0 (0.6)	292.9 (0.6)	3.19	1,580
9. C <sub>2</sub> F <sub>4</sub> on wool 30E	2.21	285.0 (1)	286.6 (0.8)	288.6 (0.40)	291.1 (0.57)	293.1 (0.46)	3.27	1,432

(continued)



TABLE 2 (Continued)

Sample	O 1s B.E. eV (ratio)	FWHM (eV)	Total intensity (counts/sec)	Corrected intensity (counts/sec)	F 1s intensity/ $10^3$ (counts/sec)	F 1s B.E. eV (ratio)	FWHM (eV)	Surface atom ratio
1	532.4 (1)	534.5 (0.54)	3,660	7,000	116.5	689.2	2.8	16.6 F/O
2	532.0 (1)	533.4 (1.2)	6,830	13,600	96.3	689.3	2.67	7 F/O
3					27.2	686.5 (1) (3.9)	2.6	2 F/O
4	532.7 (1)	533.9 (0.62)	7,240	13,900	4.95	687.1 (1) (0.5)	2.6	0.35 F/O
5	532.6 (1)	534.2 (0.4)			3.40	687.1 (1) (1.7)	2.6	
6					160.0	688.8	3.3	
7					97.8	689.3	3.3	
8	532.4 (1)	534.2 (0.8)	2,820	5,420	24.1	688.3	3.3	4.45 F/O
9	531.6 (1)	533.3 (0.5)	2,219	4,270	22.6	687.7	3.0	5.3 F/O

carbon binding energies in fluorocarbon polymers. For example, the binding energy of  $\text{CF}_2$  carbon adjacent to  $\text{CH}_2$  is 290.8 eV while carbon in tetrafluoroethylene is 292.3 eV.

Table 2 contains the results of the deconvolution of three carbon 1s electron spectra from wool fiber exposed to a hexafluoroethane plasma. The intensity of the higher binding energy carbon lines as well as the fluorine electron line intensity varied considerably for these samples. Sample 31C, whose carbon spectrum is shown in Fig. 1c, had a higher fluorine 1s line intensity and contained more intense higher binding energy carbon lines. Electron spectra from samples 31B and 31E consisted of weak fluorine lines and low intensity higher binding energy carbon lines. The five lines from spectra 31C are interpreted as follows. In addition to the reference hydrocarbon line at 285 eV, the line at 286.0 eV could contain varying contributions from carbon containing single bonded oxygen or non-fluorine containing carbon adjacent to carbon substituted with fluorine. The next three higher binding energy lines arise from carbon atoms bonded to one, two, or three fluorine atoms not adjacent to other fluorine-containing carbon atoms. The carbon line at 288.3 eV could contain some contribution from carbon containing a double bond to oxygen. The deconvoluted spectrum from sample 31B contains a single higher binding energy carbon line at 289 eV in the binding energy region expected for carbon bonded to one fluorine atom. This sample probably consisted of randomly distributed carbon bonded to one fluorine atom. The carbon electron spectra from wool fiber exposed to a tetrafluoroethylene fluorocarbon plasma are interpreted in the same way as the carbon spectrum from sample 31C. The carbon electron spectrum from sample 31E is given in Fig. 2b.

### Oxygen Electron Spectra

Oxygen 1s lines measured on the wool textiles exposed to the fluorocarbon plasmas are given in Table 2, and typical spectra are shown in Figs. 1e and 2c. These lines are believed to arise from the same functional groups discussed in the previous section on the interpretation of the oxygen spectra obtained from the plasma-polymerized fluorocarbon films deposited on polymer substrate.

### Fluorine Electron Spectra

The fluorine 1s spectra obtained from the fluorocarbon-coated wool fibers are also included in Table 2. The fluorine 1s electron spectra obtained from plasma-polymerized hexafluoroethylene

polymer on the wool fiber substrate contained shoulders and the spectra were deconvoluted into two lines. The deconvoluted fluorine 1s spectrum from sample 31E is shown in Fig. 1d. The high binding energy 1s line around 689 eV is in the region reported for fluorine covalently bound to carbon [5, 10, 14]. The lower binding energy line around 687 eV is in the region reported for fluoride ion [14]. The fluorine electron lines measured on wool textile exposed to a tetrafluoroethylene plasma were somewhat broader than those obtained from the other fluorocarbon surfaces, but symmetrical in shape. These lines were not deconvoluted.

### Surface Composition from Electron Line Intensities

Some idea of the surface composition of the fluorocarbon films can be obtained from the intensities of the fluorine and oxygen 1s lines. The calculated fluorine to oxygen atom ratio for several plasma-polymerized fluorocarbon surfaces is given in Table 2. The electron line intensities were divided by Wagner's atomic line intensity correction factors [15]. This procedure usually yields atomic ratios to within 5% [6]. The fluorine to oxygen atom ratio on the surface ranged from 16.6 to 0.3, indicating considerable variation in the fluorocarbon character of the surface as well as the amount of surface oxidation.

### CONCLUSIONS

Combining the surface core electron line intensity data and the relative electron line positions, a fairly detailed picture of the surface resulting after exposure to fluorocarbon plasmas can be obtained. Plasma polymerization of hexafluoroethane and tetrafluoroethylene onto polymer substrate yielded fluorocarbon surfaces with the following characteristics. The fluorine electron lines were quite intense, and fairly intense high binding energy carbon electron lines associated with carbon bonded to fluorine were present. The carbon binding energies were similar to those obtained from fluorocarbon surfaces containing adjacent fluorinated carbon atoms. Carbon atoms containing one, two, and three fluorine atoms are present on the surface, indicating considerable monomer breakdown under the plasma conditions employed here. Oxygen was detected on the surface, providing further evidence for surface oxidation of plasma-polymerized films.

The surface of wool fibers exposed to these fluorocarbon plasmas was quite different. The fluorine electron lines were generally much less intense. The carbon electron lines in the

region of carbon bound to fluorine were shifted to lower binding energies, indicating that the fluorinated carbon atoms were not bonded to other carbon atoms containing fluorine. Carbon atoms containing fluorine are probably randomly distributed among nonfluorinated carbons. The extent of fluorocarbon film coverage was much less in this case.

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