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# **Effective Antireflection Coatings of Transparent Polymeric Materials by Gas-Phase Surface Fluorination**

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## Effective antireflection coatings of transparent polymeric materials by gas-phase surface fluorination

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### Abstract

There is a dramatic need in solar energy collection systems for lightweight, inexpensive polymeric materials that exhibit improved performance and durability. One approach to altering the properties of polymeric materials, surface fluorination, is appealing because of its potential for low cost. The literature indicates that such properties as permeability, wettability, bondability, thermal stability, weatherability, and optical transmittance can be improved by treating the surface with gaseous fluorine. A gas phase fluorination reactor system (GPFRS) was designed, built, and used. The initial emphasis was on improving optical transmittance by having an effective antireflection coating form on the surface of a wide variety of commercially available transparent polymeric films. These included such materials as polypropylene, acrylic, polyacrylonitrile, highly cross-linked polyethylene, polyester, polycarbonate and polymethylpentene. Two techniques were used to quantify the effect of exposing the surface of the polymers to gaseous fluorine. Transparent films were characterized before and after fluorine exposure by specular transmittance measurements. Surface analysis of selected treated and untreated samples was accomplished by x-ray photoelectron spectroscopy and depth profiling. Surface analysis confirmed the deposit of fluorine at the surface and into the bulk of all specimens examined after treatment in the GPFRS. Optical measurements revealed substantial improvement in specular transmittance following surface fluorination of almost all materials considered. Increases in solar weighted specular transmittance as high as 4.6% were measured.

### Introduction

Reports indicate that several properties of polymeric films can be altered by gas phase surface fluorination. These alterations can improve permeability, wettability, and barrier properties and potentially improve resistance to attack by moisture and atmospheric pollutants.<sup>1</sup> Decreased permeability and enhanced bondability can improve glazings for metallized reflector superstrates and protective substrates.<sup>2</sup> Thermal stability can be improved with potential application to inner glazings for flat-plate collectors or absorber materials.<sup>3</sup> Fluorocarbon polymers are known to have outstanding weatherability; it is plausible that surface fluorination can also improve the weatherability of glazings. Finally, fluorinated polymers have a low refractive index, and a fluorinated surface layer can result in an antireflective coating and improve optical transmissivity.<sup>4</sup> Because the optical properties of polymeric films are particularly important to many solar applications, primary emphasis of our initial work has been on antireflection coatings obtained by surface fluorination.

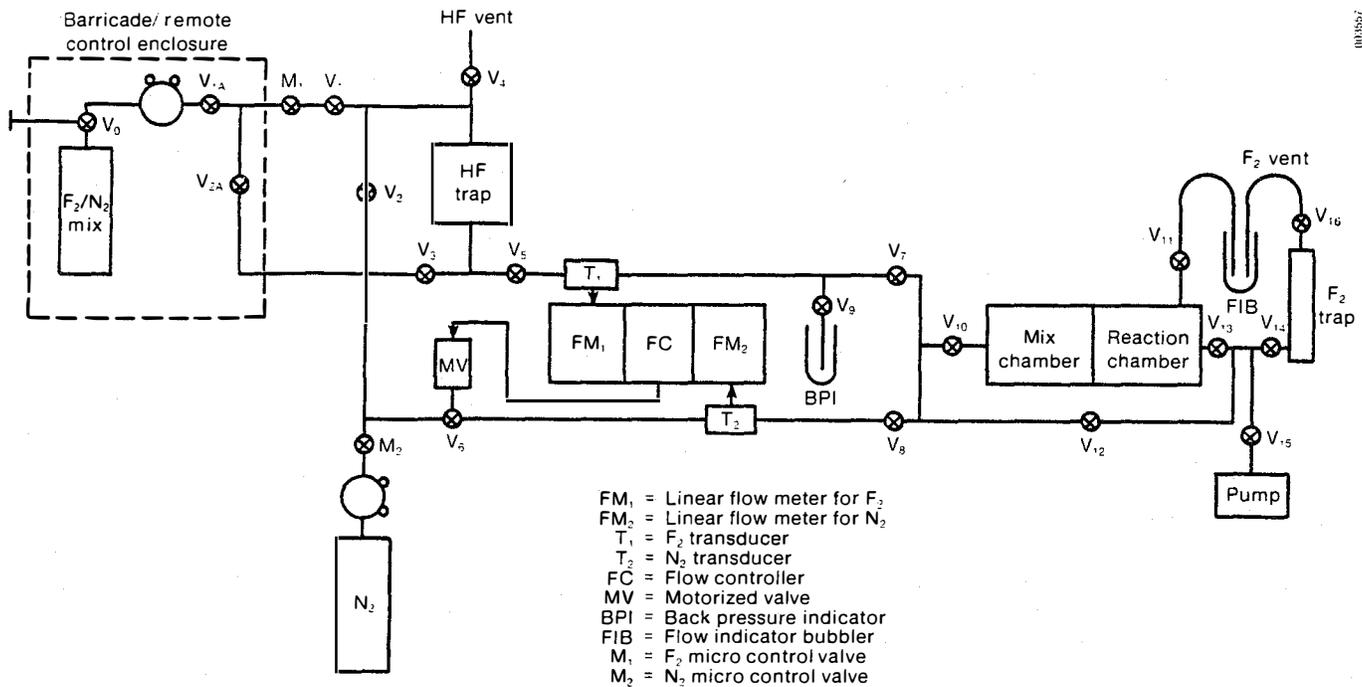
A gas phase fluorination reactor system (GPFRS) was constructed that allows the surface fluorination of a wide variety of commercially available, transparent, polymeric films. The goal is to provide a potentially inexpensive procedure for obtaining improved materials properties with initial emphasis on optical transmittance.

### The fluorination apparatus

The basic design of the GPFRS follows that of Lagow and Margrave.<sup>5</sup> A schematic layout of the present system is shown in Figure 1. Basically, the system includes a number of components specifically treated and designed to be compatible with the use of fluorine gas. A remote control barricade (Matheson Model 68-1009) encloses the fluorine gas cylinder (typically a 10%  $F_2$  mixture in a nitrogen background, available from Air Products) to allow safe shutdown in the event of leaks or uncontrolled reactions. As a further safety precaution, the barricade/ $F_2$  cylinder unit, along with the rest of the GPFRS, resides in a laboratory fume hood. Hydrogen fluoride and fluorine gas scrubbers are used to treat the effluent streams before they are discharged into the atmosphere. The former is a commercially available unit (Matheson Hydrogen Fluoride Trap Model 68-1008) using sodium bifluoride pellets ( $NaHF_2$ ) that when heated decompose into sodium fluoride ( $NaF$ ) with hydrogen fluoride ( $HF$ ) gas being carried off by a nitrogen purge. This results in a porous, highly absorbent form of a  $NaF$  that at room temperature will react with any  $HF$  impurity present in the  $F_2$  stream. The  $F_2$  trap consists of a stack of 3-14 mesh activated alumina (VWR #22894-139) housed in a 2-in.-diameter copper pipe 15 in. long. This material has been used elsewhere with much success in controlling the level of effluent  $F_2$ .<sup>6</sup> Using a MAST Series 724 oxidant detector that can measure fluorine levels to 0.01 ppm, no fluorine has been detected in the effluent from the  $F_2$  trap during normal operation. (Note that the recommended threshold limit value of  $F_2$  exposure is 1 ppm for 8 hours<sup>7</sup>).

A single cylinder of  $N_2$  allows gas to blend (to further dilute the  $F_2$  concentration) and purge the  $HF$  and  $F_2$  traps and the  $F_2$  line. Gas blending is regulated by a Teledyne Hastings-Raydist automatic flow control system. Two linear mass flowmeters and an automatic flow controller, coupled to a motorized control valve allow safe and accurate blending of the fluorine gas mixture with make-up nitrogen to obtain 1%-3% fluorine at 5 mL/min flow rates.

The mix and the reaction chambers are constructed of brass with Teflon seals. Fine copper turnings are packed into the mixing chamber to ensure uniform concentration of the  $F_2/N_2$  gas prior to introduction into the reaction chamber. Present reactor design allows up to six 2 x 2-in. film samples to be treated during a given exposure run. Details of the mix and reactor chamber design are given in Figure 2. Since  $F_2$  levels discharged through the  $F_2$  trap and vent are extremely small, the reaction chamber can be vented through valve  $V_{11}$ . This allows us to detect  $F_2$  entering the reaction chamber so we can accurately monitor sample exposure times.



Note: V<sub>0</sub> is a "T" handle to the chuck key on the F<sub>2</sub> cylinder stem. This is the prime emergency shut-down valve.

Figure 1. Gas-Phase Fluorination Reactor System

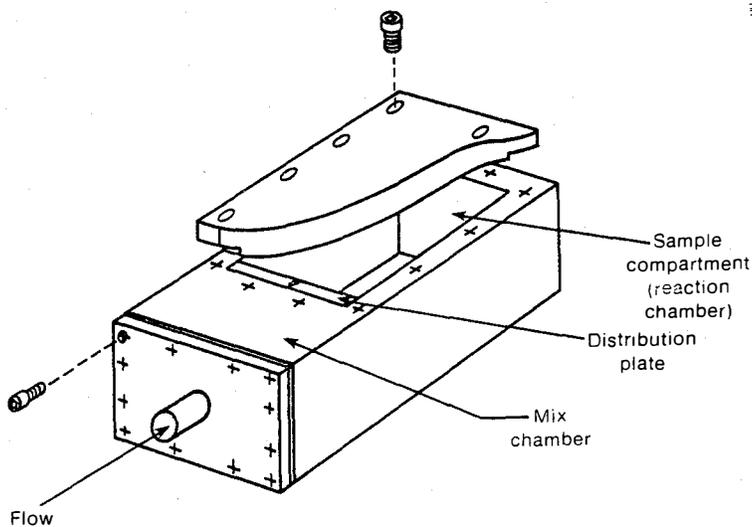


Figure 2. Fluorine Mix/Reaction Chamber

A fluorine-compatible pump station (Leybold-Heraeus D4AC) allows rapid and easy evacuation of the gas lines and reaction chamber. The F<sub>2</sub> trap can also be pumped. An oil filtration system (Leybold-Heraeus OF1000) removes F<sub>2</sub> from the oil through an aluminum oxide filter element.

The connecting gas lines are 1/4-in. copper tubing that has been appropriately passivated with F<sub>2</sub>. All valves (Matheson Model 4946) are designed specifically for use with F<sub>2</sub>. Valves M<sub>1</sub> and M<sub>2</sub> are micro-metering valves (NUPRO #SS-4BMG) that allow fine control of the F<sub>2</sub> and N<sub>2</sub> gas lines.

### Experimental

Successful fluorination of several organic materials has been reported in the literature. However, past work has not always been directed toward improved optical properties. Polymers fluorinated include polycarbonate, polymethyl methacrylate polystyrene,<sup>4</sup> polyethylene,<sup>1,2,8</sup> poly(vinyl fluoride),<sup>8</sup> polyesters and polyamides,<sup>9</sup> and polyacrylonitrile.<sup>10</sup> For purposes of evaluation, a wide variety of commercially available transparent polymeric films

were chosen for surface fluorination in the GPRFS. Samples and exposure conditions are listed in Table 1. Five exposure runs (designated I-V) were made with six specimens (1-6) included in each run. The sample numbers listed in Table 1 incorporate the run number (Roman numeral) and the specimen number (Arabic). The sample number also specifies the position of each specimen within the exposure chamber; specimens are numbered sequentially with one being the top and six being the bottom position.

Run I followed passivation of the GPRFS with a 3% F<sub>2</sub> (N<sub>2</sub> background) mixture. This level of F<sub>2</sub> was used for all subsequent exposure runs discussed in this report. To ensure surface fluorination of the poly(vinyl chloride) (PVC) films, a long exposure time (3.5 hours) was chosen for the initial experiment. A frosted coating was visible on the surface of all six specimens after the F<sub>2</sub> treatment. These coatings indicate an excessive exposure time and can be removed with dry cotton. All

subsequent experiments were conducted with shorter exposure times (one hour), and frosted (visual) coatings were not observed.

The second experiment involved polypropylene (PP) films in which sample exposure time was reduced to one hour. No surface fluorination was visible after treatment; however, optical measurements and surface analysis did demonstrate that the treatment was effective as discussed later.

In run III three materials were included: an acrylic (PMMA), polyacrylonitrile (PAN), and a highly cross-linked polyethylene (PE). The former material was chosen because of successful fluorination reported in the literature.<sup>4</sup> PAN and PE were selected since (like PVC and PP) they are inexpensive materials. A flow rate lower than previously used was tried in this run (5 rather than 10 ccm). Surface fluorination did not visually degrade any of these samples.

Three different polyester films were exposed in run IV. The fluorine flow rate was adjusted to 10 ccm. As with runs II and III, the treated films were visually indistinguishable from the untreated films.

The exposure conditions and visual results of run V were the same as runs II and IV. Exposed materials included another polyester, polycarbonate, and polymethylpentene.

Two techniques were used to quantify the effect of exposing the surfaces of transparent polymer films to gaseous fluorine. Films were optically characterized before and after fluorine exposure by specular transmittance (6° cone angle) measurements made on a Perkin-Elmer model 340 recording spectrometer. Spectra between 200 and 2600 nm were convolved with an air-mass of 1.5 solar spectrum to obtain solar-weighted transmittances. Surface analysis of selected treated and untreated samples was done using x-ray photoelectron spectroscopy (XPS), and depth profiling was done using a Leybold-Heraeus Model 10 surface analysis system.

**Table 1. Commercially Available Transparent Polymeric Films Treated by Surface Fluorination**

Sample No.	Material	Product Name	Supplier	Thickness (mils)	% F <sub>2</sub>	Flow Rate (ccm)	Time of Exposure (h)
I-1 to I-6	Poly(vinyl chloride)	CS-253 Natural	VCF Packaging Films Inc.	4	3	10	3.5
II-1 to II-6	Polypropylene	T503	Hercules Inc.	3.5	3	10	1
III-1 and III-6	Acrylic	Acrylar <sup>a</sup> X2417	3M Co.	3	3	5	1
III-2 and III-5	Polyacrylonitrile	Barex 210	Vistron Corp.	1	3	5	1
III-3 and III-4	Highly cross-linked polyethylene	RD101	Cryovac	1	3	5	1
IV-1 and IV-3	Polyester	Mylar <sup>a</sup>	DuPont	2.5	3	10	1
IV-2 and IV-5	Polyester	Llumar <sup>a</sup>	Martin Processing Inc.	1	3	10	1
IV-3 and IV-4	Polyester	Melinex <sup>a</sup> O72	ICS Americas	3	3	10	1
V-1 and V-6	Polyester	Hostaphan <sup>a</sup> 4500	American Hoechst Corp.	4	3	10	1
V-2 and V-5	Polycarbonate		Cadillac Plastics Inc.	2	3	10	1
V-3 and V-4	Polymethylpentene	TPX	Westlake Plastics	3	3	10	1

<sup>a</sup>Registered trademark

#### Optical characterization

Solar-weighted specular transmittances of the various transparent films subjected to surface fluorination are presented in Table 2. Values are listed for before and after F<sub>2</sub> exposure, as well as the change in transmittance upon treatment (after minus before). The dramatic loss in optical transmittance by PVC shown in Table 2 agrees with the visual result mentioned earlier; a frosted coating is on the surface of these films during exposure in the GPFRS. The solar-weighted specular transmittance of specimen I-1 after surface fluorination and cleaning with cotton was 38.0% compared to 88.9% prior to the F<sub>2</sub> treatment.

Polypropylene specimens (run II) were the first to give a positive indication of improved optical properties following exposure to fluorine. An average increase in specular transmittance of 2.3% is noted for the six PP specimens.

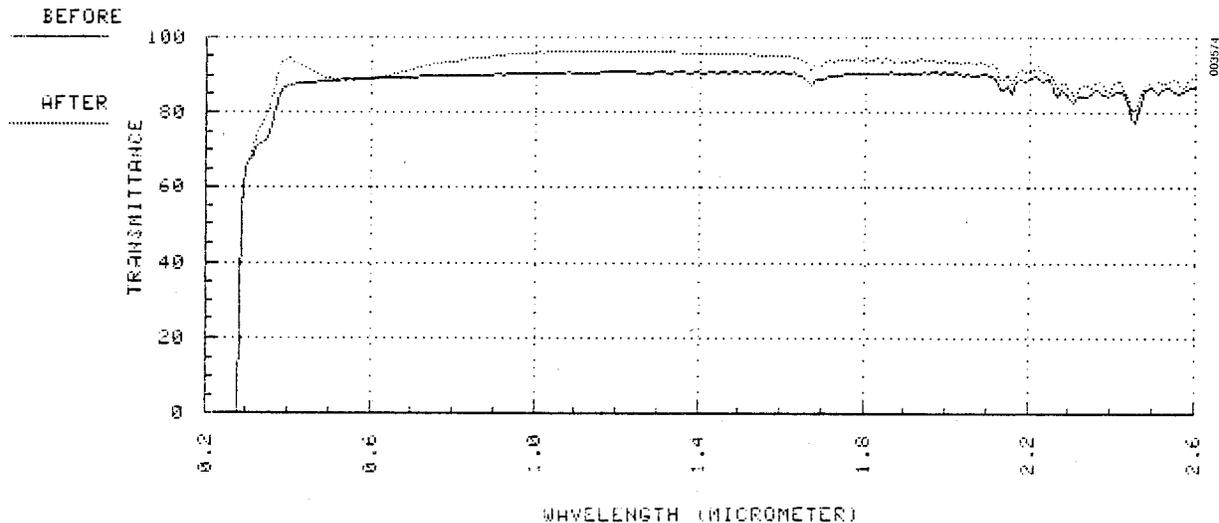
**Table 2. Solar-Weighted Specular Transmittance Measurements Before and After Surface Fluorination**

Run No.	Material	Solar-Weighted Specular Transmittance		
		Before F <sub>2</sub>	After F <sub>2</sub>	(After - Before)
I	Poly(vinyl chloride)	89.9 ± 0.2	20.1 ± 5.0	-69.8 ± 5.0
II	Polypropylene	86.8 ± 0.4	89.1 ± 0.4	2.3 ± 0.6
III	Acrylic	88.6 ± 0.03	89.0 ± 0.1	0.4 ± 0.1
III	Polyacrylonitrile	86.9 ± 0.3	87.7 ± 1.0	0.8 ± 1.0
III	Highly cross-linked polyethylene	90.2 ± 0.3	90.3 ± 0.5	0.1 ± 0.6
IV	Mylar polyester	87.0 ± 0.3	90.8 ± 0.2	3.8 ± 0.4
IV	Llumar polyester	84.3 ± 0.1	88.3 ± 0.01	4.0 ± 0.1
IV	Melinex polyester	87.1 ± 0.1	91.2 ± 0.1	4.1 ± 0.1
V	Hostaphan polyester	87.0 ± 0.1	91.6 ± 0.4	4.6 ± 0.4
V	Polycarbonate	89.1 ± 0.2	92.6 ± 0.1	3.5 ± 0.2
V	Polymethylpentene	88.0 ± 0.2	89.4 ± 0.2	1.4 ± 0.3

None of the materials exposed in the GPFRS during run III show an enhanced solar-weighted specular transmittance following surface fluorination. The only difference in exposure conditions between this run and run II is a decrease in the flow rate (5 instead of 10 cc). It is not believed that this parameter should critically control the extent of surface fluorination, although this effect should be studied systematically in future work.

All three commercially available polyester films selected for run IV showed dramatic increases in specular transmittance after F<sub>2</sub> exposure. Improvements ranged from 3.8% for Mylar to 4.0% for Llumar and 4.1% for Melinex.

A fourth polyester, Hostaphan, was included in run V along with polycarbonate (Figure 3a) and polymethylpentene films. Hostaphan exhibited the largest increase (4.6%) in specular transmittance of the 11 materials studied (Figure 3b). In general, polyester has proven to be the most promising transparent polymeric material on the basis of optical characterization. This is of particular interest because polyester can have excellent optical and mechanical properties even before fluorination. It will be important to determine how durability of the properties is affected by F<sub>2</sub> treatment.

**Figure 3a. Spectral Specular Transmittance Before vs. After F<sub>2</sub> for Polycarbonate (Sample V-2)**

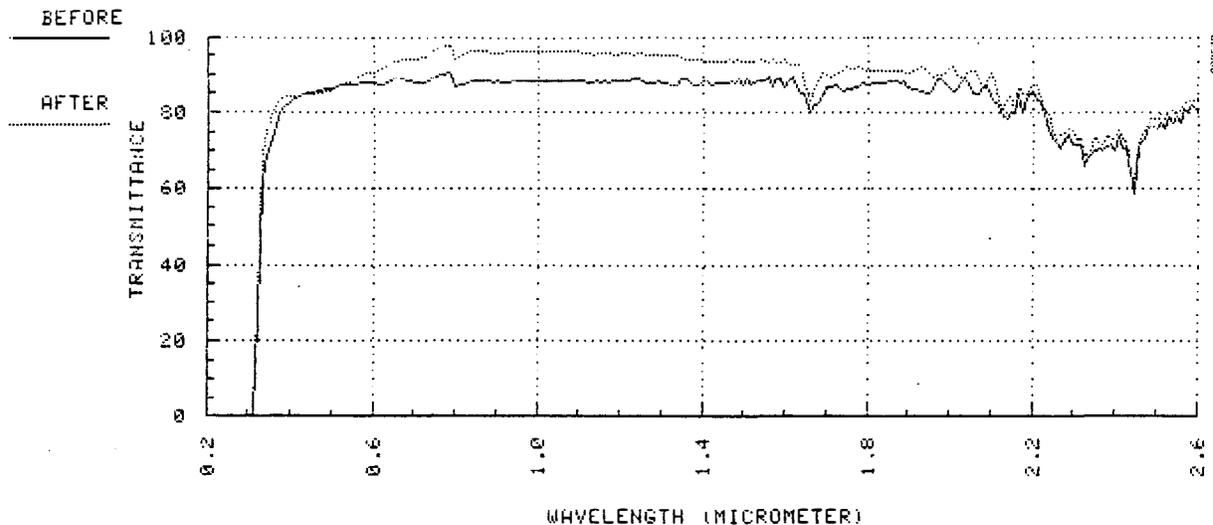


Figure 3b. Spectral Specular Transmittance Before vs. After  $F_2$  for Hostaphan Polyester (Sample V-1)

The polycarbonate film also showed a substantial rise in specular transmittance after surface fluorination (3.5%). The resulting solar-weighted transmittance of 92.6% was the largest absolute value obtained in these experiments. Polymethyl-pentene experienced a modest increase in specular transmittance (1.4%).

#### Surface analysis

PVC and PP samples were analyzed by x-ray photoelectron spectroscopy (XPS), to determine the extent of surface fluorination. Depth profiles were provided by successive 1-min argon ion etchings. Fluorine was found both at the surface and in the bulk of both fluorinated samples. Wiping the PVC sample I-1 with cotton removed all fluorine from the surface, but fluorine did persist in the bulk. Fluorine concentration as a function of depth was not readily available because of difficulties inherent in calibrating probes of polymeric materials. Substantial amounts of oxygen were evident at the surface and well into the bulk of all four specimens. The presence of oxygen, particularly in the case of PP, may be due to surface treatment during processing of the commercial film to promote adhesion.

Figure 4 shows the XPS depth profile of untreated poly(vinyl chloride) for no-etch, 1-min, and 4-min etch intervals. The carbon peak at 970 eV and the chlorine peak at 1052 eV are clearly evident. Auger and XPS oxygen peaks (at 510 and 722 eV, respectively) indicate a decreasing concentration of oxygen as a function of depth. Silicon was found as a surface contaminant (peaks at 1100 and 1154 eV of the unetched and 1-min etch profiles); the gold (1169 eV) and Auger copper (840 and 920 eV) signals were due to impurities present on the sample holder. Negative spikes were attributable to spurious power surges experienced during the XPS scans.

A small amount of fluorine was detected at the surface of the cotton-wiped fluorinated PVC specimen (568 eV of the no-etch trace in Figure 5). Fluorine was clearly evident in the bulk of this film, as the peaks at 568 and 650 eV indicate on the 1-min and 4-min etch profiles.

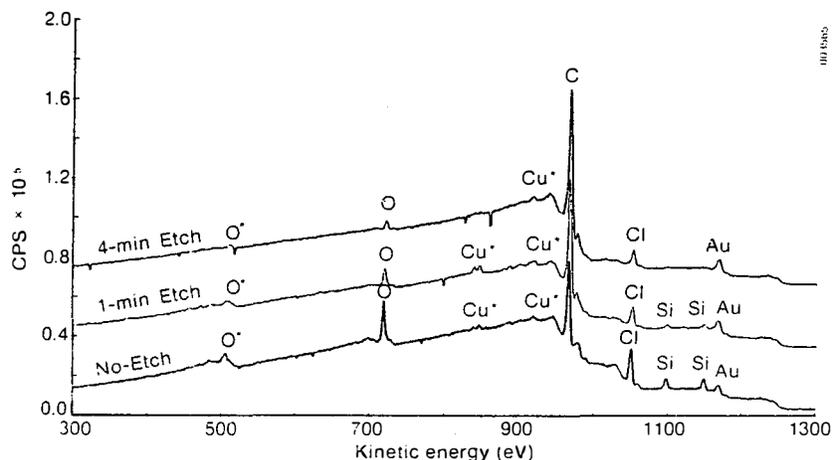


Figure 4. XPS Depth Profile of Untreated Polyvinyl Chloride

Stronger fluorine signals were found for the fluorinated polypropylene sample (Figure 6). XPS peaks at 568 and 1223 eV and Auger peaks at 605, 625, and 650 eV are readily apparent both at the surface and in the bulk. Argon implanted by the etching process was also detected at 1008 eV. The initial slopes of the XPS profiles (300-500 eV) indicate that the surface (no-etch trace) exhibits less scattering than the bulk material (1-min and 4-min etch traces). Charging of the surface caused by the argon ion etch resulted in a shift of the kinetic energy scales in (Figure 6); this is why the peaks are slightly displaced relative to one another as a function of depth.

Surface analysis was also performed on the acrylic, Lumar polyester, and polycarbonate samples (III-6, IV-2, and V-5, respectively). Fluorine was found on the surface of all three specimens.<sup>11</sup>

### Conclusions

Surface fluorination of polymeric films can alter their properties. Efforts to date have focused on verifying the presence of  $F_2$  at the surface and in the bulk of films treated by the GPFRS and on demonstrating enhanced optical properties following such treatment. The former has been shown by XPS surface analysis and depth profiling. Specular transmittance measurements before and after surface fluorination have revealed the presence of effective antireflection coatings on a large number of materials studied.

Current analysis has concentrated on investigating a wide variety of commercially available films with very little variation in the GPFRS processing variables. Future efforts should center on a promising material and the effect of changing such parameters as exposure time and concentration of fluorine gas.

Other important properties needing investigation include mechanical behavior (perhaps as a function of temperature) and permeability to various vapors and pollutants. Finally, all physical properties resulting from  $F_2$  treatment should be monitored as a function of weatherability.

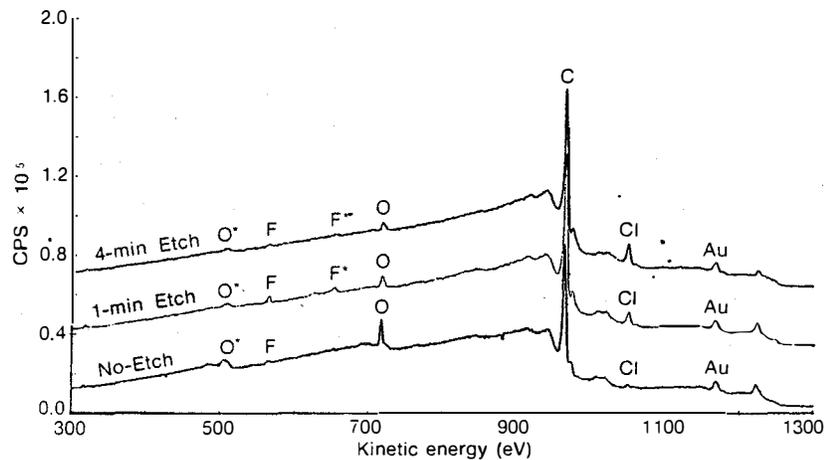


Figure 5. XPS Depth Profile of Cotton-Wiped Surface Fluorinated Polyvinyl Chloride (Sample I-1)

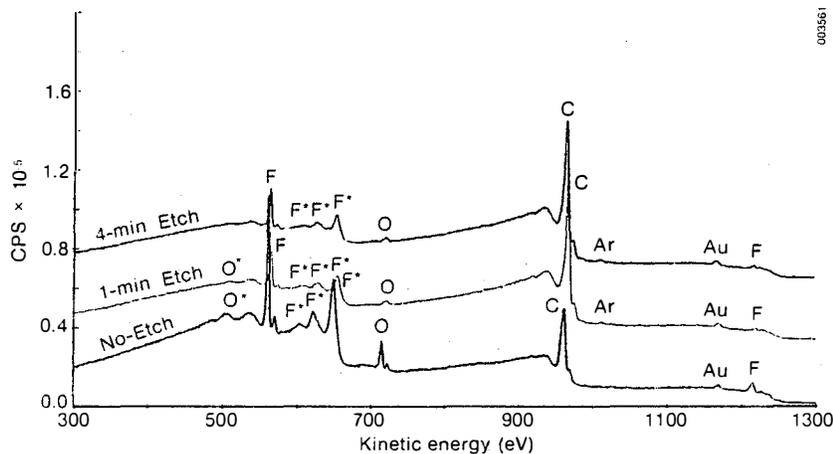


Figure 6. XPS Depth Profile of Surface Fluorinated Polypropylene (Sample II-2)

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