Silicon Contamination of Substrates in Fluorocarbon Plasmas Produced in Glass Reactors

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SYNOPSIS

Extensive research has been carried out in recent years using fluorocarbon plasmas for modification and depositions on polymer substrates. In some cases anomalous results have been obtained that are not explainable based on conventional fluorine chemistry. In this investigation pure polypropylene films were exposed to carbon tetrafluoride plasmas in a Pyrex glass reactor. At short reaction times (less than 1 min) significant amount of silicon was detected by ESCA on the surface of the films. Analysis of liquid nitrogen trapped fluorocarbon plasma gases and molecular fragments indicated high concentrations of silicon and carbon containing species, the former indicative of ablation and etching reactions of the glass reactor walls. The production of a relatively high quantity of fluorosilicon derivatives was explained by the greater affinity of silicon for fluorine than for carbon, with the tendency to readily form SiF_4. These fluorosilicon radical and ionic species generated under cold plasma conditions can easily react with polymeric substrates causing unexpected surface modifications. In addition Si–F bonds could be readily hydrolyzed to SiOH islands on the surface of the substrate to impart anomalous characteristics. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Modification of the surface properties of synthetic and natural polymers has become important in various industrial, biomedical, and other technological applications. Cold plasma techniques are some of the most efficient methods for surface modification and grafting of materials, and they affect such properties as wettability, adhesion, friction, and electrical and optical conductivity.[1-5]

Nonequilibrium plasma treatments applied in the field of polymer chemistry can be categorized into two major types of processes: (1) Surface modification of polymers by non-polymer-forming discharges such as inert gas plasmas (i.e., argon, helium etc.) and active gas plasmas (i.e., oxygen, ammonia, fluorine, etc.) and (2) polymerization–deposition and graft polymerization of conventional monomers (i.e., methyl methacrylate, acrylonitrile, etc.) and unconventional monomers (including practically all low-molecular-weight organic and organometallic derivatives).

In plasma polymerization, molecules of the starting materials are fragmented, activated, and recombined randomly into polymeric structures and deposited and/or grafted as thin films on substrate surfaces. The polymer formation mechanisms are different from conventional polymerization reactions. Because of the intense fragmentation (dehydrogenation, decarboxylation, deamination, etc.), the plasma-formed polymers are branched and crosslinked in nature, and the resultant macromolecules do not retain the structural identify of the starting materials.[1-10] Besides the recombination of plasma-generated molecular fragments on the substrate, free radical or ionic species located on the surfaces, which limit the plasma, can initiate competitive conventional polymerization processes, creating a mixture of various nature structures, making structural characterizations extremely difficult. The degree of branching and crosslinking depends mainly on the structure of the initial monomer and on the plasma parameters such as the power dissipated to the electrodes, the flow rate, and the

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pressure of the monomer in the reaction chamber, the chamber geometry, and the nature and temperature of the substrate. Exception from these mechanisms are found with a plasma-induced polymerization processes. In these cases active species (mono and poly-free radicals and ionic species) created by inert gas plasmas on a polymer or frozen monomer surfaces, initiate conventional post-polymerization reactions or graft polymerization processes in the presence of common monomers.

Etching processes can also result when plasma-generated active species initiate chemical reactions in the surface layers of the substrates and produce volatile reaction products. The competition between the polymer deposition and etching reactions control both the deposition rate and the structure of newly formed polymeric layers.

Although these phenomena have been recognized and characterized to some extent, less attention has been paid to the fact that the plasma interacts not only with the selected substrates but also with all of the surfaces that geometrically limit the plasma state, including the walls of the reactor. Atoms or molecular fragments released from these surfaces can create serious contamination problems for the desired polymeric layers. This is of particular importance for plasma reactions of fluorine and fluorinated organic compounds. These types of plasmas have been used extensively for surface functionalization, etching, polymer deposition, and graft polymerization of solid surfaces, particularly for natural and synthetic polymers. It has been shown that the plasma polymerization of fluorocarbons is always accompanied by an etching process and the concentration ratio of $[F]/[CF_x]$ in the discharge controls the competition between the etching and polymerization processes.[11-21] Fluorocarbons have also been used for etching substrates like Si or SiO_2[22,23] and glass reactor wall ablation has been noticed in such reactions.[24,25] However less data are available on reactor wall origin contamination of polymeric substrates or deposited polymeric layers during the fluorocarbon–plasma processes. The aim of this study is to demonstrate the presence of Pyrex glass reactor wall origin SiF_x species presence in a CF_4–RF plasma and their incorporation into the surface layers of a polypropylene (PP) substrate. The possible implications of such contamination are discussed.

EXPERIMENTAL

Materials and Methods

Commercially available CF_4 (Liquid Carbonic) was used without further purification. The Fortiline PP (Solvay Polymers) PP films (80 × 40 mm, high-purity film) were additive free and were used as received.

Analysis of the surface of the PP films was carried out using X-ray photoelectron spectroscopy (ESCA-Perkin Elmer Physical Electronics O 5400 Small Area System; Mg source; 15 kV, 300 W) at low and high resolution to obtain atomic percentages and to identify various fluorinated functional groups by means of chemical shifts in the C_{1s} spectra. The ESCA analysis involved the determination of carbon, silicon, fluorine, and oxygen. It should be noted that experimental techniques were not employed to eliminate charging effects, and consequently the C_{1s} peak from PP samples was shifted slightly on the binding energy scale. The binding energy values were established from the location of the C_{1s} peak from the untreated PP.

In order to collect the CF_4-plasma generated molecular fragments for analytical purposes, a specially designed stainless steel liquid nitrogen trap was constructed (Fig. 1). Valves [1] and [2] permitted the vacuum-tight isolation of volatile compounds trapped at low temperatures. A chromatography type septum, [3] assured precise sample collection for GC–MS measurements by means of a pressure tight

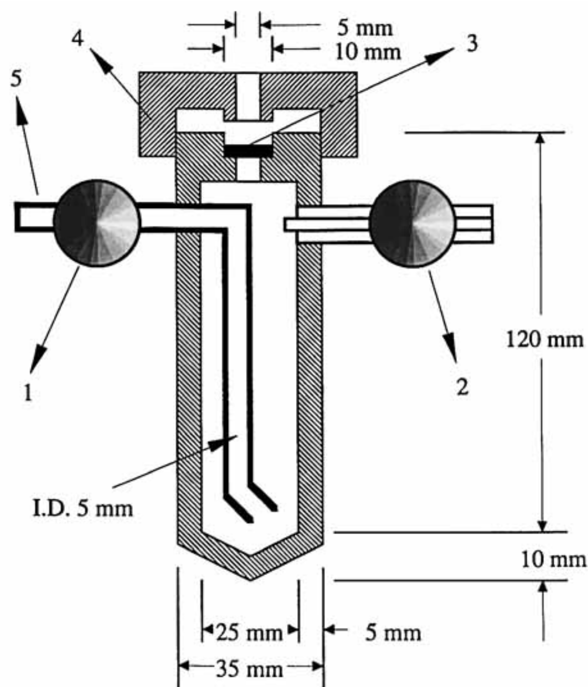


Figure 1 Schematic diagram of plasma reactor: (1) Ar container, (2) needle valve, (3) CF_4 container, (4) flexible Tygon connection, (5) stainless steel tubing, (6) coupling coil, (7) R.F. power supply, (8) Pyrex plasma reactor, (9) vacuum gauge, (10) septum, (11) stainless steel trap (liquid N_2), (12) vacuum pump.

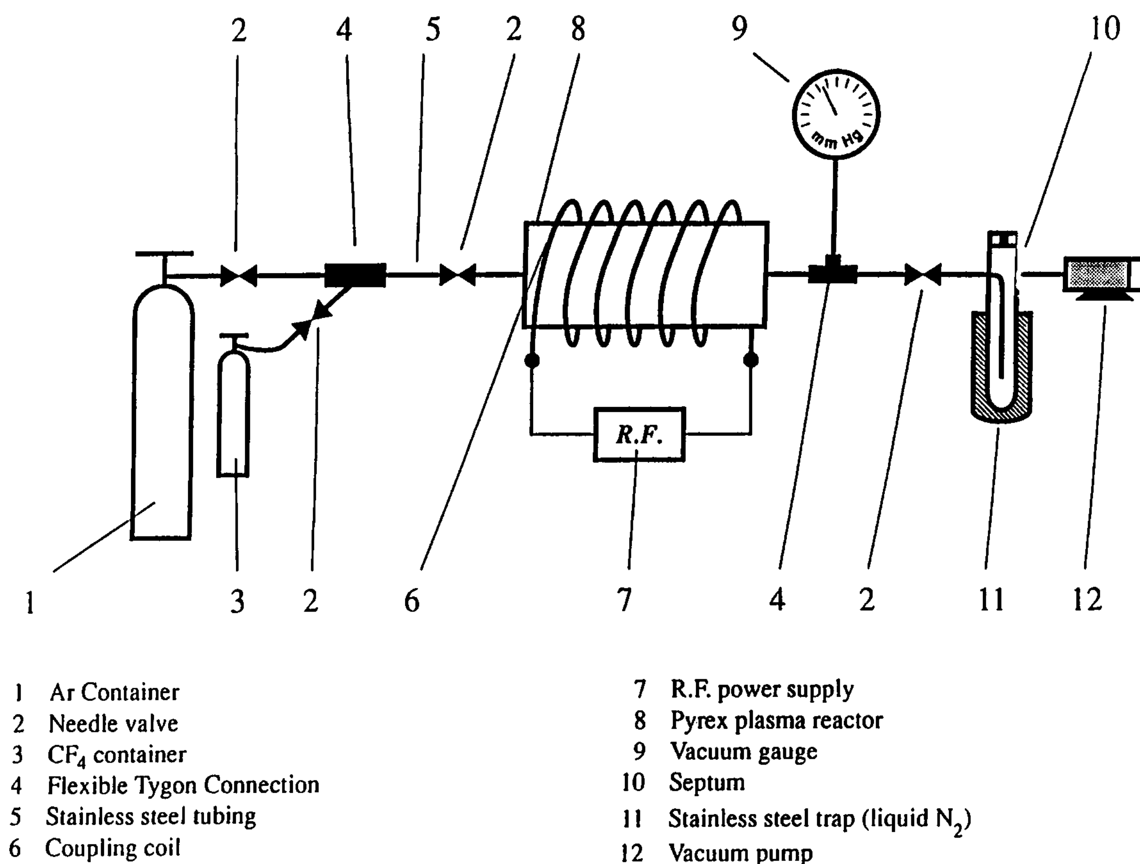
Hamilton gas syringe. The outer diameter (6 mm) of the connecting stainless steel tubing [5], matched the dimensions of the connection of the inlet line of the high-resolution MS and, in this way, provided a vacuum-proof connection to the trap.

The nature of the chemical compounds resulting from the recombination of plasma-generated active species and condensed in the liquid nitrogen trap was determined by using GS–MS (GC-Carlo Erba Fractovap 4162; MS-Kratos MS-25) and a high-resolution MS (Kratos MS-80), instrument. The following experimental conditions were used for GS–MS measurements: column-fused silica; length, 30 m, ID-0.32 mm; coating, 0.25 μm of 5% phenyl and 95% vinyl polysiloxane; injector-splitter temperature, 25°C; column temperature, 10-cm length of the column cooled for approximately 1 min by immersion in liquid nitrogen and the remainder was maintained at 25°C; electron energy, 23 eV. The high-resolution MS spectra were recorded by connecting the stainless steel trap directly to the spectrometer. The admission valve was opened after evacuating the connecting tubings. The Wiley Registry of Mass Spectral Data was used to assign structures to the experimental spectra.

Plasma Reactions

The apparatus used for CF_4 decomposition and surface fluorination of PP is shown in Figure 2. The plasma was generated by inductive coupling [6] in the tubular shaped (length 250 mm, diameter 80 mm) Pyrex glass reactor [8] to a radio frequency generator [7]. All of the connections between the argon and the CF_4 containers [1, 3] and the reaction vessel [8], gauge [9], and trap [11] were stainless steel tubing [5] and flexible Tygon connections, used only far outside of the plasma zone [4]. The only silicon-containing material present was the glass plasma reactor.

In a typical experiment a sample of PP film was placed symmetrically in the center of the reaction chamber and the chamber was evacuated to the base pressure and then vacuumed (base pressure) and repressurized (20 mmHg) several times with argon in order to remove possible gas contaminants. Car-



1 Ar Container
2 Needle valve
3 CF_4 container
4 Flexible Tygon Connection
5 Stainless steel tubing
6 Coupling coil
7 R.F. power supply
8 Pyrex plasma reactor
9 Vacuum gauge
10 Septum
11 Stainless steel trap (liquid N_2)
12 Vacuum pump

Figure 2 Diagram of plasma nitrogen cold trap.

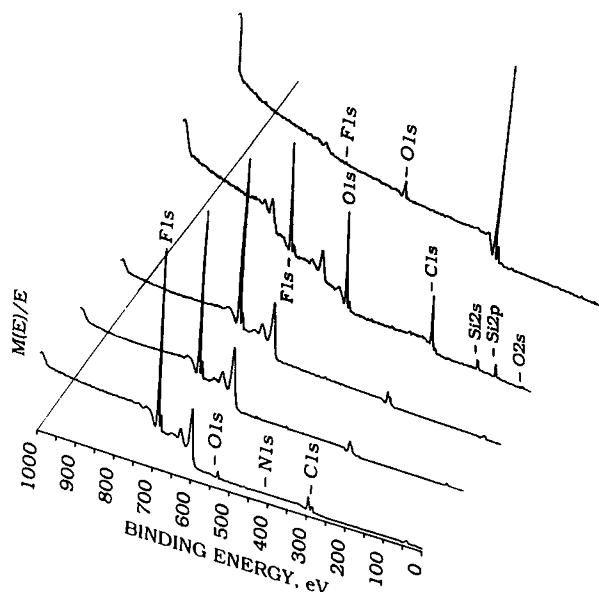


Figure 3 ESCA of untreated and CF_4-plasma-treated PP film for 1–10 mins. (From top to bottom; untreated, 1, 4, 7, and 10 min.)

bon tetrafluoride was then introduced into the reactor through the needle valve system until the pressure in the chamber stabilized to the desired value. The trap was cooled with liquid nitrogen. The plasma was ignited and maintained for the selected reaction time. At the end of the reaction, the system was evacuated and flushed several times with argon. Then the trap was isolated from the reactor by closing the corresponding valves and both the PP sample and the trap were removed from the installation.

The experimental conditions for a typical plasma treatment of PP were as follows: base pressure, 0.05 mmHg; number of cleaning cycles with argon, 3; argon pressure, 20 mmHg; working pressure in the absence of plasma, 0.4 mmHg; pressure in the presence of plasma, 0.45 mmHg; RF power dissipated to the coil, 100 W; treatment times, 1, 4, 7, and 10 min.

RESULTS AND DISCUSSIONS

ESCA survey spectra of the untreated PP film and the CF_4-plasma-treated samples are shown in Figure 3. A very small oxygen signal can be seen in all cases except the 1-min CF_4-plasma-treated PP. Intense fluorination is also observed, accompanied by a corresponding decrease in the C_{1s} peak. The survey spectra exhibit a significant silicon signal only for the sample treated for a short time period (1 min., CF_4-plasma).

Additional information on the plasma surface chemistry was obtained by recording the high-resolution ESCA spectra in the different binding energy regions (C, F, Si). Figure 4 shows the specific binding energy intervals for the C_{1s} peak from untreated PP film and for films plasma treated for 1 and 10 min. ESCA analysis of the untreated PP substrate shows a single symmetrical C_{1s} peak centered at around 285.5 eV. Exposure of PP to CF_4-plasma for 10 minutes results in significant amounts of CF_3 (295–297 eV); CF_2 (293.5–295 eV), and CF (287.5–289.5 eV) becoming attached to the surface, with a clear predominance of CF_3 functionalities at the surface. The existence of a weak C_{1s} peak (284.5–286.5 eV) in the case of PP film after 10 min of CF_4-plasma treatment indicates that a small amount of unmodified PP still exists after 10 min of plasma action. It is noteworthy that there is less intense fluorination (less strong CF_x intensities) when the

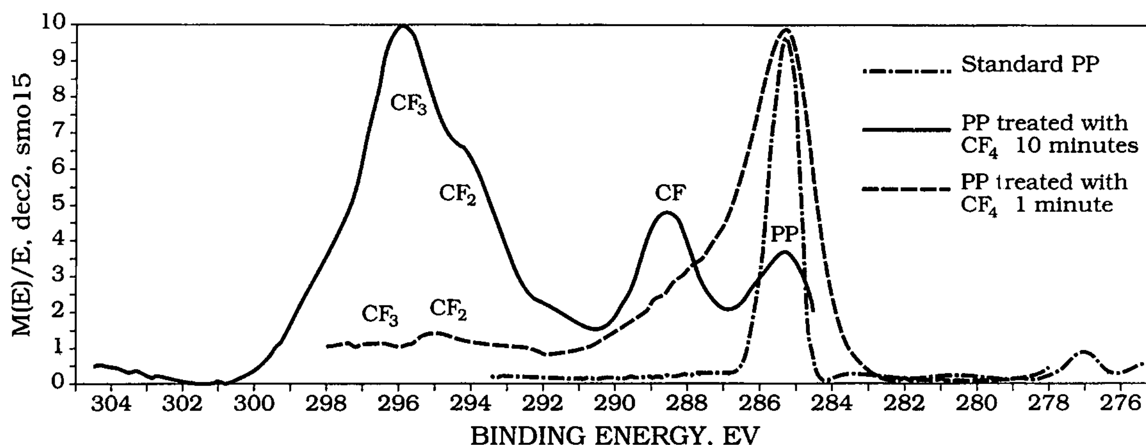


Figure 4 Expanded ESCA C_{1s} peak for untreated and CF_4-plasma-treated polypropylene film for 1–10 min.

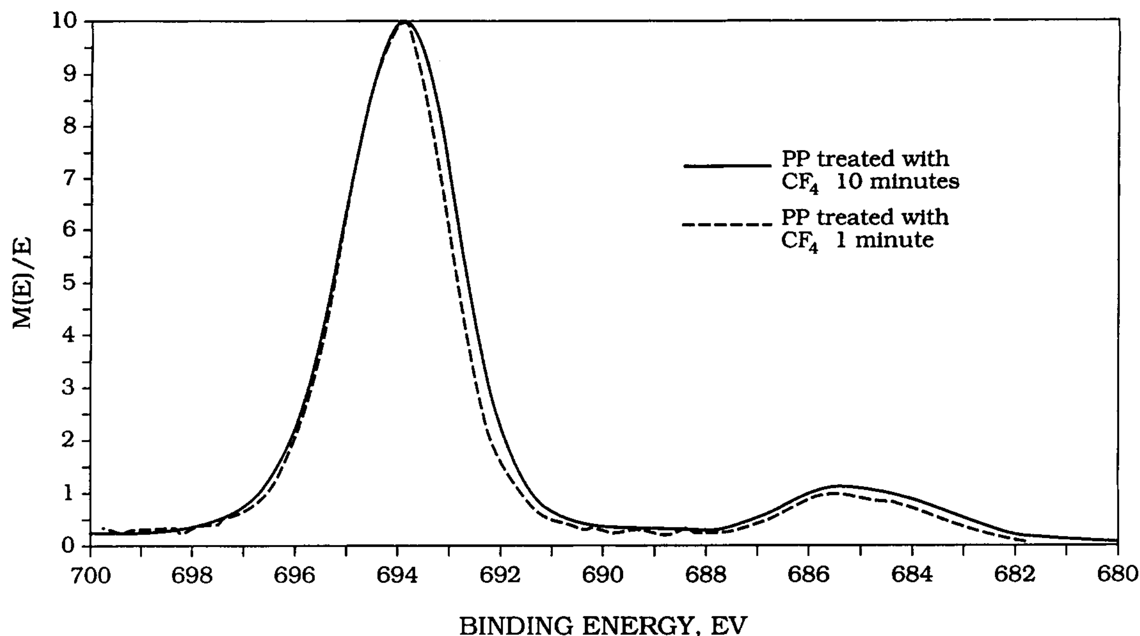


Figure 5 Expanded ESCA F_{1s} peak for PP treated with CF_4 plasma for 1 (scale factor: 0.756 Kc/S; offset: 3.634 Kc/S) and 10 (scale factor: 0.05 Kc/S; offset: 2.816 Kc/S) min.

treatment time is reduced to 1 min, accompanied by the presence of a greater amount of unmodified PP (284.5–286.5 eV). The CF functional groups (287–290 eV) of the CF_x mixture predominate at the surface of the PP treated for 1 min. High-resolution ESCA spectra from the F and Si binding energy regions emphasize the presence of F and Si atoms at the surfaces of 1- and 10-min treated samples (Figs. 5 and 6, note different scale factor). The existence of a relatively strong symmetrical F_{1s} signal (691.5–

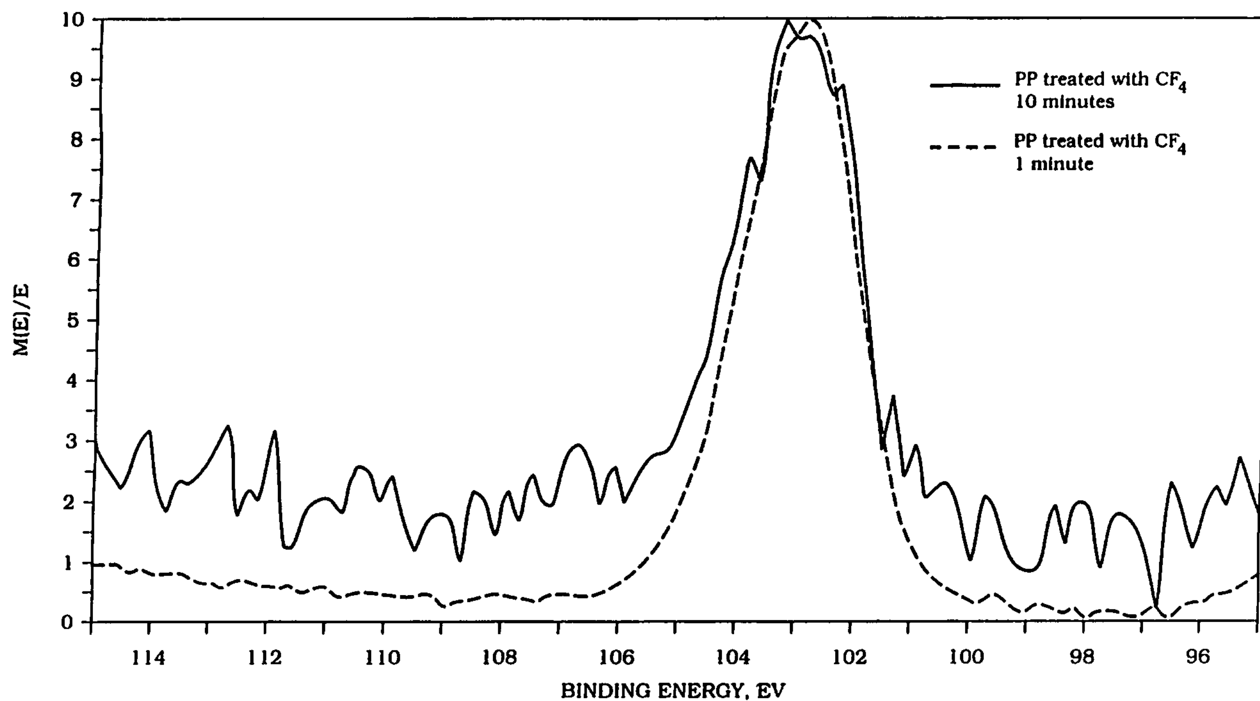


Figure 6 Expanded Si_{2p} peak for PP treated with CF_4 plasma for 1 (scale factor: 0.756 Kc/S; offset: 3.631 Kc/S) and 10 (scale factor: 0.05 Kc/S; offset: 2.816 Kc/S) min.

696.5 eV) even at short treatment times indicates the presence of intense fluorination mechanisms. The presence of an intense Si_{2p} peak (103 eV) is noticed only in the case of high-resolution ESCA spectrum of the 1-min CF_4-plasma-treated PP sample. This indicates the occurrence of significant ablation reactions at the glass reactor walls with subsequent deposition of the newly generated silicon-containing molecular fragments onto the surface of the PP films. The low Si content at higher treatment times can be explained by active fluorine atom mediated etching of Si from PP surfaces accompanied by intense surface fluorination reactions (development of a Teflon-like inert surface).

The relative atomic concentrations of C_{1s}, F_{1s}, Si_{2p}, and O_{1s} versus plasma treatment time are shown in Figures 7–9. As the plasma treatment time is increased, there is an increase in the amount of fluorination as measured by the F_{1s} peak on the polypropylene surface and a reduction in the amount of unmodified PP (Fig. 7). The silicon appears to be incorporated onto the surface of PP at short exposure times and reduced amounts are present with longer reaction times. Inverse relationship are shown for both the amount of oxygen and silicon (Fig. 8) and for the incorporation of oxygen versus unmodified PP (C_{1s}) (Fig. 9). The presence of oxygen can be explained by post plasma oxidation reactions with unsaturated bonds and trapped free radicals, by the hydrolysis of incorporated SiF_x groups under open laboratory conditions, and by reactor wall origin oxygen atom incorporation reactions.

The GC–MS and high-resolution MS data corroborate the ESCA results. Two GC peaks were identified with distinctly different mass spectra (Figs. 10 and 11). Complete separation of all products via GC was not possible because of the extremely volatile nature of some of the components of the mixture. However, SiF_4 and CF_4 could be identified in the mixture. Carbon-, silicon-, fluorine-, and hydrogen-containing ions (m/z 127, 139, 155, 167, and 186) were also observed in the two GC peaks, but the nature of the compound(s) giving rise to these ions could not be determined; the MS database did not contain spectra that matched the experimental data.

The high-resolution data confirms the GC–MS results. Accurate mass measurements unambigu-

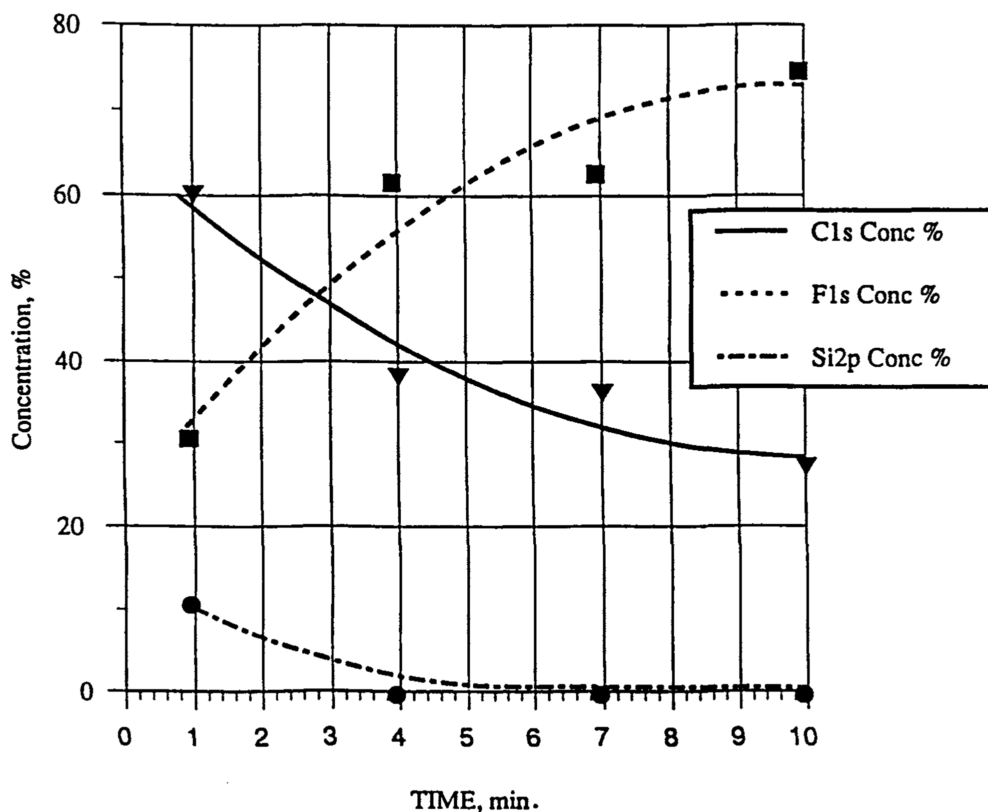


Figure 7 Relative atomic concentration of C_{1s}, F_{1s}, and Si_{2p} on PP film vs. CF_4 plasma treatment time.

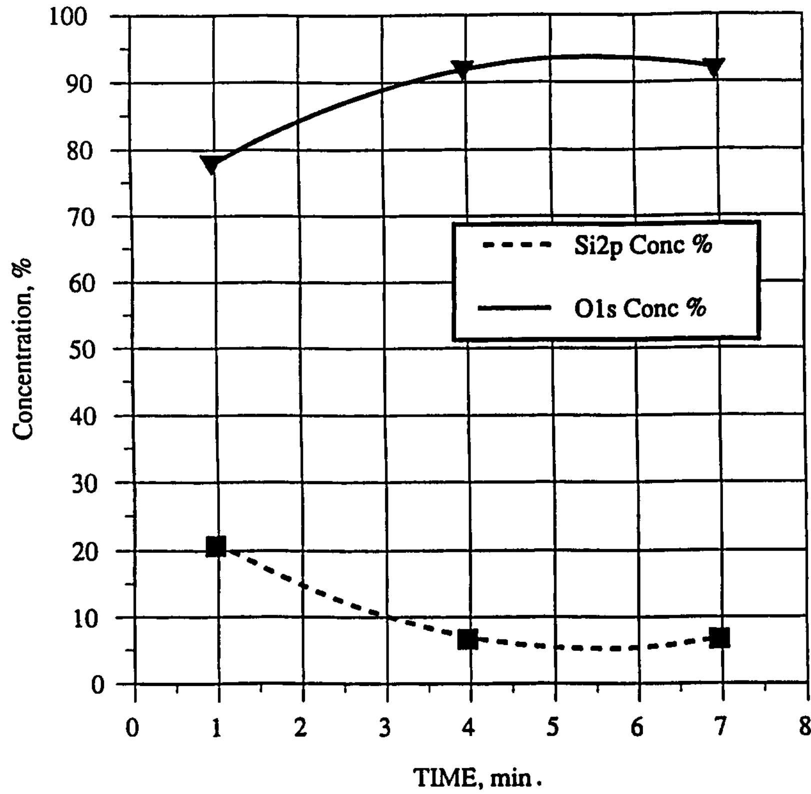


Figure 8 Relative atomic concentration of Si_{2p} and O_{1s} on PP film vs. CF_4 plasma treatment time.

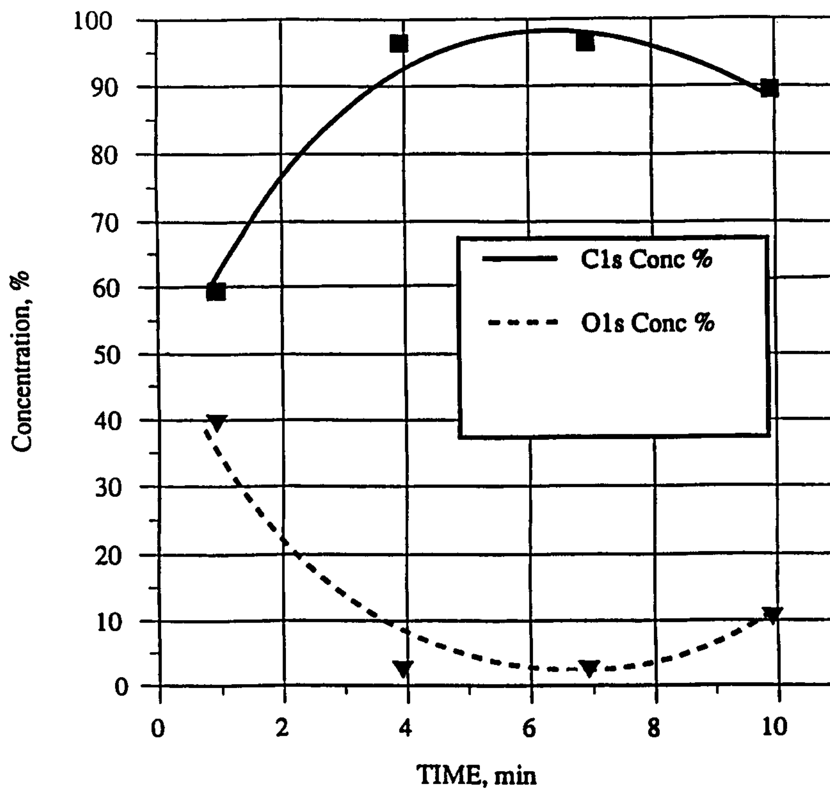


Figure 9 Relative atomic concentration of C_{1s} and O_{1s} on PP film vs. CF_4 plasma treatment time.

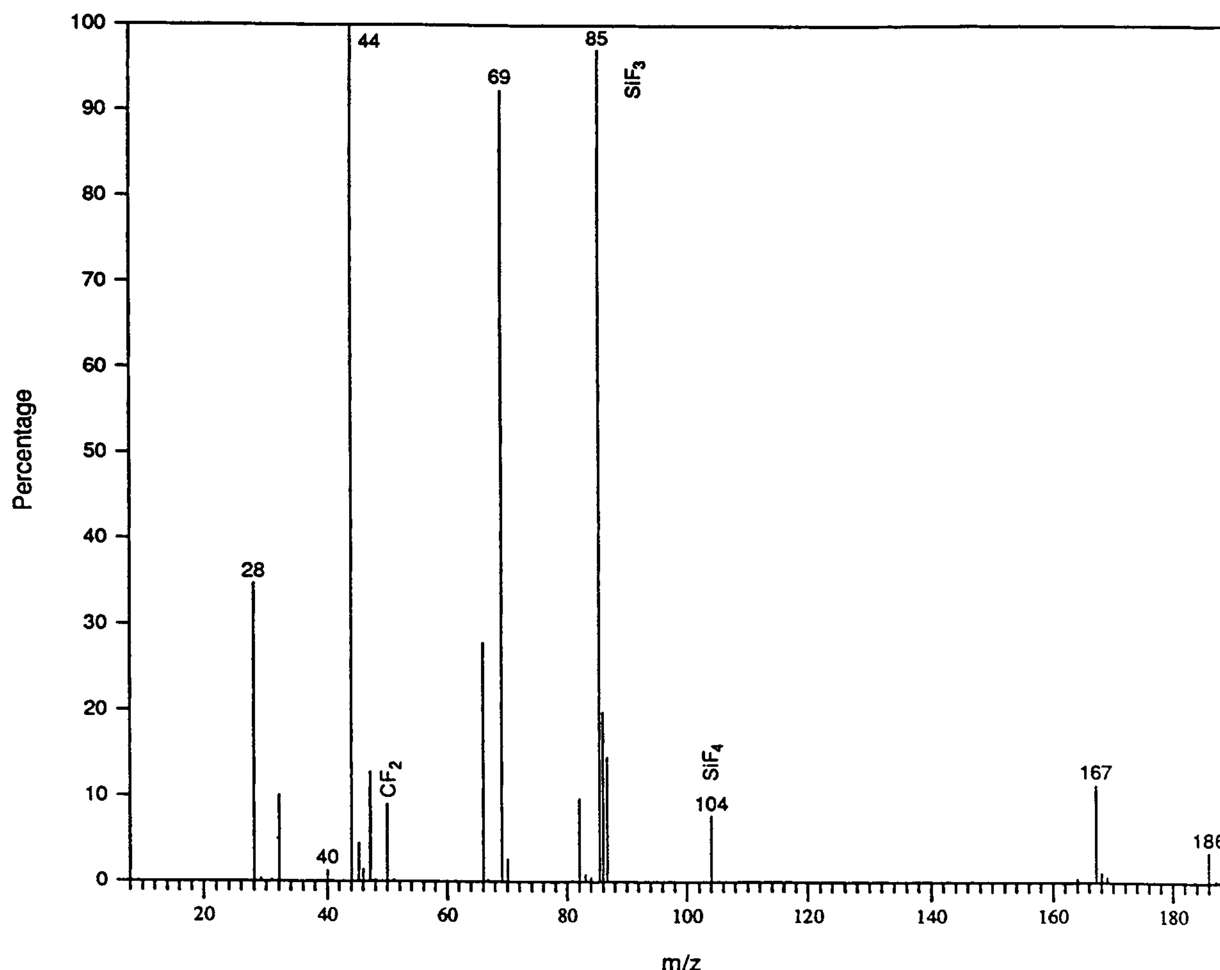
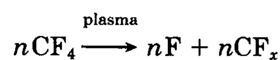


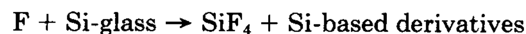
Figure 10 Mass spectrum of peak 1 from GC of trapped gaseous products from CF_4 plasma treatment of PP.

ously showed the presence of several silicon-, fluorine-, hydrogen-, and carbon-containing species (Table I) besides the presence of predominant SiF_4 and CF_4 compounds. The spectrum exhibits a very good agreement between the expected and observed isotope pattern (Table II). The fragmentation of CF_4 molecular ions is apparent and the presence of SiF_x (x = 1–4) ions is demonstrated.

Both the ESCA and the MS data demonstrate the presence of significant quantities of silicon-based derivatives on the PP substrate and in the liquid nitrogen trapped molecular mixture. These findings suggest the existence of intense etching and ablation mechanisms of the glass reactor walls and the substrate during the CF_4-plasma treatment. Extremely reactive fluorine and CF_x free radicals and ions are probably responsible for the Si extraction reactions as follows:



$$nCF_4 \xrightarrow{\text{plasma}} nF + nCF_x$$



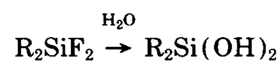
$$F + \text{Si-glass} \rightarrow SiF_4 + \text{Si-based derivatives}$$

The dominant ionic species present in CF_4 plasmas are almost always CF_3 and CF_2; CF_4 is stable only under specific conditions.[26] Silicon is observed mainly as SiF_x; presumably fragments of SiF_4 from neutral molecules. Other $C_yF_zH_w$ ions are also generated from the trapped molecular mixture as measured by MS.

The relatively high quantity of fluorosilicon derivatives can be explained by the greater affinity of Si for fluorine than for C, with the tendency to readily form SiF_4.[27] This is also the reason that at longer treatment times the Si is removed from the substrate surfaces by active fluorine-atom-mediated etching.

Figure 11 Mass spectrum of peak 2 from GC of trapped gaseous products from CF_4 plasma treatment of PP.

The fluorosilicon radicals and ionic species generated under cold plasma conditions can easily react at proper treatment times with hydrocarbon type surfaces or can be trapped into the upper surface layers, contributing to surface modifications. However, the Si—F bond is much more reactive than the C–F linkage and easily undergoes hydrolysis reactions in the presence of water and moisture under open laboratory conditions.



$$R_2SiF_2 \xrightarrow{H_2O} R_2Si(OH)_2$$

This well-known mechanism is responsible for formation of silicon-based polymers. The generation of such SiOH islands on fluorosiliconated surfaces would contribute to the character of the newly created surface properties, and these reactions could be responsible for some of the unusual properties noticed for plasma-deposited fluorocarbon polymers and/or for surface-fluorinated synthetic polymers treated in glass or quartz wall-limited reactors with fluorocarbon plasmas. Some of the unusual characteristics noted with fluorocarbon plasmas include increased water repellency accompanied by im-

Table I Exact Masses of Si, C, H, and F Based Ions of Experimental and Their Possible Theoretical Origin Correspondents

Experimental *m/z*	Theoretical *m/z*	Possible Ionic Fragments
185.9406	185.9400	$Si_3C_2F_4H_2$
166.9381	166.9416	$Si_3C_2F_3H_2$
155.0169	—	(not suggested)
96.0219	96.0187	$C_3H_3F_4$

Table II Exact Mass and Isotopic Contribution of Si and C Based Ions of Experimental and Theoretical Origin[a]

Nature of Ion	Experimental Isotopic Contribution		Theoretical Iostopic Contribution	
	m/z	%	m/z	%
SiF_4^+	103.9715	100.00	103.970549	100.00
	104.9698	9.89	104.970116	5.10
	105.9697	4.69	105.967303	3.35
SiF_3^+	84.9721	100.00	84.972144	100.00
	85.9719	4.80	85.971711	5.10
	86.9698	3.35	86.968978	3.35
SiF_2^+	65.9937	100.00	65.973739	100.00
	66.9839	4.62	66.973306	5.10
	—	—	67.970573	3.35
SiF^+	46.9764	100.00	46.975334	100.00
	47.9754	3.84	47.974901	5.10
	48.9706	1.39	48.972168	3.35
CF_3^+	68.9808	100.00	68.995215	100.12
	—	—	69.998569	1.12
$C_2F_3^+$	80.9991	100.00	80.995215	100.00
	81.9986	6.90	81.998569	2.24
	82.9971	4.60	83.001923	0.01

[a] The relative intensities are normalized to the most intensive signal in the mass spectrum (100).

proved dyeability,[28] better biopolymer adsorption,[29] contact angle anomalies,[30-32] and higher O/C (ESCA) ratios on the plasma-fluorinated surfaces.

CONCLUSIONS

1. Various silicon-based derivatives can be formed on polymer substrates when the polymers are reacted in carbon tetrafluoride cold plasmas (inductively coupled) in the presence of silicon containing surfaces such as the glass walls of the reactor.
2. Fluorine and fluorine-containing free radicals are probably responsible for the silicon extraction from the glass surfaces.
3. Halosilicon islands deposited and/or grafted to the polymer substrates in the presence of glass surfaces may be converted to polar groups (SiOH) in the presence of moisture, creating a significantly modified surface on the polymer substrate.
4. Silicon contamination could create serious problems, especially for optical and electronic applications.

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