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Silicon contamination of polypropylene films from glass reactors in a BCl_3 RF cold plasma

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Summary: Cold plasma chemistry can be used for surface modification and/or grafting of polymeric substrates for enhanced properties. In addition to interaction with the substrate, plasma reactions can also occur at other surfaces confined to the reactor. Contamination of polypropylene (PP) substrates with silicon, originating from the reactor walls in a BCl_3 plasma, has been shown to occur based on ESCA measurements and the presence of Si-based compounds in the gaseous phase has been shown by GC-MS and high resolution MS for the plasma generated molecular mixture. The Si incorporation is similar to that found with CF_4 plasmas where a shorter treatment time resulted in higher Si incorporation. These results indicate that reactor wall-origin contaminations can accompany plasma treatments, interfere with the the main reaction mechanisms and create serious problems for achieving the desired surface properties.

Introduction: Glow discharge synthesises of new polymers has been an especially active area of research in recent years, particularly for industrial applications where the advantages of producing pore-free, uniform thin films of superior physical, chemical, electrical and mechanical properties have been realized (1-5). Surface modifications and/or grafting processes are also a promising application for cold plasma polymerization reactions. Characteristics such as improved wettability, improved adhesive bonding, printability, electromagnetic radiation reflection, surface hardness, etc., can be conveniently achieved without altering the bulk properties of the polymeric substrates.

The interaction of electrical discharges with solids is restricted to thin surface layers. Depending on the physical state of the starting materials and the resulting products, etching, surface modification or coatings can be produced. The main steps in all of these processes is the adsorption of the plasma generated species and neutrals from the starting materials (monomers) on the surfaces which confine the plasma state. These molecular species and the substrate surface are modified continuously under the bombardments with ions, electrons, metastables, neutral species and photons; and finally converted, through intermediate structures such as mono- and multi-free radical or ionic species, into solid layers and desorbed volatile compounds which leave the system.

A large number of gases (O_2, Ar, H_2, NH_3, Cl_2, N_2, CF_4, CCl_4, etc.) and their mixtures, various organic compounds and classical monomers have been employed both for surface modification and etching of different substrates; and extensive analytical work has been carried out to monitor the plasma generated chemical modifications (6-14). However a significant issue has been overlooked in most of the previous work, that the plasma interacts not only with the substrates, but also with all of the surfaces which geometrically limit the plasma state, including the walls of the reactors. This is of particular importance for plasma reactions of halogen containing organic compounds. Experiments carried out with these materials, e.g. fluorocarbons, has clearly shown that the plasma polymerization mechanisms are accompanied by etching processes and the

relative ratio of F/CFx in the fluorocarbon discharge determines whether etching or polymerization predominates (15-22). Fluorocarbons have also been used for etching substrates like Si or SiO_2 (23-27) and glass reactor wall ablation has been noticed in such reactions (28, 29). However plasma induced, glass wall-origin Si incorporation into polymeric substrates has not been properly evaluated. Atoms or molecular fragments liberated from these surfaces under the action of plasma can also be incorporated into the structure of the substrates and create serious contamination problems through modification of the surface layers. A recent investigation from our laboratory demonstrated the possibility of CF_4 plasma induced Si contamination of polypropylene substrates in Pyrex plasma reactors (30). The aim of this paper is to show that another halogen atom containing compound (BCl_3) can induce similar effects under RF cold plasma conditions.

Experimental:

Materials and Methods: Commercially available boron trichloride (Aldrich, BCl_3 99.95+%, monel control valve) was used as received. An additive free, high purity polypropylene (PP) film (Fortiline) was acetone extracted by the Soxhlet method to remove any incidental contaminants and then dried at 50 ^{0}C under vacuum conditions. Both Dow Corning silicon grease and non-silicon containing Apiezon high vacuum grease were used for lubricating the only glass joint in the reactor which was located far outside the plasma region (70 mm from the plasma zone).

Analysis of the surface of PP films was carried out using X-ray photoelectron spectroscopy (ESCA- Perkin Elmer Physical Electronics 5400 Small Area System; Mg source; 15 kV, 300W) in order to establish the relative atomic concentrations. Atomic percentages for carbon (C_{1S}), oxygen (O_{1S}), chlorine (Cl_{2p}), silicon (Si_{2p}) and boron (B_{1S}) were monitored.

The chemical compounds generated by the BCl_3 plasma were trapped at liquid nitrogen temperature, sealed under vacuum conditions and identified by GC-MS (GC-Carlo Erba Fractovap 4162; MS-Kratos MS-25) and high resolution MS (Kratos MS-80). The following experimental conditions were used for GC-MS measurements : column-fused silica, length-30 m, ID-0.32 mm, coating-0.25 micrometer of 5% phenyl and 95 % methyl polysiloxane, injector splitter temperature-25 ^{0}C, column temperature profile-30 ^{0}C held 5 minutes then heated up to 280^{0}C at 20 ^{0}C/minute, electron energy - 28 eV. The high resolution mass spectra were recorded by connecting the stainless steel liquid nitrogen trap directly to the spectrometer. The admission valve was opened after evacuating the connecting tubing.

Plasma Reactions:

The apparatus used for BCl_3 decomposition and surface chlorination of PP films is shown in Figure 1. The reaction chamber was a tubular shaped (200 mm length, 80 mm diameter) Pyrex glass reactor fitted with monomer inlet and thermostated substrate holder (cold finger- cylindrical cooling jacket, OD-20 mm, ID 10 mm, positioned axially in the reactor). Low temperature alcohol was recirculated through the cooling jacket for temperature control. The plasma was sustained by an RF electromagnetic field transferred to the reaction chamber through inductive coupling. A stainless steel needle valve system assured the flow rate and the pressure control both for Ar and BCl_3. The pressure in the plasma reactor was monitored with a Hastings Vacuum Gauge (DV-4 Gauge Tube).

In order to retain the plasma generated active species-origin neutral compounds for further analytical measurements, a special stainless steel trap (Figure 2) was designed and employed in addition to the regular Pyrex glass liquid nitrogen trap used for the protection of the vacuum pump. The stainless steel valve system [1 and 2] of the trap

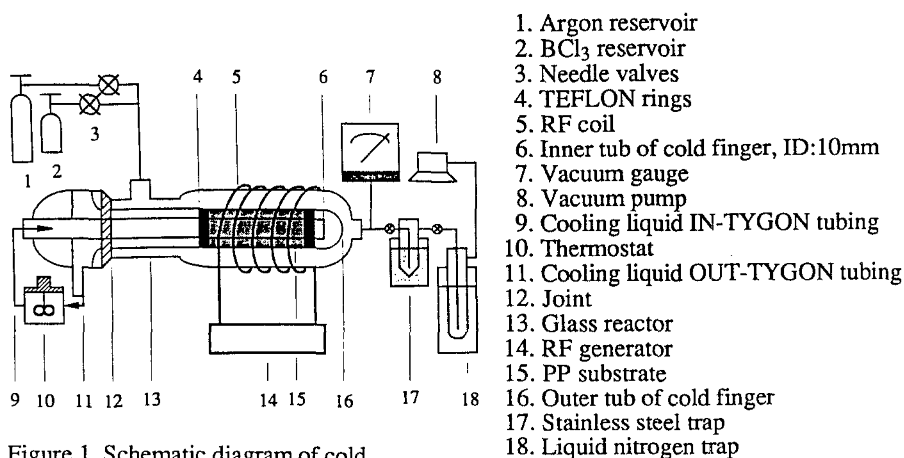

Figure 1. Schematic diagram of cold plasma installation

assured the isolation, under vacuum conditions, of the resultant molecular species and the chromatography-type septum [3] permitted precise sampling for GC-MS measurements. In a typical experiment, a sample of polypropylene [15] (100 mm length and 65 mm wide) was fastened symmetrically in the reactor on the target holder, by means of Teflon rings [4] and the chamber was evacuated to the ground pressure. Ar gas was introduced (20 mm Hg) and the system was again evacuated to the ground pressure level; this was repeated several times to eliminate moisture and oxygen adsorbed on the surfaces of the PP substrate. BCl_3 was then introduced into the reactor through the needle valve system [3] until the pressure stabilized at the desired value. The plasma was ignited, the stainless steel trap [17] cooled down with liquid nitrogen, and the plasma state was maintained for the selected reaction time. At the end of the reaction, the system was quickly evacuated and flushed several times with argon The trap was isolated from

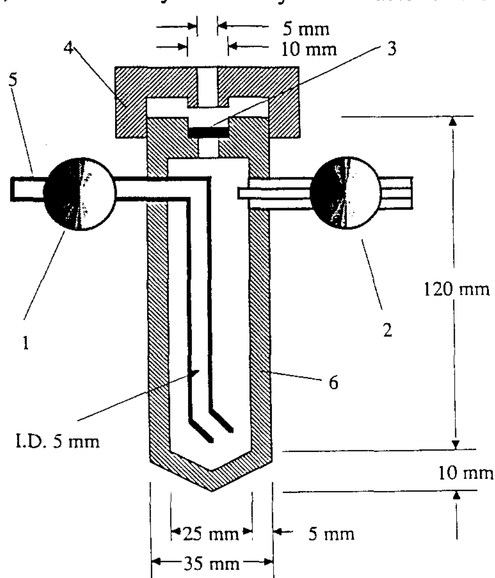

Figure 2. Cross section of stainless steel (SS) liquid nitrogen cold trap (1, 2-valves; 3-septum; 4-SS cap; 5-SS tubing; 6-body of SS trap)

the system by closing the corresponding valves and both the PP samples and the trap were removed from the installation. The samples were kept under open laboratory conditions; however sections of some of them were stored in a vacuum desiccator, during the 24 hours period which preceded the analytical measurements, in order to estimate the possible existence of moisture induced hydrolysation mechanisms. White powdery B_2O_3 -like samples, generated by hydrolysis in the Pyrex trap [18] under atmospheric conditions, were also collected and analyzed.

Typical experimental conditions for BCl_3-plasma treatment of the PP films were as follows : ground pressure - 0.05 mmHg; Ar washing cycles - 4; pressure in the absence of plasma - 0.3 mm Hg; RF power dissipated to the coil - 100 W; pressure in the presence of plasma - 0.3 mm Hg; reaction times - 1, 2, 5, 10, and 15 minutes; temperature of cold finger - minus 18 ^{0}C.

Results and Discussions:

Comparative ESCA survey spectra of BCl_3-plasma treated films at 1, 2, 5, 10, 15, and 20 minutes are shown in Figure 3. One clearly can observe the presence of Si_{2p}, C_{1s}, Cl_{2p}, and O_{1s} peaks at the characteristic binding energy values. Figure 4 is a graphic demonstration of the relative atomic concentrations of oxygen, chlorine, and silicon versus plasma treatment time. As the plasma treatment time is increased, there is an increase in the amount of chlorination, as measured by the Cl_{2p} peak, on the polypropylene surface. The silicon incorporated onto the surface of the PP films at different plasma irradiation times follows a pattern similar to that of atomic oxygen incorporation. Higher values are reached at low treatment times (maximum values at 2 minutes of plasma action) followed by a significant decrease in both the oxygen and silicon content in the following 2-15 minute time period, with a slight increase in the percentages of these atoms at even longer treatment times (15-20 minutes). CF_4-plasma treatment of PP films shows a similar Si incorporation pattern with higher quantities of Si incorporated onto the surface of the PP with short-term exposure and reduced amounts present with longer reaction times (30). However, the reverse applies to the amount of oxygen at the polymer substrate surface in the case of CF_4-plasma treatment. Moisture induced post-plasma Si-Cl bond hydrolysation mechanisms may be responsible for the similar pattern of silicon and oxygen incorporation in the BCl_3 and CF_4 irradiations; while in the case of CF_4 plasma treatments the presence of more intense fluorine atom induced surface unsaturations might be responsible for reactor wall and open laboratory

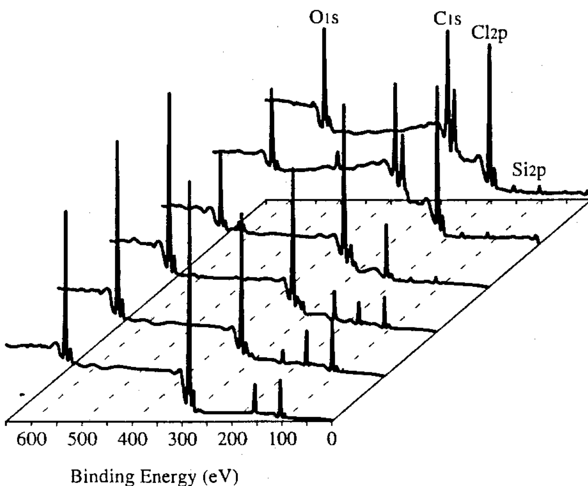

Figure 3. Survey spectra of plasma treated PP of 1, 2, 5, 10, 15 and 20 minutes

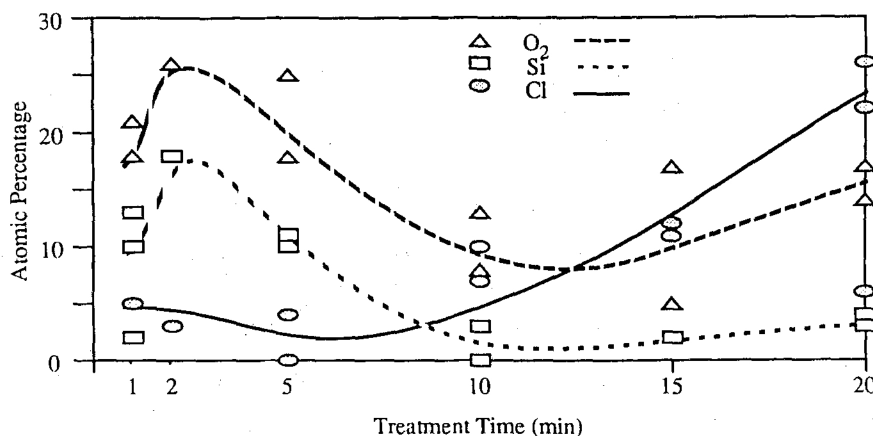

Figure 4. Relative atomic concentration of O_{1s}, Si_{2p} and Cl_{2p} on PP film versus BCl_3 plasma treatment time (The nature of vacuum grease did not influence the Si incorporation)

origin (post plasma) oxygen initiated surface oxidation. ESCA measurements on plasma treated PP films stored in a vacuum desiccator showed significantly higher atomic chlorine percentages (7% Cl at 5 minutes treatment time and 21% at 10 minutes) in comparison to the samples kept under open laboratory conditions, which yielded 4 and 9 % atomic Cl respectively. For the same treatment times, the corresponding values for Si (samples kept in desiccator and open laboratory conditions) did not indicate significant differences. These data also suggest the existence of post-plasma hydrolyzation of Si-Cl linkages for the samples stored in open laboratory conditions.

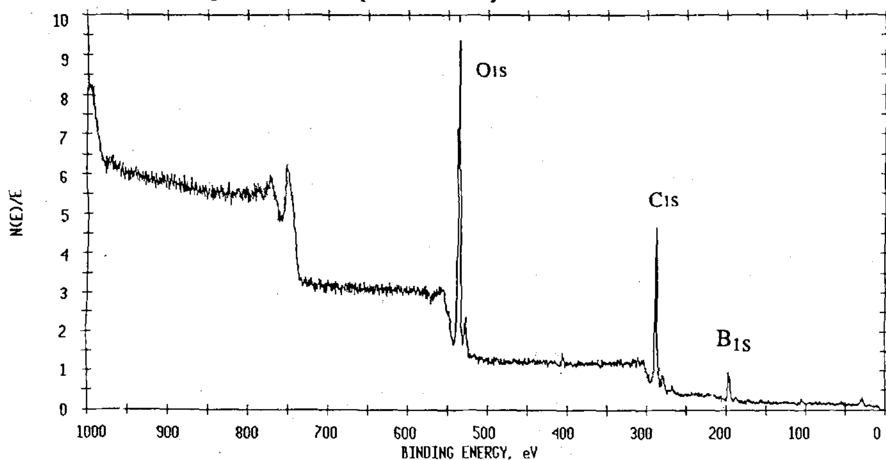

Figure 5. Survey spectrum of B_2O_3 like compounds collected in a Pyrex trap and kept under open laboratory condition

PP samples were also placed directly on the walls of the reactor (different geometrical position and the absence of cooling) and these samples exhibited comparable incorporation of atomic species (at 2 minutes treatment time: O_{1s}: 21%, Si_{2p}: 12%, Cl_{2p}: 3.2% and at 20 minutes treatment time: O_{1s}: 9.76%, Cl_{2p}: 33.5% and Si_{2p}: negligible). The lower Si content at shorter time periods and the higher Cl percentage at longer treatment times are difficult to interpret.

The ESCA spectrum and the atomic composition of the B_2O_3-like white powder collected from the Pyrex trap is shown in Figure 5. The presence of carbon suggests the existence of surface ablation of the PP during the plasma treatment.

High resolution MS measurements of trapped gaseous phase components identified BCl_3 and $SiCl_4$. The spectrum exhibits a very good agreement between the expected and observed isotope pattern (Table 1). The fragmentation of BCl_3 molecular ions can be noticed and the presence of $SiCl_x$ (x=1-4) ions is demonstrated. Because of the high volatility of halo-boron and halo-silicon compounds, incomplete separation was obtained by GC. GC-MS measurements showed the presence of $SiCl_3^+$, $SiCl_2^+$ and $SiCl^+$ ions, as well as the corresponding boron charged fragments. It was not possible to identify the minute quantity of other less-volatile compounds due to their complex nature. These entities probably arose by recombination of species from both plasma induced fragmentation of BCl_3 and from PP and reactor wall-origin etching processes. Small quantities of complex C, Si, B, O, and H containing ions (m/z 73, 93, 113, 176, 186) were also observed, but the nature of the molecular ions could not be identified. Further studies are in progress to evaluate plasma induced boron incorporation into polymeric substrates.

Table 1. Exact mass and isotopic contributions of Si and B based ions of experimental and theoretical origin*

Nature of Ion	Experimental Isotopic Contribution m/z	%	Theoretical Isotopic Composition m/z	%
$SiCl_4^+$	173.8481	13.01	173.8434	11.82
	171.8470	46.11	171.8464	50.64
	169.8517	100.00	169.8594	100.00
	167.8546	80.03	167.8523	75.22
$SiCl_3^+$	136.8835	38.20	136.8775	34.56
	134.8535	92.95	134.8805	100.00
	132.8870	100.00	132.8835	99.46
$SiCl_2^+$	101.9107	5.08	101.9087	12.67
	99.9125	63.21	99.9116	68.15
	97.9169	100.00	97.9146	100.00
$SiCl^+$	64.9461	37.85	64.9428	35.75
	62.9500	100.00	62.9458	100.00

Nature of Ion	Experimental Isotopic Contribution m/z	%	Theoretical Isotopic Composition m/z	%
BCl_3^+	119.9128	27.24	119.9099	10.50
	117.9165	87.06	117.9129	97.19
	116.9265	37.21	116.9165	23.37
	115.9217	91.46	115.9158	100.00
	114.9349	100.00	114.9195	24.66
BCl_2^+	84.9473	11.20	84.9411	10.50
	82.9504	52.06	82.9440	64.80
	81.9546	17.20	81.9476	15.98
	80.9542	100.00	80.9470	100.00
	79.9569	28.05	79.9506	24.66
BCl^+	47.9780	32.63	47.9752	32.40
	45.9796	100.00	45.9781	100.00
	44.9822	26.76	44.9818	24.66
Cl^+	36.9659	32.20	36.9659	32.34
	34.9690	100.00	34.9688	100.00

* The relative intensities are normalized to the most intense signal in the mass spectrum (100)

Conclusions:

1. ESCA measurements indicate that Si containing molecular fragments are also incorporated onto the surface of the PP substrates;
2. Shorter treatment times result in more intense Si atom incorporation. The pattern of incorporation of oxygen atoms suggests post-plasma Si-Cl bond hydrolysation;
3. GC-MS and high resolution MS data demonstrate the presence of reactor wall-origin Si based compounds in the BCl_3 plasma generated molecular mixture;
4. The implantation of halosilicon species can create unanticipated surface modifications and anomalous surface properties.

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