

INFLUENCE OF RF-COLD PLASMA TREATMENT ON THE SURFACE PROPERTIES OF SECURITY PAPER

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Security paper was exposed to SiCl_4 -RF plasma. The implantation onto the substrate surface of SiCl_x functionalities and the post-plasma formation of $\text{Si}(\text{OH})_x$ groups were demonstrated. It was shown that the presence of these functionalities are responsible for the decreased contact angle values and for the improved ink adhesion. Plasma induced reaction mechanism is discussed based on HR-ESCA spectra from model compounds and cellulose.

Introduction Security paper is repeatedly exposed to environmental and handling stress which reduces the life expectancy of the paper. Cold plasma chemistry offers unique solutions to this problem since a large spectrum of different types of surface functionalization can be achieved without altering the bulk properties of the materials [1-2]. The generation of extremely reactive species of silylium (silicinium) ions under plasma conditions opens up new ways for surface modification. Molecular fragments resulting from the gaseous phase plasma reactions interact with the surfaces in the plasma and induce surface functionalization and/or plasma-polymer-based coating processes. In this work experimental results from a systematic study on surface functionalization of security paper samples under SiCl_4 RF cold-plasma conditions are described and the newly gained surface properties are discussed in terms of the plasma induced molecular fragmentation of SiCl_4 . The surface functionalization of cellulose paper (CP) with silicon atom-based reactive species was studied using GC-MS, Low Energy Electron-MS (LEEMS) and high resolution ESCA.

Experimental The plasma treatment experiments were carried out in a parallel plate stainless steel cylindrical reactor. In a typical experiment two paper samples were positioned symmetrically on the lower electrode, the upper part of the reactor

was locked and reaction chamber was evacuated to base pressure. The second vacuum line was operated for trapping and isolated independently from the reactor. The trap was cooled down to liquid nitrogen temperature. The plasma was then ignited and the discharge was sustained for the desired time period. The experimental conditions employed during the plasma treatments were as follows: RF-power: 60-175 W; Pressure in the absence of plasma: 60-175 mT; Flow rate of gases: 2.5-12 sccm; Trapping period: 2 minutes; Treatment time: 10 seconds-1 minute.

Surface atomic composition of security paper was analyzed using ESCA (Perkin Elmer Physical Electronics O 5400 Small Area System; Mg source; 15 kV; Pass energy: 89eV; Angle: 45 degrees). The ESCA measurements involved the determination of carbon (C1s), oxygen (O1s) and silicon (Si2p). The morphology of virgin and plasma modified paper surfaces was investigated by scanning electron microscopy (JEOL JSM-35 C voltage). Contact angle estimations and surface energy component evaluations were carried out using a CAHN Dynamic Contact Angle Analyzer (Elevator speed: 150 um/sec) with vertically positioned 2 X 40 mm paper strip samples. The plasma induced molecular fragmentation of SiCl_4 was simulated by both low energy-electron MS (LEE-MS) (MS Kratos 25, electron energy-25, 50 and 70 eV) and high resolution GC-MS.

Results and Discussions A statistic central composite design in three blocks was used to determine the influence of interdependent factors on the modifications of the contact angle values. The corresponding contact angle values and the surface atomic compositions are presented in Figures 1 and 2 for plasma-treated samples. The contact angle was reduced from 36.20° to 11.18° and a much higher oxygen content (60.8%), a diminished carbon content (17.9%), and an intense silicon content (20.3%) can be noticed. A high correlation between contact angle and C/Si suggested that the significant presence of Si-OH groups under open laboratory conditions on the paper surface were responsible for the low contact angle value. SEM of the treated sample (Figure 3) revealed rougher surfaces in the surface morphology after plasma interaction. A higher specific surface area, as well as surface chemical functionalization, can play a significant role in improved adhesion.

Table 1 and Figure 4 exhibit high resolution MS data collected for SiCl_4 and Si_2Cl_6 model compounds and their mixture, and from the resulting molecular mixture in the trap from the recombination of plasma-generated active species. The m/z values and the corresponding isotopic ratios clearly indicate the presence of

SiCl_4^+ and SiCl_3^+ in all of the cases except hexachlorodisilane, in which SiCl_4^+ is not generated. Comparison of the relative ratios of these charged species for the model and plasma-generated samples clearly indicates the existence of hexachlorodisilane in the plasma-generated mixture. It is noteworthy that apart from unreacted tetrachlorosilane and hexachlorodisilane only the presence of a minute quantity of hexachlorodisiloxane was evidenced.

GC-MS data from the plasma generated mixture provides additional information. The GC spectra exhibited eight distinctive peaks and two corresponding MS patterns and assignments are presented in Figure 5 (A and B). One can notice the presence of unreacted SiCl_4 and relatively high molecular weight linear and cyclic halosiloxane structures as well as a small quantity of Si_2Cl_6 . Due to the weakness of Si-Si (78 kcal/mol) and Si-Cl (96 kcal/mol) bonds in comparison to Si-O linkages (191 kcal/mol) and the sensitivity of the two former bonds under open laboratory conditions (in presence of oxygen and moisture), the polyhalosilanes from the recombination of the SiCl_x active fragments would be instantly converted into siloxane type derivatives upon exposure to moisture. The almost total absence of halosiloxanes in the unexposed samples (HR-MS) in comparison to those analyzed by using the syringe technique (GC-MS) verifies the effect of oxygen and moisture exposure. It is important to note that by injecting larger sample quantities even higher molecular weight halosiloxane-type structures were formed. This novel approach to synthesis of polyhalosilanes and polyhalosiloxanes with the aid of RF-plasma opens up new possibilities for creating cyclic halosiloxane-nucleated star-like polyorganosiloxanes and for synthesis of ceramic-type polymeric structures.

Survey and C1s high resolution ESCA spectra of cellulose (FP) and the corresponding relative atomic compositions are presented in Figures 6. The ESCA survey spectrum demonstrates the presence of only oxygen and carbon atoms with a relatively good agreement between the theoretical and experimental (ESCA-based) surface atomic composition. The high resolution C1s pattern exhibits three distinctive peaks indicative of C-C; C-OH and C-O-C linkages. Analysis of the C1, C2 and C3 surface areas according to the structure of the cellulose repeating unit indicates that the largest peak area must correspond to C-C linkages, while the areas of the C1 and C2 peaks, associated with C-OH and C-O-C (ether type) atomic associations, should be approximately equal. However this suggestion is different from assignments made in the literature [3] where the lowest binding energy peak

was considered to be characteristic of the C-C linkages. Consequently a comparative, systematic ESCA study of cellulose and related C, O, and H containing natural and synthetic model compounds was carried out in our laboratory in order to understand the factors influencing the relative ratio of the deconvoluted C1s peaks and their affiliation.

Figure 7 shows the high resolution deconvoluted C1s spectra of PVA and PEO. One can clearly observe that smallest deconvoluted peaks for PEO are positioned at a binding energy below the binding energy of the major peak at 285 eV, the latter of which is assigned to the carbon-carbon binding energy. In contrast the smaller peak in the deconvoluted C1s spectrum of PVA is at a higher binding energy than the predominate carbon-carbon peak at 285 eV. Since PEO has carbon-ether type linkages and PVA has a carbon hydroxyl functionality, this data indicates that the peak corresponding to ether type electronic environments from PEO is located at lower binding energy values (282-283 eV) and the peaks peculiar for carbon hydroxyl functionalities are located at higher binding energy values (286.5 eV) in comparison to C-C and C-H peak energies (285 eV).

Conclusions SiCl₄ RF-cold plasma is suitable for surface modification of security paper substrates. The lowest contact angle values result from moderate plasma conditions. ESCA spectra show substantial incorporation of plasma created molecular species onto the surfaces. The greater surface roughness of the paper after treatment indicates the presence of higher specific surface area, which, along with the newly acquired chemical surface functionalities, alters the surface adhesion behavior. GC-MS and HR-MS studies in gas phase indicate that plasma induced fragmentation of SiCl₄ results predominantly in SiCl₃⁺ cations. Surface survey and high resolution ESCA data from SiCl₄-plasma treated CP strongly suggest efficient implantation of SiCl₄ (x<4) functionalities.

REFERENCES

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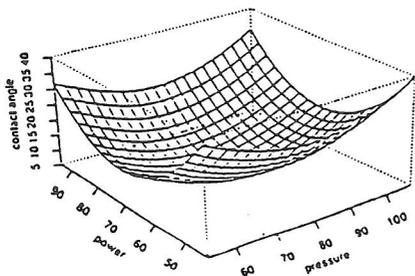


Fig.1 Contact angle plotted vs pressure and time of plasma treated SP

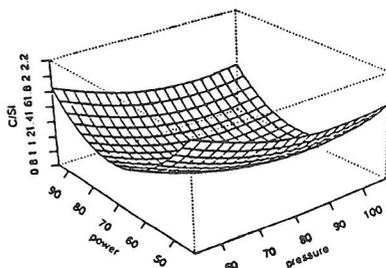


Fig.2 C/Si ratio plotted vs pressure and time of plasma treated SP



Fig.3 SEM image of plasma treated SP (x2,000)

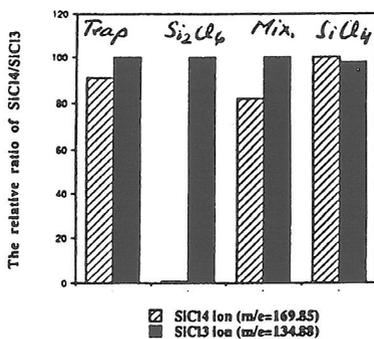


Fig.4 Relative ratios of SiCl_3^+ and SiCl_4^+ species from model and plasma-generated samples

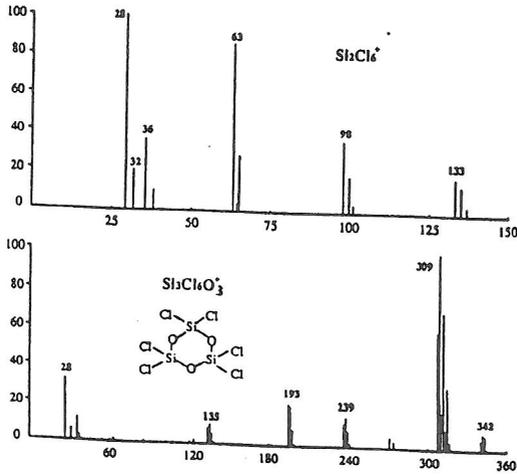


Fig.5 MS spectra of plasma-generated $Si_2Cl_6^+$ and $Si_2Cl_6O_3^+$

ESCA Survey and High Resolution C1s Peak of Unreated Filler Paper

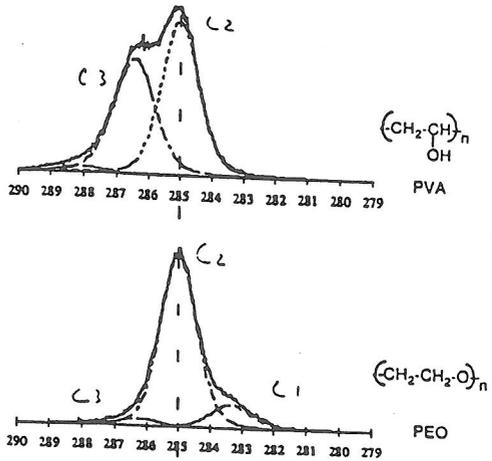
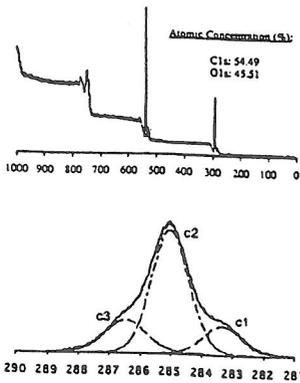


Fig.6 ESCA survey and deconvoluted C1s spectra of FP

Fig.7 ESCA deconvoluted C1s spectra of PVA and PEO