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RF-plasma vapor deposition of siloxane on paper. Part 2: Chemical evolution of paper surface

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ABSTRACT

Survey and high-resolution (HR) XPS studies indicate that OMCTSO plasma treatment created a new silicon containing functional groups and changed the hydroxyl content on the surface of paper. Four intense survey XPS spectrum peaks were observed for the OMCTSO plasma treated paper. They were the Si_{2p} at 100 eV, Si_{2s} at 160 eV, C_{1s} at 285 eV, and O_{1s} at 525 eV for the plasma modified surface. It was realized that the macromolecular chain-breaking mechanisms and plasma-induced etching processes control the number and the availability of OH-functionalities during OMCTSO plasma exposure on paper. The reaction, initiated by these species, depends mainly on the nature of chemicals in the plasma as well as on the energy level of the plasma and the nature of the surface effects in the modification of the paper. The ATR-FTIR spectrum of paper treated with OMCTSO plasma has characteristic absorption bands attributed to the Si—O and Si—O—Si formations on the surface.

1. Introduction

Surface modification of solid materials i.e., paper, is very useful in achieving changes in surface chemistry. Plasma treatment has many advantages over conventional wet chemical surface modification, giving a dry environment-friendly surface modification, without any energy-intensive multi process [1–3].

It was pointed out that silicon-containing cold plasma treatment of paper affected thin film formation at or near surfaces [4]. The mass of the deposited silicon-containing polymer under microwave plasma conditions increased linearly with time [5].

Carlsson and Strom [6] studied the effects of low-pressure cold plasma treatment on various pulp and cellulose. He reported that plasma treatment oxidized the extractives and lignin in the pulp, and that the wettability of the pulp thus increased. Denes et al. [7] investigated the effects of cold plasma $SiCl_4^-$ on unsized and sized security papers. $SiCl_4^-$ plasma increased the amount of oxygen and silicon on surfaces.

Plasma processing is rapid, clean, and depending on the choice of gas, environmentally safe. Plasma processing has gained acceptance for applications in a wide range of materials from computer microchips to synthetic fabrics and polymers.

Plasma–material surface interactions can be divided into three categories [2] such as plasma etching or ablation of material that is removed from the surface, material deposited as a thin layer on the surface, and the surface being chemically modified by species present in the plasma, a process known as plasma treatment. The detailed information on plasma processing of materials can be found elsewhere [1–3].

RF cold plasma modification is an important way to treat paper and in Part 2 of this paper I evaluated the use of cold-plasma discharge, for the first time to deposit silane by plasma chemical vapor deposition (CVD) into paper sheets by an RF-cold plasma technique. The main objective associated with such treatment is to characterize plasma chemical vapor deposited siloxane on paper by an RF-cold plasma technique. The presence of an alternating RF-electromagnetic field across the plasma causes electron acceleration, which in turn leads to bond cleavage and ionization of OMCTSO molecules, which produced silicon containing functionalities. The occurrence of siloxane on paper was assessed by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR).

2. Experimental

Surface chemical characteristics and atomic composition of the plasma treated and untreated paper samples were evaluated by the use a Perkin-Elmer PHI 5400 XPS spectrometer (Mg source; 15 kV; 300 W; pass energy: 89.45 eV; take-off angle: 15°, 45°, and 85°). Carbon (C_{1s}), oxygen (O_{1s}), and silicon (Si_{2p}) atomic compositions were evaluated and the nonequivalent binding energy peaks of carbon linkages were analyzed. To correct surface

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charge-origin binding energy shifts, calibrations were performed based on the well-known C—O (286.7 eV) C_{1s} peak of cellulose. The surface atomic concentration was calculated with software based on the peak intensity. 'In order to correct surface charge-origin binding energy shifts, calibrations were performed based on the well-known C—O (286.7 eV) C_{1s} peak of cellulose'. Three samples from each treatment were utilized for experiments.

Selected samples were also derivatized to detect the types of oxidized groups by XPS. Trifluoroaceticanhydride (TFAA) was used to detect carboxylic and hydroxyl groups, and pentafluorophenylhydrazine (PFPH) was used to identify carbonyl groups.

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used to identify the chemical linkages on the plasma functionalized paper surfaces. An ATI-Mattson, Research Series IR instrument was used, and was provided with a GRASEBY-Special Benchmark Series ATR in-compartment P/N/11160 unit. The spectra were collected in the mid-IR region (4000–450 cm^{-1}) with 4 cm^{-1} resolution using a MTC detector, cooled to liquid nitrogen temperature, and a KRS-5 crystal (thallium bromoiodide, 50 mm × 10 mm × 3 mm).

3. Results and discussion

Survey XPS spectra of untreated and OMCTSO plasma treated paper are presented in Fig. 1. Typically, untreated paper shows two strong peaks (Fig. 1A) which are carbon and oxygen characteristics of glucose. The surface atomic composition of paper dramatically changed after OMCTSO-plasma treatments. Four intense survey XPS spectrum peaks were observed for the OMCTSO plasma treated paper. They were the Si_{2p} at 100 eV, Si_{2s} at 160 eV, C_{1s} at 285 eV, and O_{1s} at 525 eV for the plasma modified surface (Fig. 1B). The plasma modification reaction conditions for the sample shown in Fig. 1B were 25 W, 5 min, and 300 mTorr. The carbon and oxygen concentrations were found to be 49.5% and 25.7%, respectively, compared to untreated paper, which was composed of 56.7% carbon and 43.3% oxygen. The oxygen (O/C) and silicon (Si/C) to carbon atomic ratios for treated paper was found to be 0.52 and 0.50, respectively.

This silicon attachment to the paper surface may represent the direct reaction of activated OMCTSO vapor with the paper surface under the glow discharge. Ion bombardment or ultraviolet photons may not only break O—Si and Si—C bonds in the OMCTSO molecule,

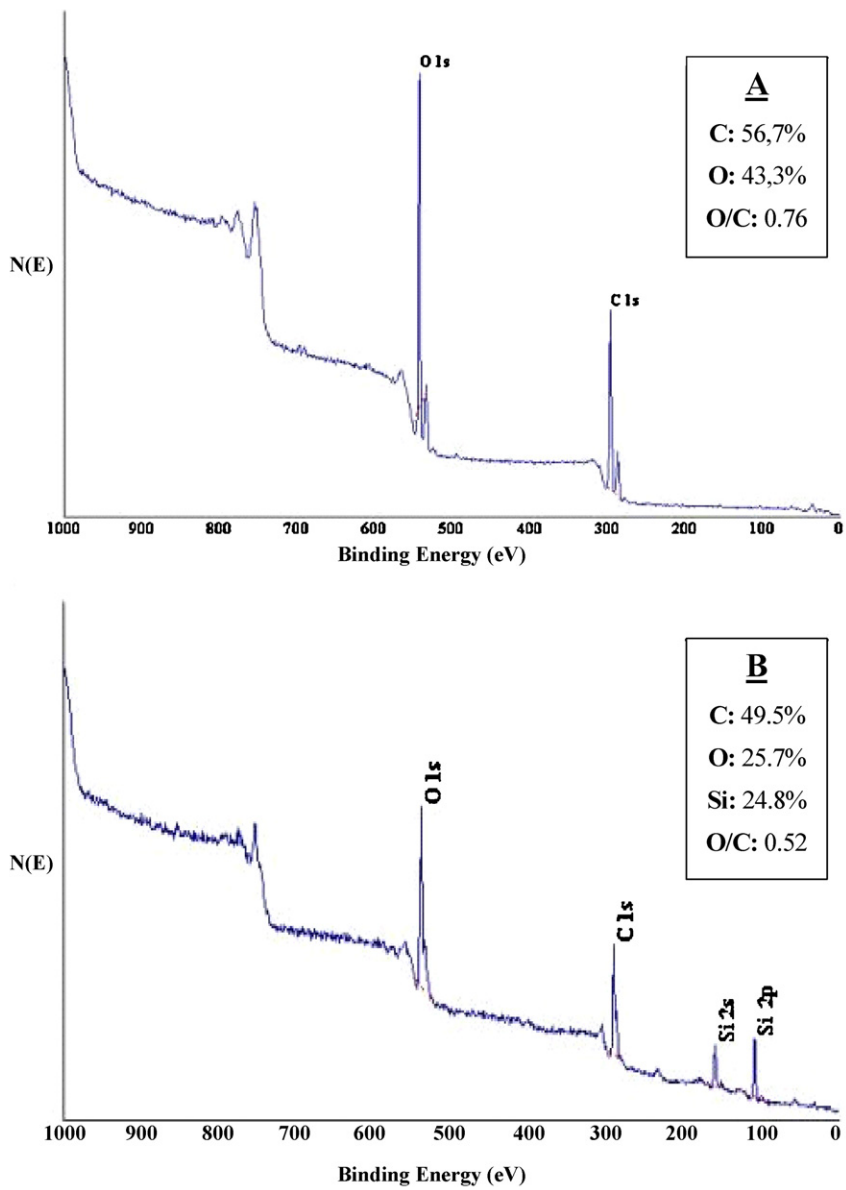

Fig. 1. XPS survey spectrum of untreated (A) and OMCTSO plasma treated paper (B).