Surface Sulfonation of Paper in SO₂+O₂ Plasmas – Hypotheses on Reaction Mechanisms

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ABSTRACT

A new approach to deposit sulfur groups on paper has been evaluated in this study by radio-frequency (RF) SO₂+O₂ plasma treatment. The survey and high-energy resolution XPS spectra provide clues to the site of modification on the paper surface. Relatively large variations in the deposited film-like layer composition can be realized by changing plasma parameters. In general, increasing RF-power provides effective implantation of sulfur, from 3.6% to 7.2%. It is clearly shown that elemental oxygen incorporation on paper directly depends on the relative ratio of SO₂/O₂.

All XPS HR C_{1s} diagrams from SO₂ + O₂ plasma treated samples show a penta model pattern. The presence of CH₂-S at 285.7 eV, O = C-O at 289.2 eV, and O-CO-O at 290.4 eV are the new groups characterized.

Keywords: RF-SO₂/O₂ plasma, paper, XPS, surface properties

INTRODUCTION

Mankind has used paper products for thousands of years. The oldest findings of paper objects date back to more than 2000 years /1/. However, during the last 50 years, there has been a tremendous development of advanced paper products for functional, biomedical, and structural applications /2, 3/.

Additive free, ordinary paper-based products could be described as temperature resistant, dielectric, and composed of cellulose, that is, the most important components influencing properties and end uses. However, functional papers possess unique material properties, such as high strength, good wear, and chemical resistance in most environments. Specially prepared structural papers are characterized by specific surface and optical properties. Advanced paper-based products are currently being used in a large number of applications, such as electrical devices, security, printing, and sensor purposes, with new applications continuously evolving /1-4/.

A promising application of paper is in the field of surface chemistry. The idea is simple and appealing; the papers are deliberately functionalized by selected moieties, which specifically react with the target species. However, the challenge is to design a suitable interface for a macroscale readout device from paper.

The cold plasma is one of the new techniques used to treat materials, without altering the bulk properties. The effect of treatment on a given substrate is determined by the chemistry of the reactions between the surface and the reactive species present in the plasma environment. For certain applications the required treatment need not be specific for example, in the modification of polymer surface properties for potential use for hydrophilic/hydrophobic purposes /5 6/.

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Zhao *et al.* /7/ found that Spunbond (SB) PET fiber presented a “sheath-core” type structure after the ($\text{SO}_2 + \text{O}_2$) plasma treatment. The sheath was a polarized layer with functional groups, and was the key to improving dyeability. Liu and Chen /8/ reported that the surface sulfonation of PVC treated with $\text{SO}_2 + \text{O}_2$ gas mixture, with plasma, depended on the volume ratio of the SO_2 and O_2 mixture. Gu *et al.* /9/ modified Bombyx mori silk fibroin (SF) film by SO_2 gas RF-plasma treatment. According to their findings the percentage of sulfur element on the surfaces of modified SF films was around 4.0%. Because of surface sulfonation, the antithrombogenicity of treated films increased remarkably. This implied the potential use of sulfonated SF for blood-contacting biomaterials /9/.

In this study, paper was selected to find alternative ways to improve certain characteristics by using RF-plasma treatments. A novel plasma process, based on surface deposition, by dissociation of $\text{SO}_2 + \text{O}_2$ gas environment was carried out using a parallel plate static reactor. The influence of SO_2 and O_2 mixture on the deposition of paper for elemental sulfur, and CO_x incorporation with treatment parameters was examined. It was believed that the RF-plasma technique would significantly modify paper surface via plasma treatment. Hence, here was an alternative method to introduce the unique sulfur structure on the paper surface. The data presented in this study go some way in helping to substantiate the validity of the paper surface modification reaction within the RF-plasma.

EXPERIMENTAL AND METHODS

The paper substrate was obtained from the USDA-Forest Products Laboratory in Madison, WI, and had an additive-free structure. The O_2 and SO_2 gases were obtained from AGA gas company, and were used as received.

Plasma reactions were carried out in an inductively coupled, stainless steel, parallel plate, a static reactor. To remove contaminants from previous experiments, the reactor was cleaned using an argon and oxygen discharge with the following parameters: power; 50-100 W, pressure; 500 mTorr, time; 1-5 min. The description of the plasma reactor can be found elsewhere /10/.

The paper samples were subjected to $\text{SO}_2 + \text{O}_2$ plasma modification under the external plasma parameters. The experimental conditions and parameters used in this study were; RF discharge power (P): 100-500 W; Treatment time (t): 1-10 min; Pressure in the absence of plasma (p): 100-500 mTorr; O_2 and SO_2 inlet feeding of SO_2/O_2 gas flow ratio (R): 0.2-1.8, and a total system pressure of 400 mTorr, at room temperature. After treatment, the samples were carefully stored in plastic bags prior to XPS analyses.

X-Ray photoelectron spectroscopy (XPS) technique was performed on a Perkin Elmer Physical Electronics 5400 small area spectrometer. with the following variables; the monochromated Mg- α X-ray source was operated at 37.5 keV, take-off angle was 45 degrees; and acquisition cycles were 5. The survey spectra were acquired from 0 to 1000 eV, and a pass energy of 89.45 eV was employed. High Resolution carbon (HR C_{1s}) XPS spectra were acquired with a step size of 1.0 eV. Both survey and HR C_{1s} spectra were used to evaluate the relative surface composition of unmodified and plasma modified samples, to estimate the presence of nonequivalent carbon functionalities.

RESULTS AND DISCUSSION

The survey XPS analyses of untreated paper indicate that the paper surface, free from any additives or contaminants, consisted of only carbon (C_{1s}) and oxygen (O_{1s}), which are the characteristics of cellulose. According to the XPS measurements, the relative surface atomic composition exhibits a slightly higher carbon (C= 57.9%), when compared to the theoretical value of cellulose (C= 54.5%). However, the relative oxygen to carbon ratio (O/C) is found to be 0.73, which is close to pure cellulose (0.83). Hence, the paper substrate that has been used in this study can be considered as cellulose substrate.

The deposition of new sulfur-based molecules on the paper by RF-plasma is evidenced by the presence of an S_{2p} peak in the XPS survey spectra at 185 eV binding energy (Figure 1). It appears that SO_2+O_2 RF-plasma exposure results in sulfur incorporation with modification of surface elemental oxygen and carbon concentration.

Fig. 1: Survey XPS spectrum of SO_2+O_2 RF plasma treated paper

However, relatively large variations in the deposited film-like layer composition could be realized by changing the plasma external parameters. A comparative summary of the surface atomic compositional changes with plasma treatment (as RF-power) is shown in Table 1. In general, increasing RF-discharge power provides effective implantation of elemental sulfur from 3.6% to 7.2%, and it appears to be well correlated with P.

Table 1

RF-Power effects on atomic concentration (%) of paper determined by XPS (5 min, 400 mTorr; R=1)

Power (Watt)	C (%)	O (%)	S (%)
0	57.9	42.1	0.0
100	59.9	36.4	3.7
150	60.7	35.7	3.6
350	58.5	36.2	5.3
400	50.7	42.2	7.2

The SO_2 concentration effects on the surface atomic concentration of papers after SO_2+O_2 RF-plasma exposure are presented in Table 2. It could be seen that increasing SO_2 gas flow from 1 to 9 sccm yielded marginally similar elemental carbon (C= 51.3-52.7%) and oxygen (O= 39.3-44.2%). It was clearly seen that elemental sulfur incorporation on paper had a directly proportional dependence on power (Table 1) and was inversely correlated with SO_2 concentration (Table 2).

The highest sulfur content of 8.0% was found at the lowest SO_2 concentration. However, oxidation appeared to be closely correlated with the SO_2 concentration present within the plasma. The highest oxygen concentration of 44.2% was found when R= 1.8. Possible reaction pathways for a SO_2+O_2 gas mixture under glow discharge were reported by some researchers /7-9,11-13/. Jiang and Hu /11/ found that the SO_2/O_2 resulted from sulfonation on poly(ester)urethane, with low powered gas plasma. Tsai and his group /12,13/ also reported that the conversion of SO_2 into elemental sulfur proceeded efficiently with the help of a radio-frequency plasma-induced system. Similar results with RF- $SO_2 + O_2$ mixture plasma treatment of paper were observed in this study.

Table 2
 SO_2 effects on atomic concentration (%) of paper determined by XPS

SO_2 flow (sccm)	C (%)	O (%)	S (%)
0	57.9	42.1	0.0
1.0	52.7	39.3	8.0
5.0	51.9	42.4	5.7
9.0	51.3	44.2	4.5

The XPS findings could be used in evaluating the surface chemical property of paper, which has been based on the determination of oxygen-to-carbon (O/C) and sulfur-to-carbon (S/C) relative atomic ratio. It is shown in Figures 2 and 3 that surface oxidation and elemental sulfur incorporation are strictly related to the RF power and SO_2/O_2 relative ratio. Hence, the different mechanism must control both effects, the increase of oxygen and sulfur on the paper surface. The presence of an RF-glow discharge field across a plasma reactor can cause electron acceleration, which in turn leads to ionization of both SO_2 and O_2 molecules.

It is possible that photon emission from the SO_2+O_2 glow discharge is the primary cause for the free radical formation, for implanting new sulfur groups on the paper surface. As C-S and O-S have high bond strength, the S and O atoms generated in the initial reactions can abstract other atoms, leading to the generation of other radicals in the cellulose chain. It is reported that when there is an oxygen functionality present in the polymer backbone (e.g., cellulose), etching and oxygen incorporation on the surface is operated together [14].

The quantitative evaluation of the XPS data was carried out by deconvolution of the C_{1s} core, using a curve fitting program. The approach used here was to optimize each fit using the following procedure. Component peak shifts were fixed at nominal values (e.g., + 2.5 eV for C-O). Once an initial fit was complete, then the new C, O, and S functional groups were tied to fit in terms of peaks, having well-characterized binding energy shifts. The typical HR C_{1s} XPS spectra of paper, treated with SO_2+O_2 RF-plasma, is presented in Figure 4. The spectrum clearly revealed diversity of new functionalities on paper surfaces. Besides the characteristic C-C at 285 eV, C-O at 286.7 eV, and O-C-O at 288 eV, peaks of cellulose, the presence of $\text{CH}_2\text{-S}$ at 285.7 eV, $\text{O}=\text{C}-\text{O}$ at 289.2 eV, and $\text{O}-\text{CO}-\text{O}$ at 290.4 eV were newly formed groups that were characterized.

Fig. 2: RF-power and SO_2/O_2 effects on surface O/C relative ratio

Fig. 3: RF-power and SO_2/O_2 effects on surface S/C relative ratio

Fig. 4: Comparative HR C_{1s} XPS spectrum of SO_2+O_2 RF plasma treated paper

Moreover, a sulfur-based functional group ($\text{CH}_2\text{-S}$ at 285.7 eV), which had a marginally similar binding energy to C-C at 285 eV, hence, HR deconvoluted C_{1s} peak at 285 eV, was assigned to contain both C-C and $\text{CH}_2\text{-S}$ groups. The fitted functionalities, relative to the aliphatic hydrocarbon peak charge, are displayed in Table 3.

Table 3
RF-power effects on atomic concentration (%) of paper determined by XPS

Power (W)	C-C & $\text{CH}_2\text{-S}$	C-O	O-C-O	O=C-O	O-CO-O
0	19.5	62.2	18.3	0	0
100	2.9	50.2	32.1	7.9	6.9
150	6.3	57.8	23.3	8.4	4.2
250	7.7	57.0	19.2	9.3	6.9
350	10.4	49.1	23.2	9.6	7.6
400	12.0	55.6	17.8	8.6	6.0

It was realized that surface functional composition was sensitive to both power and SO_2/O_2 ratio. When power was increased from 100 W to 400 W, the elemental sulfur implantation increased from 3.7 % to 7.2% when SO_2/O_2 ratio = 1 (Table 1), whereas, $\text{CH}_2\text{-S}$ and C-C ratio increased from 2.9% to 12.0%. This is an interesting observation, which

suggests the heterogeneity of paper surfaces after plasma treatment. Results clearly indicate that the sulfurous group is formed from SO_2 and O_2 dissociation, at all levels, followed by free radical conversion to the surface thin film deposition. Pons and his group /15/, observed that because of sulfur passivation, a significant decrease in the etch rate was obtained when using pure SO_2 plasmas as compared to pure O_2 plasmas. It was also presented by Pons and his group /16/, that the plasma etching process based on sidewall passivation by sulfur was proposed using SO_2+O_2 mixtures. This relationship suggested that there were two ways of increasing the sulfur on paper, namely by increasing the power or decreasing SO_2 gas flow ratio. Tsai *et al.* /12/, found that the RF-plasma technique was beneficial to convert SO_2 to elemental sulfur with CH_4/SO_2 mixture. As the CH_4 concentration was increased, most sulfur-containing products were in the form of elemental sulfur. Similar results with SO_2+O_2 plasma treatment of paper were observed in this study.

The newly formed surface functionalities, after $\text{SO}_2 + \text{O}_2$ glow discharge, appear to be well correlated on the plasma RF power (P) and SO_2/O_2 relative ratio (R). Figure 5 clearly indicates that the plasma external parameters (P and R) have a close relationship and generate C-C and $\text{CH}_2\text{-S}$ groups (C1) on paper. Similar results were observed with $\text{O}=\text{C}-\text{OH}$ (C4) (Fig. 8) and $\text{O}-\text{CO}-\text{O}$ (C5) (Fig. 9) functionalities. The increase in those groups in HR XPS C_{1s} are attributed to SO_2+O_2 gas discharge, which can generate free radicals and then react with cellulose to induce an oxidation reaction. However, C-O (C2) and $\text{O}-\text{C}-\text{O}$ (C3) groups appear to decrease with R and P (Figs. 6 and 7). It is probably because ablation and etching proceed together on cellulose. Having this information, the results have been rationalized on the basis of the accepted mechanisms of free radical formation on cellulose macromolecule versus chain scission (etching). It was proposed that free radical formation in the cellulose is possible with hydroxyl abstraction from cellulose chains /10,17/.

Fig. 5: RF-power and SO_2/O_2 ratio effects on surface C-C and $\text{CH}_2\text{-S}$ functionalities determined by XPS

Fig. 6: RF-power and SO_2/O_2 ratio effects on surface C-O functionalities determined by XPS

Fig. 7: RF-power and SO_2/O_2 ratio effects on surface O-C-O functionalities determined by XPS

Fig. 8: RF-power and SO_2/O_2 ratio effects on surface O=C-OH functionalities determined by XPS

Fig. 9: RF-power and SO_2/O_2 ratio effects on surface O-CO-O functionalities determined by XPS

It is reasonable to conclude that the formation of sulfur and oxygen containing functionalities affect sulfonation as well as intense oxidation, with macromolecular ablation of cellulose. The decreased C-OH surface areas in HR C_{1s} XPS spectra (Table 3 and Fig. 6), verify this assumption. It is well known that the reactive species in a plasma result from ionization, fragmentation, and excitation processes. In reactive gas environment (e.g., SO_2 , O_2) the functionalization with ablation and etching occur simultaneously within the plasma, resulting in the formation of small volatile degradation products /5, 6/.

CONCLUSIONS

The results suggest that elemental sulfur formation on paper surface is essential in the SO_2+O_2 RF glow discharge environment. The survey and HR C_{1s} XPS diagrams indicate an even lower SO_2/O_2 ratio, which generates a diversity of new sulfur and oxygen-based functionalities on paper surfaces, including $\text{CH}_2\text{-S}$ (285.7 eV), O=C-O (289.2 eV) and O-CO-O (290.4 eV).

It can be concluded that the new groups were introduced on paper surface at high power by a similar mechanism to that used with lower power, by direct dissociation from SO_2+O_2 gas phase and paper surface. This creates novel surface characteristics, which cannot be realized by conventional treatments.

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