Materials Research. 2017; 20(Suppl. 2): 842-850
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2016-1111

Morphological and Chemical Effects of Plasma Treatment with Oxygen (O_2) and Sulfur Hexafluoride (SF_6) on Cellulose Surface

Janine Sanches Gonzaga de Camargo[a,b]****, Aparecido Junior de Menezes***[a]***, Nilson Cristino da Cruz***[b]***,***

Elidiane Cipriano Rangel[b]***, Adriana de Oliveira Delgado-Silva***[a]

[a]*Centro de Ciências e Tecnologias para a Sustentabilidade, Universidade Federal de São Carlos, Rod. João Leme dos Santos, km 110, 18052-780, Sorocaba, SP, Brasil*
[b]*Laboratório de Plasmas Tecnológicos, Universidade Estadual Paulista, Campus Experimental de Sorocaba, Av. Três de Março, 511, 18087-180, Sorocaba, SP, Brasil*

Received: December 21, 2016; Revised: September 30, 2017; Accepted: December 14, 2017

Cellulose is a polymer widely available in nature, however its applications may be restrict due to its hydrophilic character. The creation of hierarchical structures on the surface is one of the required factors to obtain the hydrophobicity of this material. In order to compare the morphological and chemical effects caused by the action of different gases in the creation of nanostructures on the cellulose surface, samples were exposed to oxygen (O_2) and sulfur hexafluoride (SF_6) plasma treatments. The changes in morphology after treatment prove that both the gases were able to create similar nanostructures in the material. The analysis of elemental composition and identification of functional groups on the sample surface showed that chemical modifications occurred differently for each treatment. Contact angle measurements revealed that samples treated by O_2 plasma remained hydrophilic, whereas low receptivity to polar ($\theta > 120°$) and non-polar ($\theta > 100°$) liquids was observed for samples exposed to SF_6 plasma.

Keywords: *cellulose, plasma treatment, hydrophobicity, hierarchical structures.*

1. Introduction

Cellulose $(C_6H_{10}O_5)_n$ is the most abundant organic compound found in nature, having structural role on the cell wall of plants[1]. This biopolymer offers several advantages such as flexibility, biodegradability, good mechanical strength and low cost, which justifies its intense application in textile, paper and packaging industries[2,3], as well as in the production of sensors[4,5] and reinforcement for composites[6,7]. However, the use of cellulose in these areas often becomes restricted due to the hydrophilic characteristic of this material, resulting from the presence of free hydroxyl groups in its molecule[8,9]. Thus, the surface modification of cellulose to enable the reduction of their receptivity to water is essential for the development of products such as more resistant packaging[10,11], self-cleaning fabrics[12,13] and waterproof clothing[14,15].

The hydrophobic property of a surface depends mainly on the combination of adequate surface roughness and low surface energy[16]. However, studies reported show that the roughness factor can contribute more significantly to obtaining the superhydrophobicity effect[17,18], wherein the surface exhibits a water contact angle higher than 150° and low hysteresis, that can be defined as low adhesion of a liquid to the surface, so that a drop can easily slide out of the material[17].

Furthermore, the increase in surface roughness must be associated with the presence of hierarchical structures in the material, i.e., micro- and nanoscale structures[17-19]. Several methods, such as layer-by-layer[20], sol-gel[21], electrospinning[22] and lithography[23] have been used in the development of structures at different scales. In addition to these processes, another commonly applied method for the creation of these structures is the plasma etching[24,25]. The plasma, also known as the "fourth state of matter", can be defined as an ionized gas, mainly generated by electrical discharges and containing a series of charged and neutral species. The plasma processing is widely used for surface modification of different materials because it is environmentally friendly, dry, and clean[26]. Besides, this technique promotes the modification of chemical and morphological properties only in the superficial layers of the substrate, thus the original bulk remaining intact, since the plasma species do not penetrate below 10 nm of the surface[27]. The plasma can be classified according to the conditions in which it is established. In laboratories, the plasma is generated at a temperature close to the ambient temperature and is called non-equilibrium thermodynamic plasma or cold plasma. As only the temperature of the electrons is high (around 10^4 K) and the other species presented in the plasma remain at ambient temperature, including the temperature of samples, cold plasma is considered feasible in the surface modification of heat-sensitive substrates, such as cellulose[28].

The plasma etching process occurs by removing the surface material through chemical interaction between the reactive components of the plasma and the species of

---

*e-mail: janine_sanches@yahoo.com.br

the substrate, resulting in volatile products[29]. The changes generated on the surface of the material depend on several factors, such as gas pressure, applied power and exposure time of the samples to the plasma[29]. The plasma composition is another parameter that can strongly affect the properties of the substrate. In some cases, not only the topography but also the surface energy can be changed in a single step, by the choice of a different kind of precursor gas[30,31]. Besides being a flexible technique, the plasma treatment can also easily be extended to an industrial scale.

Based on these concepts, this study aimed to compare the morphological and chemical effects on the cellulose surface treated by two different gases, oxygen (O_2) and sulfur hexafluoride (SF_6), commonly used in plasma processes for the creation of nanoscale structures. The study of these effects provides a better understanding of the action of the gases and assists in the choice of the appropriate precursor according to the desired application of the material, such as hydrophobic and superhydrophobic surfaces.

2. Experimental procedure

Pulp kraft cellulose plates (supplied by Votorantim Celulose e Papel) in A4 format and 0.2 mm thick were cut into small rectangles with 20 mm x 10 mm. The samples were exposed to oxygen (O_2) and sulfur hexafluoride (SF_6) plasmas as received.

The system used for the treatments is basically composed by a cylindrical glass chamber (5L) containing two circular parallel plate electrodes, described in detail in previous work[32]. The upper electrode consists of a metallic grid, through which the gas flows into the reactor while the lower electrode acts as a sample holder. The gas admission in the chamber is controlled by high precision needle valves and the pressure of the system is monitored by the Pirani/capacitive membrane gauge. The chamber is evacuated by a rotary pump. The electrical signal for plasma generation is provided by a radiofrequency power supply (Tokyo Hy-Power, operating with 13.56 MHz) connected to an impedance matching circuit (Tokyo Hy-Power).

For the treatments, the samples were first placed on the lower electrode and then the system was evacuated to the desired base pressure.

In treatments involving the oxygen gas (O_2), the base pressure was set at 0.015 Torr and the work pressure at 0.1 Torr, with the treatment time varying from 5 to 60 minutes. The radiofrequency signal with a power of 150 W was applied to the lower electrode (sample holder), while the upper electrode remained grounded. In oxygen plasma, neutral, negative and positive species are formed by the dissociation and ionization of the molecules of the gas by the collision with electrons[29]. Since the cross section for the formation of positive ions is about 100 times higher than for negative ions[28], the first can act more intensely in assisting the chemical reactions on the surface[33]. The application of radiofrequency to the sample holder generates a negative DC bias that attracts these positive ions, causing ionic bombardment on the surface of the substrate and reactive ion etching[28,34].

For the sulfur hexafluoride gas (SF_6) treatments, the base pressure of the system reached 0.05 Torr, and the work pressure was set to 0.5 Torr. Unlike the oxygen treatment, a radiofrequency signal was applied to the upper electrode, with a power of 135 W while the lower electrode remained grounded. In the plasma phase, the breaking of the SF_6 molecules produces F atoms and SF_x radicals[30]. On the grounded electrode, the ion bombardment is very weak, since positive ions are attracted in the opposite direction. Then, the chemical etching occurs by the action of fluorine species diffused in the plasma region near the sample surface. In this treatment, the time was varied from 2 to 20 minutes.

The treatment time from oxygen gas and SF_6 gas was defined based on the work of Li et al.[35] and Kamlangkla et al.[31], respectively. In these works it is verified that each type of precursor gas acts differently in the modification of the morphology of the substrates, which influences the time spent on the treatment. Thus, in treatments involving fluorine, the removal of material from the surface is more aggressive and the alteration in its topography occurs more quickly, requiring shorter treatment times. In treatments using oxygen, the time required to obtain the same effect caused by fluorine is significantly higher, which implies longer treatments, in which the etching rate is lower.

The effect of plasma treatments on the morphology of the cellulose surface was analyzed by Scanning Electron Microscopy (SEM) with a microscope JEOL JSM-6010 LA using a detector of secondary electrons. In samples subjected to the O_2 plasma, an incident energy of 3 kV was applied. In samples exposed to SF_6 plasma, the incident energy was 2.5 to 10 kV. For the analysis, the untreated and treated samples were first coated with an Au-Pd thin layer, to avoid charging on the surface.

The presence of chemical elements on the surface of the treated samples was determined by Energy Dispersive Spectroscopy (EDS), from a detector Dry SD Hyper coupled on the scanning electron microscope, using energy of 3 kV. For each sample, five different regions of the surface with area of 90 x 125 μm^2 were analyzed, and the final results correspond to the mean of the collected values.

The identification of chemical functional groups present in surface of treated and untreated samples was performed by Fourier Transform Infrared Spectroscopy (FTIR) with a Jasco FT / IR-410 spectrometer in attenuated total reflectance mode (ATR). The spectra were obtained in the wavenumber range of 4000-600 cm^{-1}, in a total of 128 scans with a resolution of 4 cm^{-1}.

The wettability of cellulose samples was measured by the sessile drop technique in a Ramé Hart goniometer (model 100-00) with deionized water and diiodomethane. For each sample, three droplets of liquid have been deposited on different points of the surface, each with 10 measurements of the contact angle. The results correspond to the average of the 30 measurements. In order to verify the air aging effect, the contact angle measurements were performed immediately after treatment (named 0 week) and in the following 1, 2, 3 and 18 weeks. For each measurement, a new sample (that had not yet been in contact with liquids) was used.

3. Results and Discussion

3.1 Morphology

The micrographs of the untreated cellulose and the samples exposed to O_2 plasma treatment for different times are shown in Figure 1. It is noted that even for short times (Figure 1b), the surface morphology was altered after being exposed to oxygen plasma, compared to the morphology of cellulose as received (Figure 1a), in which homogeneous and smooth surface fibers are shown. The alteration in the morphology is the result of the etching process promoted by oxygen plasma species on the cellulose surface. For treatment times shorter than 15 minutes, the presence of nanostructures on the fibers surface is still subtle, because the time employed was not sufficient to promote substantial removal of material from the substrate.

On the other hand, an accentuated removal of material of the sample is evidenced by the appearance of grooves on the surface of the fibers for 30 minutes of etching time, as seen in Figure 1d (highlighted by the circle). After 60 minutes of etching, the grooves become deeper (Figure 1e, highlighted by the square) and the fibers become thinner, compared with cellulose as received, which can be better seen in Figure 2b (indicated by arrows). This effect is characteristic of treatments involving reactive gases like oxygen[24,25]. In these treatments, energetic plasma particles chemically interact with the species of the sample, removing them and forming volatile products, such as water vapor, carbon monoxide and carbon dioxide[24,25], that are then eliminated by pumping from the reactor. There is also the possibility of recombination of the removed species, favoring the formation of polar groups (e.g., hydroxyl and carboxyl groups), which if were not removed from the system, can remain in the discharge and be reincorporated into the sample[28,29].

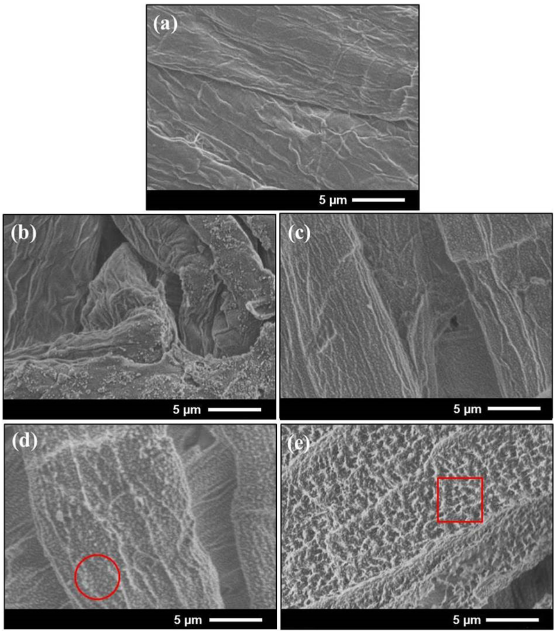

Figure 1. SEM micrographs of cellulose (a) untreated and the samples exposed to O_2 plasma treatment for (b) 5 minutes, (c) 15 minutes, (d) 30 minutes and (e) 60 minutes

According to Balu et al.[25], the etching process with oxygen can be described according to the Equations 1, 2 and 3.

$$R + O \rightarrow R\cdot + OH \tag{1}$$

$$R + OH \rightarrow R\cdot + H_2O \tag{2}$$

$$R\cdot + O \rightarrow R'O + CO + CO_2 \tag{3}$$

where R is the backbone of the cellulose and O represents radical or excited oxygen produced in the plasma processes.

The morphological change caused by the action of plasma is similar to that reported by Sapieha et al.[24], Balu et al.[25] and Xie et al.[36]. These authors attribute the creation of nanostructures to the crystalline phase revealed after the preferred reaction of plasma species with the amorphous phase of the microfibrils. Although it is necessary to apply other techniques for a better understanding of this effect, this hypothesis is corroborated by previous studies that demonstrated that the amorphous regions are more susceptible to chemical and ion etching[37-40].

The micrographs of the untreated cellulose and the samples exposed to SF_6 plasma treatment for different times presented in Figure 3 show once again that the treatment time is a factor which affects significantly the morphology of the material. The presence of nanostructures on the surface of the fibers within the first two minutes of treatment (Figure 3b, highlighted by the circle) is consequence of the high reactivity of fluorine plasma that acts by removing species of the substrate and promoting surface functionalization simultaneously. With the increase in exposure time of samples to plasma treatment, grooves arise on the surface of the fibers, which become thinner as can be seen in Figure 2c (indicated by arrows). This pronounced change in the surface morphology can be associated with weight loss due to removal of species from the cellulose surface by the action of fluorine. In their work, Hodak et al.[30] observed this weight loss in treatments involving silk and related it to an etching process, which is similar to treatments from oxygen plasma. The process of etching with fluorine occurs when

F atoms interact with the surface and abstract hydrogen atoms and hydroxyl groups, producing volatile species which are easily removed by the vacuum system. In addition to eliminating these species, the F atoms recombine with carbon atoms present on the cellulose surface by covalent bonds. This recombination may result in the reduction of the surface energy of the material, contributing to the desired hydrophobicity effect. The mechanisms of abstraction and recombination from the model proposed by Hodak et al.[30] can be described by Equations 4, 5 and 6.

$$R-C-H \xrightarrow{F\cdot} R-C\cdot + HF \quad (4)$$

Abstraction

$$R-C-OH \xrightarrow{F\cdot} R-C\cdot + F\cdot + OH\cdot \quad (5)$$

$$\text{Adsorption/Recombination} \quad R-C\cdot \xrightarrow{F\cdot} R-CF \quad (6)$$

where R is the backbone of the cellulose.

However, the excess of fluorine incorporated into the material may adversely affect its properties. According to Jinkarn et al.[41], the fluorine can promote both etching and deterioration of the fibers. The accentuated removal of material from surface (etching process) causes the appearing of pits on the cellulose fibers, seen in Figures 3d and 3e (highlighted by squares), for treatment times longer than 15 minutes. The deteriorated morphology can impair the role of the created nanostructures on the achievement of the desired surface properties.

When comparing the structures produced with the precursors oxygen (Figure 1) and fluorine (Figure 3), it is possible to observe that a similar morphology (Figure 1d and Figure 3c) could be obtained for both gases choosing the appropriated combination of the plasma treatment parameters. The obtained nanostructures associated with the microstructure characteristic of the cellulose fibers promote the hierarchical roughness on the surface of the material, necessary in modifying the surface wettability.

3.2 Composition

In order to investigate the effect of O_2 plasma treatment in the composition of the material surface, the samples were analyzed by Energy Dispersive Spectroscopy (EDS). Figure 4 presents the relative intensity O/C of detected characteristic photons for the cellulose samples treated with different exposure times. The point presented in the zero of the abscissa in the graph represents the result for cellulose as received.

The few variation in the relative intensity O/C shown in the figure suggests a balance between removal and incorporation of species, i. e., groups are reincorporated in the same proportion as they are removed. This behavior can be better observed in Figure 5 that presents a map of elemental distribution obtained from a region of the cellulose sample exposed to the oxygen plasma for 60 minutes. Although there are some more deteriorated points in the sample due to the long treatment time (highlighted in Figure 5a), it is possible to notice that the damage in the morphology cannot be directly associated with elemental concentration of carbon and oxygen (regions also highlighted in Figures 5b and 5c).

From the semi-quantitative EDS analysis, the changes on the composition of the material surface after SF_6 plasma treatment were also investigated. The results showed on Figure 6 confirm the incorporation of fluorine at the surface of cellulose and also indicate a trend of increase in relative intensity of F/C with the treatment time.

The EDS map in Figure 7 illustrates the relation between the damage in the fibers and the distribution of elemental concentration in a region of the cellulose surface submitted to the SF_6 plasma. It can be noted that the most damaged regions of the surface, evidenced by the formation of clusters of damaged fibers (pointed out in Figure 7a), correspond to the areas with higher fluorine concentration (higher color intensity in Figure 7d) and lower concentration of carbon and oxygen (indicated in Figure 7b and 7c). This observation suggests that the fluorine etching promotes functionalization at localized points on the surface where the removal of material occurs.

Thus, even though it is possible to obtain a very similar morphology independent of the precursor used, as discussed above, it is evident in the comparison of the maps of Figure 5 and Figure 7 that the concentration of the elements on the

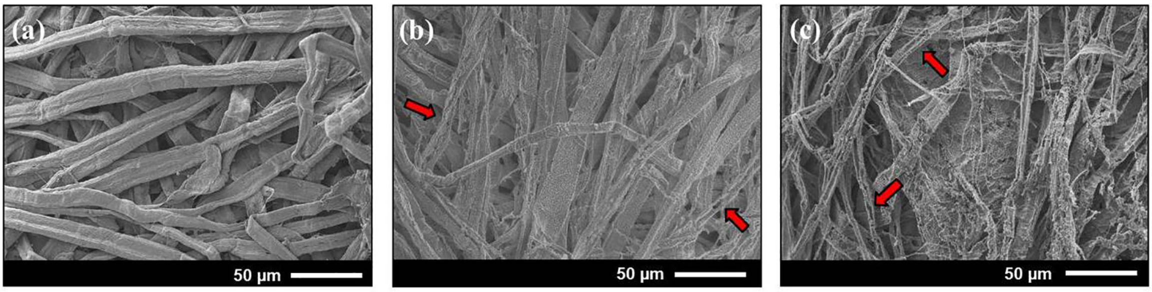

Figure 2. SEM micrographs of cellulose (a) untreated and the samples exposed to (a) O_2 plasma treatment for 60 minutes and (c) SF_6 plasma treatment for 20 minutes

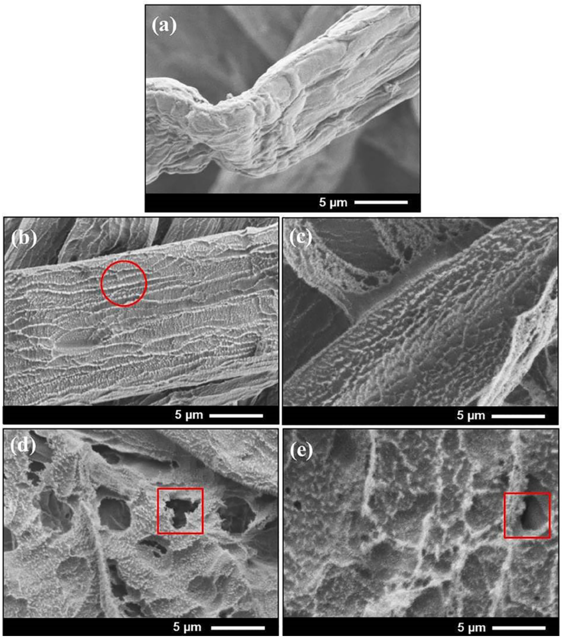

Figure 3. SEM micrographs of cellulose (a) untreated and the samples exposed to SF_6 plasma treatment for (b) 2 minutes, (c) 10 minutes, (d) 15 minutes and (e) 20 minutes

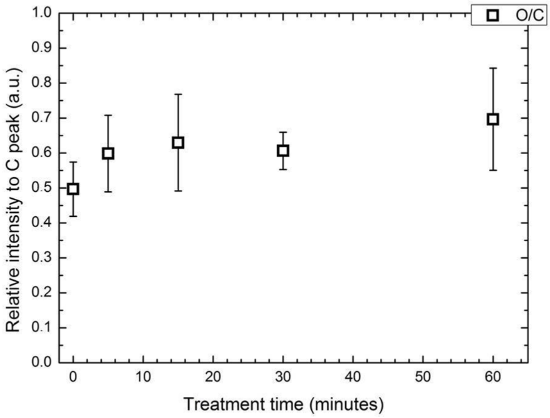

Figure 4. Relative intensity O/C of detected characteristic photons in the surface of cellulose samples treated as a function of the variation of the exposure time to O_2 plasma treatment. Points in zero correspond to results for untreated cellulose

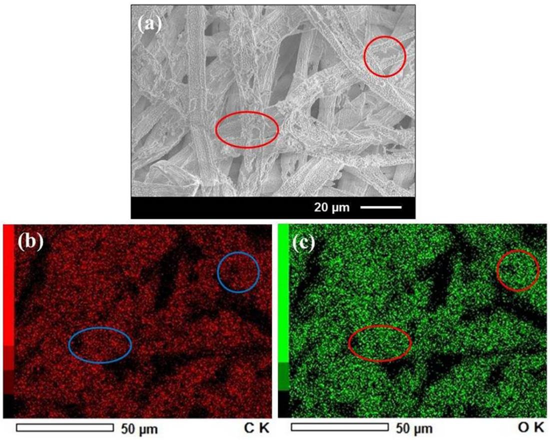

Figure 5. Micrograph of (a) treated cellulose sample for O_2 plasma treatment; and elemental maps of the major detected elements: (b) carbon and (c) oxygen. The highlighted areas in (a) correspond to the most deteriorated regions. The pointed out areas in (b) and (c) correspond to the elemental concentration of carbon and oxygen, respectively, in these same deteriorated regions

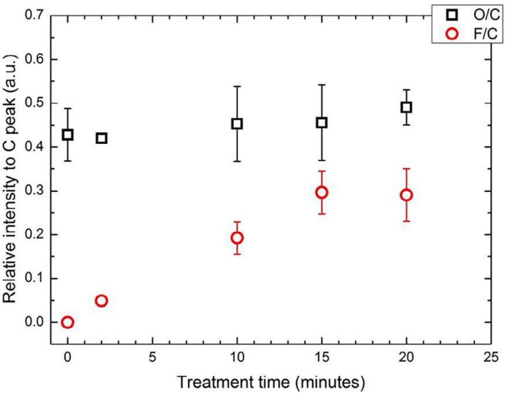

Figure 6. Relative intensity O/C and F/C of detected characteristic photons in the surface of cellulose samples treated as a function of the variation of the exposure time to SF_6 plasma treatment. Points in zero correspond to results for untreated cellulose

surface of the samples does not present the same distribution behavior for the two gases studied, which can be determinant in the performance of a surface.

Traces of sodium (Na) and silicon (Si) were also detected on the sample surface from the analysis, since these atoms were removed from the glass reactor by the action of the oxygen and fluorine plasmas and were also incorporated into the cellulose. However, the intensity of these contaminants on the surface was less than 2%.

The identification of chemical functional groups on the surface of the substrates exposed to the longest time condition, both in O_2 plasma and SF_6 plasma can also be verified in the spectra obtained by FTIR-ATR, shown in Figure 8. In the spectrum presented in Figure 8a, which refers to the untreated cellulose sample, it is possible to observe the main absorption bands of the material: the intense band located approximately in 3400 cm^{-1} is characteristic of OH stretch bonds; the band at about 2900 cm^{-1} is assigned to CH symmetric bonds and the absorption bands located in the region of 1200-1000 cm^{-1} are attributed to C-O and C-OH stretch bonds[42].

After exposing the substrate to oxygen plasma for 60 minutes, in addition to the characteristic bands of cellulose, it is also observed the appearance of a new absorption band in the region around 1700 cm^{-1}, as highlighted in the spectrum of Figure 8b. The emergence of this band confirms the formation of new unsaturated chemical groups on the surface, such as carbonyl groups (C=O)[43,44]. This result

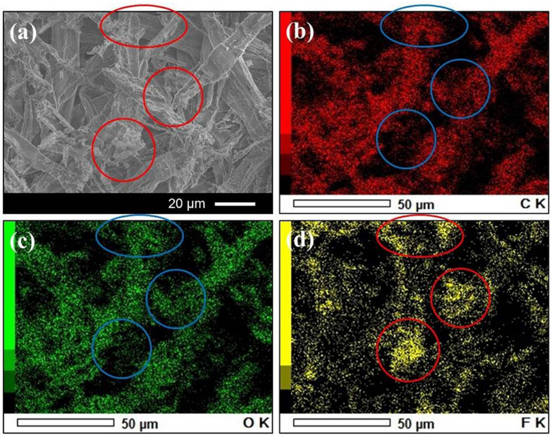

Figure 7. Micrograph of (a) treated cellulose sample in SF_6 plasma treatment and elemental maps of the major detected elements: (b) carbon, (c) oxygen and (d) fluorine. The highlighted areas in (a) correspond to the most deteriorated regions, in (b) and (c) correspond to the lower concentration of carbon and oxygen, respectively, and in (d) correspond to higher fluorine concentration

reinforces the hypothesis regarding a balance on the chemical composition of the surface, discussed from the EDS results. Oxygen plasma promotes bond breaking and H abstraction, which may result in the formation of unsaturated bonds, with balance in the elemental concentration.

The presence of a new band is also evident in the samples submitted to treatment with SF_6, as highlighted in the spectrum of Figure 8c. This absorption band in the region about 725 cm^{-1} is attributed to C-F stretch bonds[42,45], which confirms once again the occurrence of the abstraction and recombination processes characteristic of fluorine plasma etching.

3.3 Wettability

In the treatments involving O_2, the interaction of the plasma with the surface promotes the removal of species, producing free radicals. The recombination of the species may then favor the formation of polar groups in the substrate, which contributes to the increase in surface energy of the material and consequently to its hydrophilic character[46,47]. In samples submitted for this process, the contact angle measurement cannot be performed since the droplets of both liquids (water and diiodomethane) deposited on the surface were immediately absorbed. In this way, the contact angle was considered as 0º. On the other hand, the samples exposed to treatment with SF_6 presented quite different behavior and this can be confirmed in Figure 9, that depicts the results of contact angle in cellulose surface with (a) deionized water and (b) diiodomethane as a function of the treatment time in SF_6 plasma. Only the results obtained on measurements performed immediately after treatment (named 0 week) and after 18 weeks of the treatment are shown in the figure. The other measurements presented compatible values considering the error bars.

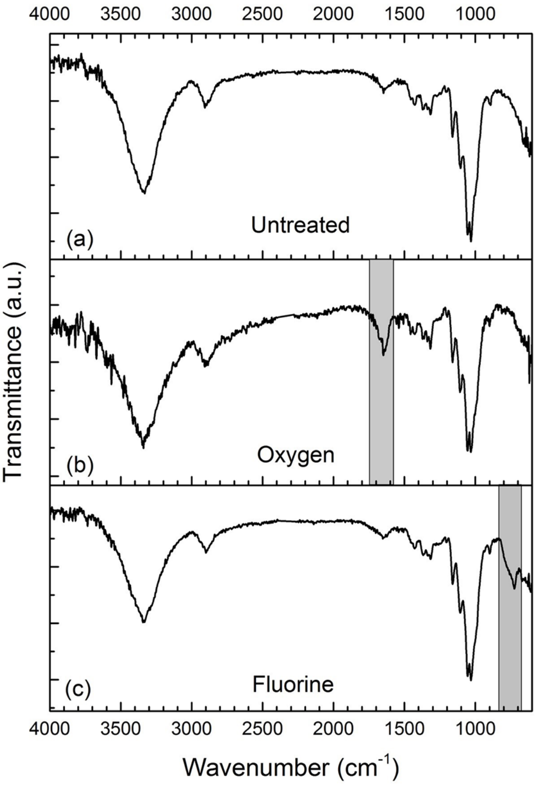

Figure 8. Infrared spectra of (a) untreated cellulose and cellulose samples treated by (b) O_2 plasma for 60 minutes and (c) SF_6 plasma for 20 minutes

In Figure 9a, it is observed that the cellulose became hydrophobic immediately after exposure to plasma for all treatment time conditions established. The effect of hydrophobicity obtained by the material can be explained by the removal of hydroxyl groups by fluorine plasma, providing the diminishment of the hydrophilicity property of cellulose, as demonstrated by Hodak et al.[30] and Kamlangkla et al.[31]. Furthermore, according to Vaswani et al.[48], the presence of fluorine on cellulose surface contributes to the reduction of the surface energy, thereby promoting increased contact angle values, as the values obtained with water and exceeding 120º.

The low receptivity can also be observed in measurements with a non-polar liquid, in which high contact angle values ($\theta > 100º$) were obtained regardless of the treatment time condition, as can be seen in Figure 9b. This reduction of wetting to both the polar (water) and the non-polar (diiodomethane) liquids may be associated with the establishment of called Cassie-Baxter state[49] by cellulose surface. In this state, the droplet of liquid deposited on a substrate remains suspended in the surface by air bubbles contained between nanostructures present on the material, thus preventing the spreading of the liquid. Several reports indicate that the presence of hierarchical structures, i.e., micro- and nanoscale structures on the material surface, contributes to the generation of an adequate roughness, which

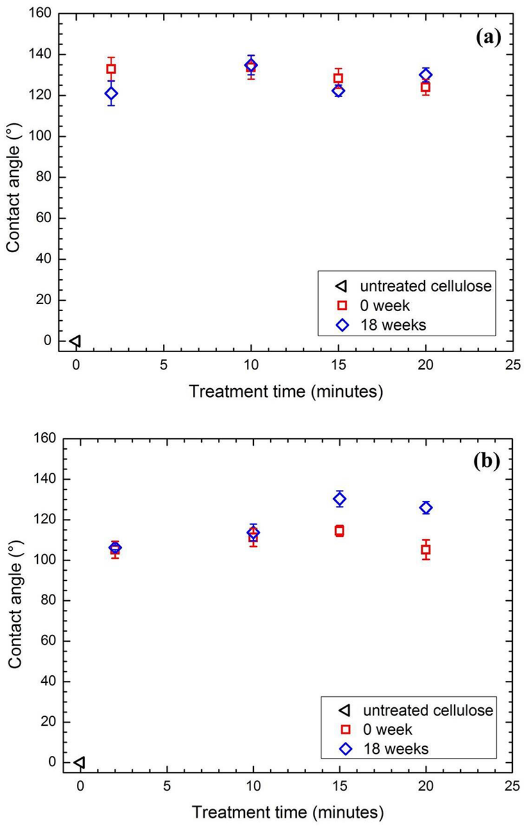

Figure 9. Contact angle in cellulose surface with (a) deionized water and (b) diiodomethane as a function of treatment time in SF_6 plasma, in measurements performed immediately after treatment (named 0 week) and after 18 weeks of treatment. The point in zero represents the contact angle of untreated cellulose

is an essential factor to achievement of this state[19,50]. Even for samples exposed for less time to treatment, the level of surface modification due to the removal of species on the substrate was sufficient to create such structures, which are clear in the micrographs shown in Figure 3 and which were responsible for the observed contact angle values with both liquids of different polarities. These results demonstrate that plasma treatment of SF_6 is capable of generating a suitable topography, with reduced surface energy and which is stable after aging time.

Despite not being possible to directly compare such results with oxygen treatment, since it has the effect of enhancing the hydrophilic behavior of cellulose, it is important to note that O_2 gas is widely used in the generation of superhydrophobic surfaces in plasma processes performed in two steps[35,36,51,52]. In this case, oxygen is responsible for creating the necessary roughness of the surface of the material, which then receives a thin coating on it. Although it is a slightly more complex process, the use of oxygen reduces the costs of treatment and can be considered more environmentally correct.

4. Conclusions

In this work, the effects promoted by the use of different gases on the cellulose surface plasma treatments were presented and discussed. The plasma treatment significantly affects the surface morphology of the cellulose. Thus, by the appropriate combination of treatment parameters, both gases, O_2 and SF_6, were able to create similar nanostructures in the material, essential for obtaining a superhydrophobic surface. Treatment times greater than 30 minutes for O_2 and 15 minutes for SF_6 caused deterioration of the samples.

The chemical modifications observed on the samples surface exposed to plasma are distinguished according to the gas precursor used. In oxygen treatment, the formation of new unsaturated functional groups (C=O) on the surface and the slight variation in the concentration of the chemical elements present in the material suggested a balance between the mechanisms of removal and incorporation of species during the plasma process. For SF_6 plasma, the incorporation of fluorine on the cellulose surface confirms the occurrence of the abstraction and recombination processes, characteristic of fluorine etching. Moreover, the surface functionalization was promoted preferentially in regions with greater removal of material, in which a marked deterioration of fibers was observed.

Distinct behaviors were also observed in relation to the wettability of the treated surfaces. For samples submitted to O_2 plasma, the hydrophilic character of the substrate remained, but in treatments involving SF_6, the cellulose surface presented a diminishment of the receptivity to both polar and non-polar liquids, with contact angle values higher than 120º for deionized water and 100º for diiodomethane, which remained stable after aging time.

5. Acknowledgments

The authors acknowledge Capes for the financial support, Votorantim Celulose e Papel (VCP) for providing the samples and Rafael Parra Ribeiro from LMCMat for SEM micrographs.

6. References

1. Pérez S, Samain D. Structure and engineering of celluloses. *Advances in Carbohydrate Chemistry and Biochemistry*. 2010;64:25-116.

2. Weber CJ, Haugaard D, Festersen R, Bertelsen G. Productions and applications of biobased packaging materials for the food industry. *Food Additives and Contaminants*. 2002;19(Suppl 1):172-177.

3. Peelman N, Ragaert P, De Meulenaer B, Adons D, Peeters R, Cardon L, et al. Application of bioplastics for food packaging. *Trends in Food Science & Technology*. 2013;32(2):128-141.

4. Li X, Tian J, Shei W. Progress in patterned paper sizing for fabrication of paper-based microfluidic sensors. *Cellulose*. 2010;17(3):649-659.

5. Ummartyotin S, Manuspiya H. A critical review on cellulose: From fundamental to an approach on sensor technology. *Renewable and Sustainable Energy Reviews*. 2015;41:402-412.

6. Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres. *Progress in Polymer Science*. 1999;24(2):221-274.

7. Pöllänen M, Suvanto M, Pakkanen TT. Cellulose reinforced high density polyethylene composites - Morphology, mechanical and thermal expansion properties. *Composites Science and Technology*. 2013;76:21-28.

8. Samyn P. Wetting and hydrophobic modification of cellulose surfaces for paper applications. *Journal of Materials Science.* 2013;48(19):6455-6498.

9. Credou J, Berthelot T. Cellulose: from biocompatible to bioactive material. *Journal of Materials Chemistry B*. 2014;2(30):4767-4788.

10. Archaviboonyobul T, Jinkarn T, Sane S, Chariyachotilert S, Kongcharoenkiat S. Water Resistance and Barrier Properties Improvement of Paperboard by Poly(Lactic Acid) Electrospraying. *Packaging Technology and Science*. 2014;27(5):341-352.

11. He M, Lu A, Zhang L. Advances in Cellulose Hydrophobicity Improvement. In: Komolprasert V, Turowski P, eds. *Food Additives and Packaging*. Washington: American Chemical Society; 2014. p. 241-274.

12. Stanssens D, Van den Abbeele H, Vonck L, Schoukens G, Deconinck M, Samyn P. Creating water-repellent and super-hydrophobic cellulose substrates by deposition of organic nanoparticles. *Materials Letters*. 2011;65(12):1781-1784.

13. Caschera D, Cortese B, Mezzi A, Brucale M, Ingo GM, Gigli G, et al. Ultra hydrophobic/superhydrophilic modified cotton textiles through functionalized diamond-like carbon coatings for self-cleaning applications. *Langmuir*. 2013;29(8):2775-2783

14. Ivanova NA, Zaretskaya AK. Simple treatment of cotton textile to impart high water repellent properties. *Applied Surface Science*. 2010;257(5):1800-1803.

15. Yazdanshenas ME, Shateri-Khalilabad M. One-Step Synthesis of Superhydrophobic Coating on Cotton Fabric by Ultrasound Irradiation. *Industrial & Engineering Chemistry Research.* 2013;52(36):12846-12854.

16. Bhushan B, Jung YC. Micro- and nanoscale characterization of hydrophobic and hydrophilic leaf surfaces. *Nanotechnology.* 2006;17(11):2758-2772.

17. Bhushan B, Jung YC, Koch K. Micro-, nano- and hierarchical structures for superhydrophobicity, self-cleaning and low adhesion. *Philosophical Transactions of the Royal Society A.* 2009;367(1894):1631-1672.

18. Bhushan B, Jung YC. Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction. *Progress in Materials Science.* 2011;56(1):1-108.

19. Song J, Rojas OJ. Approaching super-hydrophobicity from cellulosic materials: A Review. *Nordic Pulp & Paper Research Journal*. 2013;28(2):216-238.

20. Yang H, Deng Y. Preparation and physical properties of superhydrophobic papers. *Journal of Colloid and Interface Science*. 2008;325(2):588-593.

21. Liu Y, Chen X, Xin JH. Super-hydrophobic surfaces from a simple coating method: a bionic nanoengineering approach. *Nanotechnology*. 2006;17(13):3259-3263.

22. Zhu M, Zuo W, Yu H, Yang W, Chen Y. Superhydrophobic surface directly created by electrospinning based on hydrophilic material. *Journal of Materials Science*. 2006;41:3793-3797.

23. Fürstner R, Barthlott W, Neinhuis C, Walzel P. Wetting and Self-Cleaning Properties of Artificial Superhydrophobic Surfaces. *Langmuir*. 2005;21(3):956-961.

24. Sapieha S, Wrobel AM, Werthmeier MR. Plasma-assisted etching of paper. *Plasma Chemistry and Plasma Processes*. 1988;8(3):331-346.

25. Balu B, Breedveld V, Hess DW. Fabrication of "Roll-off" and "Sticky" Superhydrophobic Cellulose Surfaces via Plasma Processing. *Langmuir*. 2008;24(9):4785-4790.

26. Zanini S, Riccardi C, Orlandi M, Fornara V, Colombini MP, Donato DI, et al. Wood coated with plasma-polymer for water repellence. *Wood Science and Technology*. 2008;42:149-160.

27. Sahin HT, Manolache S, Young RA, Denes F. Surface fluorination of paper in CF_4-RF plasma environments. *Cellulose*. 2002;9(2):171-181.

28. Grill A. *Cold Plasma Materials Fabrication: From Fundamentals to Applications*. New York: Wiley-IEEE Press; 1994.

29. Yasuda H. *Plasma Polymerization*. New York: Academic Press; 1985.

30. Hodak SK, Supasai T, Paosawatyanyong B, Kamlangkla K, Pavarajarn V. Enhancement of hydrophobicity of silk fabrics by SF_6 plasma. *Applied Surface Science*. 2008;254(15):4744-4749.

31. Kamlangkla K, Paosawatyanyong B, Pavarajarn V, Hodak JH, Hodak SK. Mechanical strength and hydrophobicity of cotton fabric after SF_6 plasma treatment. *Applied Surface Science*. 2010;256(20):5888-5897.

32. Vendemiatti C, Hosokawa RS, Rangel RCC, Bortoleto JRR, Cruz NC, Rangel EC. Wettability and surface microstructure of polyamide 6 coated with $SiO_XC_YH_Z$ films. *Surface and Coatings Technology*. 2015;275:32-40.

33. Hartney MA, Hess DW, Soane DS. Oxygen plasma etching for resist stripping and multilayer lithography. *Journal of Vacuum Science and & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*. 1989;7(1). DOI: 10.1116/1.584440

34. Cardinaud C, Peignon MC, Tessier PY. Plasma etching: principles, mechanisms, application to micro- and nano-technologies. *Applied Surface Science*. 2000;164(1-4):72-83.

35. Li L, Roethel S, Breedveld V, Hess DW. Creation of low hysteresis superhydrophobic paper by deposition of hydrophilic diamond-like carbon films. *Cellulose*. 2013;20(6):3219-3226.

36. Xie L, Tang Z, Jiang L, Breedveld V, Hess DW. Creation of superhydrophobic wood surfaces by plasma etching and thin-film deposition. *Surface & Coatings Technology*. 2015;281:125-132.

37. Warner SB, Uhlmann DR, Peebles LH Jr. Ion etching of amorphous and semicrystalline fibres. *Journal of Materials Science*. 1975;10(5):758-764.

38. Donaldson L, Frankland A. Ultrastructure of iodine treated wood. *Holzforschung*. 2004;58(3):219-225.

39. Souza Lima MM, Borsali R. Rodlike Cellulose Microcrystals: Structure, Properties, and Applications. *Macromolecular Rapid Communication*. 2004;25(7):771-787.

40. Jamali A, Evans PD. Etching of wood surfaces by glow discharge plasma. *Wood Science and Technology*. 2011;45(1):169-182.

41. Jinkarn T, Thawornwiriyanan S, Boonyawan D, Rachtanapun P, Sane S. Effects of Treatment Time by Sulfur Hexafluoride (SF6) Plasma on Barrier and Mechanical Properties of Paperboard. *Packaging Technology and Science*. 2012;25(1):19-30.

42. Kuptsov AH, Zhizhin GN. *Handbook of Fourier Transform Raman and Infrared Spectra of Polymers*. Amsterdam: Elsevier Science; 1998.

43. Drake LR, Lin S, Rayson GD. Chemical Modification and Metal Binding Studies of Datura innoxia. *Environmental Science & Technology*. 1995;30(1):110-114.

44. Kapoor A, Viraraghavan T. Heavy metal biosorption sites in Aspergillus niger. *Bioresource Technology*. 1997;61(3):221-227.

45. Navarro F, Dávalos F, Denes F, Cruz LE, Young RA, Ramos J. Highly hydrophobic sisal chemithermomechanical pulp (CTMP) paper by fluorotrimethylsilane plasma treatment. *Cellulose*. 2003;10(4):411-424.

46. Park YW, Inagaki N. Surface modification of poly(vinylidene fluoride) film by remote Ar, H_2, and O_2 plasmas. *Polymer*. 2003;44(5):1569-1575.

47. Vasiljević J, Gorjanc M, Tomšič B, Orel B, Jerman I, Mozetič M, et al. The surface modification of cellulose fibres to create super-hydrophobic, oleophobic and self-cleaning properties. *Cellulose*. 2013;20(1):277-289.

48. Vaswani S, Koskinen J, Hess DW. Surface modification of paper and cellulose by plasma-assisted deposition of fluorocarbon films. *Surface & Coatings Technology*. 2005;195(2-3):121-129.

49. Cassie ABD, Baxter S. Wettability of porous surfaces. *Transactions of the Faraday Society*. 1944;40:546-551.

50. Yan YY, Gao N, Barthlott W. Mimicking natural superhydrophobic surfaces and grasping the wetting process: A review on recent progress in preparing superhydrophobic surfaces. *Advances in Colloid and Interface Science*. 2011;169(2):80-105.

51. Balu B, Kim JS, Breedveld V, Hess DW. Design of Superhydrophobic Paper/Cellulose Surfaces via Plasma Enhanced Etching and Deposition. In: Mittal KL, ed. *Contact Angle, Wettability and Adhesion, Volume 6*. Boca Raton: CRC Press; 2009.

52. Li L, Breedveld V, Hess DW. Design and Fabrication of Superamphiphobic Paper Surfaces. *ACS Applied Materials & Interfaces*. 2013;5(11):5381-5386.