

Sisal Chemo-Thermomechanical Pulp Paper with a Strongly Hydrophobic Surface Coating Produced by a Pentafluorophenyldimethylsilane Cold Plasma

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ABSTRACT: Fluorinated thin layers were created on CTMP sisal and filter paper surfaces by using pentafluorophenyldimethylsilane (PFPDMS) under RF-plasma conditions. Surface wettability and water absorption of unmodified and modified samples of both materials were evaluated through contact angle and Cobb test techniques, respectively. The mechanical strength and optical properties were also analyzed. The surface functional groups produced were evaluated using X-ray photoelectron spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA) and Attenuated Total Reflectance Fourier Transform infrared (ATR FT-IR) spectroscopy. Surface morphological changes after plasma treatment were evaluated using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). PFPDMS-plasma treatment of sisal CTMP reduced water absorption from more than 400 g (H₂O)/m² to 18 g (H₂O)/m². The contact angle was increased from less than 15° to 119°–134°. Water absorption for untreated filter paper was 220 g (H₂O)/m² and

after plasma treatment the value decreased to 13.6 g (H₂O)/m². Water drop contact angle for untreated filter paper was 24°, and after PFPDMS-plasma treatment it was 134°. Strength properties were slightly reduced in some cases and brightness was reduced in most of the trials, turning to yellow. ATR FT-IR and ESCA spectroscopy indicated a fluorinated aromatic surface, whereas AFM and SEM showed a smooth surface coating for both sisal and filter paper after PFPDMS-plasma treatment. A fully coated surface with a very high hydrophobic character was observed. This new property can be attributed to the formation of a crosslinked polymer network of covalently bound PFPDMS-based units on the paper surface as shown by the presence of C–Si, C–O–Si, C–CF_x, and C–F bonds. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 479–488, 2009

Key words: coatings; cold plasma; fluoropolymer; ESCA; surfaces

INTRODUCTION

The plasma state, recognized as the fourth state of matter, is broadly defined as a gaseous environment composed of charged and neutral species with a net zero electric charge. One of the plasma states is cold plasma or nonequilibrium plasma, also called glow discharge.¹ In the cold plasma state the electrons have sufficiently high kinetic energies to induce ionization, excitation and molecular fragmentation processes in low pressure gas environments.² These plasmas are also characterized by very low degrees of ionization; consequently, they are suitable for the

modification of organic substrates. The plasma species can also interact with solid-phase substances generating chemical and morphological changes in the very top layers of the plasma exposed substrates.¹ Therefore, cold plasma treatment is a very convenient method for surface modification of solid materials because it is restricted to shallow depth penetration. Surface modification of materials is very useful in achieving (a) changes in their wettability (more hydrophobic or hydrophilic), which could be very useful in compatibilizing dissimilar components in composites, improving adhesion between phases, and in turn the mechanical properties, and also improving the application of coatings and in printing; (b) modifying permeability to liquids or gases, with many applications—for example in food and pharmaceuticals packaging and in biomaterials; (c) stabilization to weathering and photodegradation (d) chemical functionalization for further chemical reactions such as graft polymerization; (e) improving biocompatibility, which is rendering a material more adequate to be in contact with living tissues without

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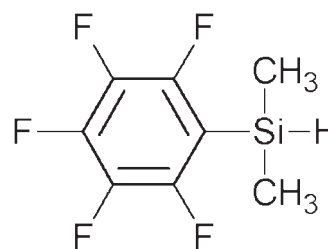
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provoking negative effects; (f) production of surfaces with low or high dielectric constants; (g) development of photoresponsive surfaces.

Plasma processing has several advantages over more traditional treatments, because it is rapid, clean, and depending on the choice of gas, environmentally safe. It can also be adapted to continuous industrial production.³ A further advantage is that the process results are relatively uniform, even over intricate shapes.⁴ Thus, plasma deposition of thin films has become an increasingly popular approach to synthesize new types of materials or as an alternative route to well-characterized organic polymer films for surface modification of substrates with complex geometries.⁵

Paper and board, which are based on cellulose, are important renewable and biodegradable materials and these are extensively used, for example, in the packaging of perishable products (foods, pharmaceuticals, perfumes, etc.). Important desirable properties that they should have in those applications are low water wettability and improved barrier behavior which can be achieved by developing surface hydrophobicity and oleophobicity. Plasma modification of cellulosic fibers for composite materials has been reviewed.⁶⁻⁸ Plasma-enhanced chemical vapor deposition can be used to apply a thin fluorocarbon coating on the surface of paper or cellulose.^{3,9-11} Fluorocarbon discharges have been widely studied because of their dual ability to promote etching of a variety of substrates and deposition of a wide range of fluorinated polymeric films.¹² The fluorination of natural and synthetic polymeric substrates is a process of great importance, because it can provide special surface properties at an accessible cost, such as chemical inertness, hydrophobicity, thermal stability, low friction, low electrical conductivity, low gas permeability, etc. It has been shown that plasma enhanced surface fluorination reactions can be carried out even on totally inert polymeric surfaces.¹³

Plasma polymerization of perfluorinated hydrocarbon monomers such as dodecafluorocyclohexane has been shown to make cellulose surfaces hydrophobic.⁹ Other fluorinated hydrocarbons have been reported to plasma-treat cellulose.^{10,14} It has been suggested that cyclic aromatic fluorocarbons like hexafluorobenzene undergo ring-opening processes under cold plasma conditions rather than defluorination mechanisms.⁹ Organic silicone compounds have been also used to develop hydrophobic surfaces in paper, Tan et al. argue that the presence of silicon in the molecule and its strong affinity to the oxygen atom of cellulose is a strong indication that plasma-deposited silicone-based films will adhere to cellulose substrates very easily and indicate advantages of organic silanes such as the ease of manipulation, because they are liquids of low toxicity.¹⁵



Structure 1 Pentafluorophenyldimethylsilane.

It would be, thus, of interest to examine the properties of cold plasma-deposited films produced from a precursor which contains in its structure a perfluorinated aromatic ring attached to dimethylsilane. The high content of fluorine atoms and the dimethyl silane functionality would provide hydrophobicity and oleophobicity, the aromatic ring would create chemical moieties amenable to crosslinking via ring-opening reactions and the silicon atom would allow for a strong attachment of the film to the cellulose or lignocellulosic substrate of paper.

This work reports the effects of plasma-deposited hydrophobic overlays on surfaces of sisal chemothermomechanical pulp (CTMP) paper (lignocellulosic) and filter paper (cellulosic) using pentafluorophenyldimethylsilane (PFPDMS) (Structure 1) under RF-plasma conditions. The degree of hydrophobicity on the treated surfaces in comparison with untreated samples is evaluated by water contact angle and Cobb tests. ATR-FTIR, Electron Spectroscopy for Chemical Analysis (ESCA), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) are used to observe chemical and morphological changes on their surfaces.

EXPERIMENTAL

Sisal CTMP and paper preparation

Depithed sisal fibers were cooked using a soda-sodium sulfite (4–6%) CTMP process. The pulp was refined in an atmospheric Sprout-Waldron 30 cm diameter disc refiner, using a D2A-509 NH disc model. A 7% consistency was used during refining until 40° SR freeness was obtained. The filter paper used was standard qualitative No. 4 Whatman.

Optical and physical testing

Physical and optical properties of hand sheets from unbleached and bleached papers were evaluated by the corresponding Tappi test methods. Brightness was measured according to Tappi T-452-OM 92 and opacity according to Tappi T-519-OM 91, using a Karl Zeiss Elrepho photoelectric reflectance photometer in conjunction with the tridimensional color scale CIE

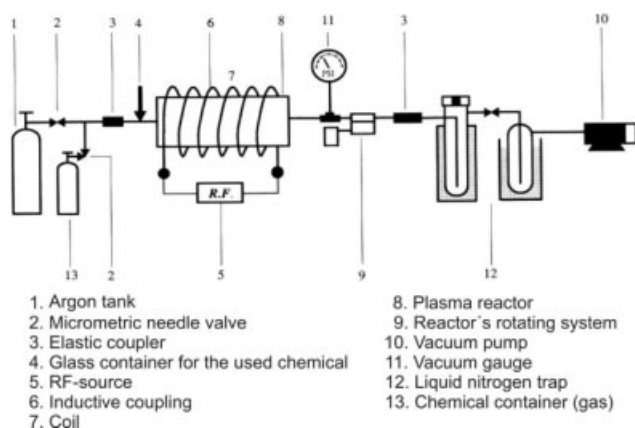


Figure 1 Inductively coupled cylindrical glass rotating, outside coil RF source plasma reactor (13.56 MHz).

$L^* a^* b^*$ in a Data Color International Elrepho 3000. The breaking length of unbleached, bleached and plasma-treated papers were analyzed according to Tappi T-494 with a pendulum type tensile strength equipment, model Nr-1047.

Plasma treatments

Plasma treatments on sisal and filter paper samples were done in an inductively coupled RF-plasma reactor (13.56 MHz), as shown schematically in Figure 1 and described by Denes et al.⁵ Experimental conditions for the plasma treatments used variable ranges obtained from preliminary trials. PFPDMS (Aldrich 99%) plasma was directly applied on the paper surface. An experimental factorial design 2^3 with three central points was used for the PFPDMS plasma treatment on sisal and filter papers. Working pressure was 100–200 mtorr, treatment time 0.5–10 min, power 40, 70, and 100 W.

Surface analysis of paper

The surface characteristics of unmodified and PFPDMS plasma-treated samples were examined using the following tools:

Water contact angle and Cobb tests

Contact angle was measured by a model OCA 20 (Germany), video-based optical contact angle measuring instrument, according to the 'sessile drop' method. The basic instrument has a high performance image processing video system with 132 MB/s data transfer rate and up to 50 images/s digitizing speed, operated by a 32 bit software SCA 20 for windows 2000/XP. Cobb tests (Tappi T-441-OM-90) were made with untreated and treated samples of both sisal and filter papers to measure water absorbency capacity. The test enables to determine the level

of water absorptiveness by the paper. The water mass absorbed during a determined time by 1 m^2 of paper under the given conditions equals to water absorptiveness in Cobb units.

Attenuated Total Reflectance Fourier Transform infrared (ATR FT-IR) spectroscopy

Measurements were carried out by means of an ATI-Mattson research series instrument provided with a Graseby special Benchmark series ATR in-compartment P/N 11160 unit, featuring a working window of $8 \text{ cm} \times 0.8 \text{ cm}$ and an optical plate Apecac type with a KRS-5 crystal. Data were collected in a range of 400 to 4000 cm^{-1} wave length, a resolution of 0.4 cm^{-1} , with 256 scans for each sample.

ESCA

ESCA analyses were performed on a Perkin-Elmer Physical Electronics 5400 small area spectrophotometer. Survey (source-Mg, 15 keV, 300 W, pass energy 89.45 eV, resolution 1.0 eV, work function 3.9 eV) and high resolution (pass energy 35.75 eV, resolution 0.1 eV, take-off angle of 45°) ESCA were used to evaluate the relative surface composition of unmodified and PFPDMS plasma-treated samples, and to estimate the presence of nonequivalent carbon functionalities, i.e., carbon (C_{1s}), oxygen (O_{1s}), fluorine (F_{1s}), and silicon (Si_{2s} , Si_{2p}) atomic composition were evaluated.

AFM

Surface morphology of untreated as well as PFPDMS plasma-treated sisal and filter papers were analyzed by AFM using a Digital Instrument Nanoscope II AFM equipment with a silicon oxide sharpened tip NP-20.

SEM

Untreated and plasma-treated samples were examined with a JEOL JSM-840 Leo 1530 scanning electron microscope, Leo Electron Microscopy Inc. Images were taken at $5000\times$ magnification.

RESULTS AND DISCUSSION

Water contact angle and Cobb tests for PFPDMS plasma-treated paper

The water contact angles obtained on untreated sisal paper were normally less than 15° ; the water droplets instantly spread on the surface and were absorbed rapidly, making it difficult to obtain accurate readings. The water contact angles observed on PFPDMS plasma-treated sisal paper were 103° – 134° .

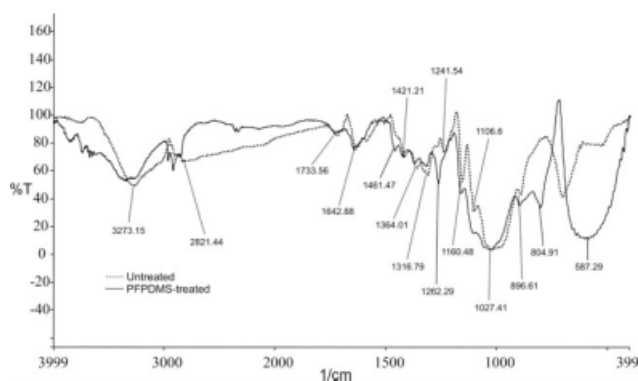


Figure 2 ATR FT-IR spectra of unbleached sisal CTMP paper, untreated (dotted line) and PFPDMS-plasma treated (continued line).

The water contact angle for untreated filter paper was 24° , increasing to values between 119° and 134° after the PFPDMS-plasma treatment. A chemical modification of cellulose fibers with pentafluorobenzoyl chloride has shown contact angles with values between 120 and 128° .¹⁶

Cobb tests made with unbleached and bleached sisal papers showed that PFPDMS treatment (working pressure of 140 mTorr, 3–5.5 min treatment time, power of 70 W) reduced the water absorption capacity from more than 400 g of water/m² (untreated) to values as low as 18 g of water/m² (treated). Similar results for liquid penetration resistance were achieved with the same paper treated with plasma of fluorotrimethylsilane at 70 W, 150 mTorr of working pressure, and 7.5 min of treatment time,¹⁷ and only slightly above the absorbency of 15 g of water/m² obtained by Tan et al.¹⁵ for filter paper treated with hexamethyldisilazane-plasma. Cobb tests made with untreated filter paper resulted in an absorbency of 220 g of water/m². When the filter paper was treated with PFPDMS plasma for 3–5.5 min, with a power of 70 Watts, and a pressure of 140 Torr, the resulting Cobb absorbency was 13.6 g of water/m².

Paper properties after PFPDMS-plasma treatment

PFPDMS-plasma treatment reduces paper tensile strength slightly by around 2.2% for unbleached sisal paper, and around 3.4% for bleached sisal paper. On the other hand, brightness is reduced considerably to around 56% for unbleached and 74% for bleached sisal paper. This is explained by observing that PFPDMS when applied to the surface by plasma treatment imparts a yellow color to the paper.

ATR FT-IR analysis of CTMP paper

Figure 2 shows the Attenuated Total Reflectance Fourier Transform Infrared (ATR FT-IR) spectra for

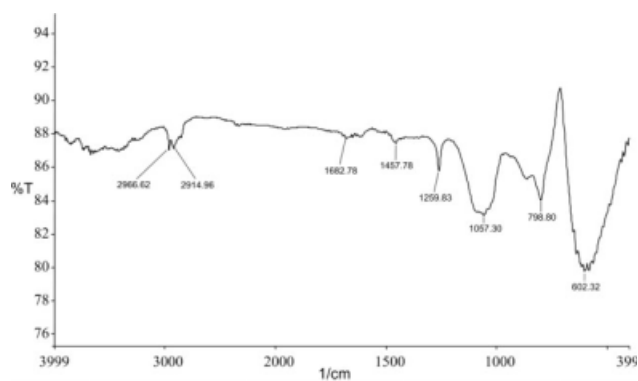


Figure 3 High resolution difference ATR FT-IR spectra, between untreated and treated CTMP sisal paper.

the unbleached sisal CTMP paper before and after PFPDMS-plasma treatment. Figure 3 shows the high resolution ATR FT-IR differential spectrum from Figure 2 revealing considerable differences in certain bands^{18–23} as summarized in Table I. It confirms the presence of aromatic rings at 1682, 1655 and 1457 cm⁻¹, C=C (stretching), Si-CH₃ groups at 1260 cm⁻¹ and 1057 cm⁻¹, Si-O-C bonds at 798 cm⁻¹ and probably Si-OH at 602.32 cm⁻¹. The C-F stretching band expected at around 1100 cm⁻¹ is obscured by the very strong Si-CH₃ band. These results show that the PFPDMS-plasma treatment of sisal paper generates deposition and polymerization of fluorine and silane compounds mainly with C=C, Si-CH₃, Si-O-C and Si-OH bonds.

ATR FT-IR analysis of filter paper

Figure 4 shows the ATR FT-IR spectra of filter paper before and after PFPDMS-plasma treatment. Table II shows the main bands which differentiate one spectrum from the other. It confirms the presence of aromatic rings at 1639 cm⁻¹ and 1610 cm⁻¹, C=C (stretching), Si-CH₃ groups at 1052 cm⁻¹, Si-O-C bonds at 753 cm⁻¹ and probably Si-OH at 586 cm⁻¹. The C-F stretching band expected at around 1100 cm⁻¹ is again obscured by the very strong

TABLE I
ATR FT-IR Characteristic Bands of Sisal CTMP Paper Treated with PFPDMS-Plasma

Transmittance band	Assignment
1682 cm ⁻¹ , 1655 cm ⁻¹ , 1457 cm ⁻¹	C=C stretching (aromatic)
1259 cm ⁻¹	Si-CH ₃ symmetrical bending
1057 cm ⁻¹	Si-CH ₃ stretching
798 cm ⁻¹	Si-OH stretching
602 cm ⁻¹	Si-C stretching
1100 cm ⁻¹	C-F stretching

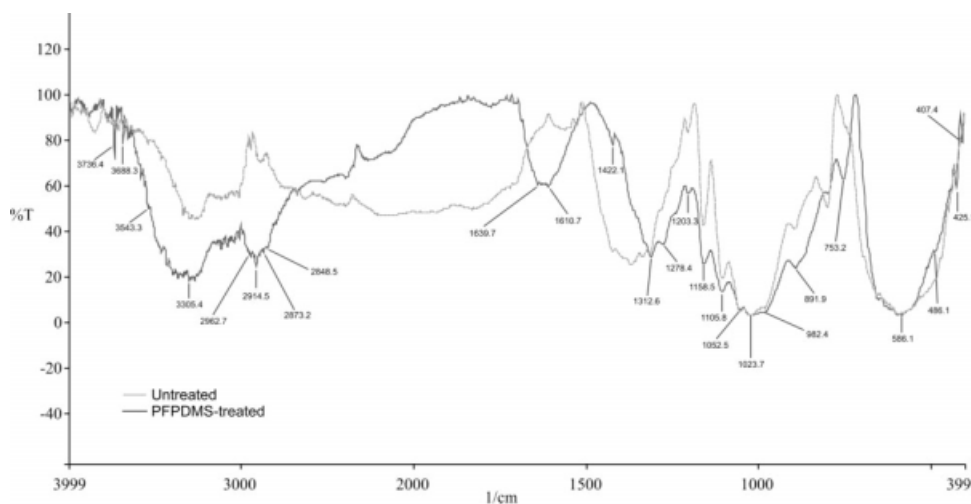


Figure 4 ATR FT-IR spectra of untreated, and PFPDMS plasma-treated filter paper.

Si-CH₃ band. These results show that the PFPDMS-plasma treatment of filter paper generates deposition and polymerization of fluorine and silane compounds mainly, again, with C=C, Si-CH₃, Si-O-C and Si-OH bonds.

ESCA analysis of sisal paper

Survey ESCA spectra of unbleached sisal paper showed the presence of C_{1s} and O_{1s} peaks with a relative atomic composition of 64.9% and 35.1%, respectively. After PFPDMS-plasma treatment, the survey ESCA spectra, in addition to the C_{1s} and O_{1s} peaks, also show the presence of F_{1s} and Si_{2p} peaks, indicating the presence of fluorine and silicon atom-based functionalities on the paper surface. PFPDMS plasma treatment of unbleached sisal paper for 3 min reduced C_{1s} carbon content to 54.1% and O_{1s} oxygen content to 9.2%. Fluorine and silicon content are in relative amounts of 31.7 and 5.0%, respectively. C_{1s} carbon high resolution ESCA spectra for PFPDMS plasma treatments of 0 (untreated control), 0.5, 1, and 3.0 min were deconvoluted with the curve fitting technique; the corresponding spectra for sisal paper are shown in Figure 5.

TABLE II
ATR FT-IR Characteristic Bands of Filter Paper Treated with PFPDMS-Plasma

Transmittance band	Assignment
1610–1640 cm ⁻¹	C=C stretching (aromatic)
1262 cm ⁻¹	Si-CH ₃ symmetrical bending
1100 cm ⁻¹	C-F stretching
1052 cm ⁻¹	Si-CH ₃ stretching
753 cm ⁻¹	Si-OH stretching
586 cm ⁻¹	Si-C stretching

The spectra reveal chemical changes on the surface caused by the treatment, resulting in different modal patterns as a function of plasma treatment time. For untreated paper [Fig. 5(a)], the first region corresponds to C-C, C=C, and C-H bonds, which normally influences the 284.7–285 eV binding energy region^{1,18} bonds which are related to the presence of lignin-based components and also to some extractives related to hydrocarbon peaks,²⁴ the relative percentage area for this region is 40.6%; the second region corresponds to C-O-C and C-OH,¹ they normally influence the 286.0 to 286.7 eV region, and the relative area is 44.9%; the third region corresponds to C=O bond²⁴ which influences the 287.5–288.3 eV binding energy region and to O-C-O bond in the 288–288.1 eV region¹⁸ with a relative area of 12.3%; there is also the existence of a fourth region, which corresponds to C(=O)OH bond groups²⁴ in the 288.7–289.2 eV region with a relative area of 2.2%.

Figure 5(b) shows the high-resolution ESCA spectra for the sisal paper treated with PFPDMS-plasma for 30 s. The modal pattern features six regions. The first at 282.7 eV is associated to Mg, originated from the instrument; the second region with a relative area of 24.6% corresponds to C-Si bonds originating from PFPDMS, and influences the 284.3 eV region. The third region with a relative area of 24.6% corresponds to C-C, C=C and C-H bonds that influence the 285 eV region, and also to C-O-Si bonds, another possible bond originating from the PFPDMS-plasma treatment, which influences the 284.8 eV region. The fourth region with a relative area of 28.4% corresponds to C-O-C and C-OH bonds in the 286.7 eV region, and also to C-CF_x bonds, yet another possible bond originating from the PFPDMS treatment, which influences the 286.6 eV region. The fifth region with a relative area of 11.9% corresponds to O-C-O and C=O bonds at

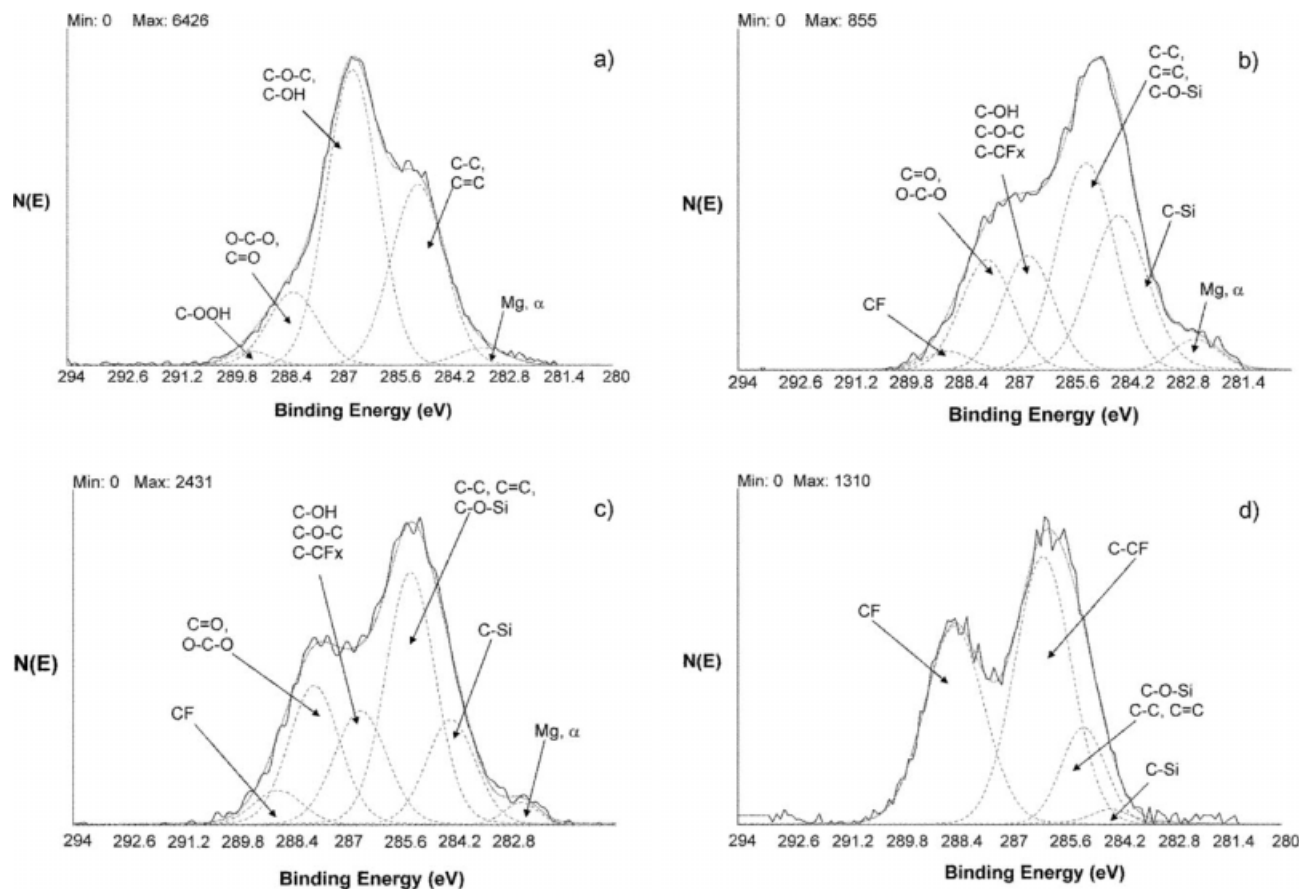


Figure 5 High-resolution ESCA spectra for (a) untreated, and PFPDMS plasma-treated sisal paper for (b) 0.5 min, (c) 1 min, and (d) 3 min.

288 eV, and the sixth region with a relative area of 5.7% corresponds to C—F bonds, also a bond originating from the PFPDMS-plasma treatment, and influences the 288.5 eV region. The spectrum in Figure 5(c) shows the C—Si bond at 284.25 eV with a relative area of 16.0%, the C—C, C=C and C—O—Si bonds at 285.29 eV with a relative area of 38.5%, the C—O—C, C—OH and C—CF_x bonds at 286.58 eV with a relative area of 18.5%, the C—O—C—O and C=O bonds at 287.77 eV with a relative area of 21.9% and the C—F bond at 288.71 eV with a relative area of 5.1%.

Figure 5(d) shows the high-resolution ESCA spectrum for the paper treated with PFPDMS-plasma for 3 min. This spectrum shows almost exclusively the bonds originating from the PFPDMS-plasma treatment, i.e., the C—Si bond at 284.3 eV with a relative area of 2.7%, the C—O—Si bond at 284.8 eV with a relative area of 16.6%, the C—CF_x bond at 286.6 eV with a relative area of 45%, and the C—F bond at 288.5 eV with a relative area of 35.7%.

ESCA analysis of filter paper

Survey ESCA spectra of untreated filter paper shows the presence of C_{1s} and O_{1s} peaks with a relative

atomic composition of 53.9 and 46.1%, respectively. After the PFPDMS-plasma treatment, the survey ESCA spectra in addition to the C_{1s} and O_{1s} peaks also show the presence of F_{1s} and Si_{2p} peaks, indicating the presence of fluorine and silicon atom-based functionalities on the paper surface. Figure 6a shows the high-resolution ESCA spectra for untreated filter paper. The first region with a relative area of 19.4% corresponds to C—C, C=C, and C—H bonds, at 284.7–285.3 eV binding energy region.¹⁸ It is much smaller than for sisal paper due to the absence of lignin and extractives.²⁴ The second region with a relative area of 65.7% corresponds to C—O—C and C—OH bonds¹ at the 286.0 to 287.5 eV regions. The third region with a relative area of 11.8% corresponds to the C=O bond²⁴ at the 287.5–288.3 eV binding energy region, and to the O—C—O bond at the 288–288.1 eV region.¹⁸ A smaller fourth region with a relative area of 3.1% corresponds to the C(=O)OH bond²⁴ at the 288.7–289.2 eV binding energy region.

Figure 6(b) shows the high-resolution ESCA spectra for filter paper treated with PFPDMS-plasma during 0.5 min. The first region corresponds to Mg, from the instrument at 282.7 eV, the second region

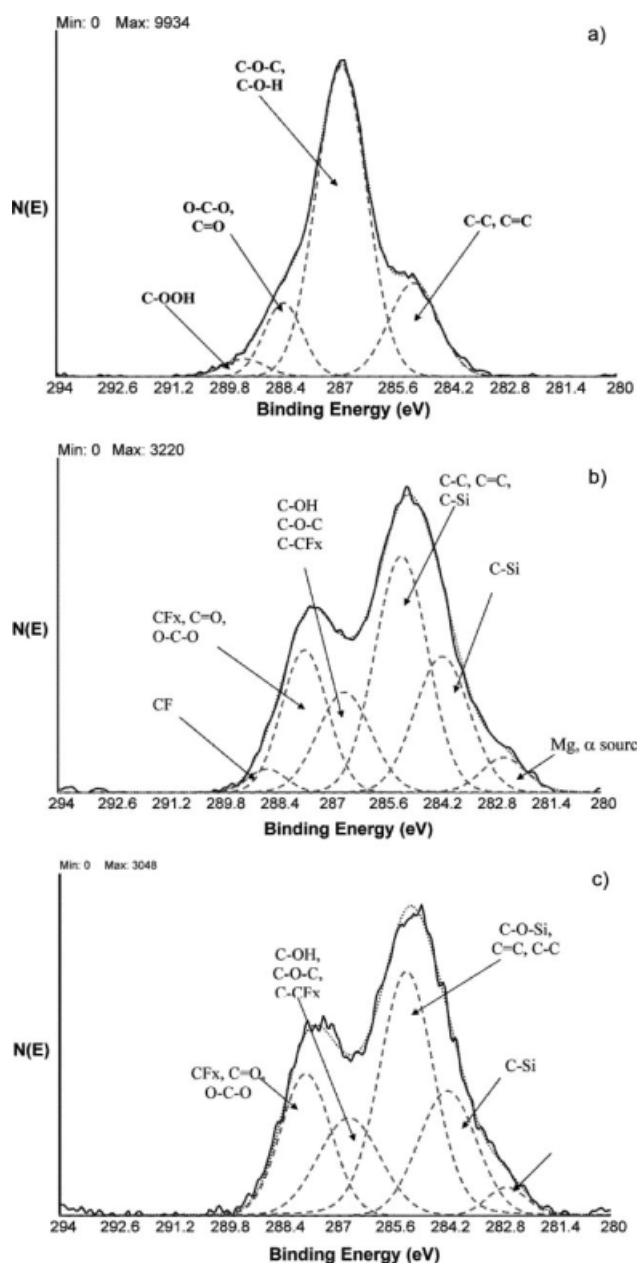


Figure 6 High-resolution ESCA spectra for (a) untreated filter paper, (b) PFPDMS-plasma treated for 0.5 min and (c) PFPDMS-plasma treated for 3 min.

corresponds to C—Si bonds from PFPDMS at 284.2 eV region, with relative area of 22.7%. The third region corresponds to C—C, C=C, C—H and also C—O—Si bonds, with a 38.2% relative area, a bond resulting from the PFPDMS-plasma treatment that influences the 285.2 eV region. The fourth region corresponds to C—O—C and C—OH bonds in the 286.7 eV region with a 16.5% relative area, but also to C—CF_x bonds, another bond possibly resulting from the PFPDMS treatment, which influences the 286.6 eV region. The fifth region corresponds to O—C—O, C=O and CF_x bonds at 287.5 eV region with a relative area of

19.9%. The sixth region corresponds to C—F bond with a relative area of 2.7% at 289 eV region.

Filter paper treated with PFPDMS-plasma for 3 min has a C_{1s} carbon content of 58.6%, O_{1s} oxygen content of only 7.1%, fluorine in a relative proportion of 31.9% and silicon content are in a relative amount of 2.4%. Figure 6(c) shows the high-resolution ESCA spectra for the filter paper treated with PFPDMS-plasma during 3 min. Besides the first region which corresponds to Mg, from the equipment at 282.7 eV, this spectrum shows practically only bonds related to the PFPDMS-plasma treatment, i.e., the C—Si bond at 284.2 eV with a relative area of 20.8%, the C—O—Si bond at 285.2 eV with a relative area of 40.8%, the C—CF_x bond at 286.6 eV with a relative area of 17.7%, and the C—F_x at 287.7 eV with a relative area of 20.7%.

It is evident from inspection and from the interpretation of the above ESCA results that with increasing time exposure to the PFPDMS plasma in all samples, the amount of carbon atoms which produce higher energy photoelectrons increases and decreases the relative amount of oxygen. This tendency provides a reasonable case in which it can be said that more PFPDMS-based film is deposited with longer plasma application times, at least up to 3 min, which is the time that has been previously demonstrated to reach a maximum deposition, based on the maximum production of free radicals quantified by electron spin resonance ESR studies.²⁵ It also can be observed that the peaks corresponding to unsaturated carbon atoms diminish markedly at longer treatment times, which is in accord with the interpretation that the fluorinated aromatic benzene ring is opened and probably serves as reactive intermediate to crosslinking and polymerization. Crosslinking also is supported by the existence of strong and broad bands in the 800–850 cm⁻¹ region of the FTIR spectrum of the plasma-treated papers.²⁶

AFM

Figure 7 shows the morphological changes for untreated and PFPDMS-plasma treated sisal paper evaluated by means of AFM. Figure 7(a) depicts the CTMP unbleached paper without plasma treatment, Figure 7(b) shows a three-dimensional view of the same sample. From both illustrations the rough surface of the paper becomes evident. Figure 7(c,d) (also three-dimensional views) shows the same sample after 3 min of PFPDMS-plasma treatment. The rough surface of the untreated paper has acquired a uniform smooth fine-grained coating. The cross-linked nature of the deposited macromolecular structure and the presence of the well-coated surface explain the highly hydrophobic nature of the PFPDMS-plasma modified paper.

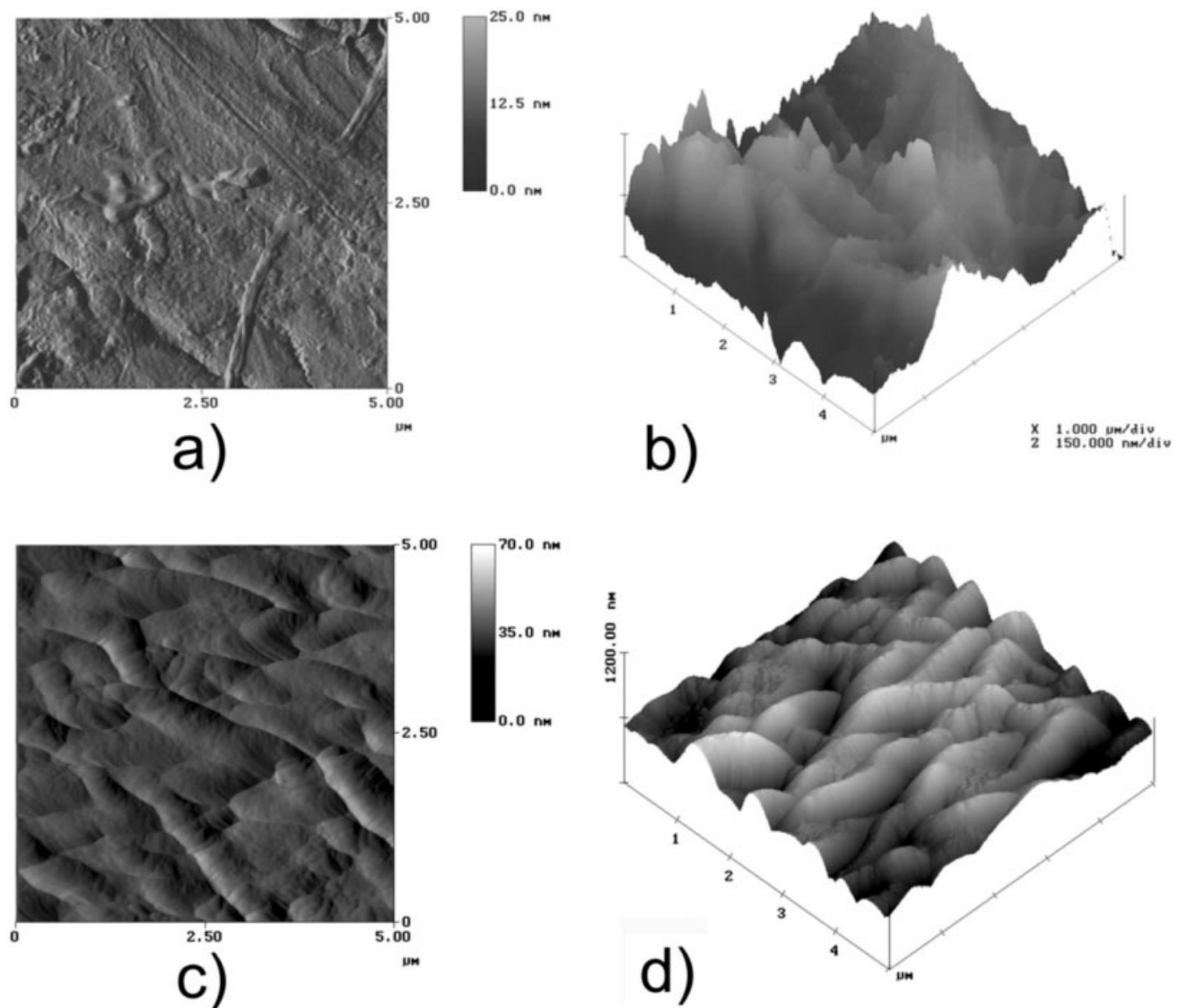


Figure 7 AFM images of unbleached CTMP, 5 μm ; (a) surface view and (b) three-dimensional image of untreated sisal paper; (c) surface view and (d) three-dimensional image after 3 min PFPDMS-plasma treatment.

Figure 8 shows the morphological surface changes for untreated and PFPDMS-plasma treated filter paper, evaluated using AFM. Figure 8(a) depicts a filter paper surface without plasma treatment; Figure 8(b) shows the same sample in a three-dimensional view. From both illustrations the rough surface of the paper becomes evident. Figure 8(c,d) (three-dimensional view) show the same sample after 3 min PFPDMS-plasma treatment. The rough surface of the untreated paper has also acquired a uniform smooth fine-grained coating.

SEM

Morphological changes of untreated and PFPDMS-plasma treated paper were examined with a scanning electron microscope. Figure 9 shows the SEM photomicrographs for unbleached CTMP paper with-

out and with PFPDMS-plasma treatment. Figure 9(a) depicts a normal unbleached paper fiber, Figure 9(b) depicts a surface that has acquired a continuous layer of plastic-like material which corresponds to a crosslinked macromolecular structure of PFPDMS-plasma deposited material.

Both AFM and SEM prove that the polymeric films formed with conditions used produce fairly smooth top layers that reduce greatly the porosity and roughness of the surfaces. This may be not very desirable in specific cases, particularly when it is desired to keep certain breathability of the materials, such as in food packaging or biomedical applications. Cobb's water absorption test proves that the water passage is hindered. Moreover, the hydrophobicity in terms of large contact angles and very low stickiness is severely affected when the surface roughness is diminished, as is explained by Cassie's

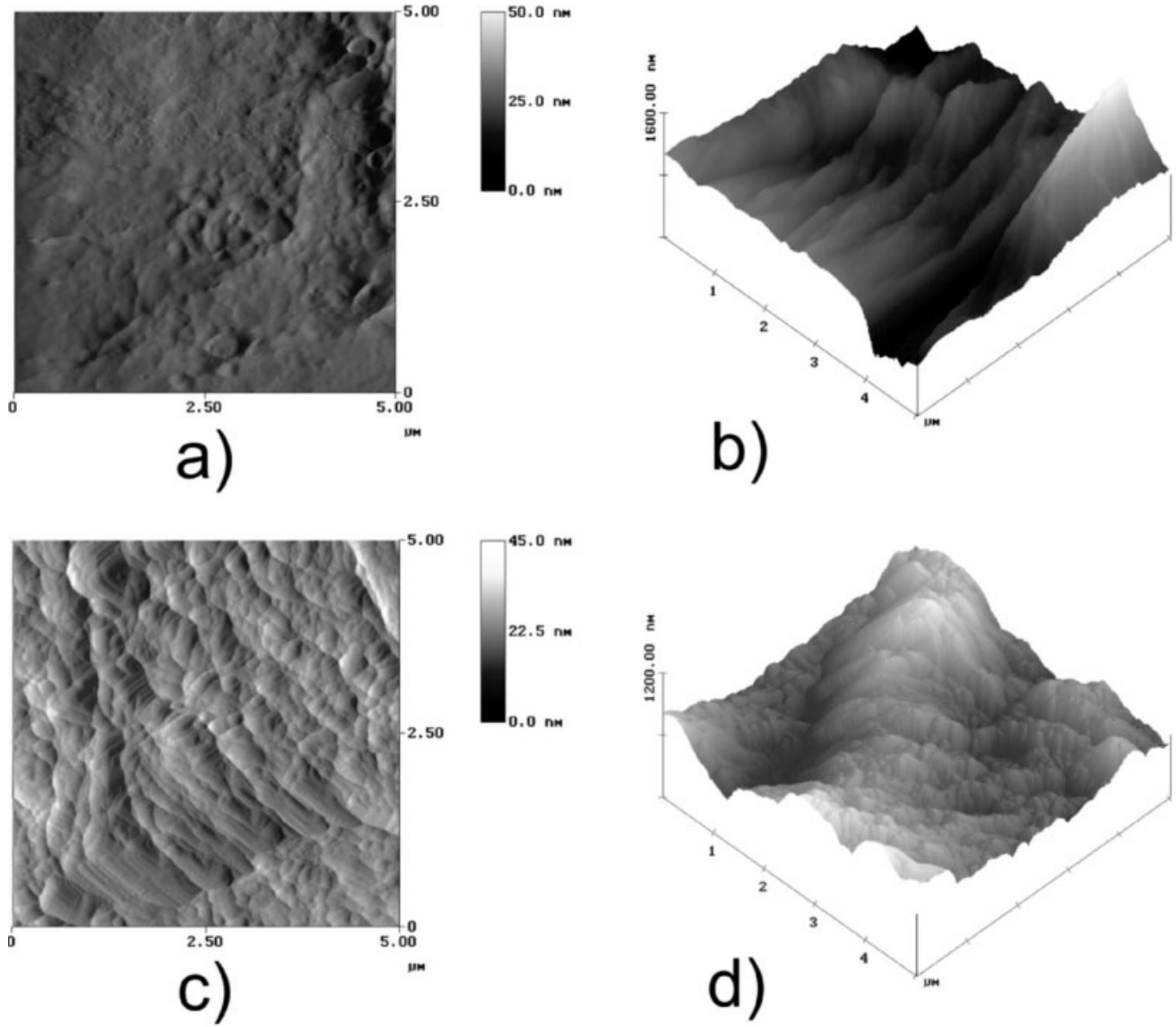


Figure 8 AFM images of filter paper, 5 μm ; (a) surface view and (b) three-dimensional image of untreated sisal paper; (c) surface view and (d) three-dimensional image after 3 min PFPDMS-plasma treatment.

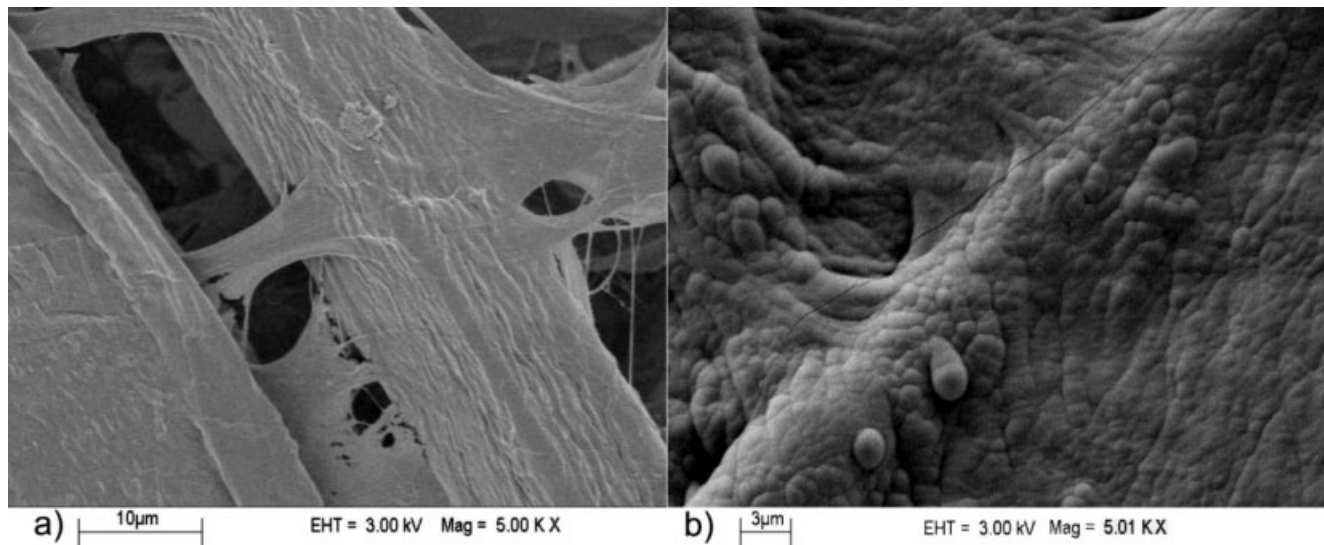


Figure 9 SEM photomicrographs of CTMP sisal paper: (a) untreated, (b) PFPDMS-plasma treated, both at $\times 5000$ magnification.

model, which assumes that a liquid does not completely wet a rough hydrophobic surface, and attributes the increased contact angle to the presence of air pockets at the liquid–solid interface.¹⁴ If the surface were to be kept rough, and increase in 20° to 30° could be reached, a contact angle of almost 170° has been reported for organofluorine-plasma coated cellulose surfaces.^{10,14}

CONCLUSIONS

CTMP sisal paper and virgin cellulose filter paper constitute feasible substrates for the implantation of fluorine and silicon organic groups by a PFPDMS-plasma treatment, resulting in a highly hydrophobic paper surface under optimal plasma conditions.

For sisal paper, the water contact angle after the PFPDMS-plasma treatment is increased from less than 15° to values from 119° to 134°. For filter paper, contact angle was increased from around 24° to values higher than 129° after a 30 s plasma treatment and to 134° after 3 to 5.5 min treatment time.

Cobb tests made on the untreated and treated samples for unbleached papers showed that water absorbency capacity was reduced from a more than 400 g of water/m² to values as low as 18 g of water/m². The low level was obtained under processing conditions of 70 W power, 140 mTorr PFPDMS working pressure and 3–5.5 min treatment time.

ATR FT-IR and ESCA prove that fluorinated organic layers were formed, although AFM and SEM analysis show a smooth surface for both sisal and filter paper after PFPDMS-plasma treatment, showing a completely covered surface with a highly cross-linked polymerized network, likely to be linked to the paper surface by C–Si, C–O–Si bonds.

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References

- Denes, A. R.; Young, R. A. *Holzforchung* 1999, 53, 632.
- Denes, F.; Young, R. A.; Sarmadi, M. *J Photopolymer Sci Technol* 1997, 10, 91.
- Gaiolas, C.; Costa, A. P.; Nunes, M.; Santos Silva, M. J.; Belgacem, M. N. *Plasma Process Polym* 2008, 5, 444.
- Barton, D.; Bradley, J. W.; Steele, D. A.; Short, R. D. *J Phys Chem B* 1999, 103, 4423.
- Denes, F.; Sarmadi, A. M.; Hop, C. E. C. A.; Young, R. A. *J Appl Polym Sci* 1994, 54, 55.
- Morales, J.; Olayo, M. G.; Cruz, G. J.; Herrera-Franco, P.; Olayo, R. *J Appl Polym Sci* 2006, 101, 3821.
- Martin, A. R.; Manolache, S.; Denes, F. S.; Mattoso, L. H. C. *J Appl Polym Sci* 2002, 85, 2145.
- Zaninia, T. S.; Riccardia, C.; Canevalic, C.; Orlandib, M.; Zoiab, L.; Tolppa, E.-L. *Surface Coat Technol* 2005, 200, 556.
- Denes, F.; Hua, Z. Q. *J Appl Polym Sci* 1999, 71, 1627.
- Vaswania, S.; Koskinenb, J.; Hess, D. W. *Surface Coat Technol* 2005, 195, 121.
- Sahin, H. T.; Manolache, S.; Young, R. A.; Denes, F.; *Cellulose* 2002, 9, 171.
- Butoi, C. I.; Macckie, N. M.; Gamble, L. J D.; Castner, G.; Barnd, J.; Miller, A. M.; Fisher' E. R. *Chem Mater* 2000, 12 2014.
- Denes, F.; Hua, Z. Q.; Young, R. A.; Shohet, J. L. *Plasmas Polym* 1997, 2, 1.
- Balu, B.; Breedveld, V.; Hess, D. W.; *Langmuir* 2008, 24, 4785.
- Tan, H.; da Silva, M. L. P.; Demarquette, N. R.; *J Mater Chem* 2001, 11, 1019.
- Cunha, A. G.; Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Gandini, A.; Orblin, E.; Fardim, P. *Biomacromolecules* 2007, 8, 1347.
- Ramos, J.; Navarro, F.; Dávalos, F.; Denes, F.S.; Young, R. A. 2002. 7th European Workshop on Lignocellulosics and Pulp Proceedings. Turku/Åbo, Finland. August 26–29.
- Fonseca, J. L. C.; Tasker, S.; Apperley, D. C.; Badyal' J. P. S.; *Macromolecules* 1996, 29, 1705.
- Inagaki, N. *Plasma Surface Modification and Plasma Polymerization*; Technomic Publ. Co. Inc.: USA, 1996, p 216.
- Naum, C.; Manolache, S.; Denes, F. *Langmuir* 2000, 16, 749.
- Socrates, G. 1980. *Infrared Characteristic Group Frequences*, John Wiley.
- Chaussé, A.; Chehimi, M. C.; Karsi, N.; Pinson, J.; Podvorica, F.; Vautrin-UI, C. *Chem Mater* 2002, 14, 392.
- Pretsch, E.; Clerc, T.; Seibil, J.; Simon, W. In *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Fresenius, W.; Huber, J. F. K.; Pungor, E.; Rechnitz, G. A.; Simon, W.; West, T. H. S., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong, 1989.
- France, M.; Short, R. D. *Langmuir* 1998, 14, 4827.
- Sabharwal, S. S.; Denes, F.; Nielsen, L.; Young, R. A. *J Agric Food Chem* 1993, 41, 2202.
- Navarro, F.; Dávalos, F.; Denes, F.; Cruz, L. E.; Young, R. A.; Ramos, J. *Cellulose* 2003, 10, 411.