# Chemical analysis of a cornstarch film surface modified by SF$_6$ plasma treatment

Anastácia E.F. Santos, Daniele C. Bastos, Monica L.V.J. da Silva, Rossana M.S.M. Thiré, Renata A. Simão*

*PEMM/COPPE, Universidade Federal do Rio de Janeiro, PO Box 68505, 21945-970, Rio de Janeiro, RJ, Brazil*

## ARTICLE INFO

## ABSTRACT

SF$_6$ plasmas were employed to improve the water repellency of cornstarch films by producing physical as well as chemical modifications of the film surface. Samples were placed in the cathode of a capacitively coupled plasma enhanced chemical vapor deposition (PECVD) reactor. Local surface modifications resulting from SF$_6$ plasma treatment were evaluated using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Photoelectron spectroscopy (XPS) and Raman spectroscopy were used to characterize sulfur and fluoride incorporation on the surface as well as changes in the chemical state of carbon. The results indicate that fluoride and sulfur incorporation is dependent on the self bias, and fluoride is preferentially incorporated at self-biases higher than 100 V. The carbon chemical state changed, and an amorphous-like layer was formed upon treatment. Surface reticulation was observed, indicated by the formation of a structure that resembled starch recrystallization. Optimized treatment conditions led to water contact angles over 120°.

## 1. Introduction

The development of bioplastics derived from renewable resources has been encouraged by the increasing interest in the reduction of the amount of plastic waste in the environment. Due to its total biodegradability, low cost and worldwide availability from a large number of crops, there has been much interest in the application of thermoplastic starch (TPS) as the base element for the production of single-use biodegradable plastic items. However, technological application of thermoplastic starch as a bioplastic has been limited by its inherent hydrophilicity. Starch-based materials are susceptible to moisture uptake during storage, which may cause changes in dimensional stability and both mechanical and barrier properties (Hulleman, Kalisvaart, Janssen, Feil, & Vliegenthart, 1999). Similar to starch, other polysaccharides like carrageenan are being tested to produce edible or environmentally friendly plastics. In this case, the natural polymer is associated with fat to enhance its water barrier properties. The authors related the surface stability upon water contact to the dynamic contact angle behavior. A variation in shape and size of the water droplet was observed over time, and the results were related to either water absorption, evaporation or polymer dissolution (Karbowiak, Debeaufort, Champion, & Voilley, 2006). A new approach to overcome the great hydrophilicity and water sensitivity of natural polymer-based films might be the protection of starch based materials from humidity changes with a thin polymeric layer, deposited by plasma

polymerization (Thiré, Simão, & Andrade, 2005). Additionally, it is well established that fluoride-containing plasmas can be used to modify surface hydrophilicity. The flat surfaces of low surface energy materials such as carbon fluorine compounds have a maximum contact angle with water of about 120° (Nishino, Meguro, Nakamae, Matsushita, & Ueda, 1999). Surfaces with higher contact angles can be obtained by structuring these surfaces with an appropriate roughness. Surfaces presenting contact angles as high as 150° are called super-hydrophobic surfaces (Bico, Marzolin, & Quere, 1999; Cassie & Baxter, 1954; Dorrer & Rühe, 2006; Shibuichi, Onda, Satoh, & Tsujii, 1996). To obtain such high contact angles, roughness size and topography have to be controlled in such a way that drops are suspended on top of the roughness features, with air trapped underneath.

As pointed out by Dorrer and Rühe (2006), in their analysis of artificially prepared rough surfaces composed of micromachined silicon chemically modified with fluoride groups, contact angle can be varied on surfaces by varying the distances and sizes of posts, varying the area of the water droplet spanning the trapped air. The best conditions obtained by the authors were surfaces composed of posts of 4 μm in size and spaced 16 μm.

Highly hydrophilic/hydrophobic contrast surfaces on polyethylene terephthalate (PET) substrates were formed by a shadow mask technique in an electron cyclotron resonance generated sulfur hexafluoride plasma atmosphere. XPS analysis indicated that the unmasked PET surfaces contained a high proportion of CF$_2$–CF$_2$ groups, and therefore were hydrophobic with a large water contact angle (Chuang & Chu, 2011).

Plasma treatment was carried out on PET surfaces, generating surface roughness at different length scales to maximize the

* Corresponding author. Tel.: +55 21 2562 8527; fax: +55 21 2290 6626.
*E-mail address:* renata@metalmat.ufrj.br (R.A. Simão).

stability of the superhydrophobic or superhydrophilic properties, depending on the surface chemistry. These properties were maintained during storage and resisted moderate mechanical stress (Fernández-Blásquez, Fell, Bonaccurso, & del Campo, 2011).

SF$_6$ plasma treatment enhances starch film hydrophobicity, as reported elsewhere. Plasma treatment at −100 V self bias led to surfaces presenting 130° contact angle with water. Surface topography changes were clearly observed, and hydrophobicity was attributed to the creation of surface roughness, fluoride incorporation and surface reticulation (Bastos, Santos, da Silva, & Simão, 2009).

The hydrophobicity improvement of Thai silk fabrics achieved via SF$_6$ plasma treatment showed that fluorine atoms were efficiently attached to the treated silk surface via plasma deposition (Hodak, Supasai, Paosawatyanyoung, Kamlangkla, & Pavarajarn, 2008; Suanpoot et al., 2008). Cold plasma treatments created fluorine-rich layers on the surface of starch–aspen foam tray samples, enhancing their hydrophobic properties (Chuang & Chu, 2011).

In the present study, we analyzed the significant reduction of the water sensitivity of cornstarch films upon plasma treatment with sulfur hexafluoride (SF$_6$). This was accomplished by controlling plasma parameters such as self bias and treatment time and observing the global and local chemical variation of the surface using different analysis techniques.

## 2. Experimental procedures

Regular cornstarch composed of 26–30% amylase and 74–70% amylopectin with less than 0.5% gluten and 12% moisture content was supplied by Corn Products Brazil Ltda. (São Paulo, Brazil). Cornstarch was dispersed in distilled water under reflux (5%, w/v) and kept under stirring for 300 s. Analytical grade glycerol (15%, w/w) was purchased from Vetec Química Fina Ltda. (Rio de Janeiro, Brazil) and added as a plasticizer. After casting, films with thickness ranging from 70 to 100 μm were obtained.

The cornstarch films were used as substrates for surface treatment with sulfur hexafluoride (SF$_6$). Cornstarch substrates were placed on the cathode of a glow discharge reactor operating at 13.56 MHz. The vacuum chamber was operated below 8 Pa, and different cathode self-bias voltages ($V_b$) were applied for different treatment periods. To avoid excessive solvent loss, the chamber base pressure was always kept above 6 Pa, as described elsewhere (Thiré et al., 2005). To characterize the different surface treatments, small pieces of silicon wafers that had previously been coated with amorphous carbon films were placed on the cathode close to the cornstarch films.

The influence of the plasma treatment on the hydrophilicity of starch films was determined from water contact angle measurements obtained using a NRL A-100-00 Ramé-Hart Goniometer. The evolution of the droplet shape was recorded with a CCD camera every 15 s over the measurement time of 600 s.

The elemental composition of the surface was evaluated by X-ray photoelectron spectroscopy (XPS) using a Phoibos 100 spectrometer equipped with a monochromatic MgK( source. XPS measurements were performed on both the corn starch films and the amorphous carbon films with surfaces modified by the same SF$_6$ treatments. The elements present were identified from survey spectra recorded at 50 eV pass energy. High-resolution spectra were recorded from individual peaks at 20 eV pass energy.

A Topometrix Accurex II (Topometrix, Santa Clara, USA) instrument, equipped with a non-contact AFM probe head and a 100 mm Tripot scanner, was used to image the samples. The tips (Topometrix 1660 e) were made of silicon and mounted on a cantilever with a spring constant of ca. 40 N/m and resonance
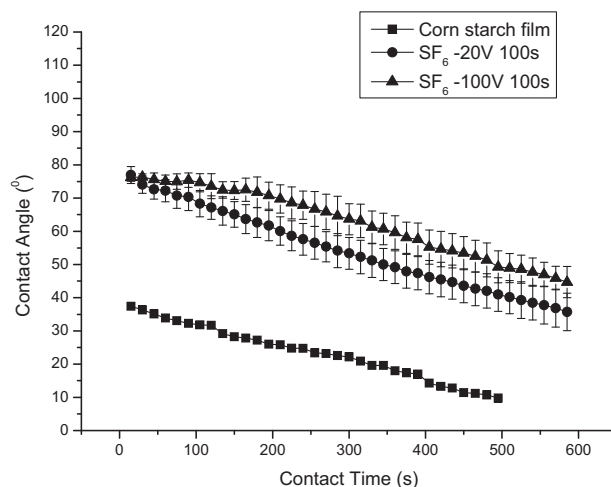


**Fig. 1.** Contact angle dynamics for cornstarch films treated with SF$_6$ plasma at different self-bias potentials and the same treatment time.

frequencies in the 100–150 kHz range. Scanning was carried out at the free cantilever oscillation frequency and different amplitudes, depending on the stability and contrast obtained. The amplitude was set higher than 80 nm, and the set point was fixed at 10–30% of the free oscillation amplitude to guarantee that the microscope was operating in intermittent contact mode. Samples were fixed on double-sided adhesive tapes, and the AFM images of the upper surface were obtained in air.

SEM micrograph at 3500× magnification of corn starch SF$_6$-treated films were obtained with JEOL JSM (model 6460 LV; Tokyo, Japan) with a tungsten filament operated at 15 kV. The samples were coated with 250 Å of gold.

Confocal Raman spectroscopy was performed in a Witec alpha300 R Confocal Raman Microscope System operating with a 50 mW laser ($\lambda$ = 532 nm). Surface depth profiles were obtained at different locations, and images of selected bands were compared.

## 3. Results

The films produced in this study were partially gelatinized, presenting a granular region formed by the swollen granular envelopes and a continuous region composed mainly of amylose molecules. The granule surface presented a roughness that was different from that of the matrix, confirming that the granule surface can possess a different molecular structure than the matrix (Thiré, Simão, & Andrade, 2003).

Dynamic contact angles were measured for the cornstarch thermoplastic films before and after 100 s of SF$_6$ plasma treatment at different self bias potentials; the data obtained are presented in Fig. 1. The cornstarch films presented an initial contact angle with water of 45°. After 600 s of wetting, the contact angle decreased to almost zero. Surfaces treated with SF$_6$ plasma at −20 V self-bias presented an initial contact angle with a water droplet of 75°, and the measured angle also decreased continuously with time. After SF$_6$ plasma treatment at a self-bias of −100 V, the cornstarch film surface presented the same initial contact angle observed for the −20 V treatment, but the contact angle remained stable for almost 180 s. After 180 s, the measured angle decreased continuously with time, reaching a value of 42.7° after 600 s.

The variation of the measured contact angle for the cornstarch film was previously reported (Thiré et al., 2005) and was related to the complete absorption of the water droplet into the polymeric film. The difference in stability observed for the analyzed surface

**Table 1**
Binding energies (eV) and the corresponding amount (%) in different samples.

| Binding energy (eV) | Amount (%) in different samples | | |
|---|---|---|---|
| | $-20$ V SF$_6$ plasma on a-C:H | $-100$ V SF$_6$ plasma on a-C:H | $-100$ V SF$_6$ plasma on starch films |
| 285.4 (C–C sp$^2$/sp$^3$) | 77.3 | 77.2 | 17.9 |
| 287.1 (C–CF ionic) | 15.9 | 17.1 | 41.1 |
| 288.15 (O=C–OR; O=C–OH) | – | – | 25.1 |
| 289.6 (C–F covalent) | 6.8 | 5.7 | 15.9 |
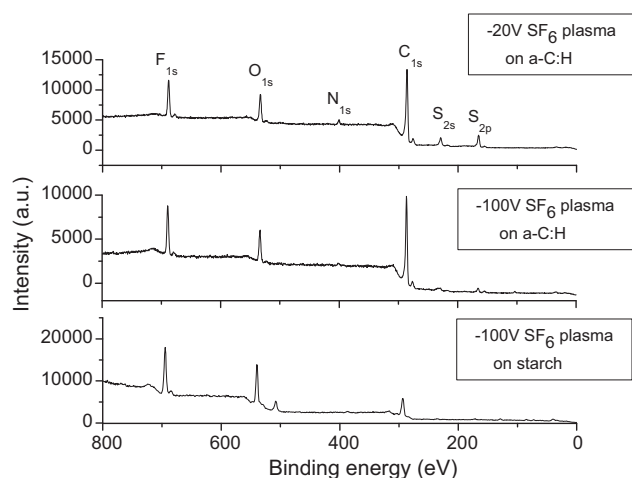


**Fig. 2.** Photoelectron spectroscopy spectra of SF$_6$ a-C:H film and starch film after plasma treatment at different voltages.

treatments was related either to chemical or to topographic effects (Bastos et al., 2009; Thiré et al., 2003).

X-ray photoelectron spectroscopy (XPS) measurements were performed on SF$_6$-treated starch film surfaces and compared with previously reported results (Saad, Gaiani, Mullet, Scher, & Cuq, 2011). XPS spectra of the amorphous carbon films treated at $-20$ V and $-100$ V for 60 s, and the XPS data of starch films treated at $-100$ V for 60 s are presented in Fig. 2. The data indicate that the SF$_6$ plasma treatment leads to fluoride incorporation on the film surface for all treatments. It can also be observed that sulfur incorporation is strongly dependent on the plasma self-bias.

Detailed spectral analysis of the carbon XPS peak is presented in Table 1. The spectrum indicates that, independent of treatment bias, the C$_{1s}$ contribution remains, primarily composed of three mains peaks at 285.4 eV, 287.1 eV, and 289.6 eV. The peak at 285.4 eV is related to sp$^2$ and sp$^3$ carbon, as presented in amorphous carbon films (Ayala, Costa, Prioli, & Freire, 2004). The peak at 287.1 eV (C–CF) may be related to carbon atoms bonded to another carbon in the neighborhood of a fluorine and amounts for 15.9% and 17.1% of the total intensity of the carbon peak for films treated with $-20$ V and $-100$ V self-bias, respectively. The band at 289.6 eV (C–F) corresponds to the C$_{1s}$ binding energy of a carbon atom directly bonded to a fluorine atom (Bastos et al., 2009). This peak accounts for 6.8% and 5.7% of the total peak intensity for films treated with $-20$ V and $-100$ V self-bias, respectively. Based on these results, it can be said that the amount and type of carbon–fluoride bonding

did not vary significantly with self-bias, as observed for the C$_{1s}$ chemical states. No peak was observed with higher binding energy.

XPS chemical analysis was also performed on cornstarch films treated with SF$_6$. The results, also presented in Table 1, indicate a relative increase in the number of fluoride modified groups, accounting for 41.1% for the C–CF and 15.9% for the C–F peak. The peak at 288.15 eV can be attributed to O=C–OR and O=C–OH in the glucose units (Thiré et al., 2003). The SF$_6$-plasma treated films show a decrease of the atomic abundance at 285.4 eV and an increase at 287.1 eV and 288.15 eV in comparison with the untreated starch (Saad et al., 2011), which can be explained by the fact that the C=O and C–F bonds were preferentially formed in relation to the C–C (285.4 eV) bonds.

Detailed analysis of the fluoride F$_{1s}$ XPS peak, shown in Table 2, indicates the presence of three peaks at 687.5 eV, 689.0 eV and 690.5 eV. The intensity of the third peak accounts for less than 5% of the total intensity for both treatments applied to amorphous carbon substrates. The peak at 689 eV is related to C–F bonds in ≡CF, =CF$_2$, and –CF$_3$ groups, while the peak at 687.5 eV is related to C$_4$F bonding as presented in graphite. It can be observed that, for surfaces treated at $-100$ V, roughly the same amount of the first two species was obtained. Additionally, the quantity of the species related to the peak at 687.5 eV was double that of the peak at 689.0 eV for surfaces treated at $-20$ V, indicating that $-20$ V plasma did not provide enough energy to induce strong bonding between C and F. Table 2 also presents the chemical analysis of the corn starch films after plasma treatment with $-100$ V SF$_6$ plasma for 60 s, and it can be observed that the main contribution to the fluoride peak is due to the C–F bonds on the ≡CF, =CF$_2$, and –CF$_3$ groups. The presence of a peak at 679.5 eV that amounts for 6.8% of the total intensity is also observed.

The chemical state of sulfur does not vary with treatment condition, but it can be observed that four times more sulfur than fluoride is incorporated into the surface of films treated at $-20$ V compared to the ones treated at $-100$ V self-bias SF$_6$ plasma. Sulfur was hardly detected on corn starch films treated with $-100$ V SF$_6$ plasma (Fig. 2). The carbon–fluorine interactions in a material can range from ionic to covalent. Covalent carbon–fluorine bonds show higher core electron binding energies than bonds that are more ionic in character. The method of fluorination affects the nature of the fluorine bonds. In the starch-treated films, ionic fluorine is predominant because the C–OH terminal bonds are disrupted and fluorine is incorporated, increasing the hydrophobicity of the starch-treated films.

To evaluate the effect of treatment time on the surface hydrophobicity, starch films were treated at $-100$ V self-bias for different periods of time. These data are presented in Fig. 3. It can

**Table 2**
Binding energies (eV) and the corresponding amount (%) in different samples.

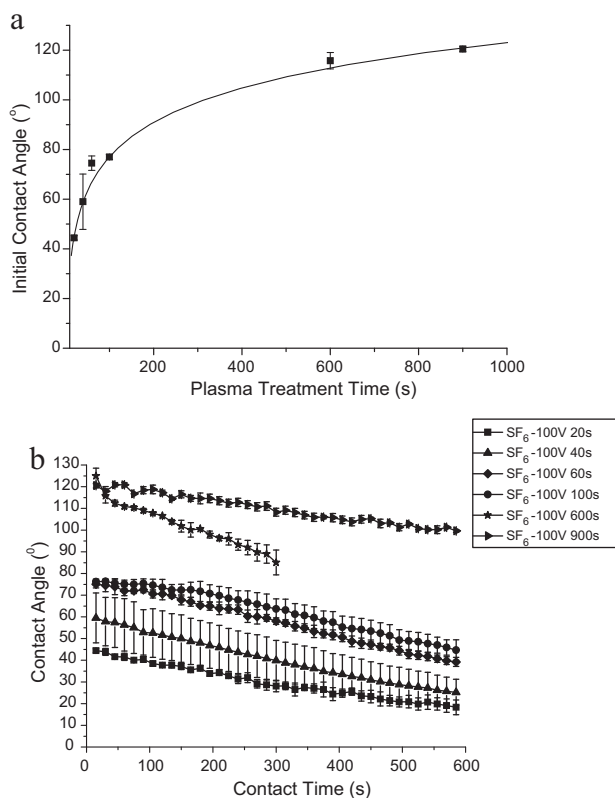| Binding energy (eV) | Amount (%) in different samples | | |
|---|---|---|---|
| | $-20$ V SF$_6$ plasma on a-C:H | $-100$ V SF$_6$ plasma on a-C:H | $-100$ V SF$_6$ plasma on starch films |
| 679.5 | – | – | 6.8 |
| 687.5 (C–F ionic) | 64 | 48 | 3.5 |
| 689.0 (C–F covalent) | 32 | 48 | 89.7 |
| 690.5 | 4 | 4 | 0.0 |

**Fig. 4.** Contact angle dynamics for corn starch films treated with $SF_6$ plasma at different self-bias potentials and the same treatment time.



**Fig. 3.** (a) Initial contact angle with water of corn starch films submitted to $SF_6$ plasmas at $-100$ V; (b) contact angle dynamics measured for corn starch films treated with $SF_6$ plasma at $-100$ V and different treatment time.
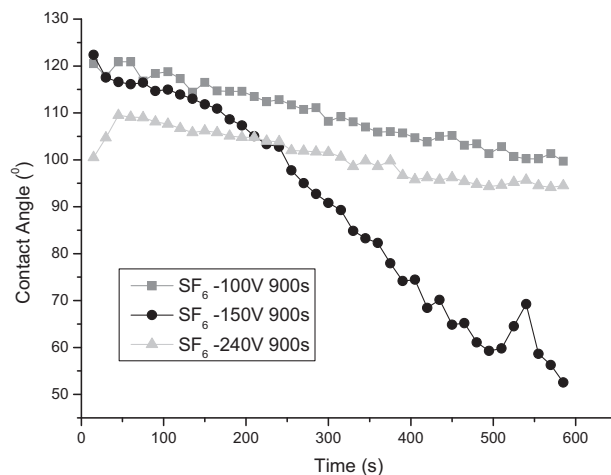
be observed that the initial contact angle varied logarithmically with treatment time. Starch films that initially presented a contact angle of $45°$ with water presented a contact angle of almost $120°$ after exposure of the surface to $SF_6$ plasma for 600 s. It was observed that the surface composition does not vary significantly with the treatment time.

To guarantee the optimal plasma treatment conditions, treatment time was fixed at 900 s, and the self-bias voltage was varied to include values higher than $-100$ V. These results are presented in Fig. 4. Dynamic contact angle measurements indicate that the surface treated with $-100$ V plasma for 900 s was reasonably stable to water contact; the contact angle varied from $120°$ to $110°$ after 600 s of contact between the droplet and the surface.
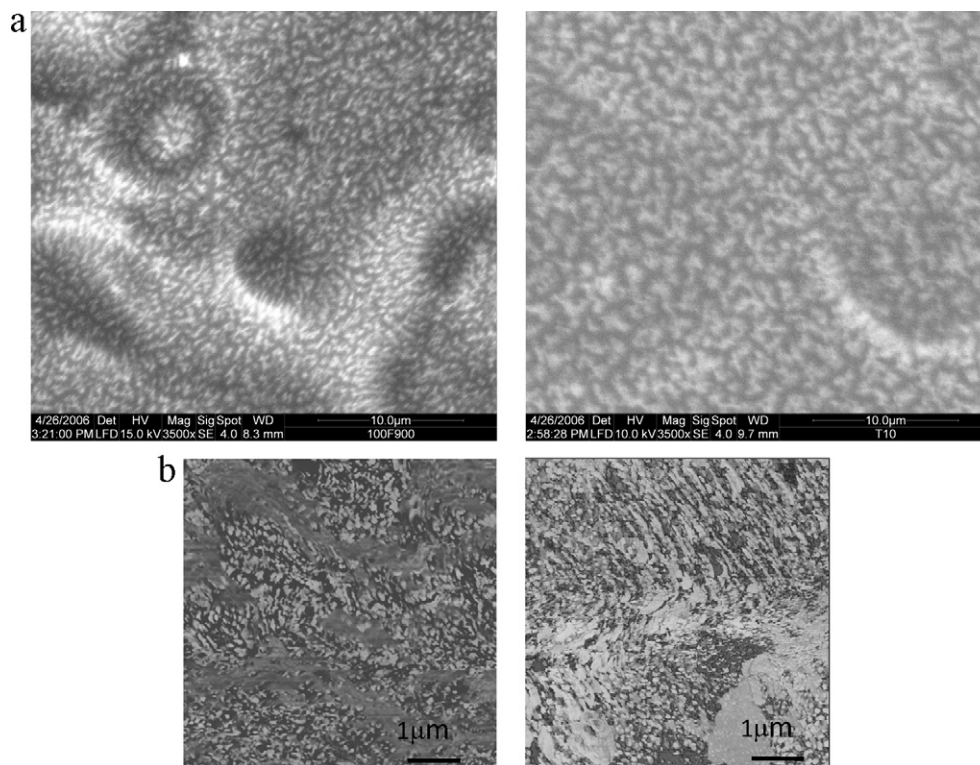


**Fig. 5.** (a) SEM images of cornstarch film treated with $SF_6$ plasma at $-100$ V and $-200$ V, respectively. (b) AFM phase contrast images of cornstarch film treated with $SF_6$ plasma at $-100$ V and $-200$ V for 900 s, respectively.
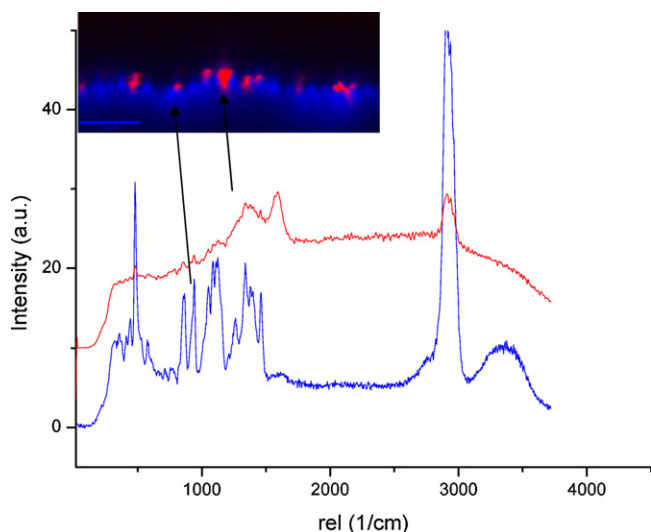
**Fig. 6.** Confocal Raman spectroscopy on $SF_6$ plasma-treated films at $-200\,V$ for 900 s: (a) typical Raman spectrum obtained for this film (b) difference spectrum obtained when graphic in (a) is subtracted from the starch film spectrum. This spectrum was obtained mainly in the lighter areas in the image shown in the insert.

It can be observed that surface stability to water contact was reduced when self-biases higher than $-100\,V$ were employed, and although the initial contact angle was roughly the same, the angle varied significantly after the initial contact.

Surface modification induced by plasma treatment was also confirmed by SEM as presented in Fig. 5a. A significant decrease in the overall granular envelope morphology can be observed, indicating major surface changes. AFM phase contrast images of samples treated at $-100\,V$ and $-200\,V$ for 900 s indicates the formation of a structure that resembles starch recrystallization (Fig. 5b).

Confocal Raman Spectroscopy was performed on the films treated with $SF_6$ plasma at $-200\,V$ for 900 s, and data are presented in Fig. 6. Fig. 6(a) shows the typical Raman spectrum obtained for these films. Comparing this spectrum with that of partially gelatinized starch films, a slight variation of the Raman bands can be observed for films treated with $SF_6$ plasma. Fig. 6(b) presents the difference spectrum obtained when the graphic in Fig. 6(a) is subtracted from the starch film spectrum. The difference spectrum is characteristic of the D and G bands of amorphous carbon, indicating that plasma treatment can induce the restructuring of carbon, causing both reticulation and amorphization of the carbon skeleton.

## 4. Discussion and conclusions

As reported by Olthoff, Van Brunt, Benck, and Roberts (1996), $SF_6$ plasma is dominated by the presence of atomic fluoride species resulting primarily from electron-impact excitation

$$e + F \rightarrow F^* + e \rightarrow F + h\nu + e$$
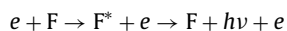
with minor contribution from the process of dissociative excitation

$$e + SF_x \rightarrow SF_{x-1} + F^* + e$$

Laser plasma data analysis (Olthoff et al., 1996) showed sharp peaks in the time averaged emission intensity close to both electrode surfaces. This indicates a narrow sheath region and the formation of a double-layer close to the cathode surface, leading to an enhancement of the ionization rate in these regions. Additionally, an increase in $SF_6$ dissociation was observed to be related to an increase in the plasma potential. Therefore, the incorporation of different species can be found, depending on plasma self-bias. In this

study we found that at higher self bias voltages, the dissociation rate increased and the density and energy of $F^*$ species colliding with the starch film surface was also enhanced. The energy was insufficient to fuse the film surface when self-biases lower than $-100\,V$ were employed. This is indicated by the similar global surface topography before and after plasma etching. Plasma treatment introduced a greater density of atomic excited fluoride related to $SF_x$ species to the surface when compared to lower self bias treatments.

It can be inferred that the stabilization of the contact angle for starch films treated with $SF_6$ plasma for times greater than 600 s might be related to the cross-linking among D-glucose units of starch, in addition to fluoride incorporation in the film. The cross-linking might prevent the reorientation of the surface starch molecules, and the aging process would be retarded. The reactions of starch in the $SF_6$ plasma zone should be similar to those proposed for cross-linking by an argon glow discharge plasma (Zou, Liu, & Eliasson, 2004). The helical structure of native starch leads to hydrophobic channels in which polarizable organic molecules or charged species can be absorbed. Fluoride species were easily absorbed into the helical channels, where charge and energy were transferred to the hydrogen atom of the C-2 hydroxyl group through collision of fluoride species with this group. At the same time, the effect of the plasma electric field should induce a further polarization of the O–H bonds of some hydroxyl groups, causing the covalent bond to become electrovalent to some degree. With the energy transferred by $F^*$ via another collision, two kinds of OH groups have a high probability to dehydrate, causing the crosslinking of two $\alpha$-D-glucose units.

Strong plasma treatment can also lead to a stronger reorientation of the surface chains with the formation of covalent bonds, as confirmed by Raman spectroscopy where the formation of the carbon D and G Raman bands were clearly assigned.

## Acknowledgments

## References

Ayala, P., Costa, M. E. H. M., Prioli, R. & Freire, F. L., Jr. (2004). Nano- and micro-scale wear of fluorinated carbon films. *Surface and Coatings Technology*, *182*, 335–341.

Bastos, D. C., Santos, A. E. F., da Silva, M. L. V. J. & Simão, R. A. (2009). Hydrophobic corn starch thermoplastic films produced by plasma treatment. *Ultramicroscopy*, *109*, 1089–1093.

Bico, J., Marzolin, C. & Quere, D. (1999). Pearl drops. *Europhysics Letters*, *47*(2), 220–226.

Cassie, A. B. D. & Baxter, S. (1954). Wettability of porous surfaces. *Transactions of Faraday Society*, *40*, 546–551.

Chuang, M.-J. & Chu, A.-K. (2011). Formation of a high hydrophilic/hydrophobic contrast surface on PET substrates by ECR generated sulfur hexafluoride plasma. *Applied Surface Science*, *257*, 3943–3947.

Dorrer, C. & Rühe, J. (2006). Advancing and receding motion of droplets on ultrahydrophobic post surfaces. *Langmuir*, *22*, 7652–7657.

Fernández-Blásquez, J. P., Fell, D., Bonaccurso, E. & del Campo, A. (2011). Superhydrophilic and superhydrophobic nanostructured surfaces via plasma treatment. *Journal of Colloid and Interface Science*, *357*, 234–238.

Hodak, S. K., Supasai, T., Paosawatyanyoung, B., Kamlangkla, K. & Pavarajarn, V. (2008). Enhancement of the hydrophobicity of silk fabrics by $SF_6$ plasma. *Applied Surface Science*, *254*, 4744–4749.

Hulleman, S. H. D., Kalisvaart, M. G., Janssen, F. H. P., Feil, H. & Vliegenthart, J. F. G. (1999). Origins of B-type crystallinity in glycerol-plasticised, compression-moulded potato starches. *Carbohydrate Polymers*, *39*, 351–360.

Karbowiak, T., Debeaufort, F., Champion, D. & Voilley, A. (2006). Wetting properties at the surface of IOTA-carrageenan-based edible films. *Journal of Colloid and Interface Science*, *294*, 400–410.

Nishino, T., Meguro, M., Nakamae, K., Matsushita, M. & Ueda, Y. (1999). The lowest surface free energy base don $-CF_3$ alignment. *Langmuir*, *15*(13), 4321–4323.

Olthoff, J. K., Van Brunt, R. J., Benck, E. C. & Roberts, J. R. (1996). Optical and mass spectrometric investigations o ions and neutral species in $SF_6$ radio frequency discharges. *Physical Review Letters*, *54*(2), 1876–1887.

Saad, M., Gaiani, C., Mullet, M., Scher, J. & Cuq, B. (2011). X-ray photoelectron spectroscopy for wheat powders: Measurement of surface chemical composition. *Journal of Agricultural and Food Chemistry*, *59*, 1527–1540.

Shibuichi, S., Onda, T., Satoh, N. & Tsujii, K. (1996). Super water-repellent surfaces resulting from fractal structure. *Journal of Physical Chemistry*, *100*(50), 19512–19517.

Suanpoot, P., Kueseng, K., Ortmann, S., Kaufmann, R., Umongno, C., Nimmanpipug, P., et al. (2008). Surface analysis of hydrophobicity of Thai silk treated by SF$_6$ plasma. *Surface and Coatings Technology*, *202*, 5543–5549.

Thiré, R. M. S. M., Simão, R. A. & Andrade, C. T. (2005). Surface modification of maize starch films by low-pressure glow 1-butene plasma. *Carbohydrate Polymers*, *61*, 407–413.

Thiré, R. M. S. M., Simão, R. A. & Andrade, C. T. (2003). High resolution imaging of the microstructure of maize starch films. *Carbohydrate Polymers*, *54*, 149–158.

Zou, J.-J., Liu, C.-J. & Eliasson, B. (2004). Modification of starch by glow discharge plasma. *Carbohydrate Polymers*, *55*, 23–26.