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Inducing surface hydrophobization on cornstarch film by SF_6 and HMDSO plasma treatment

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ABSTRACT

The development of thermoplastic materials based on starch has become a promising alternative for reducing plastic waste. To this end, plasma treatments were used to enhance the hydrophobicity of cornstarch films. Cornstarch films plasticized using glycerol and distilled water were prepared by casting. A surface modification method was employed using different precursor gases, HMDSO and SF_6, and a combined treatment using HMDSO followed by SF_6 (HMDSO/SF_6) and then the reverse, using SF_6 first followed by HMDSO (SF_6/HMDSO). The results indicated that the induced surface morphology determines the contact angle. It was observed that all films became hydrophobic, and films that were initially treated with SF_6 showed the greatest hydrophobicity if no further coating was applied, or if the treated surface was further coated using HMDSO. Under both of these treatment conditions the contact angle was greater than 110°.

1. Introduction

Although polymers from the petroleum industry have great importance in modern society, the search for eco-friendly materials increases the interest in the use of biodegradable products, particularly plastics. Starches from different botanical sources are the most promising biopolymers for this purpose. The interest in using starch as the base material for the production of biodegradable plastics is due to its total biodegradability, low cost and worldwide availability from a large number of crops.The starch is not a true thermoplastic, but when submitted to a thermo-mechanical process in the presence of a plasticizer such as water, glycerol or sorbitol, it loses its granular structure and acquires semicrystallinity similar to the behavior of a molten thermoplastic. The films produced using these methods show high water susceptibility, limiting their technological application (Soest, Hulleman, Wit, & Vliegenthart, 1996).

Polymer coating technology is currently an actively researched field in science as it can lead to final products with enhanced properties characterized by desirable bulk and surface properties. Low-power plasmas can induce the polymerization of a precursor gas on the substrate surface and introduce functional groups under specific plasma conditions (Hulleman, Kalisvaart, Janssen, Feil, & Vliegenthart, 1999; Jenkins & Donald, 1998; Santos, Bastos, Silva, Thiré, & Simão, 2012; Vaydia, Bhattacharya, & Zhang, 1995). Two successful methods that have been reported in the literature for inducing surface hydrophobization are the use of chemical vapor deposition – CVD plasma – either with sulfur hexafluoride (SF_6) or with hexamethyldisiloxane (HMDSO) as precursor gases (Andrade, Simão, Thiré, & Achete, 2005; Bastos, Santos, Silva, & Simão, 2009; Cruz-Barba, Manolache, & Denes, 2002; Hegemann, Brunner, & Oehr, 2001; Hulleman et al., 1999; Jenkins & Donald, 1998; Santos et al., 2012; Selli, Mazzone, et al., 2001; Selli, Riccardi, Massafra, & Marcandalli, 2001; Simão, da Silva, Martins, Thiré, & Andrade, 2007; Vaydia et al., 1995; Zanini, Massini, Mietta, Grimoldi, & Riccardi, 2008).

SF_6 plasma is used to introduce fluoride on treated surfaces resulting in contact angles greater than 130° due to fluoride incorporation together with surface reticulation (Bastos et al., 2009). Surfaces treated with HMDSO plasma present a high retention of methyl groups. Different wetting properties depending on plasma treatment and surface-induced design can be created (Behnisch et al., 1998; Simão et al., 2007; Zanini et al., 2008). Sulfur hexafluoride, SF_6, is a source of fluorine for etching processes under radio frequency plasma (RF) conditions as well as a gas-phase dielectric used in high-power electrical and physics industries. Fluorine atoms were found to efficiently attach to polymer surfaces by the use of SF_6 plasma treatment (Bastos et al., 2009). The wettability of Thai silk has been improved by SF_6 plasma treatment (Selli, Riccardi, et al., 2001; Suanpoot et al., 2008). Similar processing was

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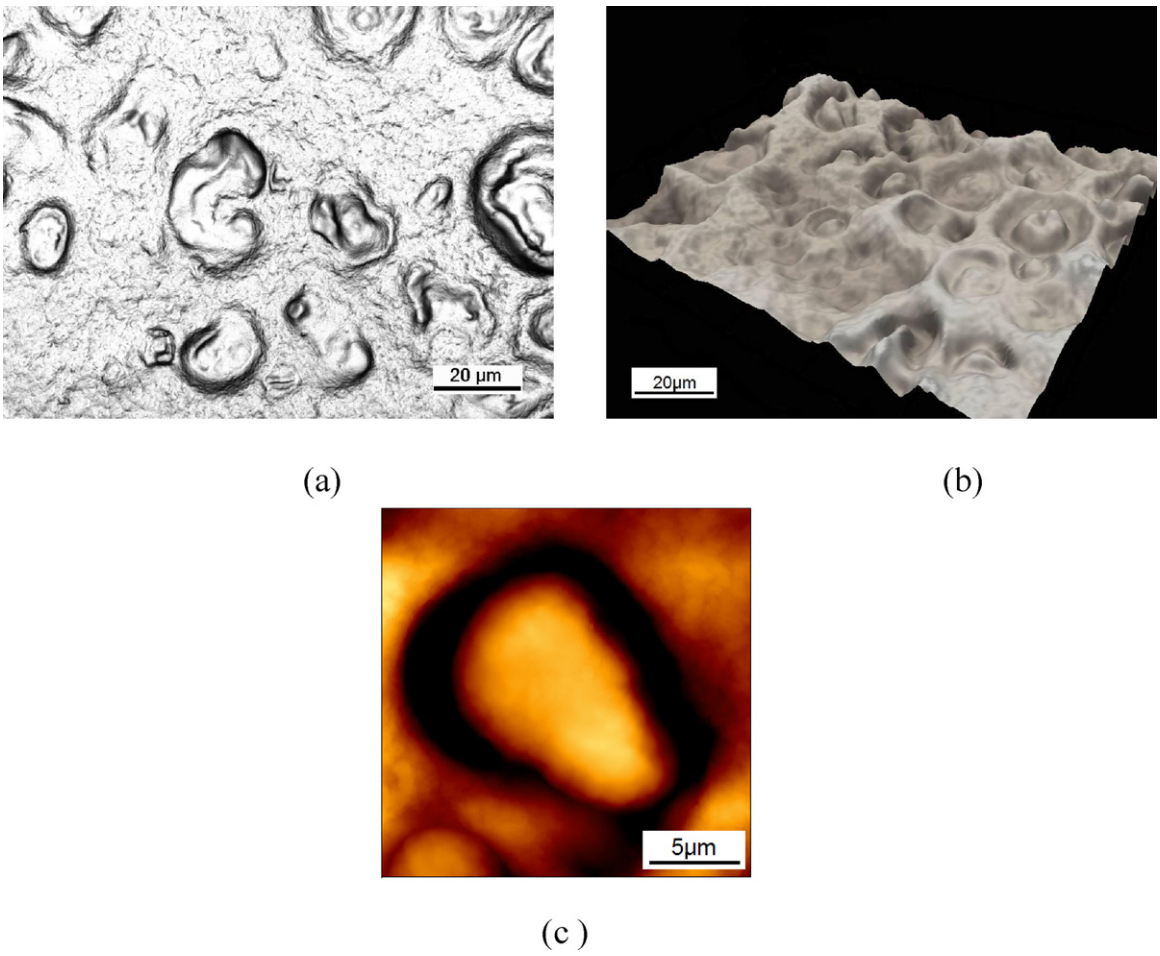


Fig. 1. Surface morphology of the partially gelatinized cornstarch film produced by casting: (a and b) laser confocal optical microscopy and (c) AFM images.

effective on a starch surface (Bastos et al., 2009), in which the surface became hydrophobic, and the interface between the starch surface and water droplet was significantly stabilized due to the association of different factors: surface structuring, fluoride incorporation and surface reticulation.

Hexamethyldisiloxane, HMDSO, is an organo-silicon compound with the formula $O[Si(CH_3)_3]_2$. It is reported as a precursor gas for low pressure plasma discharges used for producing soft coatings of $SiO_xC_yH_z$ with high contents of methylene and methyl groups and for generating hydrophobic surfaces (Behnisch et al., 1998; Bellel et al., 2006; Schwardz, Schmidt, & Ohl, 1998).

In this study, SF_6 plasma treatment and HMDSO plasma coating were compared as different means of hydrophobization of thermoplasticized starch surfaces. For comparison, all treatments were performed under the same conditions; their combined effect was also determined by applying both plasmas successively. Thus, a surface modification method was employed using different precursor gases, but the same conditions of self-bias voltage of −200 V for 10 min: HMDSO and SF_6, and a combined treatment using HMDSO followed by SF_6 (HMDSO/SF_6) and then the reverse, using SF_6 first followed by HMDSO (SF_6/HMDSO).

The main aim of this work was to try a different mean to obtain a hydrophobic surface either by surface reticulation or by coating using roughness to enhance the observed effect. The modifications of the plasma treated surfaces were investigated through atomic force microscopy (AFM), confocal laser scanning microscopy (CLSM), contact angle measurements and X-ray photoelectron spectroscopy (XPS).

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 stirred for 5 min. 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.

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. The same cathode self-bias voltage, $V_b = -200$ V, and the same treatment time, 10 min, were used for every treatment. The flux of gas was independently controlled by a set of micro-leak valves and it was not necessary any extra mean for plasma ignition. The reactor and the details of the experimental SF_6 and HMDSO conditions were described elsewhere (Bastos et al., 2009; Zanini et al., 2005). HMDSO films presented a thickness of 500 nm as measured by Dektak contact perfilometry.

An Atomic Force Microscope (1M Plus, JPK Instruments, Germany) was used to image the samples. Images were obtained in dynamic mode using a Micromasch NSC 14/AIBS cantilever with nominal spring constant of 5 N/m. Force–distance curves were systematically obtained mapping a selected 10 μm × 10 μm region of the sample in an 8 × 8 points matrix. Curves were automatically analyzed for slope and adhesion of the retrace curve providing distribution maps. Force–distance curve data were obtained using the

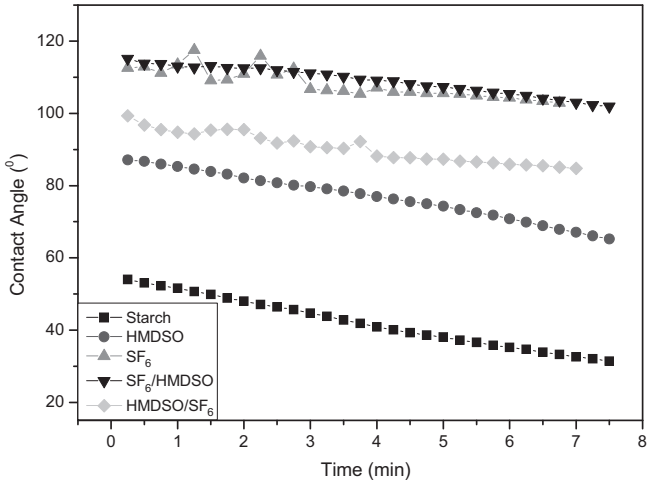


Fig. 2. Time evolution of the water contact angle for cornstarch films before and after plasma treatments, self-bias −200 V for 10 min.

same cantilever used to image the samples in the intermittent contact mode. After imaging, the tip was retracted and the oscillation was turned off to acquire the curves. Samples were probed again with the same tip at the same location, and no detectable surface damage was observed.

The influence of the plasma treatment on the hydrophilicity of starch films was determined by water contact angle measurements with an NRL A-100-00 Rame-Hart Goniometer. The time evolution of the droplet water (2.5 μL) shape was recorded using a video camera every 15 s for a total of 10 min.

An OLYMPUS LEXT/OLS 3100 Confocal Laser Scanning Microscope was used to obtain some of the images in this study. The magnification used varied between 2400× and 9600× using an objective lense of 100× magnification. Three-dimensional images were also acquired.

The elemental composition of the surface was evaluated by X-ray photoelectron spectroscopy (XPS). XPS analysis was performed in a multi-technique system (SPECS) equipped with a hemispherical analyzer PHOIBOS-100 using AlKα X-ray radiation at the background pressure in the range of 10^{-8} Pa. Peak analysis was performed after subtraction of a Shirley background using Gaussian–Lorenzian peak shapes obtained from the Casa XPS software package. The signal of C_{1s}, at 285.4 eV, was selected for energy calibration.

3. Results

Fig. 1 presents confocal optical microscopy images, (a) and (b), and atomic force microscopy, (c), of cornstarch film obtained by casting. Gelatinization time was not enough for complete granules disruption, a structure characteristic of a partially gelatinized starch film was observed. Two different regions were distinguished: one continuous phase, composed mainly of amylose that was released from the granules during the gelatinization process, and a phase of swollen granules composed mainly of amylopectin (Thiré, Simão, & Andrade, 2003). Between the two regions a depression was observed; this depression was observed inside the granular region, Fig. 1(b). This depression was first observed by atomic force microscopy (Hegemann et al., 2001) but was initially attributed to composition or tip effects. In this study, the presence of the same depressions, as observed through confocal microscopy as well as atomic force microscopy, discounted the possibility of tip–surface effects. Fig. 2 shows the dynamics of contact angle of water droplets in contact with the surface of cornstarch film. All measurements

Table 1
Detailed XPS analysis untreated cornstarch film: binding energies (eV) and the corresponding amount (%).

Binding energy (eV)	Amount (%)
285.6 (C—C; C—H)	29
287.7 (C—O; C—N)	54
290.4 (O—C—O; C=O)	16
292.7 (O=C—OH; O=C—OR)	1

were performed one week after plasma surface modification. The droplet profile, obtained from the average of three drops in different regions of the sample, was followed for 10 min to evaluate surface stability. No droplet spreading was observed. It was observed that untreated starch film had an initial water contact angle of 55° which quickly decreased over time if the droplet was left on the surface by water absorption. In contrast, after all plasma treatments employed the film surfaces presented a hydrophobic character with initial contact angles above 85°. It was also observed that the variation of the contact angle with time was dependent on the plasma treatment. HMDSO coated surfaces had an initial water contact angle up to 85° which decreased to 75° after 7 min of water contact. If the coated surface was further treated with SF_6 (HMDSO/SF_6), the water contact angle improved and an initial contact angle over 100° was obtained. The best results were obtained when cornstarch films were only treated with SF_6, were an initial contact angle of 115° was observed and a variation of less than 10% was measured after 7 min of water contact. Similar results were obtained when the surface was treated first with SF_6 and then plasma coated with HMDSO (SF_6/HMDSO). The contact angle variation with time was smaller for cornstarch films modified first using SF_6 plasma treatment without any further surface modification. These results suggested that the HMDSO coating alone is not enough to prevent water from being absorbed by the substrate because the coating may present microporosity that could allow water molecules to penetrate the substrate. When SF_6 plasma was applied either to the substrate or the coated surface, some degree of reticulation was induced to guarantee surface protection against water. Long time surface stability was observed by measuring films stored at 50% RH and 25 °C form more than one year. Contact angle do not change with storage time.

XPS analysis was performed on untreated cornstarch film and on plasma-treated samples. The detailed XPS analysis of untreated cornstarch film is presented in Table 1.

The spectrum indicates that the C_{1s} contribution is primarily composed of four mains peaks at 285.6 eV, 287.7 eV, 290.4 eV and 292.7 eV. Similar results were obtained before by Saad, Gaiani, Mullet, Scher, and Cuq (2011) for starch granules. Differences are related to the gelatinization process in which starch granules forms a viscous mass consisting of a continuous phase of solubilized amylose and a discontinuous phase of remnant granules (Simonin, Guyon, Orlowska, Lamballerie, & Le-Bail, 2011).

The peak at 285.6 eV is related to C making a single bond with C or H (C—C, C—H) in side chains. The peak at 287.7 eV may be related to carbon making a single bond with O or N (C—O; C—N) in alcohol, amine, or amide functions. The band at 290.4 eV corresponds to C making two single bonds or one double bond with O (O—C—O or C=O) in hemiacetal and acetal functions in polysaccharides. The peak at 292.7 eV is related to C making one double or single bond with O (O=C—OH or O=C—OR) in ester and carboxyl functions of polysaccharides (Saad et al., 2011).

The XPS analysis of SF_6 plasma-treated starch films was already presented before (Santos et al., 2012) and indicated a significant increase in the (O—C—O or C=O) functions as well as fluoride incorporation as observed in Table 2. After SF_6 plasma treatment, an increase of the O/C ratio (63%), compared with that of untreated

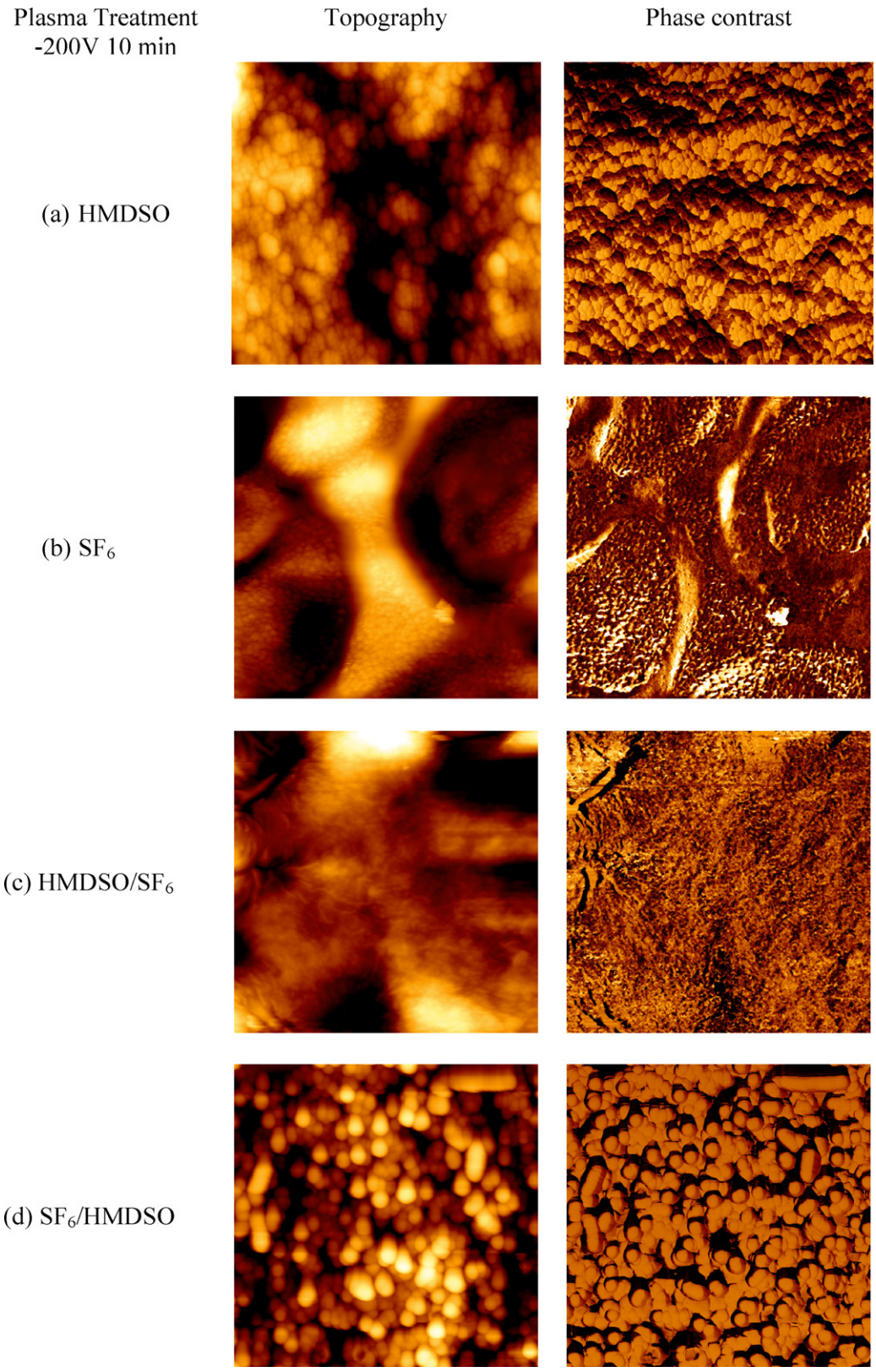
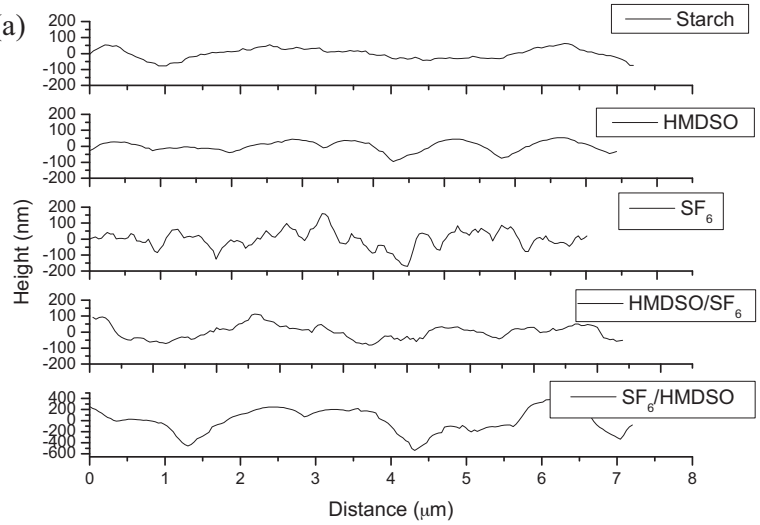


Fig. 3. AFM topographic and phase contrast images (20 μm × 20 μm) of plasticized cornstarch films after plasma treatments, self-bias −200 V for 10 min.

starch (40%) was observed. Deconvolution of the C_{1s} peak for HMDSO and HMDSO/SF_6 plasma-treated samples showed similar percentages of carbon and oxygen, where an O/C ratio of approximately 0.5 was obtained. In the HMDSO/SF_6 treated film, the presence of Si is negligible, indicating that the main effect of SF_6 plasma was the etching out of silicon (Zanini et al., 2008) and fluoride incorporation, which lead to an enhancement of the hydrophobicity of this sample.

Deconvolution of Si_{2p} peak for HMDSO and SF_6/HMDSO treated samples are presented in Table 3. The major contribution of HMDSO

(a)



(b)

Sample	Roughness (nm)
Starch	25 ± 8
HMDSO	33 ± 8
SF_6	58 ± 11
HMDSO/SF_6	40 ± 9
SF_6/HMDSO	190 ± 70

Fig. 4. (a) Line profiles obtained from AFM imaging of different samples. All profiles are presented with the same vertical scale, except the line profile from the SF_6/HMDSO sample, which presented a significant change in roughness. (b) Roughness obtained from 10 different 8 μm line scans extracted from the presented AFM images.

film was $Si(—O)_2$ while SF_6 induced silicon oxidation where the major contribution to the Si_{2p} peak was $Si(—O)_3$. HMDSO deposition over the SF_6 plasma-treated starch (SF_6/HMDSO) induced modifications in the chemistry of the film. It was observed that the presence of fluoride within the plasma increased the oxygen concentration in relation to the film deposited over bare starch, increasing both the O/C and the O/Si ratios. In the SF_6/HMDSO film the proportion of $Si(—O)_2$ decreased in favor of the more highly oxidized $Si(—O)_3$ environment (Alexander, Short, Jones, Michaeli, & Blomfield, 1999).

Surface morphology variation in the plasma treated samples was observed using atomic force microscopy, and the results are presented in Fig. 3(a)–(d). Fig. 3 presents both topography and phase contrast images obtained from the interface between granules and the matrix for the different plasma treatments employed.

Typical line profiles for lines obtained at the granular, and the matrix regions are presented in Fig. 4(a) as well as the root mean square (RMS) roughness for the different treated surfaces. It can be observed that after HMDSO coating of cornstarch films both roughness and phase contrast distribution were different for matrix and granular regions. The measured roughness is comparable to the one observed for the substrate, untreated TPS, as presented in Fig. 4(b). The high degree of variation related to the measurements was due to sample non-homogeneity as well as to different matrix and granular region roughnesses. SF_6 plasma treatment on this surface did not induce a significant increase in roughness that varied from (33 ± 8) nm for HMDSO to (40 ± 9) nm for HMDSO/SF_6 films. For both surfaces, SF_6 plasma treatments resulted in a substantial increase for surface roughness on the nanometer scale. The roughness was measured to be at least double that observed for the untreated starch sample and the observed corrugation presented a smaller length scale compared with the one observed for the substrate. The highest increase in roughness was measured for the SF_6/HMDSO films. It can be observed in Fig. 3(b) and (d) that a major increase in roughness was induced by the

Table 3
Deconvolution of Si_{2p} peak for HMDSO and SF_6/HMDSO plasma-treated samples.

Functions	Amount (%)	
	HMDSO	SF_6/HMDSO
$Si(—O)_1$	18.0	28.0
$Si(—O)_2$	44.0	21.0
$Si(—O)_3$	32.0	43.0
$Si(—O)_4$	6.0	8.0

Table 2
Atomic concentrations of samples from XPS analysis.

Plasma treatment	%C	%O	%F	%Si	%S	O/C	F/C	O/Si
Cornstarch	71.5	28.5	–	–	–	0.40	–	–
SF_6	50.5	32.1	16.2	–	1.2	0.63	0.32	–
HMDSO	49.9	23.9	–	26.2	–	0.48	–	0.91
HMDSO/SF_6	47.4	25.1	27.4	–	–	0.53	0.58	–
SF_6/HMDSO	43.0	31.3	1.2	24.5	–	0.73	0.03	1.28

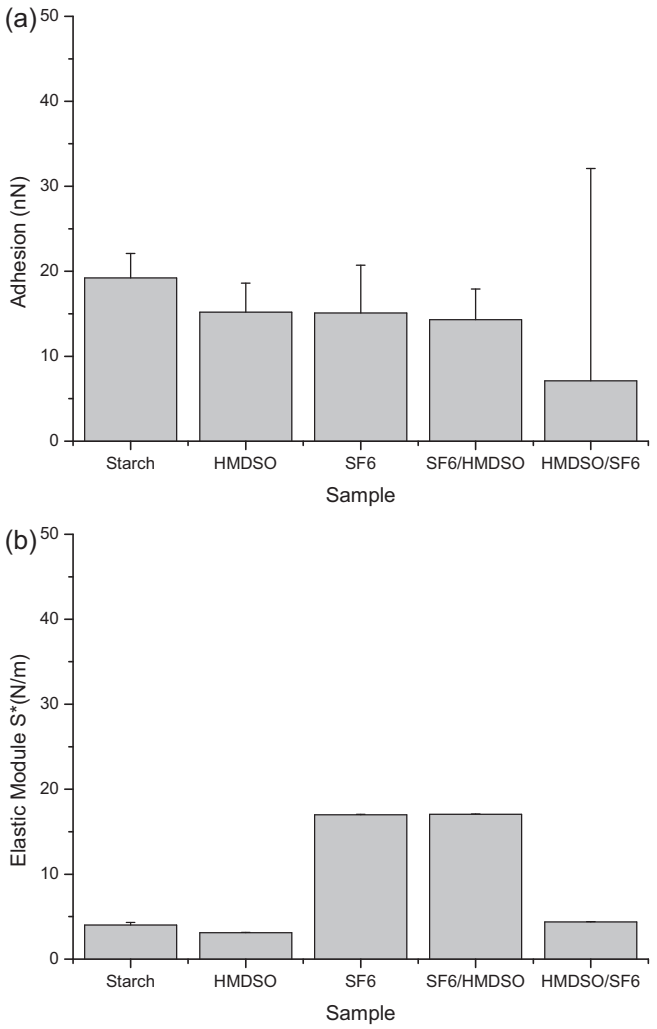


Fig. 5. Data from AFM force–distance curves: (a) Adhesion and (b) elastic spring constant, S^*, of the surface of cornstarch films after plasma treatments at −200 V for 10 min.

SF_6 plasma treatment before HMDSO surface coating. Although the image presented in Fig. 3(d) greatly resembles an image obtained with a blunt tip, the same image was observed using at least four different new tips from different sources, including super sharp tips. Increase in roughness may be due to Si etching in the surface.

Atomic force microscopy was also used to provide further information on surface stability and reticulation induced by plasma treatment these results were used to compute local surface hydrophilicity. A statistically significant set of force–distance curves was obtained for each sample. This procedure was performed to build up a map of surface interactions against a silicon tip. Both surface effective elastic modulus and surface–tip adhesion forces were measured, and the results are presented in Fig. 5(a) and (b). All measurements were performed in air (50 ± 2)% humidity using the same NSC14/AIBS (Micromasch) with a spring constant of (5.0 ± 0.5) N/m. Tip–surface adhesion may be caused by capillarity induced by the presence of a contamination layer containing water on the surface of both tip and sample (Lieberman & Lichtenberg, 1994). In Fig. 5(a), the adhesion forces between the silicon tip and the sample are presented. It was observed that adhesion forces values showed high scattering making interpretation difficult. A significantly higher adhesion was observed for the untreated substrate, and smaller values were observed for samples coated first with HMDSO and then treated with SF_6. This result can be related to the higher hydrophilicity of the substrate and the lower local roughness of the HMDSO/SF_6 sample, respectively. When the sample is hydrophilic, as the cornstarch film is, it retains a thick layer of water that adheres to the silicon tip by capillary action that increases the measured adhesive forces. In contrast, when a hydrophobic smooth layer is deposited over the hydrophilic sample, the contamination layer is unable to fully form and the measured adhesion is lower due to lower capillary condensation between the tip and the hydrophobic substrate, as described by Fujihira et al. (1996) and Xiao and Quian (2000). When a high roughness hydrophobic layer is deposited onto the surface, the high adhesion forces may be related to multiple contact point adhesion rather than to capillarity (Sedin & Rowlen, 2000). More studies must be performed to clarify this point. The values for the effective elastic spring constant of the surface are presented in Fig. 5(b). It can be observed that the starch sample presented an effective elastic spring constant of 4 N/m, with less than 7.5% variation. This error can be attributed to the surface inhomogeneity because the granular region and the matrix may be composed of different molecules. The HMDSO coating did not significantly modify the elastic spring constant of the surface as measured by AFM (Schneider et al., 2006). However, when starch samples were modified by SF_6 plasma treatment, a substantial increase of the elastic spring constant was observed. This increase in elastic spring constant might be related to surface reticulation. The HMDSO coating produced over the reticulated starch surface, presented the same elastic spring constant as the uncoated reticulated surface. Little data scattering was observed for the measurement of the elastic spring constant of all plasma-modified samples, indicating that all coatings may be producing a homogeneous layer as was previously observed in the phase contrast images.

4. Conclusion

This study showed that HMDSO coatings can be produced on the surface of starch films and that these coatings are intrinsically hydrophobic. The final contact angle of a system based on starch is highly dependent on the microstructure created on the surface and the surface roughness, these being the main factors that induced surface hydrophobicity in addition to starch reticulation. The presence or absence of a dense coating produced by HMDSO plasma on the surface did not affect the contact angle when starch was previously reticulated. Additionally, the water contact angle is dependent not only on the top most surface layer, but also on the hydrophilic character and densification of the polymeric surface. The reticulated substrate is rougher and more hydrophobic surface produced, thus, it prevents water that could potentially migrate through the defects of the coating from being absorbed. The HMDSO films produced were soft, and the elastic spring constant did not change after SF_6 plasma treatment, indicating that the surface does not undergo a reticulation process. A significant increase in the contact angle and a decrease of the absorption kinetics were observed after the HMDSO film treatment with SF_6 plasma, and this effect can be attributed to fluoride incorporation on the film.

SF_6/HMDSO-treated film was the most hydrophobic of the samples, and the interface between the starch surface and a water droplet did not change with time, indicating that water is not adsorbed on the surface, due to the association of different factors: substrate surface reticulation, increase of the O/C ratio and a significant increase in the surface roughness.

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