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Sulphur Hexafluoride Plasma Treatment to Enhance the Hydrophobicity of CVD Carbon Coatings Produced on Cornstarch Plasticized Films

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Summary: In this work, a new coating strategy was successfully developed and promising results indicate a significant reduction of the water sensibility of cornstarch films coated by chemical vapour deposition (CVD). Amorphous carbon coatings (a-C:H) produced from methane (CH_4) were submitted to different sulphur hexafluoride plasma treatments. The best results were obtained for cornstarch films coated with a 50 nm-thick CH_4 plasma coating and treated with SF_6 for 60 s. This surface modification led to a significant increase in the surface hydrophobicity, with measured contact angle of 85°. Atomic force microscopy (AFM) was used to evaluate local surface modifications upon the a-C:H coating and after the SF_6 plasma treatment. Results indicate that the cornstarch films were homogeneously coated using CH_4. SF_6 treatment led to a plasma etching of the surface, changing completely the observed morphology. Fluorine was incorporated to the surface.

Keywords: atomic force microscopy (AFM); biopolymers; plasma processing and deposition; thermoplastic starch; wettability

Introduction

Polymer coating technology is currently an important field in science as it can lead to final products with enhanced properties characterized by desired bulk and surface properties. Hydrocarbon low power plasmas can induce the polymerization[1–3] of a precursor gas on the substrate surface and it might introduce functional groups, such as hydroxyl and carboxylic groups onto a polymer substrate, under specific plasma conditions. Carbon coatings called amorphous hydrogenated carbon (a-C:H) exhibit special physical properties related to micro-hardness, optical refractive index and water repellence.[1,4] In addition, since a-C:H coatings contain only carbon and hydrogen, they are considered to be environmentally safe.

The development of bioplastics derived from renewable resources has been encouraged by the increasing interest in reducing 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 single-use biodegradable plastic items. Starch is inexpensive, totally biodegradable and is available in large quantities from certain crops (i.e. corn and wheat) produced in abundance in the available market.[5] Native starch is composed of two polymers, amylose and amylopectin, both of them constituted of α-D-glucose repeating units. Amylose is mostly linear, whilst amylopectin is highly branched.

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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 the dimensional stability and the mechanical and barrier properties.[6] A new approach to overcome this difficulty might be to protect the starch based materials from humidity changes with a thin polymeric layer, deposited by plasma polymerization.[7–9] In the present work, we studied the possibility of reducing the water sensitivity of cornstarch films by depositing carbon coatings from hydrocarbon gases. A subsequent surface treatment with sulphur hexafluoride (SF_6) on the amorphous carbon coated films was also evaluated. Fluorinate compounds is often used to create hydrophobic and ultrahydrophobic (contact angle superior to 150°).[3]

Experimental Details

Food grade cornstarch was supplied by Refinações de Milho Brasil Ltda (São Paulo, Brazil). High-purity methane was purchased from White Martins Gases Industriais (Rio de Janeiro, Brazil). Analytical grade glycerol was purchased from Vetec Química Fina Ltda. (Rio de Janeiro, Brazil) and was used as received.

Films were prepared by dispersing cornstarch in distilled water under reflux (5% w/v) and stirring for 300 s (time of gelatinization). Glycerol (15% w/w) was added as plasticizer. The hot dispersion was poured onto a Petri dish and allowed to dry at 340 K for 12 h. This process led to incomplete gelatinization of starch granules as already reported.[10] The films were peeled off and reconditioned for at least 10 days at 50% relative humidity before measurements. Produced films were clear, homogeneous and easily released from Petri dishes presenting measured thickness (digital micrometer Mitutoyo n° 293-265, Mitutoyo Corp., Japan) ranging from 70 to 100 μm.

Coatings of different thicknesses were deposited by glow discharge produced from methane (CH_4) under a pressure of 10 Pa with varying cathode self-bias voltages (V_b) and different deposition times. Cornstarch substrates were placed on the cathode of a glow discharge reactor, operating at 13.56 MHz. In order to characterize the chemical properties of the different coatings produced, small pieces of silicon wafers were placed closely to the cornstarch films inside the deposition chamber. The chamber base pressure was always kept above 6 Pa to avoid excessive solvent loss, as described elsewhere.[7] After the a-C:H coating, the cornstarch and silicon substrates were submitted to a surface treatment with sulphur hexafluoride (SF_6). SF_6 plasma treatment was carried out in the same manner. The time of treatment was fixed in 60 s.

The influence of the plasma deposition and subsequent treatment on the wettability of starch films was determined by water contact angle measurements with a NRL A-100-00 Ramé-Hart Goniometer (Mountain Lakes, USA). A 2.5 μl-water droplet was applied on the surface of the as casted and the plasma-modified cornstarch films. The time evolution of the droplet on the surface was recorded each 15 s.

Scanning probe microscopy analysis was carried out with a Topometrix Acurrex-IIL system. Morphology of the cornstarch substrates and their coatings was analyzed in intermittent contact mode using silicon tips (MikroMasch^{TM} NSC16) mounted on a cantilever with a spring constant of ca. 40 N/m and resonance frequencies in the range of 170 kHz. 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 to 30% of the free oscillation amplitude in order to guarantee that the microscopy was operating in intermittent contact mode. Samples were fixed on double-coated adhesive tapes and the atomic force microscopy (AFM) images were obtained in air.

Results and Discussion

Native cornstarch occurs as semicrystalline granules with varied sizes and shapes and can be converted into thermoplastic materials by casting in the presence of plasticizers, such as water and glycerol as well as other low molecular weight polyols.[5] Different methane (CH_4) plasma conditions and deposition times were employed to coat cornstarch films with a-C:H with the purpose of enhancing their water resistance. The efficiency of the process depends strongly on the deposition procedure and parameters. Contact angle measurements indicates that a 50 nm-thick coatings produced from methane, produced at −100 V self-bias, enhanced considerably the hydrophobicity of the films (Figure 1). It can be observed that initial contact angle with water increased from 35° to more than 80° upon coating. Although an increasing in water resistance is clearly observed, the measured contact angle restored its initial value after 540 s of contact between the water droplet and the surface, indicating a poor stability of the surface when wetted. In general, plasma-treated polymer surfaces show an aging effect due to the reorientation of mobile groups or segments at the polymer surface.[2] In order to try to further increase water resistance and surface stability, a-C:H coated films were also treated with SF_6 plasma. After 60 s of SF_6 treatment the initial contact angle increases to 85°. Besides the enhancement of the measured initial contact angle with water, wetted surface stability was also slightly increased upon SF_6 plasma treatment as the measured contact angle was observed to be 43° after 600 s of contact between the water droplet and the surface.

Amorphous hydrogenated carbon (a-C:H) coating and SF_6 treatment were also carried out in silicon wafers in order to evaluate chemical and physical properties of the resulted film surface. Figure 2 presents the X-ray photoelectron spectroscopy (XPS) spectra of the a-C:H coating after SF_6 plasma treatment. It can be

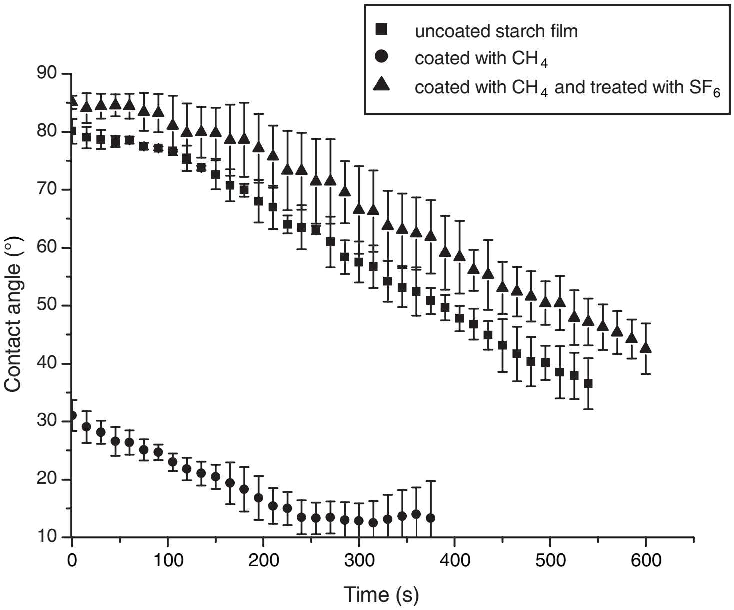

Figure 1.

Variation of water contact angles with time for different samples. (a) Uncoated cornstarch film; (b) film coated with a 50 nm-thick a-C:H coating produced from CH_4 plasma at −100 V; (c) film coated as in (b) and treated with −100 V SF_6 plasma for 60 s.

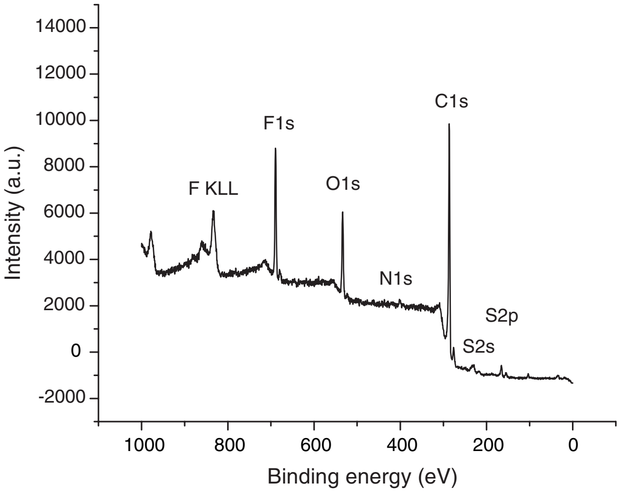

Figure 2.
XPS spectra of a-C:H coatings treated with SF_6 at −100 V for 60 s.

observed that fluorine was strongly incorporated to the surface. Sulphur was also found on the coating surface but at lower amount. Under the chosen treatment conditions (−100 V self-bias), SF_6 plasma acted as a convenient source of fluorine atoms incorporation. The oxygen and nitrogen presented on the sample surface is believed

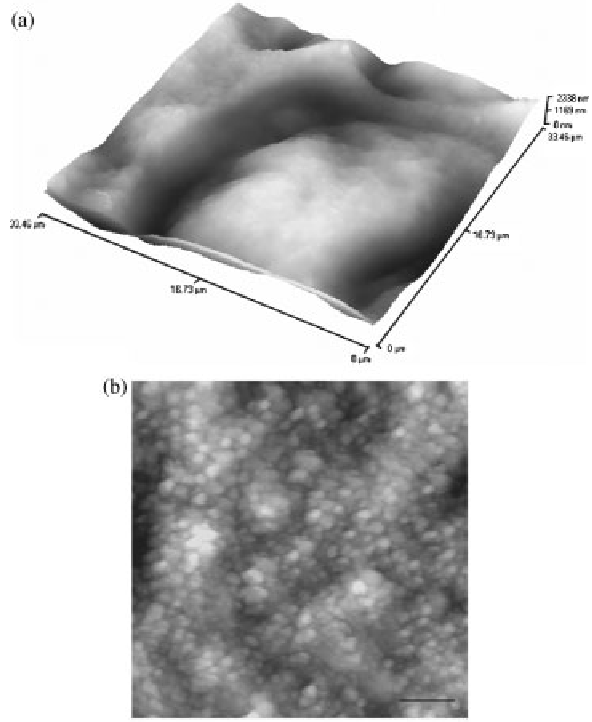

Figure 3.
(a) AFM image of the surface of matrix and granular envelope regions of cornstarch film coated with 50 nm thick a-C:H produced at −100 V. (b) Detailed image of the matrix. Scale bar = 400 nm. Z-scale amounts 190 nm.

to be due to absorption of atmospheric air when transferring the samples from the deposition chamber to the analysis system.

In fluorine-containing plasmas, surface reactions, etching and plasma polymerization can occur simultaneously.[2] The operating parameters, gas feed and the chemical nature of the polymer substrate dictate which reactions predominate. Since sulphur is not a backbone element of the polymer, an SF_6 plasma, having a zero $[CF_x]/[F]$ ratio, is an etching plasma which results in surface grafiting of fluorine functionalities rather than polymer deposition.[2] Profilometer measurements corroborate this hypothesis since results indicated a strong etching of the a-C:H coating, which did not led to its complete removal (data not shown).

Figure 3 presents AFM typical images of 50 nm thick coatings produced from methane at −100 V. As reported previously[10], the surface of partially gelatinized cornstarch films was composed by granular envelopes surrounded by a amylose-rich matrix. In Figure 3a, both granular envelope and the continuous matrix can be observed. This result indicates that the overall surface morphology of cast cornstarch films was preserved upon a-C:H coating. Higher resolution image of the matrix shows the presence of round shaped structures (Figure 3b). Images with similar morphology were obtained for granular envelope region. This observation corroborates previous works reporting that upon a-C:H coating, using either 1-butene[7] or 1,3-butadiene[8] as precursors gas, an homogeneous surface composed mainly of irregular oval shaped structures was observed on both matrix and granular regions. However, the size of surface features varied according to the precursor gas. The typically values observed for major

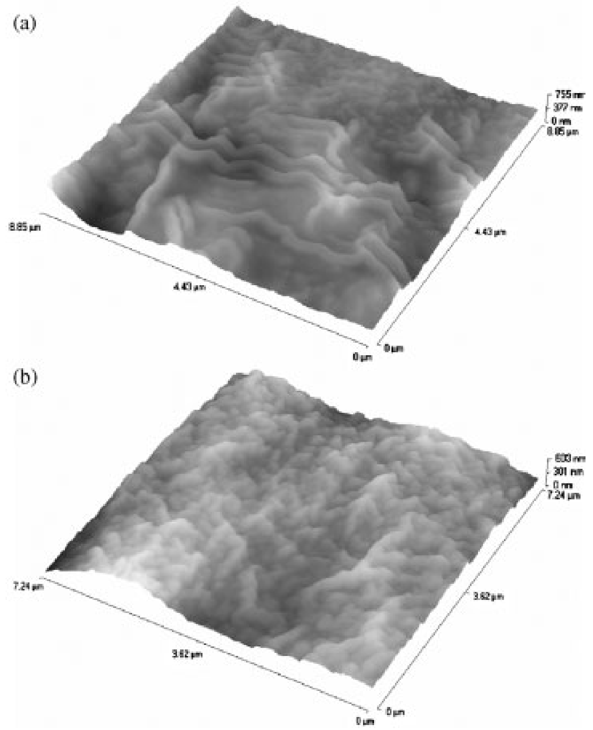

Figure 4.
AFM image of (a) granular and (b) matrix regions of cornstarch films coated with a-C:H and treated with SF_6 at −100 V for 60 s.

axis of features were 67 nm for methane, 104 nm for butane and 130 nm for butadiene, in average.

Regarding the coated surface after SF_6 plasma treatment, it was observed that the surface morphology changed considerably as a function of the time of plasma exposition. A completely different morphology was observed after a treatment time of 60 s, as shown in Figure 4. Surface details observed on both granular and matrix regions revealed long aligned structures. The typical lateral dimension of the structures was 200 nm, which could not be related to individual polymeric chains, but it might be referred to bundles. Some residual round shaped structures remained on the granular envelope surface. It can be inferred that the aligned structures might be originated from internal stress created inside the coating due to SF_6-etching process and might resemble somehow the amylsa and amylopectine molecular arrangement.

Conclusions

In this paper, a novel process for hydrophobic surface creation on cornstarch films was proposed and tested. This process is based on plasma polymerization in methane atmosphere followed by sulphur hexafluoride plasma treatment. Treated cornstarch films had their water-repellent properties improved. Although fluorine was incorporated in coating surface, the subsequent SF_6 plasma treatment for 60 s did not enhance significantly the hydrophobicity of a:C-H-coated films. This result might be related to the high surface etching rate that was promoted by fluorine-containing plasma. Important differences in morphological features for uncoated and SF_6 treated films were revealed in high magnification AFM images.

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