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Surface Modification of Starch Films by Plasma

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Summary: Many studies have shown that starch is a good alternative to produce biodegradable plastics. Corn starch based films were prepared by solvent evaporation using water and glycerol as plasticizers and their surfaces were modified by chemical vapor deposition (CVD) employing different plasma treatments in order to induce different surface wettability characteristics. Three different surfaces were produced: (i) starch modified by helium (He) plasma at −100 V for 10 min; (ii) starch coated using hexamethyldisiloxane (HMDSO) monomer at −60 V for 20 min;and (iii) starch surface modification by He plasma at −100 V for 10 min followed by coating with HMDSO monomer at −60 V for 20 min. The results indicated that He plasma treatment under this condition was not able to induce changes in the surface wettability, but HMDSO coating led to surface hydrophobization, both of the as-prepared starch films and the He-modified surfaces.

Keywords: atomic force microscopy (AFM); cold plasma; films; HMDSO; starch

Introduction

A large amount of non-biodegradable waste is discarded daily, prompting strong concern due to the environmental impact.[1] In this regard, interest in developing thermoplastic materials composed mainly of starch has grown in recent years,[2,3] since this polymer has good biodegradability, low production cost and is available from many renewable sources, such as corn and wheat.

However, starch plastics are highly susceptible to deterioration by water due to their hydrophilic character. An alternative way to make them usable would be to change their hydrophilicity by plasma treatment using different gases, to prevent contact between water and the material.[4] Cold plasma technology has been widely used to modify the surface of polymeric materials, as it is a clean coating method that does not change the bulk properties of the material.

HMDSO, with the formula $C_6H_{18}OSi_2$, has been widely used for plasma polymerization because of its highly organic character and high vapor pressure.[5] Furthermore, coatings like $SiO_xC_yH_z$ are produced with a high levels of methyl and methylene groups, creating hydrophobic surfaces.[6] On the other hand, He plasma can break chemical bonds, without inducing chemical reactions on the substrate.[7] In this study, He plasma treatment and HMDSO plasma coating were compared as different means of hydrophobization of thermoplasticized starch (TPS) surfaces. TPS surfaces were treated with He plasma, He plasma followed by HMDSO and HMDSO plasma. Surface modifications were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurements and Fourier-transform infrared spectroscopy (FTIR).

Experimental Part

Regular corn starch 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). Corn

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starch 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 mm were obtained. Corn starch substrates were placed on the cathode of a glow discharge reactor operating at 13.56 MHz. The vacuum chamber was operated below 8 Pa. Three different surfaces were produced: (i) starch modified by helium (He) plasma at −100 V for 10 min; (ii) starch coated using hexametylsiloxane (HMDSO) monomer at −60 V for 20 min and (iii) starch surface modification by He plasma at −100 V for 10 min followed by coating with HMDSO monomer at −60 V for 20 min. A schematic representation of the RF plasma-polymerization reactor is shown in Figure 1. The details of the experimental conditions were described elsewhere.[8,9] SEM micrograph at 5000× magnification of untreated starch film and of the films produced by the different treatments were obtained with JEOL JSM (model 6460 LV) and Inspect S 50 operated at 12. 5 and 15 kV. The samples were coated with 250 Å of gold. 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. 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 Ramé-Hart Goniometer. The time evolution of the droplet water (2.5 mL) shape was recorded using a video camera every 15 s for a total of 10 min. Fourier Transform-Infrared spectra were acquired using a FTIR-Nicolet 6700 (Thermo Scientific). The films were mounted on an attenuated total reflectance (ATR) accessory equipped with ZnSe crystal prior to scanning. The spectra were obtained with an accumulation of 100 scans and with a resolution of 4 cm^{-1}.

Results and Discussion

TPS films produced are partially gelatinized and starch-swollen grains can still be observed on the surface.[4] Figure 2 presents SEM image of the untreated starch film as well as the images related to the plasma treated samples. Figure 2 (b) shows that the interface regions between swollen granule and the matrix is not so well defined as those observed for the untreated sample (Figure 2(a)). Figure (c) and (d) shows that, although the HMDSO coatings homogeneously cover all the surfaces, the coatings do not greatly change the overall corn

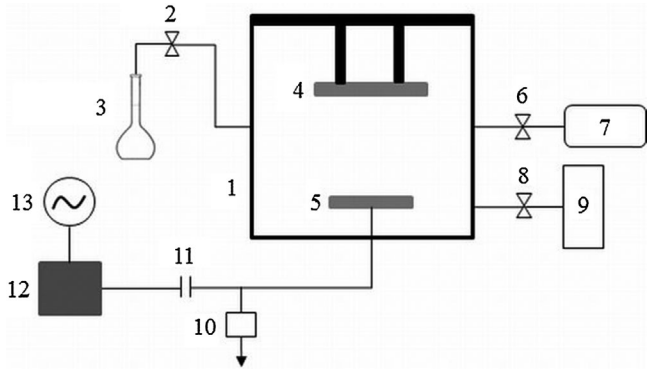

Figure 1.
Schematic diagram of the plasma reactor used for RF plasma-polymerization (1. plasma reactor, 2. needle valve, 3. HMDSO monomer, 4. anode, 5. cathode, 6. needle valve, 7. precursor gas (He), 8. valve, 9. vacuum system, 10. DC self-bias voltage, 11. coupling capacitor, 12. impedance matching, 13. RF power source).

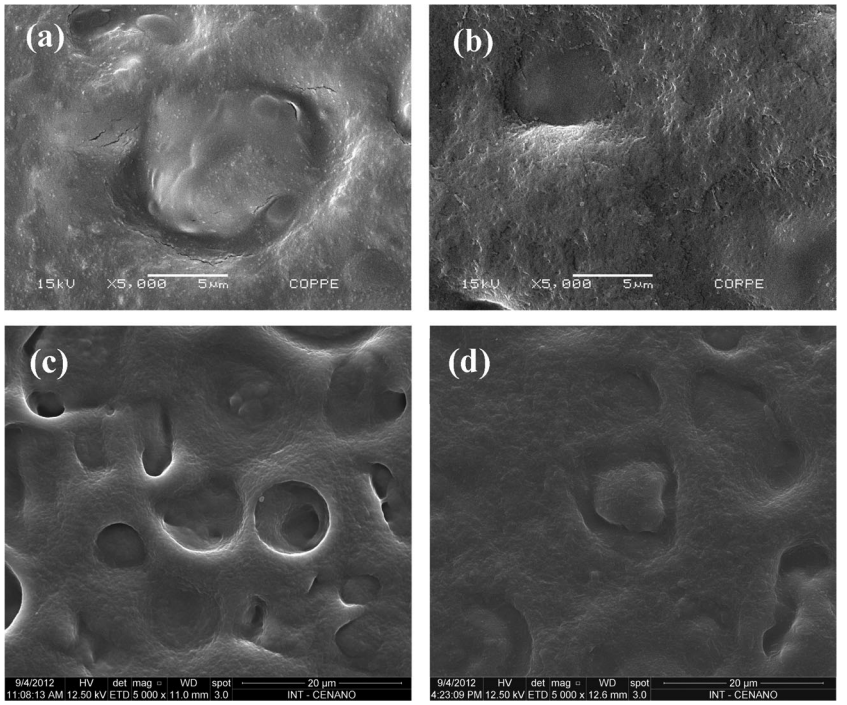

Figure 2.
SEM images: (a) untreated starch film, (b) starch film treated with He at −100 V for 10 min, (c) starch film coated with HMDSO plasma (−60 V for 20 min) and (d) starch film treated with He plasma (−100 V for 10 min) followed by HMDSO plasma (−60 V for 20 min).

starch film, because grains of gelatinized starch can still be observed.

Figure 3 shows the topographic AFM image of the untreated sample and of the sample treated with He at −100 V for 10 min.

Figure 3 (a) shows a region with continuous phase, composed mainly of amylose that was released from the granules during the gelatinization process, and a phase with swollen granules composed mainly of amylopectin.[9]

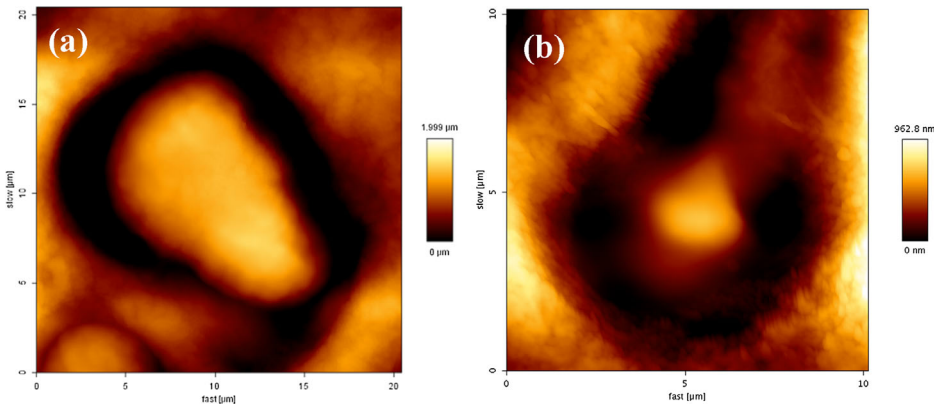

Figure 3.
Topographic AFM images: (a) untreated starch film and of (b) the starch film treated with He at −100 V for 10 min.

Moreover it can be observed that the treatment with He at −100 V for 10 min changed the surface of the starch film, with the appearance of small protrusions (Figure 3(b)). According to the literature,[10,11] samples treated with He are rougher than the untreated film, which proves that He is effective in causing surface etching.

Figure 4 presents topographic and phase-contrast images of untreated starch

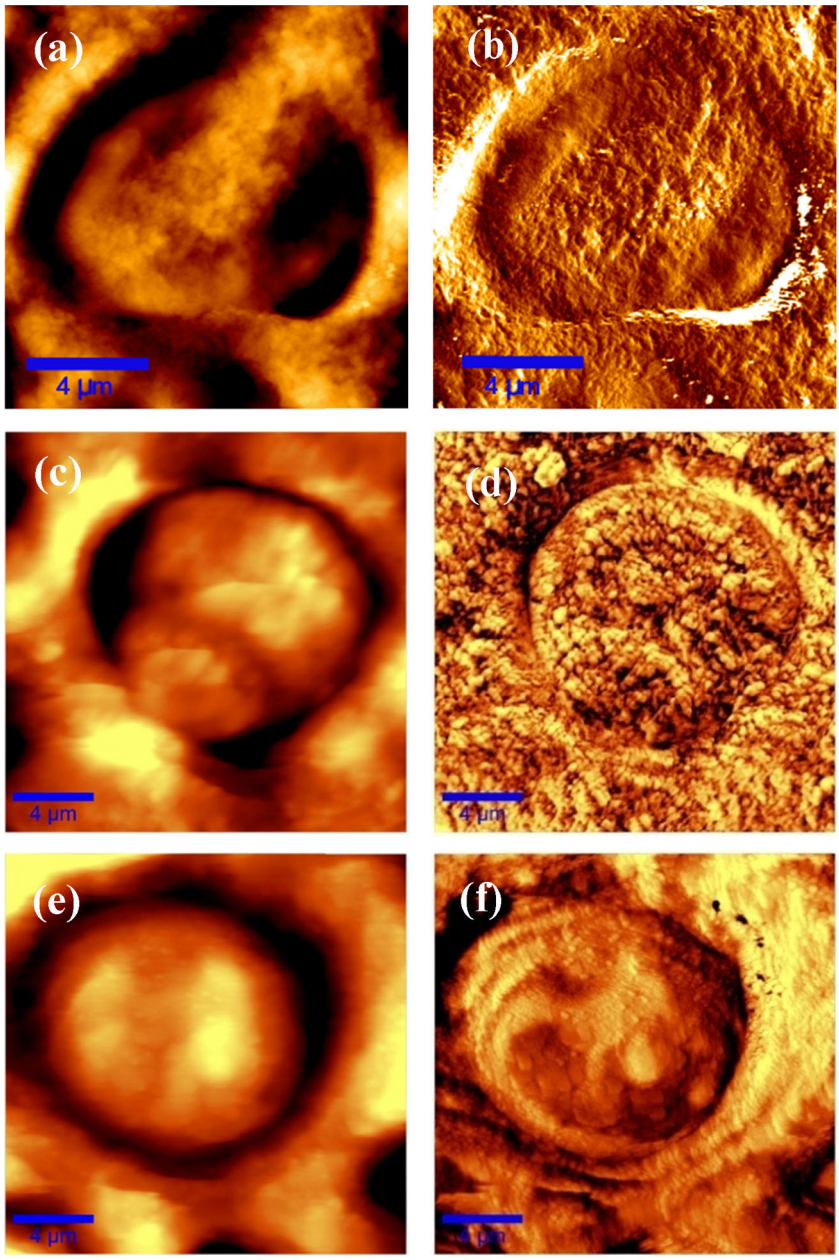

Figure 4.
AFM image – untreated starch film: (a) topography and (b) phase contrast; starch film coated with HMDSO plasma (−60 V for 20 min): (c) topography and (d) phase contrast; starch film treated with He plasma (−100 V for 10 min) followed by HMDSO plasma (−60 V for 20 min): (e) topography and (f) phase contrast.

film and of the films produced by the different treatments. It can be seen that the deposition of HMDSO on the surface of the starch films treated and not treated with He created a layer containing small granules and that this coating did not greatly change the topography corroborating with SEM images.

The influence of the plasma treatment on the hydrophilicity of TPS films was determined by measuring the water contact angle dynamics (Figure 5). This Figure shows that the hydrophilicity of the untreated starch film and that treated with He for 10 min is practically the same. However, the samples coated with HMDSO and He/HMDSO showed hydrophobic behavior with water contact angles above 100°. The droplet stability can be analysed observing the water contact angle variation with the time the droplet was left laying on the surface. It can be observed that the water contact angle decreased less than 10% after 600 s of contact between the droplet and the surface.

Table 1 and Table 2 presents the vibration modes of starch and HMDSO investigated by FTIR spectra, respectively. Figure 6 shows the FTIR spectra obtained for the untreated starch film and also for different plasma treatments. It can be observed that the spectra related to untreated starch and that treated with He plasma are very similar, with can be explained by the fact that these films have the same chemical composition. On the other hand, the FTIR spectra for TPS films after treatment with plasma HMDSO and He/HMDSO showed a significant reduction in the absorption band at 3280 cm^{-1} (related to the OH group). Furthermore, the bands present in the spectra of the untreated starch film and that

Table 1.
Vibration modes of starch investigated by FTIR spectra.

Infrared band assignment	Wavenumber cm^{-1}
whole glucose ring stretching vibrations[12,13]	765, 861, 929, 992
–C–O–C– stretching vibration in glucosebonds[12]	1082, 1159
tightly bound water present in the starch[12]	1648
vibration of C–H stretches[12]	2923
related to the OH group[12]	3280

Table 2.
Vibration modes of HMDSO investigated by FTIR spectra.

Infrared band assignment	Wavenumber cm^{-1}
Si–O–Si bending vibration[14]	795
Si–C and CH_3 rocking vibrations[15]	840
Si–O–Si stretching vibration[15]	1015
CH_3 bending in Si–$(CH_3)_x$[14]	1260
Si–H stretching in (Si–O_2–SiH)[14]	2145
CH_3 stretching[15]	2965

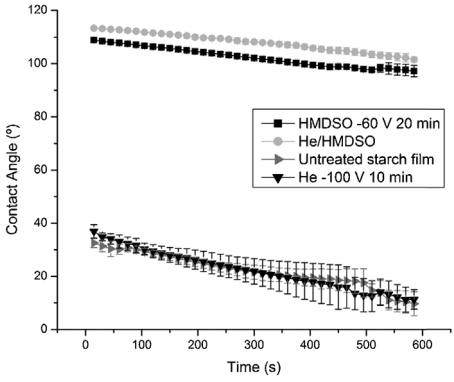

Figure 5.
Contact angle for the untreated TPS film and TPS films treated with plasma.

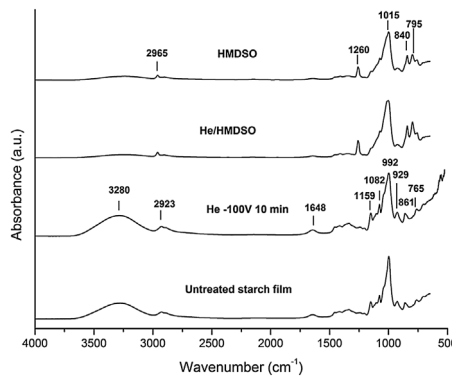

Figure 6.
FTIR spectra for the untreated starch film and for different plasma treatments.

treated with He plasma were suppressed when compared with the spectra of the films treated with HMDSO plasma and He plasma followed by HMDSO, giving rise to absorption bands for the HMDSO coating.

Conclusion

Starch films were successfully modified by plasma using either He as well as HMDSO plasma. He plasma promoted surface etching, making it more prone to receive treatment with a reactive gas. Atomic force microscopy images showed the appearance of small granules due to plasma HMDSO coating. The combined treatment of He followed by HMDSO resulted in a more homogeneous film and even smaller granules compared to the films produced without the preliminary use of He. The treatment with HMDSO and He/HMDSO plasma suppressed the FTIR bands of starch giving rise to absorption bands for the HMDSO coating, indicating that the coating is homogeneous. Both HMDSO plasma as well as the combined treatment of He/HMDSO induced surface hydrophobization, with surfaces presenting a water contact angles above 100°. The roughness created by He plasma was not effective in increasing water contact angle of the modified surface.

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