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Surface modification of maize starch films by low-pressure glow 1-butene plasma

Cristina T. Andrade[a,*], Renata A. Simão[b], Rossana M.S.M. Thiré[a,b], Carlos A. Achete[b]

[a] *Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525, 21945-970 Rio de Janeiro, Brazil*
[b] *PEMM/COPPE, Universidade Federal do Rio de Janeiro, P.O. Box 68505, 21945-970 Rio de Janeiro, Brazil*

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Abstract

Plasma polymerisation was used to modify the surface of maize starch films in order to reduce their water affinity. Films were prepared by casting starch suspensions heated for different periods of time. Glycerol was added as a plasticiser. To produce a hydrogenated-carbon coating, films were exposed to low-pressure glow plasma generated in 1-butene gas from a radio frequency diode sputtering system. Atomic force microscopy (AFM) was used to investigate possible changes in surface morphology and roughness of plasma-coated films in relation to the corresponding substrates. AFM phase contrast images at high magnification revealed characteristic features at the surfaces of plasma-coated starch films. Water absorption experiments and contact angle measurements were carried out to verify the effect of deposited layers on the water sensitivity of those surface-modified films. The results indicated that the coating process reduced significantly the hydrophilic character of starch films.

Keywords: Thermoplastic starch; Plasma polymerisation; Atomic force microscopy; Water sensitivity

1. Introduction

The development of bioplastics derived from renewable resources has been encouraged by the increasing interest to reduce the amount of plastic waste in the environment. Nowadays, some of the bioplastics available in the market are used in specific applications, such as in fast food tableware, packaging and agriculture, where biodegradability is desirable. Due to its total biodegradability, low cost and worldwide availability from a large number of crops, starch is considered an attractive source for production of biodegradable materials (Bastioli, 1998; Soest & Vliegenthart, 1997). However, the technological application of starch as a bioplastic has been limited by its inherent hydrophilicity. The presence of hydroxyl groups in the polysaccharide molecules makes starch-based materials susceptible to moisture uptake and to the resulting changes in dimensional stability, mechanical and barrier properties (Hulleman, Kalisvaart, Janssen, Feil, & Vliegenhart, 1999; Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). A new approach to overcome this difficulty might be to protect starch materials from humidity changes with a thin polymeric layer, deposited by plasma polymerisation.

Deposition of thin films by plasma polymerisation offers several advantages over conventional coating techniques; the process may occur in a single reaction step, good adhesion between film and substrate is generally achieved, the deposition of the film is fairly uniform over the entire surface, and problems with residual solvents are avoided (Chan, Ko, & Hiraoka, 1996).

Plasma technology has become an important industrial process, used to alter chemical and physical properties of polymeric surfaces without affecting their bulk properties. This process, also known as glow discharge polymerisation (Yasuda, 1981), is a specific type of plasma chemistry, and consists of complex reactions between charged and neutral plasma species, between plasma and surface species, and between surface species (Chan et al., 1996; Kaplan, 2004; Shi, 1996; Yasuda, 1981). Unlike conventional polymers, plasma polymers do not consist of chains with a regular repeating unit, but tend to form cross-linked networks (Chan et al., 1996; Shi, 1996). Hydrocarbons used in plasma

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* Corresponding author. Tel.: +55 21 25627208; fax: +55 21 22701317.
E-mail address: ctandrade@ima.ufrj.br (C.T. Andrade).

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polymerisation may not contain conventionally polymerisable groups. Hydrocarbon molecules are dissociated and ionised; radicals and ions that impinge on substrates lead to the growth of the so-called amorphous hydrogenated-carbon (a-C:H) films (Rabbani, 2004; Schwarz-Selinger, Keudell, & Jacob, 1999). Since a-C:H coatings contain only carbon and hydrogen, they are considered to be environmentally safe (Jacob, 1998). These films have been widely used as protective coating materials due to their special surface properties, such as micro-hardness, optical refractive index, and water repellence (Chan et al., 1996; Magalhães, & Souza, 2002; Schwarz-Selinger et al., 1999; Vasquez-Borucki, Jacob, & Achete, 2000)

Some reports in the literature are related to the modification of starch by glow discharge polymerisation. The surface processing of granular starches in ethylene plasma was investigated; depending on the botanical origin of starch, plasma polymerisation was characterised either as graft polymerisation of ethylene onto starch or as homopolymerisation. Under the reaction conditions applied, starch depolymerisation was relatively low, and cereal starches were shown to be more resistant to the action of plasma than tuber starches. In all cases, the granular structure of the starches was preserved (Lii, Liao, Stobinski, & Tomasik, 2002). Starch foils were coated in a radio frequency glow discharge with two different monomers, hexamethyldisilazane (HMDSN) and hexamethyldisiloxane (HMDSO), in mixtures with argon. The thickness of the deposited layer was determined by the increase of the sample weight. At 17% HMDSN and 11% HMDSO in argon feeds, and at radio frequency discharge powers of 5 and 2 W, respectively, water-repellent properties were improved (Behnisch et al., 1998).

In the present work, a-C:H coatings were deposited onto maize starch films in 1-butene plasma atmosphere, with the aim of reducing the hydrophilic character of the films surface. In order to prevent macromolecular degradation, mild working conditions were used. Atomic force microscopy (AFM) was used to investigate possible modifications in morphology and roughness caused by glow discharge polymerisation. Other experiments were carried out to evaluate the wetting properties of coated surfaces in relation to their substrates.

2. Materials and methods

2.1. Materials

Food grade maize starch, composed of 26–30% amylose and 74–70% amylopectin, and with less than 0.5% gluten was supplied by Corn Products Brazil (São Paulo, Brazil). High-purity 1-butene was supplied by White Martins Gases Industriais (Rio de Janeiro, Brazil). Analytical grade glycerol was purchased from Vetec Química Fina Ltd (Rio de Janeiro, Brazil) and was used as received.

2.2. Methods

2.2.1. Preparation of films

Maize starch (5 g) was dispersed in 50 ml distilled and deionised water at room temperature. Suspensions were diluted with 50 ml water previously heated to 95 °C and then kept under stirring and reflux conditions for different periods of time, 5 and 90 min. Glycerol (0.75 g) was added as a plasticiser. The hot suspensions were poured onto polyethylene Petri dishes and allowed to dry at 50 °C for 12 h. Films were peeled off and conditioned for at least 10 days at 50% relative humidity (RH) before plasma treatment. Starch suspensions plasticised with glycerol that were heated for 5 and 90 min gave rise to films that have been called 5MG and 90MG, respectively. The thickness of the films (70–100 μm) was measured with a digital micrometre (Mitutoyo no. 293–265, Mitutoyo Corporation, Japan).

2.2.2. Plasma deposition

A glass chamber fitted with parallel plate electrodes, 370 cm^2 in area and 3.5 cm apart from each other, capacitively coupled to a Varian Associates radio frequency (r.f.) diode sputtering system (Palo Alto, USA), was used to produce 1-butene plasma atmosphere. Maize starch films and silicon wavers (680 μm in thickness), used as reference to measure the thickness of deposited layers, were fixed on the cathode (upper electrode). For cleaning, the chamber was evacuated to a base pressure of 6 Pa. 1-Butene was admitted into the chamber through an inlet situated between the two electrodes, and the operating pressure was maintained at 8 Pa for 15 min. The r.f. generator was turned on, and the cathode was driven by a negative voltage pulse of -60 V, equal to the self-bias voltage (V_b). The treatment was performed at a constant level of r.f. power for periods of time long enough to produce coatings of 20–230 nm in thickness. Before opening the chamber, the flux of gas was kept constant for at least 15 min. The thickness of the deposited layers was measured with a commercial Dektak IIA Stylus profilometre (Veeco Instruments, Woodbury, USA).

2.2.3. Water absorption

Water absorption of uncoated and plasma-coated starch films was evaluated as the weight gain after 0.8 cm^2 sample area was put in contact with a column of distilled water for 3 min. The result was expressed in terms of water absorption capacity of coated films relatively to their respective substrates (WAC), and was given by Eq. (1)

$$\mathrm{WAC} = \frac{(\mathrm{IW}_{\mathrm{coated}} - \mathrm{IW}_{\mathrm{substrate}})}{\mathrm{IW}_{\mathrm{substrate}}} \times 100 \quad (1)$$

where WAC is the water absorption capacity of the coated film relatively to its substrate (%), $\mathrm{IW}_{\mathrm{coated}}$ is the weight gain of the coated film (%), and $\mathrm{IW}_{\mathrm{substrate}}$ is the weight gain of the substrate (%).

This method was used because of the characteristics of the samples; starch films obtained by casting were very thin, water was easily absorbed, and the samples were rapidly dissolved when immersed in water, even for a short period of time. In the case of coated films, only one surface was covered by the a-C:H layer. The physical stability of uncoated films in contact with the water column was maintained up to 3 min; longer periods of time promoted excessive swelling and even their disruption, which could nullify the experiment.

2.2.4. Contact angle measurements

The effect of the a-C:H coating on the hydrophilicity of starch films was determined by water contact angle measurements with a NRL A-100-00 Ramé-Hart Goniometre (Mountain Lakes, USA). A 2.5 µl droplet of water was applied on the surface of uncoated and plasma-coated starch films. The evolution of the droplet shape was recorded each 15 s by a video camera; an image analysis software was used to determine the contact angle evolution. Water drop height and width were simultaneously measured.

2.2.5. Atomic force microscopy (AFM)

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

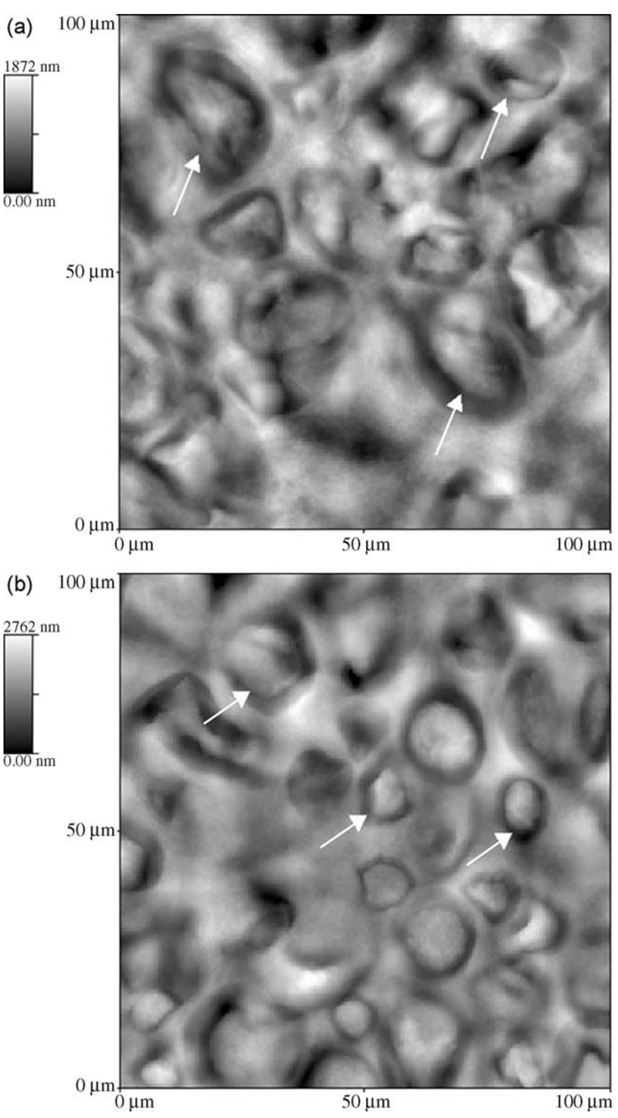

Fig. 1. AFM topographic images of uncoated (a) and 1-butene plasma-coated (b) 5MG maize starch films.

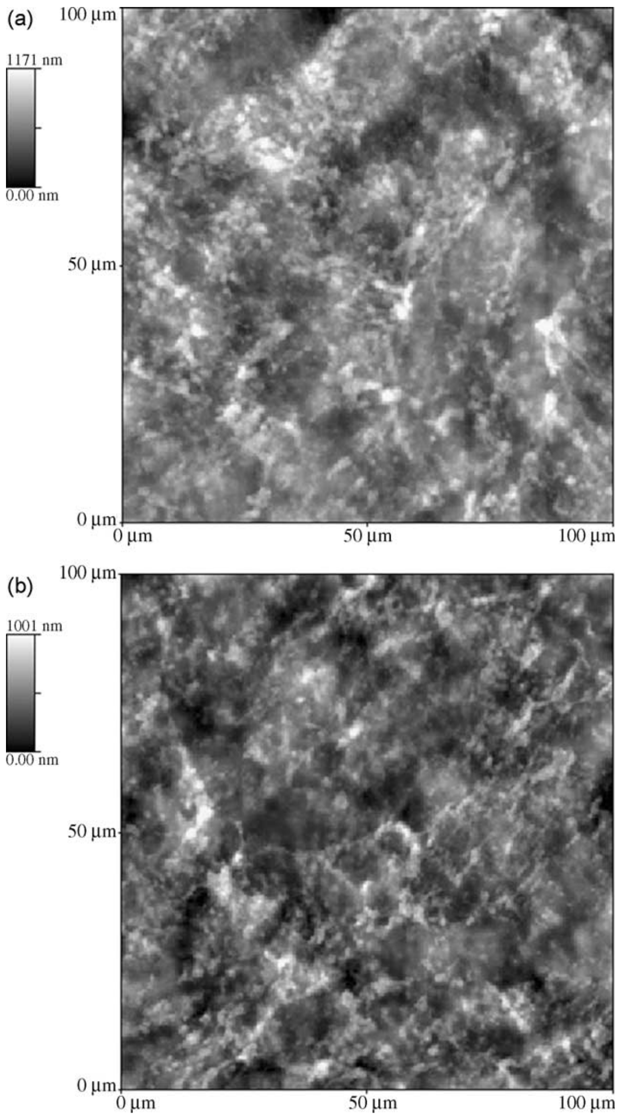

Fig. 2. AFM topographic images of uncoated (a) and 1-butene plasma-coated (b) 90MG maize starch films.

guarantee that the microscope was operating in intermittent contact mode. Samples were fixed on double-coated adhesive tapes and the AFM images of the upper surface were obtained in air. Changes in the sample vertical position are presented as height images. Changes in the phase angle difference between the oscillations of the cantilever and the standard signal, which drives the piezoelectric crystal during the intermittent contact mode, are presented as phase images. The software supplied with the equipment was used to determine the root mean square roughness (RMS roughness).

3. Results and discussion

Milder experimental conditions than normally used in plasma polymerisations were adopted to avoid damage to starch films, known to be sensitive to vacuum. In the process, the chamber was pumped to a base pressure of 6 Pa, and cleaning was achieved by purging the chamber with the plasma precursor gas (1-butene), instead of using high vacuum (Coutinho, Araújo, Thiré, Simão, & Achete, 2003). As a result, no macroscopic cracks were observed on the coated films. After plasma deposition, the starch films presented a pale yellow colour, whose intensity depended on the thickness of the coating. No tendency to delamination was observed for a-C:H layers, which suggests a good adhesion between starch substrate and deposited coating.

Figs. 1 and 2 show AFM topographic images of typical regions on surfaces of 5MG and 90MG starch films, respectively, before and after plasma deposition. As reported previously (Thiré, Simão, & Andrade, 2003), in Fig. 1(a), the surfaces of 5MG films show granular envelopes surrounded by a matrix composed mostly of

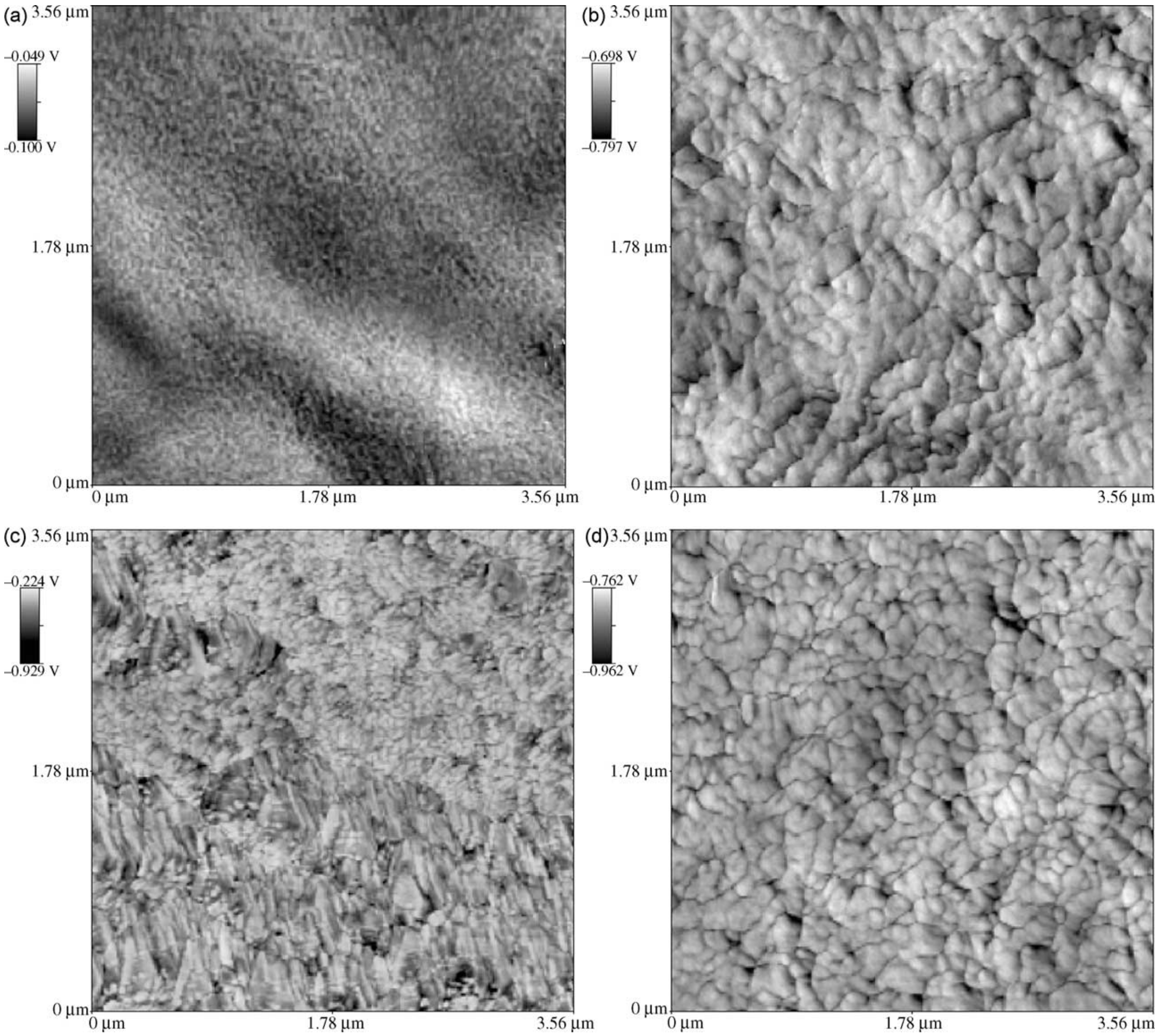

Fig. 3. AFM phase contrast images of different regions of a 5MG film; a granular envelope before (a) and after (b) plasma deposition, and the matrix region before (c) and after (d) plasma deposition.

amylose. Differences in height allowed identifying smooth and rough regions on the more homogeneous surfaces of 90MG films, shown in Fig. 2(a). In all cases studied, independently of the particular substrate and the coating thickness, no significant morphological change was observed on the surfaces of plasma-coated films. It is possible to identify granular envelopes (indicated by arrows) and the matrix region on coated 5MG films, such as in Fig. 1(b), and similarly more homogeneous regions on coated 90MG films, as in Fig. 2(b). The reduced thickness of the deposited coatings and the homogeneous covering of the substrate may explain the similar morphological characteristics between uncoated and plasma-coated films, as observed in topographic images at low magnification.

Typical images at higher magnification of the two regions of 5MG films are shown in Fig. 3, before and after plasma deposition. Before plasma deposition, the surface of granular envelopes, as in Fig. 3(a), differs from the matrix region shown in Fig. 3(c). In these phase contrast images, after plasma deposition, other characteristics are revealed at the surfaces of granular envelopes (Fig. 3(b)) and of the matrix region (Fig. 3(d)). While in the substrate matrix elongated and ordered features may be observed, the surface of plasma-coated 5MG films consists of irregular oval structures, typically 104 nm in major axis. Images with similar morphology were obtained for plasma-coated 90MG films.

The roughness of the films was determined from 100 μm × 100 μm AFM topographic images. Plasma deposition did not affect significantly the overall roughness of coated films, when compared to the corresponding uncoated films (Table 1). Roughness was measured separately for granular and matrix regions. For 5MG films, coating led to no significant changes in roughness, for both granular and matrix regions. Meaningful increases in roughness were evidenced when granular and matrix regions of 90MG films were measured separately. Moreover, it may be observed that these values for plasma-coated 90MG films increased as a function of coating thickness.

Table 1
Overall, granular region and matrix RMS roughness determined for uncoated and plasma-coated films

Starch film	Thickness of deposited layer (nm)	RMS roughness (nm)		
		Overall	Granular region	Matrix
Uncoated 5MG	–	454 ± 16	8.3 ± 0.2	24 ± 4
Plasma-coated 5MG	21	457 ± 18	7.6 ± 0.6	23 ± 2
	120	446 ± 22	8 ± 1	21 ± 4
Uncoated 90MG	–	227 ± 25	22 ± 3	39 ± 4
Plasma-coated 90MG	20	229 ± 20	37 ± 3	49 ± 3
	86	258 ± 14	47 ± 4	56 ± 6
	213	–[a]	58 ± 4	69 ± 2

[a] Non-determined.

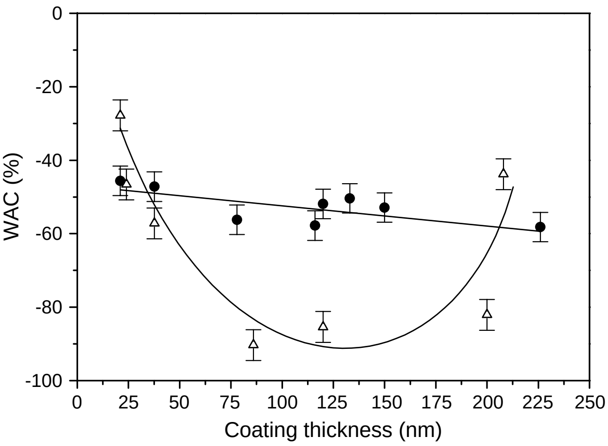

Fig. 4. Water absorption capacity of 5MG (●) and 90MG (△) 1-butene plasma-coated starch films relatively to their respective substrates (WAC), as a function of the thickness of the deposited layer.

Two different analyses were performed to evaluate the water-repellent properties of the modified starch films; measurements of water absorption capacity (WAC) of the coated films were carried out relatively to the corresponding substrates and contact angle measurements. Fig. 4 shows results from measurements of WAC for 1-butene plasma-coated 5MG and 90MG films in relation to their substrates, as a function of the thickness of the deposited layer. When starch films obtained from suspensions heated for 5 min (5MG films) were used as substrates for plasma polymerisation, an average reduction of (52 ± 4)% in water absorption was achieved, independently of coating thickness. For coated 90MG films, a maximum reduction of (90 ± 5)% was observed for coatings with 80 nm in thickness.

The efficiency of a-C:H coatings as a water barrier for 90MG films increased with thickness up to a critical value. Formation of micro-cracks on deposited layers of larger thickness may be the cause of this behaviour. In general, when a plasma-polymerised coating is deposited on a substrate, the coating tends to buckle up. As the thickness of the coating increases, accumulation of stress may cause cracking or delamination. This phenomenon, interpreted as arising from compressive stress developed during the deposition process, has been associated with high cross-linking density (Chan et al., 1996). The susceptibility of the substrate to plasma atmosphere should also be taken into consideration (Yasuda, 1981).

Results of contact angle measurements are shown for plasma-coated 5MG films (Fig. 5) and for plasma-coated 90MG films (Fig. 6) and their respective substrates. The contact angle formed between a water drop placed on the surface of a material and its variation with time is related to the wettability of the material. For uncoated starch films, the initial contact angles are low because of their hydrophilic nature; in particular, 5MG films (Fig. 5) showed initial contact angles approximately 53% lower than those observed for 90MG films (Fig. 6). The origin of this difference is presently unclear.

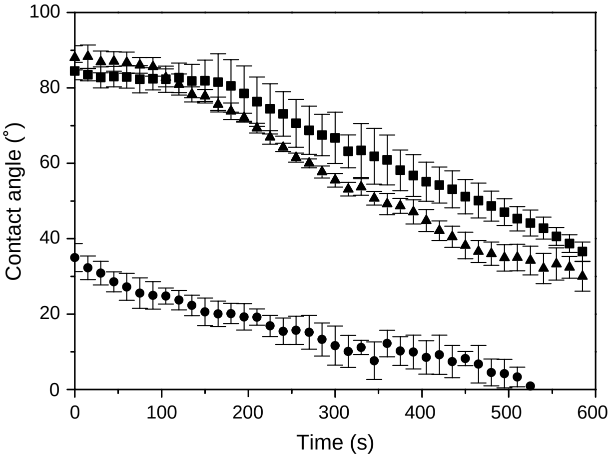

Fig. 5. Water contact angle values as a function of contact time for uncoated (●) and plasma-coated 5MG films with deposited layers 38 nm (▲) and 120 nm (■) in thickness.

Figs. 5 and 6 also show the variation of contact angles of water with time for 5MG and 90MG films, respectively. For uncoated starch films, the contact angles decreased rapidly with time. For plasma-coated films, the contact angles remained nearly constant up to 4 min, except for the 90MG film with deposited layer 213 nm in thickness. In this case, after a short period of time, a faster decrease in contact angle values was observed. For the other plasma-coated 90MG films, it is worth noting that the thickness of the deposited layers was lower or slightly higher than the critical thickness (80 nm) shown in Fig. 4. These results corroborate the behaviour previously observed in relation to water absorption capacity.

The simultaneous action of absorption, spreading and evaporation may explain the decrease in drop height and in contact angle values as a function of time. In the present work, evaporation should be taken into account, since measurements were carried out under ambient conditions. Variations in drop width and drop height as a function of time for uncoated and coated 5MG films can be observed in Fig. 7. Similar results were observed for 90MG films. In both cases, no increase in drop width was observed. Decreasing drops widths and drop heights indicate absorption or evaporation of water; thus, spreading seems not to contribute to the process. The fast decrease of contact angles visualised for uncoated films may be attributed mainly to the rapid absorption of the drop.

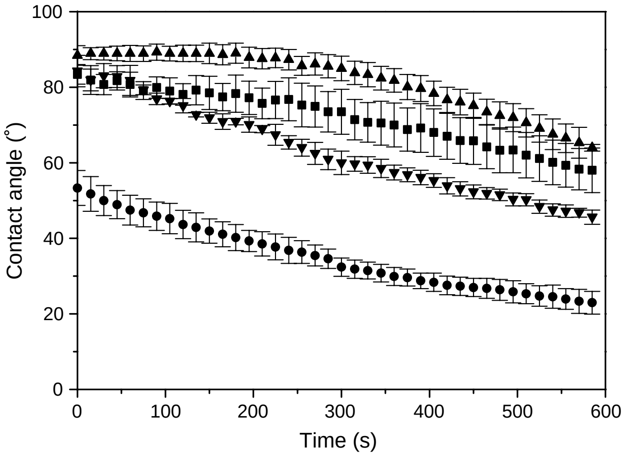

Fig. 6. Water contact angle values as a function of contact time for uncoated (●) and plasma-coated 90MG films with deposited layers 21 nm (▲), 86 nm (■), and 213 nm (▼) in thickness.

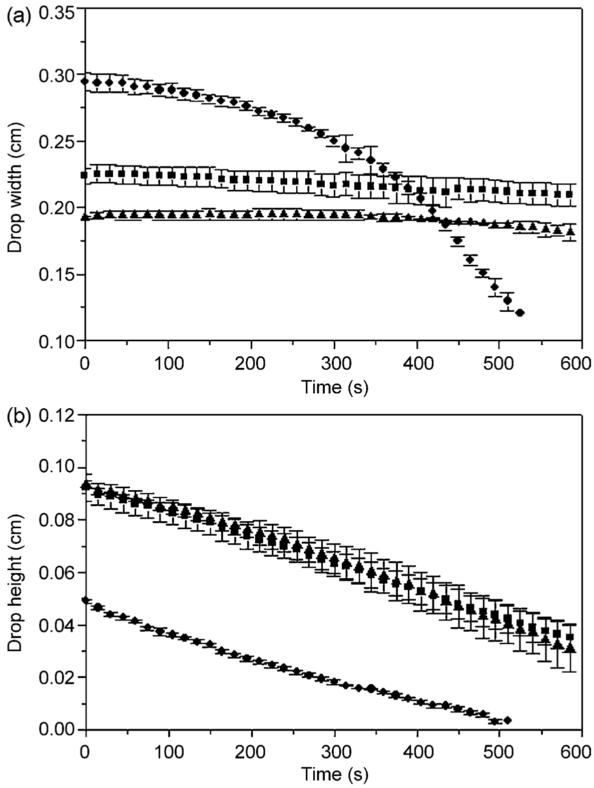

Fig. 7. Variation of water drop width (a) and height (b) as a function of contact time for uncoated (●) and plasma-coated 5MG films with deposited layers 38 nm (▲) and 120 nm (■) in thickness.

Despite evaporation, for coated 5MG and 90MG films, at the beginning of the measurements, the water drop remained in equilibrium with the hydrophobic surface for some period of time. After this period, the increase in entropy favours absorption of the drop. The evolution of contact angle values with time is faster for 5MG films than for 90MG films, for both uncoated and coated films. Such behaviour may be explained at least by the more homogeneous nature of 90MG films.

4. Conclusion

Formation of hydrophobic coatings on starch films was achieved by low-pressure plasma polymerisation in 1-butene atmosphere. Similar morphological features for uncoated and plasma-coated films were observed in AFM topographic images at low magnification. Significant differences were revealed in AFM phase contrast images at higher magnification. Coated films had their water-repellent properties improved. Differences in roughness and in water-repellent properties of coated films depended on the preparation of starch substrates. Substrates prepared from non-completely gelatinised starch suspensions presented higher overall roughness, not significantly altered by the thickness of the deposited coatings, which had only a slight influence on the water absorption capacity of the coated films under the experimental conditions used. Substrates prepared from starch suspensions that had been heated for longer periods of time presented lower roughness values, which increased with the thickness of the deposited coatings. For these films, the thickness of the deposited coatings influenced water absorption capacity and contact angle of water. Roughness of uncoated and coated films exerts an important role on the evolution of contact angles with time; more homogeneous surfaces showed a lower water absorption rate.

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