Effect of Oxidation Level on the Dual Modification of Banana Starch: The Mechanical and Barrier Properties of Its Films

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ABSTRACT: Banana starch was oxidized at three different levels and then acetylated. The double-modified starch was used for film preparation. The physical, mechanical, and barrier properties were tested. The oxidation level increased the whiteness of the film, and the second modification (acetylation) did not affect this parameter. The solubility increased with temperature and oxidation level. However, acetylation decreased the solubility value. At the longest storage times, the solubility decreased because of starch reorganization inside the polymeric matrix. In general, oxidation increased the tensile strength of the films, and a slight increase was observed when the oxidized starch was acetylated. This effect was more noticeable at the longest storage time. The oxidation level decreased the percentage elongation at break, and a slight effect due to acetylation was observed. The film of oxidized–acetylated starch showed a higher elastic modulus value than its oxidized counterpart. The water vapor permeability increased with oxidation level, but the acetylation decreased this parameter. The oxidation increased the hydrophilic character of the starch because of the formation of carbonyl and carboxyl groups that showed more affinity for water molecules. When the oxidized banana starch was acetylated, a decrease in the water vapor permeability was found because the acetylation increased the hydrophobic character of the starch due to the ester group. Films prepared with the double-modified banana starch had some improved physical, mechanical, and barrier properties, and they may be used in specific applications. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 822–829, 2009

Key words: barrier; blends; films; modification; polysaccharides

INTRODUCTION

Environmental contamination produced by the uncontrollable final deposition of synthetic oil derivatives, commonly known as plastics, have increased interest in biodegradable materials such as starch in the substitution of conventional plastic materials such as polyethylene and polystyrene.[1] In past decades, the investigation of films based on biopolymers has been intense; these types of films have the potential to reduce traditional packaging and, hence, contamination, and additionally, they act as a barrier to prevent excessive water loss, gases, and solutes.[2]

Essentially, plastic films are used to extend the storage life and quality of food as they modulate processes or respiration and delay changes in aroma, taste, appearance, and texture characteristics.[3] Biodegradable films overall contain hydrophilic components such as proteins and polysaccharides; from these, the use of starch is accentuated as a raw material for the production of films because it is biodegradable, economical, abundant, and relatively easy to handle.[4] The interest in banana starch has increased because of its molecular and structural characteristics, which might be used for the development of new products with better physicochemical and functional properties.[5,6] The native starch presents certain limitations that lessen its use and application in industry. These limitations are associated with its low shear stress resistance, thermal decomposition, high retrogradation, and syneresis. These difficulties might be overcome by chemical modifications. Recently, Zamudio-Flores et al.[7] reported that by oxidation of the native starch banana, it was possible to obtain films with higher

mechanical properties; nevertheless, the water loss permeability increased because of the hydrophilic characteristics of the oxidized starch. To control this unwanted hydrophilic aspect, the use of hydrophobic materials such as waxes and oils have been included; however, these additives act negatively on the mechanical properties.[7–9] Various researchers have reported that, with chemical modification by acetylation, it is possible to reduce the hydrophilic characteristic of the starch used in films and coating materials.[10–13] The objectives of our study were then to produce banana starch films double-modified by oxidation and acetylation and to evaluate their mechanical and barrier properties at different storage times.

EXPERIMENTAL

Materials

Unripe bananas (*Musa paradisiaca* L.) were purchased at the local market of Cuautla, Morelos, México.

Starch isolation

The starch was isolated with a pilot-scale procedure.[14] The powder was ground to pass a U.S. no. 100 sieve and stored at room temperature (25°C) in a glass container.

Preparation of the oxidized starches

A starch slurry was prepared according to Wang and Wang[15] with slight modifications by the addition of distilled water to 200 g of starch (dry basis) to a final weight of 500 g in a 1-L reaction vessel. We maintained the starch slurry at 35°C by occasionally turning off the heating power, and the pH was adjusted to 9.5 with $2M$ aqueous NaOH. An aqueous sodium hypochlorite solution with 0.5% (w/v) active chlorine was slowly added to the starch slurry over 30 min with the pH maintained at 9.5 with $0.5M$ H_2SO_4. After the addition of the NaOCl solution, the pH of the slurry was maintained at 9.5 with $1M$ NaOH for an additional 50 min. The pH of the slurry was then adjusted to 7.0 with $0.5M$ H_2SO_4, and the slurry was passed to a 1-L flask to precipitate the starch. The reaction mixture was decanted, washed with several volumes of deionized water, and dried in a convection oven at 50°C for 48 h. The same procedure was applied to banana starch treated with active chlorine concentrations of 1.0 and 1.5%.

Starch acetylation

The methodology reported by Wurzburg[16] was used. Starch (162 g) was mixed with 220 mL of dis-

TABLE I
Sample Identification of Films

Sample	Sample identification
Native starch	NS
Acetylated starch	AS
Oxidized starch (0.5% active chlorine)	OS(0.5)
Oxidized (0.5% active chlorine) and acetylated starch	OS(0.5)A
Oxidized starch (1.0% active chlorine)	OS(1.0)
Oxidized (1.0% active chlorine) and acetylated starch	OS(1.0)A
Oxidized starch (1.5% active chlorine)	OS(1.5)
Oxidized (1.5% active chlorine) and acetylated starch	OS(1.5)A

tilled water, and the dispersion was maintained with a magnetic stirrer. The pH was adjusted (8.0) with a solution of NaOH (3%), and 0.1 mol of anhydride acetic was added drop by drop. Simultaneously, the pH was maintained between 8.0 and 8.4 with the NaOH solution (3%). When the anhydride acetic was added, the pH was adjusted at 4.5 with $0.5N$ HCl. The slurry was centrifuged (1500 rpm for 15 min), the supernatant was removed by decantation, and the solid was resuspended in distilled water; this procedure was repeated three times. The starch was dried in a convection oven at 45°C for 24 h and sieved through 100 U.S. mesh (0.150 mm).

Dual modification

The starch dual modification was carried out with the oxidation as previously described and acetylation.

Starch pasting

To determine the viscosity (Brabender units) profile of the starches, the American Association of Cereal Chemists (AACC)[17] methodology was followed. A starch dispersion containing 5% (w/v) total solids was prepared; 100 mL of the sample was transferred into the bowl of a microviscoamylograph (Brabender OHG, Duisburg, Germany). The machine was programmed to run a heating–cooking–cooling cycle that began at 30°C, increased to 95°C, and cooled to 50°C, each for 20 min. A heating rate of 1.5°C/min was used along the whole cycle with an agitation speed of 125 rpm.

Film preparation

The films were prepared with a concentration of banana starch of 4% (w/w, dry basis) and a concentration of glycerol of 2% (w/w). For details of the formulation of the films and abbreviations used, see Table I. Starch and glycerol were mixed directly

with distilled water to make lots with a total weight of 100 g. The film-forming dispersions were transferred quantitatively to the cup of a viscoamylograph (Brabender OHG), heated from 30 to 95°C, and maintained at 95°C for 10 min, with regular stirring (125 rpm) and a constant heating rate (3°C/min). The films were prepared by casting, where gelatinized suspensions (20 mL) were immediately poured into polyethylene Petri dishes (110 × 20 mm). The starch suspensions were dried at 65°C in an oven for 5 h. Afterward, the films were removed from the Petri dishes and stored at 25 ± 2°C and a relative humidity (RH) of 57%, which was provided by a saturated solution of NaBr.

Moisture content

The moisture content was determined gravimetrically (by heating to 130 ± 2°C for 2 h) with 500 mg of sample. Five measurements were done for each film.

Evaluation of color

The evaluation was carried out on the surface of the films (at least five replicates). A Universal colorimeter (Milton Roy, Color Mate model, Rochester, NY) was used with a D65 illuminant and an observation angle of 10°. The luminosity factor ($L*$) was obtained with a white standard ($L* = 100$).

Solubility of the film in water

Pieces (2 × 3 cm) were cut from each film and stored for 7 days in a desiccator (ca. 0% RH). The samples were weighed and placed in glass vessels with 80 mL of deionized water. The samples were maintained with constant agitation for 1 h at 25 or 80°C and were dried at 60°C until a constant weight was reached. The percentage soluble total material was calculated as follows:

$$\% \, \text{Solubility} = \frac{(\text{Initial dry weight} - \text{Final dry weight})}{\text{Initial dry weight}} \times 100$$

The samples were analyzed at least three times each.

Mechanical properties

The mechanical measurements consisted of a test to determine the tensile strength (TS), percentage elongation at break (%E), and elastic modulus (EM). The maximum breaking force, deformation at break (extension at the moment of rupture, in millimeters),

and EM were obtained from force versus deformation curves according to ASTM 882-95[18] with a texture analyzer equipped with 25-kg load cell (TA-XT2i, Stable Micro Systems, Surrey, United Kingdom). For the tests of tension, films were cut into rectangles 8 cm long and 1 cm wide. The rectangles were maintained for at least 3 days in a desiccator containing a saturated NaBr solution (57% RH). The separation among the gauges was 6 cm. The ends of the film were fixed in each of the subjection gauges. The speed of deformation was 24 mm/min. The thickness of the films was assessed with a manual micrometer (Mitutoyo Co., Kobe, Japan) in 10 random positions of the film. The average of these determinations was 0.120 ± 0.010 mm. This average value was used to calculate the cross-sectional area of the films (the area was equal to the thickness multiplied by the width of each film). We calculated TS by dividing the maximum force exerted on the film during fracture by the cross-sectional area. %E was expressed as the percentage change of the original length of the specimen between the grips at break. EM was determined from the slope of the linear regression performed on the initial points on the stress–strain curves.

Water vapor permeability (WVP)

WVP tests were conducted with ASTM method E96[19] with some modifications. Each film sample was sealed over a circular opening of 0.000282 m² in a permeation cell that was stored at 25°C in a desiccator. To maintain a 75% RH gradient across the film, silica gel ($\approx$ 0% RH) was placed inside the cell, and a sodium chloride saturated solution (75% RH) was used in the desiccator. Water vapor transport was determined from the weight gain of the permeation cell. After steady-state conditions were reached (ca. 2 h), eight weight measurements were made over 24 h. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. The slope of each line was calculated by linear regression ($r^2 > 0.98$), and the water vapor transmission rate was calculated from the slope of the straight line (grams/second) divided by the cell area (square meters). After the permeation tests, the film thickness was measured, and WVP (g Pa^{-1} s^{-1} m^{-1}) was determined.

Statistical analysis

Experiments were arranged in a completely randomized design. An analysis of variance was carried out with the statistical program Sigma-Stat version 2.03 (Aspire Software International, Ashburn, VA).[20] Media comparison was done by Tukey's multiple test ($P \leq 0.05$).[21]
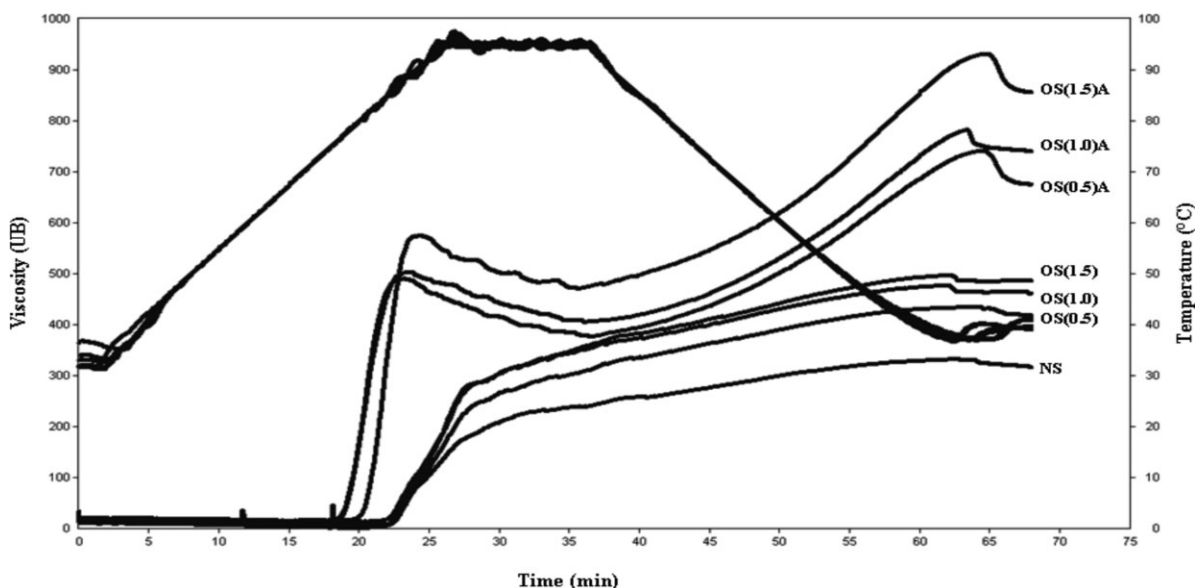
Figure 1 Pasting profile of the modified starches (for sample identification, see Table I).

RESULTS AND DISCUSSION

Starch pasting

The dual modification produced an increase in the peak viscosity compared to its oxidized counterpart and the native sample (Fig. 1); this effect was more noticeable when the level of oxidation increased. The changes in the pasting profile indicated alterations in the starch structure during the chemical modification, as was demonstrated in cassava starch modified by crosslinking and acetylation.[22]

Moisture content of the films

The moisture content of the films decreased because of the acetylation (Table II). This pattern occurred because the acetylation increased the hydrophobic character of the banana starch.[23] The moisture content is important because of the antiplasticization

TABLE II
Evaluation of the Color and Moisture Content of the Films

Film	Humidity (%)	$L*$
NS	$9.10 \pm 1.20_a$	$82.30 \pm 1.70_a$
AS	$6.10 \pm 1.10_b$	$83.10 \pm 1.20_a$
OS(0.5)	$10.20 \pm 1.30_a$	$85.70 \pm 1.30_b$
OS(0.5)A	$8.10 \pm 1.20_a$	$86.50 \pm 1.10_b$
OS(1.0)	$14.40 \pm 1.60_{c,d}$	$90.10 \pm 0.75_c$
OS(1.0)A	$11.20 \pm 1.30_a$	$89.90 \pm 1.80_c$
OS(1.5)	$16.20 \pm 1.70_d$	$95.21 \pm 1.23_d$
OS(1.5)A	$13.30 \pm 1.50_c$	$94.85 \pm 1.05_d$

The means of five replicates plus or minus the standard error are shown. The means inside each column with the same subscript letter are not significantly different ($\alpha = 0.05$). For sample identification, see Table I.
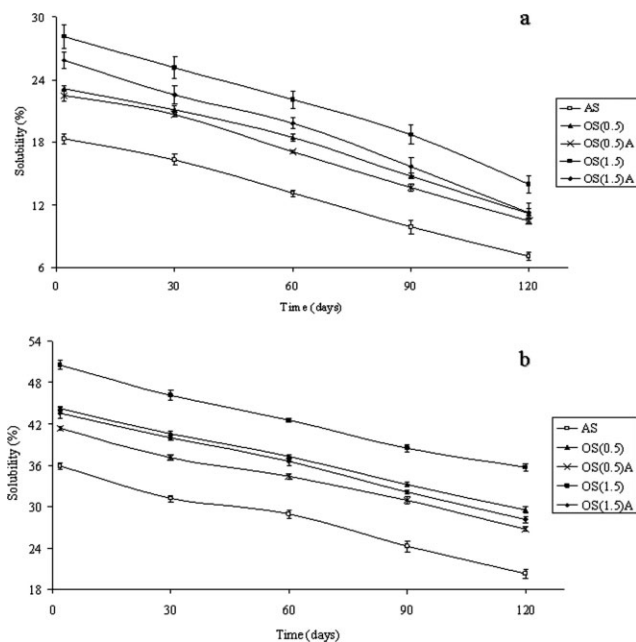
effect of the polymers, which influences the polymer–polymer interactions and, consequently, the physicochemical and functional characteristics of the films during processing and storage.[24]

Color of the films

In general, the whiteness of the films increased with oxidation level, but when the oxidized banana starch was acetylated, the whiteness of the film did not change (Table II). The oxidation of banana starch produced a whiteness sample, and a higher $L*$ value was found when the oxidation level increased.[25] The whiteness of the film is important in diverse applications because, in some cases, the protection of the product from light is necessary to avoid rancidity; moreover, transparency of the films is mostly required by consumers to observe the characteristics of the product.

Solubility of the film in water

The temperature had an important effect on the solubility of the film because, at the lowest tested temperature [25°C; Fig. 2(a)], lower solubility values were found than at 80°C [Fig. 2(b)]. This effect was due to the thermal degradation of the starch of the film, with a concomitant increase in the solubility of the material. A similar pattern was reported in films elaborated with blended corn starch, chitosan, and glycerol[26] and with rice starch plasticized with glycerol, sorbitol, and poly(ethylene glycol).[27] When the storage time of the film increased, the solubility decreased because, at the longest storage time, the reorganization of the starch components (amylose and amylopectin) was carried out; this increased the

Figure 2 Percentage solubility of the films evaluated at (a) 25 and (b) 80°C (for sample identification, see Table I).

crystallinity and, consequently, decreased the solubility of the films. In general, the film type elaborated with starches of modified banana had similar behavior at both temperatures. The film elaborated with the acetylated banana starch had the lowest solubility value, whereas the film made of banana starch had the highest concentration of active chlorine (1.5%) and also showed the highest solubility. This test showed that when the oxidation level increased, the solubility increased. However, when the oxidized starch was acetylated, a decrease in the solubility was observed. This pattern occurred

because acetylation increased the hydrophobic character of the starch and, consequently, of the film and decreased the solubility.[12] In the same sense, oxidation produces major hydrophilic characteristics in starch and its films, which increases the solubility value.[3] The double modification produced a film with an intermediate solubility value compared to its respective oxidized and acetylated starches. The solubility in water of the film is an important factor in the elimination of the material and its degradation because, at higher solubilities, polymers are more susceptible to degradation.

Mechanical properties

The acetylation of the starch increased the TS of the film, which indicated that the film was more rigid (Fig. 3). This pattern occurred because the hydrophobic groups present in the acetylated starch produced interaction with the plasticizer agent and increased its mechanical properties. This was not surprising, as it is well known that the strength of a material below the glass-transition temperature is mainly assured by short-range interactions such as hydrogen bonding or Van der Waals interactions.[28] When storage time increased, TS increased too. The reorganization of the starch components in the system was responsible for this pattern.[29] The effect of oxidation on TS was evident because, when the oxidation level in the film increased, TS increased (Fig. 3). The oxidation of the starch produced carbonyl and carboxyl groups,[25] which increased the interactions between the starch components and produced a more rigid film. In general, %E presented an inverse pattern compared to TS because the film elaborated with the native starch had the highest
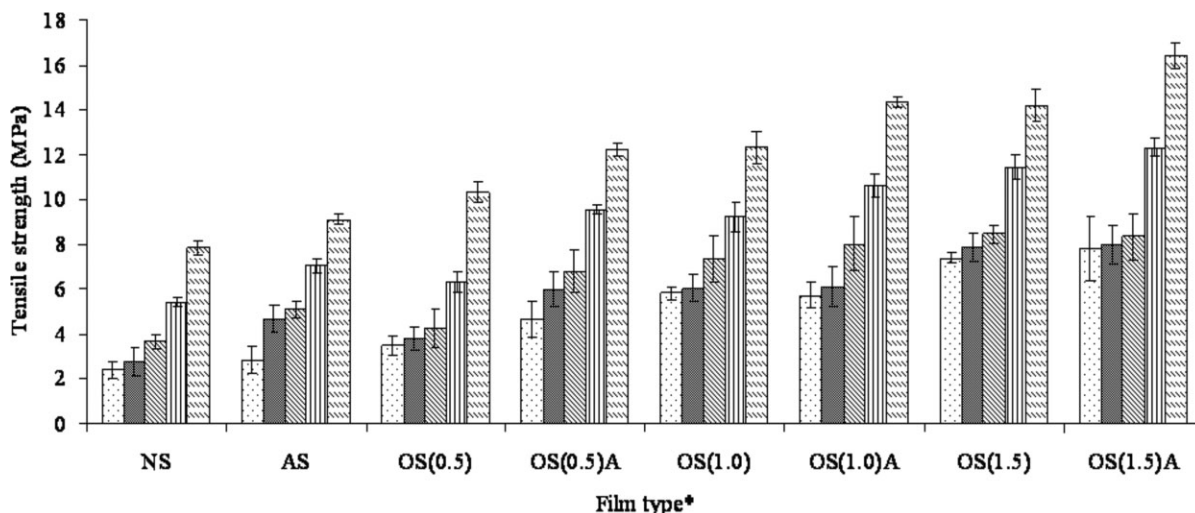

Figure 3 Effect of the oxidation level and acetylation on TS of the oxidized starch films: (☐) recently elaborated and evaluated at (▨) 30, (▧) 60, (▥) 90, and (▱) 120 days (*see Table I).
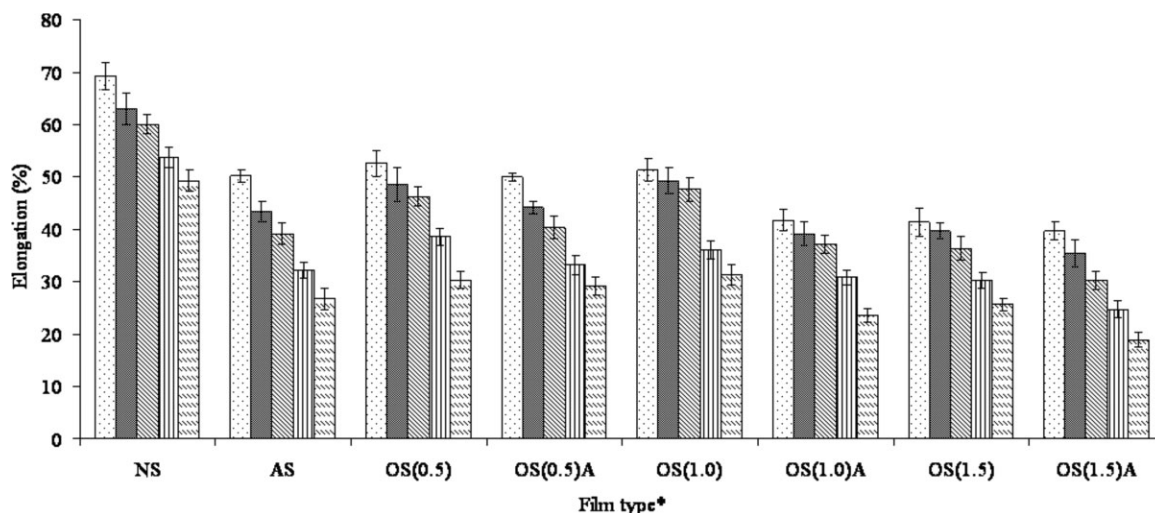
Figure 4 Effect of the oxidation level and acetylation on %*E* of the oxidized starch films: (▫) recently elaborated and evaluated at (▦) 30, (▨) 60, (▥) 90, and (▨) 120 days (*see Table I).

values and those films with oxidized starch at 1.5% active chlorine had the lowest values (Fig. 4). These values of %*E* were in agreement with the TS value because, when the film was more rigid (high TS value), the %*E* value was low. The acetylation of the oxidized banana starch had a slight effect on %*E* because, when the film of the oxidized starch was compared with that where the starch was oxidized and acetylated (at the same storage time), a higher value of %*E* was found in the former film. The interactions of the starch components in the chemically double-modified starch were more stable, which increased the rigidity of the film and decreased its %*E* value. No important effect on EM was present in the films elaborated with native and acetylated starch (Fig. 5). The film elaborated with oxidized–acetylated starch showed a higher EM value than its

oxidized counterpart. The films showed an increase in EM value with the oxidation level. EM testing measures the rigidity of a material.

WVP

In general, the oxidation level increased the WVP of the films (Fig. 6). This pattern occurred because the oxidation increased the hydrophilic character of the starch, and consequently, the film transferred a higher amount of water molecules because the oxidation produced carbonyl and carboxyl groups, which had a higher affinity for water.[30] When the oxidized banana starch was acetylated, a decrease in WVP was found because the acetylation increased the hydrophobic character of the starch by the ester group, which decreased the hygroscopicity of the
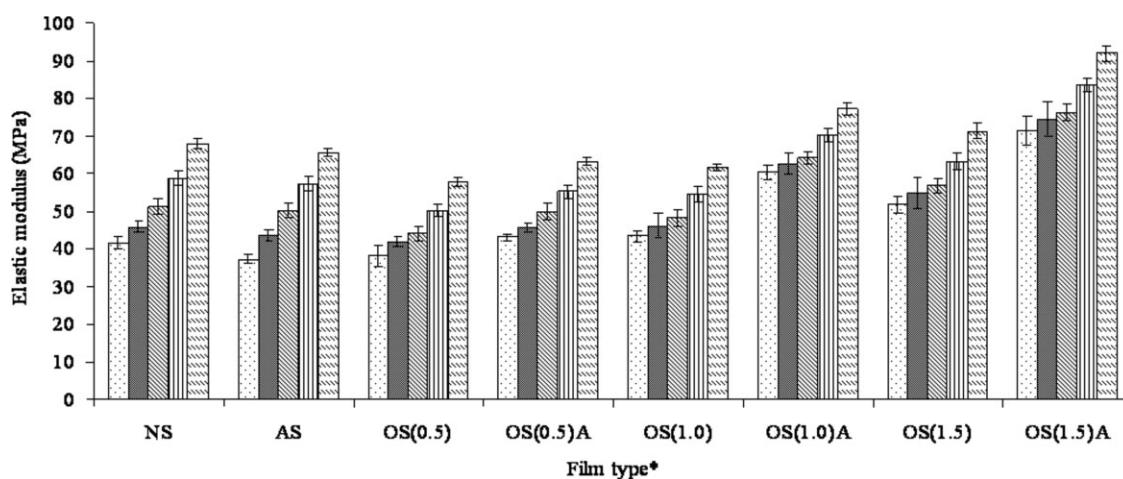

Figure 5 Effect of the oxidation level and acetylation on EM of the oxidized starch films: (▫) recently elaborated and evaluated at (▦) 30, (▨) 60, (▥) 90, and (▨) 120 days (*see Table I).
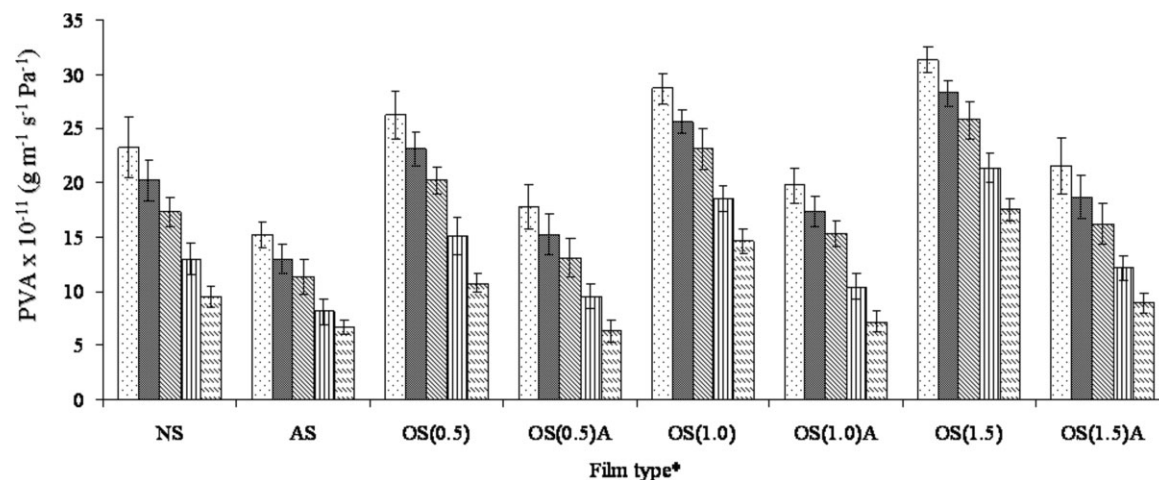
Figure 6 Effect of the oxidation level and acetylation on WVP of the oxidized starch films: (▫) recently elaborated and evaluated at (▨) 30, (▨) 60, (▥) 90, and (▭) 120 days (*see Table I). PVA, WVP $\times 10^{-11}$.

starch.[11,12,28] At the longest storage time, WVP decreased because of an increase in the crystallinity level of the film, which produced an arrangement of the starch molecules that decreased the interactions between the OH^- groups of the glucose units of the starch with the H^+ of the water molecules.[31] WVP depends on factors such as the ratio between crystalline and amorphous zones.[32] Also, WVP decreased with increasing crystalline zones because permeation occurred through the amorphous zones of the films.[33] This is an important feature because the main function of food packaging is often to prevent or at least decrease moisture transfer between the food and the surrounding atmosphere or between two components of a heterogeneous food product, so WVP should be as low as possible.[34]

CONCLUSIONS

The whiteness of the films increased with the oxidation level, and the acetylation did not produce any change in this parameter. The oxidation level increased the solubility of the film, but the acetylation decreased this functional property. The film elaborated with the double-modified starch had an intermediate value of whiteness compared to its oxidized and acetylated counterparts. At the longest storage time, the solubility of the films decreased. The oxidation increased the TS of the film, and when the oxidized starch was acetylated, this parameter improved. Higher values were obtained when the storage time was increased. The control films (no storage) did not show important changes in %E in the differently modified starches used in the elaboration. The effect was more notorious when storage time increased. The %E value decreased when the oxidation level increased, and the effect was more evident. WVP increased with the oxida-

tion level, but acetylation decreased this parameter. The double modification of banana starch can produce biodegradable films with improved functional and mechanical characteristics for specific applications.

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