Influence of the Oxidation and Acetylation of Banana Starch on the Mechanical and Water Barrier Properties of Modified Starch and Modified Starch/Chitosan Blend Films

Paul Baruk Zamudio-Flores,[1] Apolonio Vargas Torres,[2] René Salgado-Delgado,[2] Luis Arturo Bello-Pérez[1]

[1]*Centro de Desarrollo de Productos Bióticos, Instituto Politécnico Nacional, Kilometro 8.5 Carretera Yautepec-Jojutla, Colonia San Isidro, CP 62731, Yautepec, Morelos, Mexico*
[2]*Posgrado-Departamento de Ingeniería Química y Bioquímica, Instituto Tecnológico de Zacatepec, Calzada Tecnológico Número 27, CP 62780, Zacatepec, Morelos, Mexico*

ABSTRACT: Banana starch was oxidized at three different levels and afterwards acetylated. The double-modified starch was used for film preparation with the addition of chitosan. The physical, mechanical, and barrier properties were tested. The oxidation level increased the moisture content of the film, but the acetylation and the addition of chitosan decreased this characteristic. The oxidation level increased the whiteness of the film, but the second modification (acetylation) and the addition of chitosan to the blend did not affect this parameter. The solubility increased with the temperature and the oxidation level but decreased with the storage time of the film. The oxidation increased and the acetylation reduced the solubility with respect to the native starch film. The dual modification produced a solubility value less than that of its oxidized counterpart, and the addition of chitosan produced the highest solubility value. The addition of chitosan increased the tensile strength of the film, and the effect was higher with the oxidation level and longest storage time. The addition of chitosan produced a higher elongation value than that of its double-modified film, but at the longest storage time, this parameter decreased. The water vapor permeability increased with the oxidation level because of the hydrophilic character, but the acetylation reduced this parameter because the acetylation increased the hydrophobic character of the starch due to the ester group. Films prepared with the double-modified banana starch and the addition of chitosan had some improved physical, mechanical, and barrier properties, and they may be used in specific applications. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 991–998, 2010

Key words: barrier; biodegradable; polysaccharides

INTRODUCTION

Bananas are among the most important products worldwide with a high deterioration rate. In Mexico, bananas are economically the second most important fruit. Approximately 77,301 Ha is harvested, and this produce 2.2 million tons; 95% is consumed in the national market, with only 5% designated for export.[1] In the same sense, approximately 10% of the banana production is lost because of attacks by insects and microorganisms that produce damage in the fruit, which eventually cannot be commercial-ized.[2] Unripe bananas have a high starch content (70–80% of the dry pulp).[3] Starch consists of two polymer of different structures and molecular weights: amylose and amylopectin. Amylose is the essential linear component with a molecular weight less than that of amylopectin, and it has the property of film formation.[4–6] The film formation of starch depends on the botanical source from which this polysaccharide is isolated. For this reason, the search for novel starches is an objective of diverse research groups; for instance, banana starch presents an amylose content (35%) higher than that of conventional starches (maize, wheat, and potato).[7] However, it is well documented that native starch (NS) has limitations in functional properties; for this reason, banana starch has been modified with diverse chemical treatments such as oxidation,[8] acetylation,[9] lintneri-zation,[10] alcohol–alkaline treatment,[11] and crosslink-ing.[12] Zamudio-Flores et al.[13] reported that the oxidation of banana starch increased the capacity for film formation with improved mechanical properties, but the water vapor permeability (WVP)

increased (in comparison with a film prepared with native banana starch) because the oxidation increased the hydrophilic character of the starch. In this sense, to control the hydrophilic character of films, hydrophobic agents such as waxes and oils have been used, but these additives influence the mechanical properties.[13–15]

Other researchers[16–20] have reported that starch acetylation can be used to decrease the hydrophilic character. A dual modification is a combined chemical treatment with the objective of taking advantage of each property obtained with the two modifications. Very little information is available on the dual modification of starch for film elaboration. Also, to improve the characteristics of films, blends of starch with other biopolymers such as gelatin,[21] κ-carragenin,[22] and chitosan[23,24] have been tested. Diverse arguments for the blending of chitosan with starch are as follows: (1) chitosan (obtained after *N*-deacetylation of chitin) is the second most abundant biopolymer in nature (after cellulose), and (2) chitosan has the functional property of producing films and membranes with characteristics such as high clarity, resistance, and flexibility that present an adequate barrier to oxygen.[25] The objective of this study was to elaborate films of starch with dual chemical modification (oxidization and then acetylation) and with chitosan added and to evaluate the mechanical and barrier properties at different storage times.

EXPERIMENTAL

Raw materials

Unripened bananas (*Musa paradisiaca* L.) were purchased at the local market of Cuautla, Mexico. Chitosan (85% deacetylated) was obtained from Sigma Chemical Co. (St. Louis, MO), and glycerol was acquired from Fermont (Productos Químicos Monterrey, Monterrey, Mexico).

Starch isolation

The starch was isolated with a pilot-scale procedure.[26] The powder was ground to pass a US 100 sieve and was stored at room temperature (25°C) in a glass container.

Chemical modification methods for starch

Oxidation

Starch slurry was prepared according to Wang and Wang[27] 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. The starch slurry was maintained at 35°C (the heating power was occasionally turned off), and the pH was

adjusted to 9.5 with $2M$ aqueous sodium hydroxide (NaOH). An aqueous sodium hypochlorite (NaOCL) solution with 0.5% (w/v) active chlorine was slowly added to the starch slurry over 30 min while the pH was maintained at 9.5 with $0.5M$ sulfuric acid (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 an active chlorine concentration of 1.0 or 1.5%.

Acetylation

The methodology reported by Wurzburg[28] was used. Starch (162 g) was mixed with 220 mL of distilled 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 acetic anhydride was added, the pH was adjusted at 4.5 with $0.5N$ hydrochloric acid. 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 a US 100 mesh (0.150 mm).[29]

Dual modification

The oxidized starch was thereafter acetylated as described previously.

Preparation of the starch films

The films were prepared with a banana starch (native or modified) concentration of 4% (w/w on a dry basis) and a glycerol concentration of 2% (w/w). For details of the formulations 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 films, containing a 1 : 1 starch/chitosan ratio, were prepared through the mixing of starch, glycerol, and chitosan (3% w/w) dissolved in 100 mL of 1% acetic acid, as reported by Butler et al.[30] The film-forming dispersions were transferred quantitatively to the cup of a visco-amylograph (Brabender OHG, Duisburg, Germany), 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

TABLE I
Samples and Sample Identification of Films

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

prepared by casting: gelatinized suspensions (20 mL) were immediately poured onto polyethylene Petri dishes (110 × 20 mm^2). The starch suspensions were dried at 65°C in an oven for 5 h. Afterwards, 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 sodium bromide (NaBr).

Characterization of the recently prepared starch/chitosan blend films

Moisture content

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

Evaluation of color

The evaluation was carried out on the surface of the films (at least five replicates). A universal colorimeter (Color Mate, Milton Roy 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 (luminosity factor = 100).

Characterization of the recently prepared or aged starch and starch/chitosan blend films

X-ray diffraction

Samples were analyzed between $2\theta = 2°$ and $2\theta = 60°$ with a step size of $2\theta = 0.02°$ in an X-ray diffractometer (2100, Rigaku, Amsterdam, the Netherlands) using Cu Kα radiation (wavelength = 0.1543 nm) at

30 kV and 16 mA. The diffractometer was equipped with a 1° divergence slit and a 0.1-mm receiving slit.

Solubility of the film in water

Pieces (2 × 3 cm) were cut from each film and were 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°C or at 80°C and were dried at 60°C until a constant weight was obtained. The percentage of the soluble total material was calculated as follows:

$$\text{Solubility } (\%) = [(\text{Initial dry weight} - \text{Final dry weight}) \times 100]/\text{Initial dry weight}$$

The samples were analyzed at least in triplicate.

Mechanical properties

The mechanical measurements consisted of tests to determine the tensile strength, elongation at break (%), and elastic modulus. The maximum breaking force, deformation at break [extension at the moment of rupture (mm)], and elastic modulus were obtained from force–deformation curves according to ASTM 882-95[31] with a texture analyzer (TA-XT2i, Stable Micro Systems, Surrey, United Kingdom) equipped with a 25-kg load cell. For the tension test, 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). Separation among gauges was 6 cm. The ends of the films 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) at 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). The tensile strength was calculated by the division of the maximum force exerted on the film during fracture by the cross-sectional area. The elongation at break (%) was expressed as the percentage of the change in the original length of a specimen between grips at break. The elastic modulus was determined from the slope of the linear regression performed on the initial points on the stress–strain curves.

WVP

WVP tests were conducted with ASTM method E96[32] with some modifications. Each film sample was sealed over a circular opening of 0.000282 m^2 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 taken 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 (g/s) divided by the cell area (m^2). After the permeation tests, the film thickness and WVP (g Pa^{-1} s^{-1} m^{-1}) were measured.

Statistical analysis

Experiments were arranged in a completely randomized design. An analysis of variance (ANOVA) was carried out with the statistical program Sigma-Stat (version 2.03).[33] A medium comparison was done with Tukey's multiple test ($p \leq 0.05$).[34]

RESULTS AND DISCUSSION

Characterization of the recently prepared starch/chitosan blend films

Moisture content of the films

The moisture content of the films decreased with acetylation (Table II) because this modification increased the hydrophobic character of the starch on account of the introduction of hydrophobic ester groups (R—COO—R').[35–37] This pattern agrees with the higher moisture content determined for oxidized banana starch versus its double-modified counterpart.[38] The addition of chitosan to the OS(0.5)AC film led to a decrease in the moisture content. A similar pattern was found in the OS(1.0)AC and OS(1.5)AC films; however, the difference from its counterpart without chitosan was not significant. That slight decrease in the moisture content with the addition of chitosan was due to the hydrophobicity of its acetyl groups, but in the film elaborated with banana starch oxidized at a higher NaOCl level, the hydrophilic character of this starch was predominant. Films prepared with cassava starch, with chitosan added, showed a hydrophobic effect[23] similar to that determined here.

Color of the films

The films elaborated with oxidized banana starch had higher L^* values, and this increased when the oxidation level rose, but no significant change was found with the acetylation and the addition of chito-

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

Film	Moisture (%)	L^*
NS	9.10 ± 1.20^a	82.30 ± 1.70^a
AS	6.10 ± 1.10^b	83.10 ± 1.20^a
OS(0.5)	10.20 ± 1.30^a	85.70 ± 1.30^b
OS(0.5)A	8.10 ± 1.20^a	86.50 ± 1.10^b
OS(0.5)AC	6.70 ± 0.90^b	87.20 ± 0.90^b
OS(1.0)	$14.40 \pm 1.60^{c,d}$	90.10 ± 0.75^c
OS(1.0)A	11.20 ± 1.30^a	89.90 ± 1.80^c
OS(1.0)AC	10.30 ± 1.10^a	90.55 ± 1.35^c
OS(1.5)	16.20 ± 1.70^d	95.21 ± 1.23^d
OS(1.5)A	13.80 ± 1.00^c	94.85 ± 1.05^d
OS(1.5)AC	12.60 ± 1.20^c	95.45 ± 1.20^d

The data are the means of five replicates plus or minus the standard error. Means inside each column with the same letter are not significantly different ($\alpha = 0.05$). For sample identification, see Table I.

san (Table II). The principal effect of the luminosity of the films was due to the oxidation, as reported in studies of oxidized banana starch[8,38] and films elaborated with oxidized banana starch.[39] The addition of chitosan showed that both polymers had compatibility because no alteration of the L^* value in the films was observed. This parameter is important in diverse applications of films in which a visual characteristic of the product is required.

Characterization of the recently prepared or aged starch and starch/chitosan blend films

X-ray diffraction

The recently prepared films and those stored for 30 days, even those with chitosan added, did not show crystallinity peaks (Fig. 1). When the storage time increased (60 days), crystallinity peaks appeared because of starch reorganization, and this characteristic influenced the mechanical properties of the films. The films prepared with the double-modified banana starch [OS(0.5)A] showed peaks at 2θ values of 19, 23, and 25° (Fig. 1, top), as reported previously,[13] and these increased with longer storage times. The film elaborated with the double-modified banana starch (with chitosan added) and stored up to 60 days (Fig. 1, bottom) did not present peaks at 2θ values of 19 and 25° but presented a peak at $2\theta = 23$°. An additional peak with a higher intensity at $2\theta = 33$° was present for this film because of the interaction between chitosan and starch chains. Interactions among polymer chains were produced by the formation of hydrogen bonding[40] during the storage of the films.

Solubility of the films in water

Figure 2 presents the solubility values of the films at two temperatures. Higher solubility values were
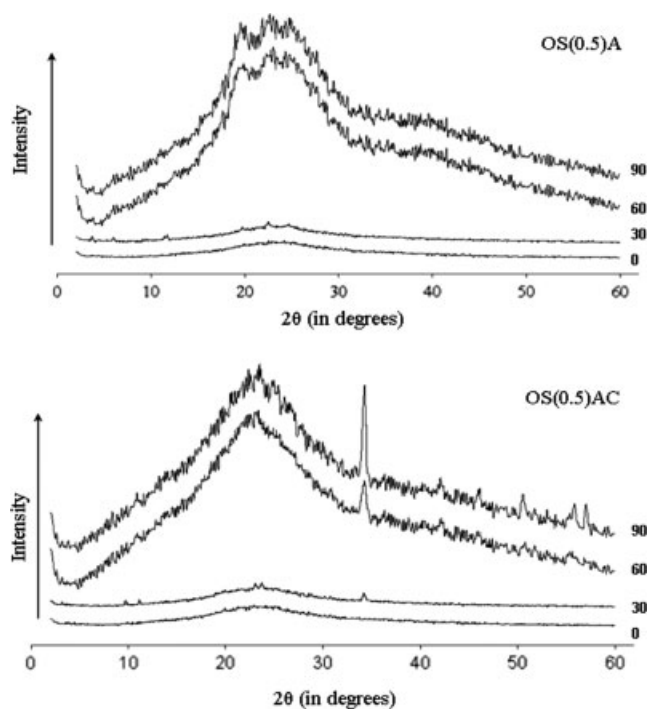
Figure 1 X-ray diffraction patterns of aged films at different times: double-modified banana starch (top) and double-modified banana starch with chitosan added (bottom). For sample identification, see Table I.

found at 80°C than at 25°C because of the disorganization of the polymers present in the films. Similar patterns have been reported for films prepared with native rice starch,[41] native corn starch,[24] chemically modified corn starch,[42] and banana starch.[39] The acetylation decreased ($p < 0.05$) the solubility value of the films because of the hydrophobic character imparted by this kind of modification. The hydroxyl groups (OH^-) of the glucose units of starch were substituted by hydrophobic ester groups (CO^-) of the acetic anhydride.[43] This is in agreement with the lowest solubility value determined in the film elaborated with acetylated starch (AS). When chitosan was added, for example, to the OS(1.5)A film, the solubility value increased because of the hydrophilic character imparted by the cationic character of chitosan, in which interactions between hydroxyl groups of water molecules and amine groups of chitosan could be carried out.[44] In general, the behavior shown by the films at both temperatures was similar because a decrease in the solubility values was found when the storage time increased. This pattern was related to a reorganization of the polymers forming the film, with a concomitant increase in the crystallinity (Fig. 1). The solubility value of a film indicates its integrity in an aqueous system because higher solubility is due to minor resistance to dissolution in water.[45–47] In some applications, films with low solubility are required with the objective of

maintaining the structural integrity (e.g., films to cover fruits and vegetables). However, in other applications, high solubility of the film can be preferred (e.g., edible films for candies).[46–48]

Mechanical properties

The oxidation level increased the tensile strength of the films, but when the second chemical modification was incorporated into the starch, no effect on this mechanical property was evidenced in the film (Fig. 3). However, the incorporation of chitosan led to an important increase in the tensile strength of the film (Fig. 3). This effect was due to interactions between carbonyl and carboxyl groups of the oxidized starch with the amine groups of the chitosan that reinforced the film structure.[43] In general, the films stored at different times presented an increase in the tensile strength; this pattern was produced by reorganization of the starch chains produced during the production of the filmogenic solution, as demonstrated in the X-ray study. The linear short chains obtained during the step of film preparation were available for interactions through intermolecular hydrogen bonds,[24–26] and this effect was higher when the storage time was increased.

In general, the dual modification did not affect the elongation of the films when they were compared with their oxidized and acetylated counterparts. A slight decrease in the elongation value was found at the highest oxidation level in comparison with those
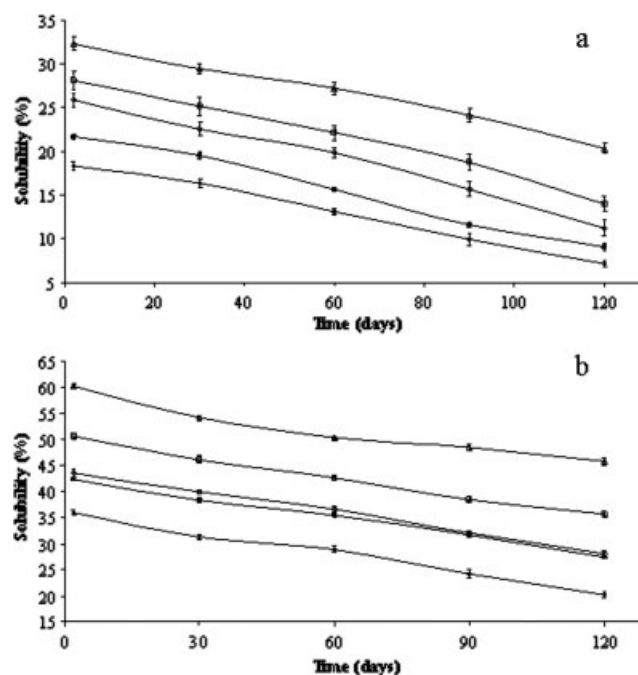
Figure 2 Solubility (%) of the films evaluated at (a) 25 and (b) 80°C: (■) NS, (◆) AS, (□) OS1.5, (◇) OS1.5A, and (△) OS1.5AC. For sample identification, see Table I.
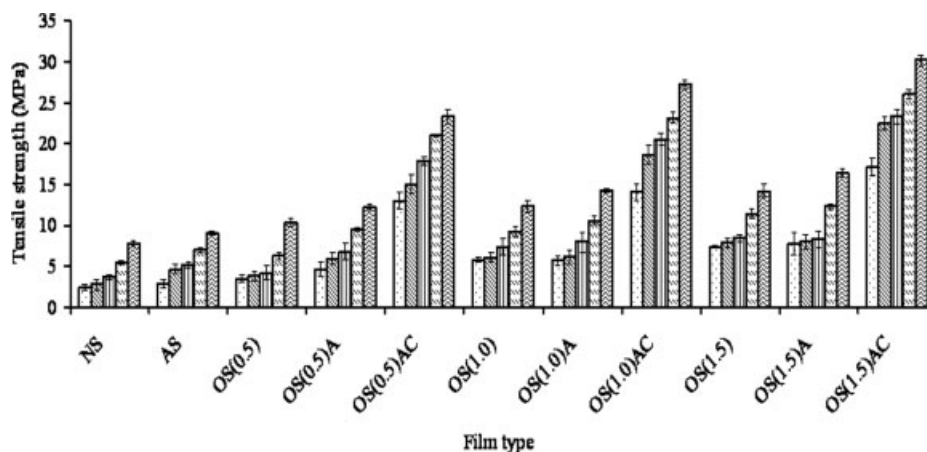
Figure 3 Effect of acetylation and chitosan on the tensile strength of oxidized starch films: (▭) recently elaborated and evaluated at (▨) 30, (▥) 60, (▨) 90, and (▧) 120 days. For sample identification, see Table I.

films elaborated with oxidized banana starch at concentrations of 0.5 and 1.0% (Fig. 4). When chitosan was added, the films had higher elongation values than the oxidized films and those with the dual modification, but when the films with chitosan added were compared, a decrease in the elongation value was determined when the oxidation value increased.

The control film presented the highest elongation value (Fig. 4) because the chemical modification of the starch reduced this parameter of the films. This pattern might be due to the interactions among the diverse components of the film. Similar elongation values have been reported in films elaborated with maize starch and chitosan[24–26] and cassava starch with chitosan.[23] When the storage time increased, the elongation value decreased, and this showed that an inverse relationship was present between the tensile strength and the elongation value.[30,49] Figure 5 shows the elastic modulus, which is related to the rigidity of a material.[50] The addition of chitosan to the film produced a significant difference ($p < 0.05$)
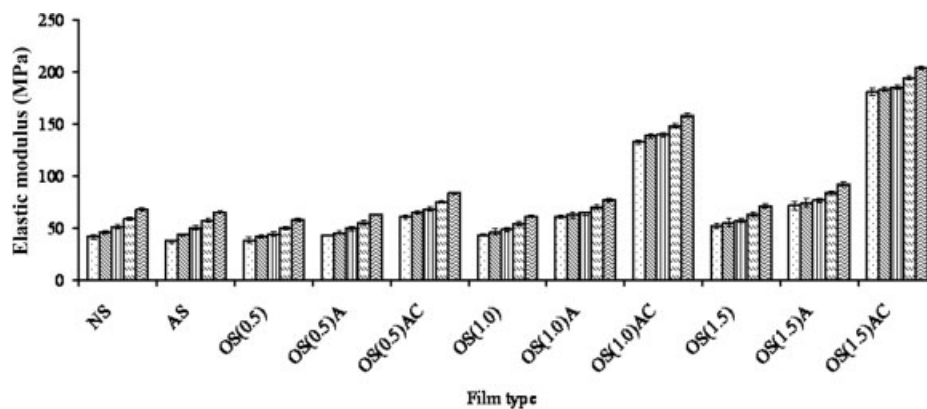
in the elastic modulus values of those elaborated with OS(1.0)A and OS(1.5)A; this pattern originated from the formation of intermolecular hydrogen bonds between the amine groups (NH_3^+) of the chitosan chains and the carboxyl groups (COO^-) of the oxidized starch at the highest level. When the storage time increased, the elastic modulus value rose, and this was related to the increase in the crystallinity of the films (Fig. 1) due to reorganization of the amylose.[4]

WVP

The oxidation level increased the WVP of the film due to the hydrophilic character of the starch because the oxidation produced carbonyl and carboxyl groups,[8,38] which showed a higher affinity for the water molecules, and the film had the capacity to transfer a greater amount of water. When acetylation was applied to oxidized banana starch, the WVP decreased significantly ($p < 0.05$; Fig. 6) because the hydrophilic character decreased with
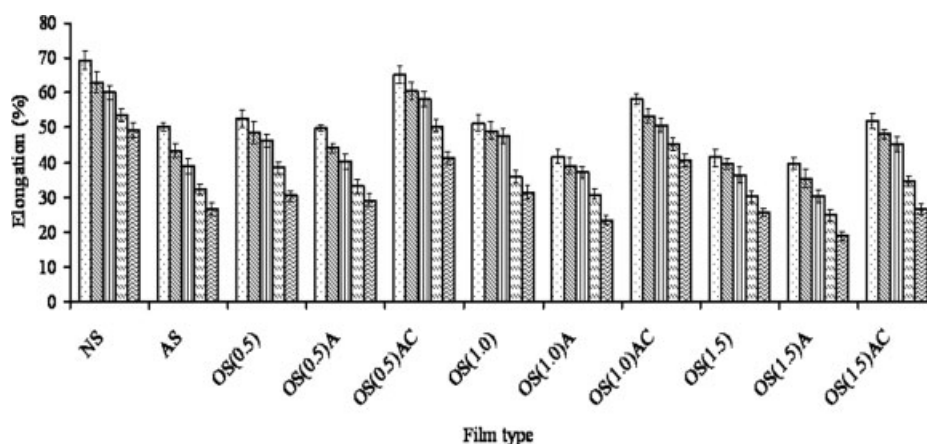
Figure 4 Effect of acetylation and chitosan on the elongation (%) of oxidized starch films: (▭) recently elaborated and evaluated at (▨) 30, (▥) 60, (▨) 90, and (▧) 120 days. For sample identification, see Table I.
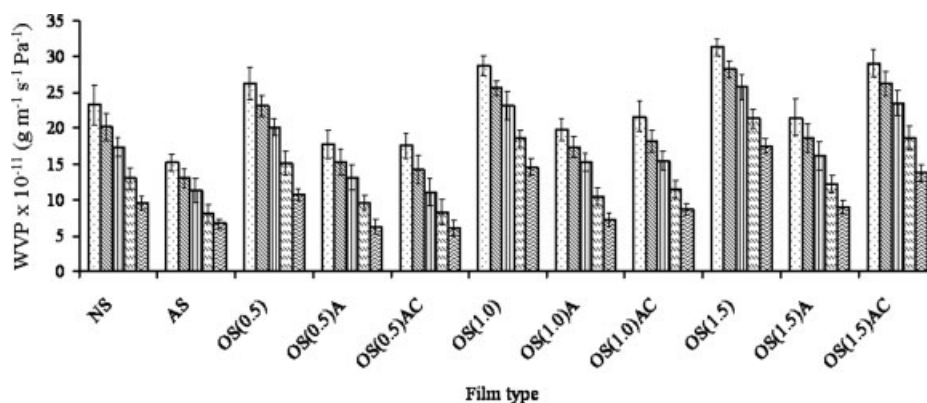
Figure 5 Effect of acetylation and chitosan on the elastic modulus of oxidized starch films: (▢) recently elaborated and evaluated at (▨) 30, (▥) 60, (▨) 90, and (▨) 120 days. For sample identification, see Table I.

the increase in the hydrophobicity by acetylation; this occurred because this chemical modification introduced hydrophobic ester groups.[43] This explanation is in agreement with the lowest WVP of the film elaborated with AS. The addition of chitosan decreased the WVP of the film because of the hydrophobicity of this polymer in the presence of hydrophobic acetyl groups of the partially deacetylated chitosan.[23] A statistical difference ($p > 0.05$) was not observed in the WVP of the films elaborated with the modified starches with chitosan added [OS(0.5)A and OS(1.0)A] because the hydrophilic–hydrophobic character of the blend was not significantly modified. The film elaborated with the OS(1.5)AC blend showed a WVP value between those obtained by the films prepared with OS(1.5) and OS(1.5)A. When the storage time increased, the WVP decreased; this was due to the increase in the crystallinity of the film produced by the arrangement of the starch molecules, in which the interactions between the OH^- groups of the glucose units and the H^+ groups of the water molecules were minimized.[51]

CONCLUSIONS

The acetylation of the starch decreased the moisture content of the films, but the addition of chitosan did not substantially change this parameter. The whiteness of the films increased with the oxidation level, but the acetylation and addition of chitosan did not produce any change in this parameter. The acetylation decreased the solubility of the films, but the addition of chitosan increased this parameter. The oxidation level increased the tensile strength of the films, but the acetylation did not produce changes in the mechanical properties; however, the incorporation of the chitosan led to an important increase in the tensile strength of the films. In general, the double modification did not affect the elongation of the films when they were compared with their oxidized and acetylated counterparts. The addition of chitosan produced higher elongation values than those of the oxidized and double-modified counterparts. At the longest storage time, the elongation value decreased, and this showed that an inverse relation was present between the tensile strength and the

Figure 6 Effect of acetylation and chitosan on WVP of oxidized starch films: (▢) recently elaborated and evaluated at (▨) 30, (▥) 60, (▨) 90, and (▨) 120 days. For sample identification, see Table I.

elongation value. The oxidation of the starch increased the WVP, but the second modification (acetylation) decreased this parameter. The addition of chitosan decreased the WVP of the films even more. Interactions between polymer chains in the aged films were due to the formation of crystallinity peaks. The double modification of banana starch and the addition of chitosan could produce biodegradable films with improved functional and mechanical characteristics for specific applications.

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