

Structural And Physical Properties Of Films From Native And Modified Banana Starch With Two Plasticizers

Perla Alanís-López, Emmanuel Flores-Huicochea, Isidra Guadalupe Ruiz-Martínez, Javier Solorza-Feria

Center for Research on Biotic Products (CEPROBI-IPN), National Polytechnic Institute. Calle Ceprobi 8, Col. San Isidro, Yautepec, Morelos, ZC. 62731. MEXICO.

Corresponding Autor: J. Solorza-Feria

ABSTRACT: Films were made with either native banana starch or oxidized (*Musa paradisiaca* L.) starch, modified with 2% or 3% of active chlorine. Glycerol: sorbitol at ratios 70:30 and 50:50 (w/w) were used as plasticizers. The substitution degree of oxidized starches ranged from 0.035 to 0.073. Films solubility increased with the level of oxidation at the plasticizers ratio glycerol: sorbitol 50:50 w/w, presenting the highest luminosity value. Water vapor permeability from native starch films increased with storage time, while for those from oxidized starch (2%) and oxidized starch (3%), it was a function of time of storage. Films from oxidized starch (2%) and oxidized starch (3%) with the plasticizers ratio 70:30, increased its strength compared to those from native starch. The glass transition temperature of the starch films decreased in samples with oxidized starch.

KEYWORDS: modified starch, degradable films, plasticizers, physical properties

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I INTRODUCTION

Shifts imposed by the growing environmental awareness motivate researches looking for edible films and coatings which could also be friendly with the environment, and health of consumers. Biodegradable films are flexible materials that can be prepared from biological macromolecules, which usually conform a continuous matrix. Chemically synthesized polymeric films are widely used for packaging in the food industry, because they are easily and inexpensively produced from uniform raw materials and are both flexible and durable. A serious disadvantage of these films is that they are not biodegradable. The growth of environmental concerns over nonbiodegradable petrochemical-based plastics raised interest in the use of biodegradable alternatives, originating from renewable sources [1] [2]. Among the biopolymers commonly used for film production are proteins and polysaccharides as starch, as well as lipids, and its derivatives.

Starch is abundant and readily available from various sources worldwide, such as Banana, which is a general term involving a number of species or hybrids in the genus *Musa* of the family Musaceae. Almost all of the known edible-fruited cultivars arose from two diploid species, *Musa acuminata*, and *Musa balbisiana*, which are native to Southeast Asia. As is the case for most tropical products, due to special climatic conditions needed to grow bananas, they are mainly produced in developing countries [3]. Starch is constituted by two biopolymers, namely: amylose and amylopectin, which in addition to present different structure and function, they are susceptible to physical, chemical and enzymatic modification. Since starch has some affinity to water, which is attributed to amylose, it also has the ability to film formation [4].

This is generating investigations focused on developing films from starch, to contribute to solve the contamination problem generated by plastic materials. Starch oxidation may modify efficiently some starch properties and, by adding a plasticizer to its structure, a homogeneous mixture macromolecule-plasticizer can be produced. Studies on the effect of polyols (e.g. glycerol, sorbitol, and poly-ethylene-glycol) used as plasticizers in film formation from biopolymers have been reported [5] [6], where the outstanding plasticizing effect of glycerol and in a lesser degree that of sorbitol has been evidenced. Some researches on biodegradable films from native starches and plasticizers are commonly found in the literature, but those on modified starches are still needed, since they are far away from complete. That is why the aim of this study was the obtainment and

partial characterization of films from banana (*Musa paradisiaca* L.) starch, modified by oxidation with two concentrations of sodium hypochlorite and two plasticizers (glycerol and sorbitol) addition.

II MATERIALS AND METHODS

Materials

Common laboratory glassware and reagent grade chemicals were used. Unripe hard green banana fruits were purchased from the local market in Cuautla Morelos, Mexico.

Obtainment of Starch

To isolate the starch from the bananas, the method mentioned in Argüello-García, et al [7] was followed. The total starch content was evaluated by the method of Goñi et al [8]. The apparent amylose content was obtained using the method of Gilbert and Spragg [9], using potato starch as standard.

Starch oxidation

It was done as suggested by Wang and Wang [10]. To obtain oxidized banana starch (OXS), native banana starch (NS) and sodium hypochlorite solution (NaOCl) were used. Oxidized starch obtained with 2% and 3% (w/w) of active chlorine were named OXS-2 and OXS-3 respectively. About 35 g starch/100 g slurry was prepared using deionized water. This was set at 35 °C by using a magnetic stirrer with a heating system; since the oxidation reaction is performed best at alkaline conditions, as indicated by the method, the pH was adjusted to 9.5 with a (1 N) NaOH solution. Then, 50 mL of sodium hypochlorite solution were added at a constant rate, slowly and during exactly 30 min, with constant stirring of the reaction mixture into the flask, using a (1 N) H₂SO₄ solution, to maintain the pH at 9.5. The mixture was let to react 50 more min, keeping the same pH value with the mentioned NaOH solution. To continue, the pH was set to 7.0 with (1 N) H₂SO₄ solution and the starch separated by decantation. All remaining oxidized starch was washed four times with deionized water and dried in a convection oven at 45 °C for 48 h. Finally, the starch was ground and kept in hermetic containers until further use.

Starch carbonyl groups content

The carbonyl groups (C=O), as a measurement of the aldehydes content, were determined by the titration method of Smith [11]. About 4 g (dry basis) of native and oxidized starch were weighed separately, then, the samples were suspended in 100 mL of distilled water, this was gelatinized by heating at 90 °C for 20 min, then cooled down to ambient temperature, the pH was adjusted to 3.2 with HCl 0.1 N, and 15 mL of hydroxylamine chlorhydrate were added before taking each sample into a water bath at 40 °C, with slow agitation for 4 h. The excess of hydroxylamine that reacted with hydroxyl groups was titrated to a pH value of 3.2 with 0.1 N HCl. All tests were done in triplicate. The carbonyl groups content was calculated as follows:

$$\% \text{ Carbonyl} = \frac{[(\text{control} - \text{sample}) \text{ mL} \times \text{N acid} \times 0.028 \times 100]}{\text{Sample weight (dry basis) in g}} \quad (1)$$

Starch carboxyl groups content

The modified banana starch carboxyl group content (COOH), was determined according to the modified method of Chattopadhyay et al [12], as follows. About 2 g of oxidized starch were weighed and mixed with 25 mL of 0.1N HCl with constant agitation during 30 min, using a magnetic stirrer. The starch dispersion was filtered at vacuum and washed with 400 mL of distilled water, the starch paste formed was carefully transferred to an Erlenmeyer flask, and then, it was gelatinized in a water bath with boiling water for 15 min with constant stirring, after this step, about 150 mL of deionized water was added to the sample of starch paste, which was then cooled down to a temperature between 34 to 39°C, finally the sample was titrated with a 0.01N NaOH solution to a pH of 8.3. The same above procedure was applied to the native starch or control. To evaluate de carboxyl content, the following formulae were applied.

$$\frac{\text{Miliequivalents of acid}}{100 \text{ g of starch}} = \frac{[(\text{Sample} - \text{Control}) \text{ mL} \times \text{N NaOH}]}{\text{Sample weight (dry basis) in g}} \quad (2)$$

$$\% \text{ Carboxyl} = \frac{\text{Miliequivalents of acid}}{100 \text{ g of starch}} \times 0.045 \quad (3)$$

Films preparation

The films were manufactured by casting, as suggested by Mali et al [13]. Authors like Thomazine et al [5] used various ratios of glycerol:sorbitol (e.g.40:60, 60:40, 80:20 and 100:0) to plasticize gelatins solutions during films formation, finding a higher plasticizing effect of glycerol when it predominated. To investigate the effect of a different plasticizer concentration, a banana starch suspension having 4% (w/w) total solids of which

70 % was starch and 30 % plasticizers, in distilled water, was prepared with either native banana starch (NS) or oxidized banana starch (OXS-2, OXS-3). A plasticizer solution with two polyols (glycerol and sorbitol) at one of two ratios (either 70:30 or 50:50 w/w) was added to the mentioned suspension and mixed thoroughly, making a sample with 100 g in weight, which was put into a water bath at 80°C for 10 min to achieve starch gelatinization and the mixture solubilization, giving place to a filmogenic solution. Then, each solution was poured into sterile Petri dishes and dried in an oven at 65 ± 1 °C during 5 h. After this time, the films were detached and stored for 7 days in a desiccator containing saturated sodium bromide, that provided a relative humidity (RH) of about 57% inside, at 25 ± 1 °C. A total of six types of films were prepared (NS 70:30, NS 50:50, OXS-2 70:30, OXS-2 50:50, OXS-3 70:30, and OXS-3 50:50).

The thickness of the films was measured randomly at five different points with a digital micrometer (Mitutoyo, Japan) of each sample of 10 cm diameter, taking five different samples and the average was calculated.

Films solubility

The solubility (%) values were evaluated by using the Modified methodology suggested by Gontard, et al [14]. Rectangular pieces of film of 2 x 3 cm, were cut and stored for 48 h, in a desiccator almost exempted of moisture with silica gel. Then, the samples were weighed and placed into 100 mL beakers with 50 mL of distilled water containing sodium azide (0.02% w/v) at room temperature (about 25 °C), maintained under constant stirring for 1 h. After soaking, the solution containing the film samples was filtered, the insoluble matter was dried at 100 ± 2 °C for 2 h and the resulting material was weighed till obtaining a constant value to determine the final dry weight. Measurements were done at least three times. To estimate the solubility, the following equation was applied.

$$\% \text{ solubility} = \frac{\text{Initial dry weight} - \text{Final dry weight}}{\text{Initial fresh weight} - \text{Final dry weight}} * 100 \quad (4)$$

Luminosity degree

A random model was used to choose the surface points on the films to determine the color. A colorimeter (Color Analyzer, Color Mate OEM, Milton Roy™ Co., USA) with a D65 illuminant and observation angle of 10° was used. Five readings were taken for each sample, doing each test in triplicate. The measurements were done using the CIELAB (L^* , a^* , b^*) system. Chromaticity (C) and hue angle (°h) were evaluated using the following equations:

$$C = (a^{*2} + b^{*2})^{\frac{1}{2}} \quad (5)$$

$$^{\circ}h = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad \text{for } a^* > 0 \text{ and } b^* \geq 0 \quad (6)$$

$$^{\circ}h = 180 + \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad \text{for } a^* < 0 \quad (7)$$

Water vapor permeability

The water vapor permeability (WVP) of all films, was carried out using the ASTM method E 96-80 (1993), also known as the cup or test cell method. Film samples of similar thickness with a circular shape (about 0.00181 m²) were stored for five days at 25°C in a desiccator with a saturated solution of NaBr (57% RH). Then, the films were sealed over circular openings of the same area in permeation cells that were stored in another desiccator. To have about 92.5% RH, an over saturated solution of KNO₃ was placed inside each cell and a saturated solution of NaCl was placed into the desiccator (75% RH). Water vapor transfer was evaluated from the weight gain of the permeation cell. Once reaching steady state conditions (about 2 h), weight measurements were done over a period of 24 h. Variations in the cell weight were registered and plotted as a function of time. Linear regression ($R^2 \geq 0.99$) was used to calculate the slope of each line, and the water vapor transmission rate (WVT) was calculated from the slope of the straight line (g/s) divided by the cell area (m²). Once permeation tests were done, the film thickness was measured and WVP in g Pa⁻¹ s⁻¹ m⁻¹ was evaluated by applying the following equation.

$$WVP = \left[\frac{WVT}{S(R_1 - R_2)} \right] d \quad (8)$$

Where: S is the saturated water vapor partial pressure at the test temperature, R_1 is the RH of the desiccator, R_2 is the RH of the permeation cell, d the film thickness (m), and WVT, is the water vapor transmission rate given by the equation 7.

$$WVT = \frac{G}{tA} \quad (9)$$

Where G is the weight change, t is the time when G takes place and A, is the transference area.

Mechanical Properties

Film samples with thickness mean values of 1mm, measured by digital micrometer (Mitutoyo™, Tokyo, Japan), were selected for mechanical tests, that were performed in a M-93 TA-XT2i-Texture Analyzer (Stable Micro Systems™, Scarsdale, NY), equipped with a 10 Kg load cell, following the official method ASTM D-888-95a. Pieces of films with 10 cm long and 1 cm wide, were affixed to both ends of a test strip to hold it in place and to keep the grips of the testing machine from cutting the film. A constant extension rate of 24 mm/min was applied to samples having 8 cm of real test distance between gauges, and the tensile strength (TS, MPa) was measured. The tensile stress was calculated with the following equation:

$$TS = \frac{\text{Maximum force over film during fracture}}{\text{area of transversal section (thickness} \times \text{width)}} \quad (10)$$

Thermal Properties

The thermal properties of the films were determined using a DSC (TA™ Instruments, New Castle, DE, USA). Before the analysis, about 10 mg of films were conditioned for 7 days in aluminum pans in a desiccator with NaBr (HR≈ 57%). The temperature range used was from -150 to 130 °C with a heating rate of about 10° C/min in an inert atmosphere (50 mL/min of N₂, 99.9% purity). All samples were subjected to this heating range twice, taking the second run as the effective one. The glass transition (mid-point) temperature (T_g) was calculated using the software Universal Analysis V1.7F (TA™ Instruments). As an independent test, the melting temperature and enthalpy of all films were determined under the same conditioning procedure mentioned above (weight and RH), except that the temperature range used was from 25 to 300 °C. All tests were run in triplicate.

Statistical analysis

The results were subjected to one-way analysis of variance (ANOVA) at a significance level or probability of 5 % (P < 0.05) and in a case of significance, the Tukey multiple comparisons method was applied at the same probability [15]. The Sigma Stat ver. 2.03 statistical program was used.

III RESULTS AND DISCUSSION

During the oxidation process, the carbonyl and carboxyl groups are produced from hydroxyl groups on starch molecules, the carbonyl groups are the first product of oxidation, and then the carboxyl groups are formed [10]. The carbonyl and carboxyl content of the oxidized starches are shown in Table 1, the carbonyl values between OXS-2 and OXS-3 starches did not show significant differences (P > 0.05).

Since oxidation was undertaken under alkaline conditions (pH= 9.5), the formation of carboxyl groups was favored during the production of the specimens OXS-2 and OXS-3, in comparison with the oxidation under acid conditions, as in the case when other oxidant agents have been used [10]. Also, Wing and Willett [16], conducted a study with three types of starches, that were oxidized with hydrogen peroxide and ferrous sulfate. They found that an increase in hydrogen peroxide, increased the oxidation level (higher carbonyl and carboxyl content). Kuakpetoon and Wang [17], studied starch from different type of maizes, namely; waxy maize, common or normal maize, maize with 50% amylose and maize with 70% amylose, finding that as the active chlorine concentration to oxidize the starches increased from 0.8 to 5%, more carbonyl and carboxyl groups were generated, being the carboxyl content which increased faster than the carbonyl group, going from 0.48 for starch with 70% amylose, till 0.76 for starch from waxy maize, suggesting a complete reaction that involved oxidation of hydroxyl groups of starch, first to carbonyl and then to carboxyl group, stipulating that the oxidation had taken place in the starch amorphous lamella consisting of amylose. The sample which presented the highest carboxyl content was OXS-2 (Table 1), being lower than that reported by Wang and Wang [10] for normal starch, nonetheless, these authors reported a similar degree of oxidation (0.177%).

The thickness affect the film properties and needs controlling to obtain a uniform material, it may vary with the formulation, volume of filmogenic solution poured into plates and processing conditions. The thickness values among the various films were within the range 0.20±0.005 mm to 0.22±0.008 mm (data not shown), with no significant differences (P > 0.05) among them, neither because of starch modification nor for the plasticizers ratio. Thus, this could be due, especially to the consistent amount of the filmogenic solutions used and drying conditions, for the various formulations during the films manufacture.

The percentage of solubility is one of the most important properties of films and for those studied, the solubility ranged between 26.54 and 32.77% at 25 °C, as shown in Fig. 1. Overall, except for films from OXS-3, the films with the lowest solubility, were those produced with glycerol and sorbitol 50:50 w/w. In general, the films solubility increased with increase in the concentration of active chlorine used during the oxidation process of starch, since it increased the polar groups, making them more hydrophilic. This increase in solubility, might well be related to an increase in the interactions between the compounds derived from the starch depolymerization and water as a result of the oxidation. In this study, for film samples from OXS-3 (70:30), this combination seemed to reduce the dehydration capacity of the films. But on the other hand, for the other films,

the highest film solubility value was obtained with the same mentioned ratio of glycerol and sorbitol, due to the hydrophilic character of these polyols, being consistent with the results reported by Laohakunjit and Noomhorm [18], in a study carried out in rice starch films plasticized with various glycerol and sorbitol concentrations; showing that films with glycerol displayed higher solubility than those with sorbitol, since glycerol presented a higher interaction with water (hygroscopicity), making its incorporation into a hydrogen bridge network easier.

In contrast Kim and Ustunol [19], found that films plasticized with sorbitol were completely water soluble, while those plasticized with glycerol were just partially soluble. A low film solubility is required during storage, while a high film solubility, may be advantageous during cooking of food products coated with this sort of films.

Film color is a relevant property when the film is used in foods as coating. The different film formulations presented overall significant differences ($P < 0.05$), respect to the luminosity parameter (Fig. 2). The films from OXS-3 presented the highest L^* values, followed by those of NS, but these films displayed similar color intensity irrespective of the plasticizer ratios, which is not consistent with the work of López et al [4], who found that films with less glycerol addition were more transparent. Also, the expected "clearing" effect of starch oxidation because of amylose depolymerization [17], was not observed in films from OXS-2, which presented a predomination in L^* value in samples with the ratio 50:50 w/w gly-sor.

The lowest of all L^* values were those of the films obtained from oxidized starches OXS-2, suggesting that the 2% chlorine used to modify the starch, was not enough to produce a change in the films color. Nonetheless, the differences in color observed between NS and OXS-3 film samples, might be due to the higher amount of minor components (lipid, protein residues) present in native starch as compared to oxidized starch, where the oxidation reaction and subsequent washings, eventually got rid of most of those components. Table 2 shows the WVP of banana starch films determined at 30 and 60 days of storage. The films with the higher level of oxidation (OXS-3), seemed to favor a greater water vapor diffusion through the films, at 30 days of storage, as seen with its higher WVP values, but this trend was not maintained up to 60 days of storage, where overall, the effect of glycerol was more notorious.

The WVP of the film produced with NS and plasticizers ratio 50:50, showed significant differences respect to the value at 60 storage days, with an increase in such a value. This could be due to the trend of the film conferred by glycerol, to hydrate by adsorbing water as the storage time passed out, favoring an increase in the film WVP. The WVP of the NS (70:30) film at 30 storage days also showed significant difference respect to the value at 60 days of storage (Table 2). This increment was higher than that obtained for films with plasticizers ratio 50:50, and might well be due to a higher glycerol content, which caused higher film water affinity or hygroscopicity [20]. Films from OXS-2 and OXS-3 with plasticizers ratio 50:50, at 30 storage days, presented notorious different WPV values.

The WVP values of film samples from OXS-2 (50:50) did not show significant differences ($P > 0.05$) respect to values at 60 days of storage. However, OXS-3 film with the same ratio gly:sor at 60 storage days, showed statistical difference ($P < 0.05$) respect to WPV values at 30 storage days, having at the longer period, a lower value than that at the shorter storage period. This was possibly due to oxidation and plasticizers, because at this oxidation level, with the same plasticizers ratio; plasticizers migration and sorbitol crystallization occurred during storage, lowering the free volume in the films [20].

The WPV values of films from OXS-2 and OXS-3, with gly:sor ratio 70:30, at 30 storage days, were significantly different to those at 60 storage days. Probably the higher glycerol content made the films more sensitive to water, reorganizing the biopolymer structure and increasing the free volume. Similar results were reported by Thomazine et al [5], in gelatin films plasticized with various concentrations of glycerol and sorbitol, finding that as the glycerol concentration increased, the films were more hygroscopic than those plasticized by sorbitol. For the film from OXS-3, the WPV value registered at 60 storage days, also decreased significantly respect to the shorter storage period, probably due to film components crystallization, as stipulated by Kim et al [21], who found the same trend in films from potato starch, evidencing that glassy polymers are not in thermodynamic equilibrium, concluding that the free volume fraction decreased with storage time, decreasing in consequence the WPV.

The results from tensile strength (TS) of the films from native and oxidized banana starch are shown in Fig. 3. Tests were undertaken in samples at fifteen days from manufacture, when the relative humidity had reached real stability. An increase in TS for all films from oxidized starches respect to those from native starch can be observed. The films from NS (70:30), presented notoriously the lowest TS values, while those prepared with OXS-2 and OXS-3 at the same plasticizers ratio, displayed the highest values.

This could be due to the presence of carbonyl and carboxyl groups in the oxidized starches, as well as to the hydroxyl groups from the plasticizers molecules, giving place to a cross-linked structure. Also, the amylose and amylopectin, were able to form hydrogen bridges, which furnished high structural integrity and thus, a higher stress was required to break such films [22]. That is to say: in films from modified starch, the

resulting amylose and amylopectin depolymerization from the oxidation, gave place to short-chain components that linked to glycerol, facilitating a closer or tight structure [17], which required a higher stress to be broken. In films from oxidized starch with plasticizers ratio 50:50, the TS values did not show significant difference between them, suggesting that to observe a notorious effect on the the TS, a higher glycerol proportion was required.

Being a semi-crystalline material, most probably samples experienced in the amorphous part of its structure, the glass transition; while in its crystalline portion, the crystals melting was manifested. The Glass transition of an amorphous or partially amorphous polymer is typically described as a transition from a brittle glassy to a highly viscous or a liquid-like rubber, it is of great importance for the mechanical properties of materials. Addition of plasticizers such as water, glycols and sugars, lower the glass transition temperature and make the material more rubber-like [23].

Table 3 shows the thermal parameters of both the glass transition and melting temperature of the mentioned films. The main glass transitions were observed between -23 to -3.41°C, probably due to sorbitol, while the one seen between -87.95 to -50.61°C, might be due to glycerol. Transitions presumably due to starch were not reproducible and difficult to identify (not shown).

Previous works have reported glass transition temperatures between -80 to -86°C for glycerol. Some authors [24], have shown evidence that plasticizers as glycerol, tend to notoriously decrease the glass transition temperature of starch systems, which is consistent with the results obtained in this work, where the glycerol addition, decreased the glass transition temperatures in all film samples.

Respect to the combined effect of glycerol and sorbitol addition on the starch glass transition, not that many results have been reported. Habitante et al [25], studied aqueous systems of cassava starch and glycerol, suggesting that in a system conformed by a biopolymer and a polyol, this will experience some phase separation, finding that cassava starch systems with 20 and 40% glycerol addition, displayed the highest molecular interaction, and when glycerol concentration addition increased, the solution presented a behavior controlled by the starch granules water molecules migration, due to the glycerol hypertonic character, which affected the phase transition measured by calorimetry. In this work, it was also seen that starch oxidation decreased the glass transition temperature of sorbitol, glycerol and starch within the film.

The melting temperature of the films, showed an increase in its values when the proportion of glycerol increased, irrespective of the starch treatment, suggesting that a more stable system of the polymeric chains was achieved, requiring a higher temperature to be destabilized. Also, this parameter decreased overall, as the oxidation level increased (Table 3). However, an undefined trend is observed in the films enthalpy data, which could possibly be associated with the weakening of the intermolecular bonds among the various film components, giving as a consequence such low values. Further research might be needed to make clear this tendency but so far quite interesting results have been obtained.

IV. CONCLUSION

1. The starch oxidation degree was a function of the active chlorine concentration. The solubility increased with the level of oxidation, being the most soluble film the one from OXS-3 (50Gly:50Sor).
2. Films from OXS-3 (50Gly:50Sor) presented the highest luminosity (L^*) value, followed by films from NS and OXS-2. The WVP of films from NS increased with storage time, all films from OXS-3 however, showed a decrease in WVP with storage time.
3. Films from oxidized starches with the plasticizers ratio 70Gly:30Sor, increased the tensile strength, compared to those from native starch, probably because oxidation favored an increase in intermolecular attraction, facilitating a closer or tight structure, which required a higher stress to be broken.
4. The glass transition temperatures of the starch films decreased in samples with oxidized starch, with probable plasticizers phase separation. The melting point of the starch films increased with the glycerol content, possibly due to the mentioned increase in the interactions among the starch macromolecules.

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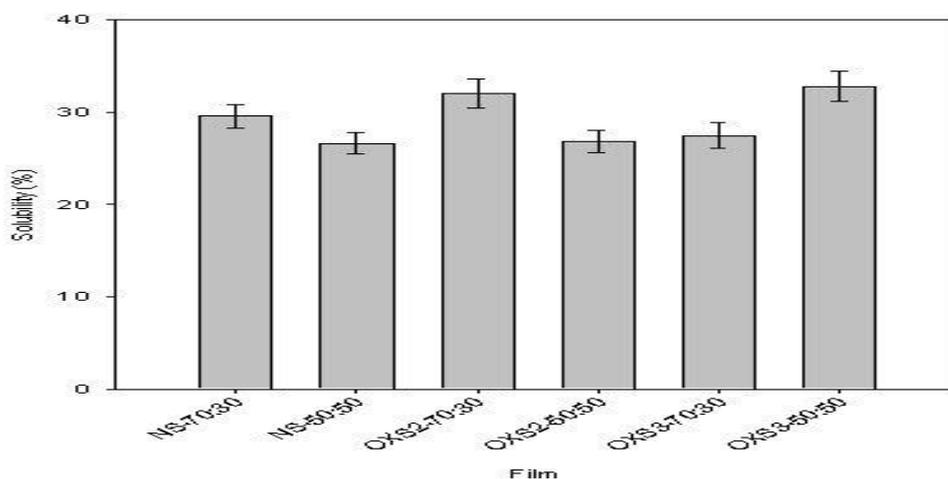


Figure 1: Effect of banana starch oxidation and plasticizers (glycerol-sorbitol) addition on the solubility of films at 25° C

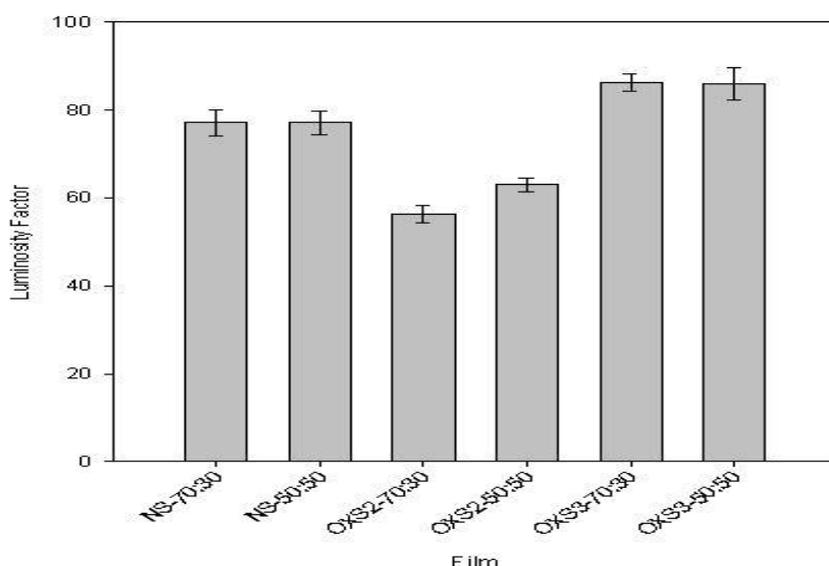


Fig. 1: color of films from native and oxidized banana starch, with plasticizers (glycerol-sorbitol) addition

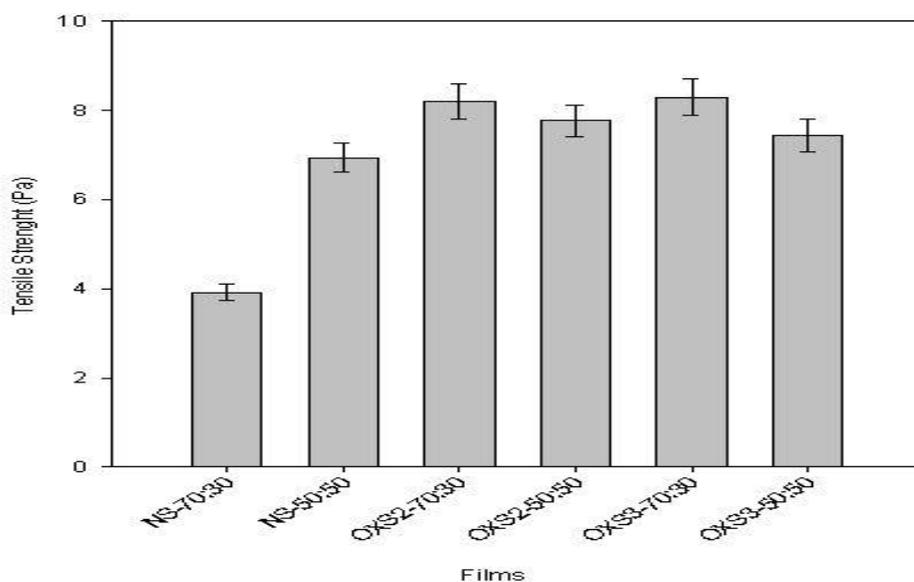


Fig. 2: Tensil strength of films from native and oxidized banana starch with plasticizers (glycerol-sorbitol) addition

Table 1. Chemical analysis of banana starch oxidized with 2 and 3% of NaOCl*

Starch sample	Carbonyl (%)	Carboxyl (%)	Apparent amylose ¹	Total starch ¹
NS	ND	ND	30.36 ± 0.100 ^a	87.02 ± 0.30 ^a
OXS-2	0.039 ± 0.002 ^a	0.073 ± 0.0008 ^a	12.1 ± 0.32 ^b	88.27 ± 0.09 ^b
OXS-3	0.061 ± 0.008 ^b	0.035 ± 0.001 ^b	7.29 ± 0.20 ^c	89.01 ± 0.04 ^b

*Mean values of three replicates ± standard error. Different letters within the same column indicates significant differences (P < 0.05). ¹Results are in dry basis. NS (native starch), OXS-2 (starch oxidized with 2 % sodium hypochlorite), and OXS-3 (starch oxidized with 3 % sodium hypochlorite). ND = not detected. Superscript “a” was assigned to the first figure of each column

Table 2. Effect of storage time on water vapor permeability of films from native and oxidized starch with two plasticizers*

Type of film	WVP x 10 ⁻¹¹ (g Pa ⁻¹ s ⁻¹ m ⁻¹)	
	30 days of storage	60 days of storage
NS 70:30	11.77 ± 0.34 ^a	23.79 ± 0.41 ^b
NS 50:50	16.2 ± 0.18 ^c	25.21 ± 0.15 ^d
OXS-2 70:30	11.03 ± 0.12 ^e	13.26 ± 0.17 ^e
OXS-2 50:50	16.99 ± 0.45 ^f	18.72 ± 0.37 ^e
OXS-3 70:30	29.27 ± 0.14 ^h	12.78 ± 0.40 ^f
OXS-3 50:50	26.61 ± 0.34 ^j	23.14 ± 0.10 ^k

*mean values of three replicates ± standard error. Analysis was done for each film sample among the storage times data. Different letters within the same row indicates significant difference (P < 0.05)

Table 3. Thermal parameters of films from native and oxidized starch with two plasticizers

Type of film	T _g (°C) sorbitol	T _g (°C) glycerol	T _g (°C) starch	T _p (°C)	ΔH (J/g)
NS 70:30	-23.94± 2.06	-87.95±9.59	83.86±8.24	258.04±26.09	0.6379±0.03
NS 50:50	-11.19±1.05	Nd	135.76±16.25	238.53±23.21	0.7792±0.041
OXS-2 70:30	-3.41±0.36	-67.21±7.56	106.67±11.50	257.87±25.76	0.6123±0.034
OXS-2 50:50	-17.07±1.68	-77.82±9.34	83.84±7.75	244.65±29.52	0.1896±0.02
OXS-3 70:30	Nd	Nd	98.7±10.12	245.85±26.79	0.0092±0.001
OXS-3 50:50	-6.05±0.67	-80.71±9.05	156.4±16.67	189.11±22.93	0.3410±0.017

*mean values of three replicates ± standard error. T_g= glass transition temperature, T_p= peak melting temperature, ΔH= melting enthalpy, Nd= not detected

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