Research article

Development and characterization of dual-modified yam (*Dioscorea rotundata*) starch-based films

Germán Narváez-Gómez [a,b], Jorge Figueroa-Flórez [b], Jairo Salcedo-Mendoza [b], Carmen Pérez-Cervera [c], Ricardo Andrade-Pizarro [d,*]

[a] *Master of Agri-Food Sciences, University of Córdoba, Montería, Colombia*
[b] *Department of Agroindustrial Engineering, University of Sucre, Sincelejo, Colombia*
[c] *DANM/ Desarrollo y Aplicación de Nuevos Materiales, Escuela de Ingenierías y Arquitectura, Universidad Pontificia Bolivariana, Montería, Colombia*
[d] *Department of Food Engineering, University of Córdoba, Montería, Colombia*

ARTICLE INFO

ABSTRACT

The current consumer demand for fresh food and the interest in caring for the environment have driven the development of biodegradable film packaging to replace synthetic films to preserve the integrity of food. The objective of this work was to evaluate the effects of starch modifications (oxidized, cross-linked, and dual: oxidized/cross-linked), starch concentration (1 and 2%), and glycerol concentration (5 and 15%) on water vapor permeability (WVP), mechanical properties (tensile strength and elongation), optical, and structural properties of films based on "hawthorn" yam starch. The WVP of the films was 4.4×10^{-10} to 1.5×10^{-9} g/m*s*Pa, where the films with oxidized yam starch showed a 58.04% reduction concerning the native starch. The tensile strength of oxidized yam starch films showed a decrease of 17.51% with an increase in glycerol concentration. For the 1% starch concentration, elongation increased by 17.03% when the glycerol concentration was increased from 5 to 15%. Modification of starch, starch concentration, and glycerol have a significant effect on the barrier, mechanical, physical, and structural properties of films made with yam starch, where films made with oxidized yam starches at a concentration of 1% starch and 5% glycerol showed the best responses of the properties evaluated.

1. Introduction

Edible films offer an alternative method of food preservation. Biodegradable materials are used in their elaboration to mitigate the environmental pollution caused by the large quantity of synthetic or petroleum-derived packaging and containers. The materials used in the production of edible films and coatings are proteins, lipids, and polysaccharides. One of the most widely used biopolymers is starch, which has the advantage of being odorless, colorless, and presenting a high barrier to gases [1, 2, 3].

Starch is composed of amylose (linear) and amylopectin (branched), whose composition varies according to the biological source. The amylose/amylopectin ratio defines the functional properties of starches. Gelling temperature, paste viscosity, and gel formation are associated with amylose, while retrogradation is associated with amylopectin. The amylose/amylopectin ratio provides specific properties for the development of edible films, amylose being the most relevant one [4]. Yam starches have a higher amylose content (29–40.75%) than potato, rice, and cassava starches [5, 6].

Native starch-based edible films have limitations due to their poor water vapor barrier, low flexibility, cracking, and decreased wettability [7, 8]. To overcome the deficiencies presented by native starches, chemical modifications can be made (oxidized, hydroxypropyl, cross-linked, and a combination of these) that can improve the barrier properties and mixed with plasticizers such as glycerol, mechanical properties and appearance, such as color, can be improved [5, 7, 9, 10].

Edible films made from hydroxypropyl starches of cassava and potato, as well as phosphate yam starch plasticized with glycerol, tend to decrease water vapor permeability and increase their percentage of elongation and fracture stress in comparison to those made from native starches [11, 12]. Potato and banana oxidized starch films plasticized with glycerol show differences in the behavior of their mechanical and barrier properties; while in oxidized potato starch films the water vapor permeability and fracture stress decrease, in those made from oxidized banana starch, these properties increase [13].

---

* Corresponding author.
E-mail address: rdandrade@correo.unicordoba.edu.co (R. Andrade-Pizarro).

To further improve the properties of biodegradable films, dual modification of starches has been introduced. It has been found that films obtained with doubly modified starches, such as those made from rice starch (hydroxypropylation-crosslinking) [14], cassava starch (crosslinking-oxidation and oxidation-crosslinking) [15], potato starch (acetylation-crosslinking) [16], maize starch (debranching - hydroxypropylation) [17], sweet potato (crosslinking-hydroxypropylation) [18], and achira starch (acid hydrolyzation-succinylation) [19] show better behavior in some properties, presenting a decrease in water vapor permeability and an increase in the percentage of elongation and fracture stress in comparison to films made from single-modified starches. Besides, filmogenic solutions of dual-modified starches from potato and oats, as well as rice and elephant foot yam (*Amorphophallus paeoniifolius*) exhibit reduced viscosity, retrogradation, increased solubility, stability, and clarity of the pastes [14, 20, 21].

The properties of edible films made from starches are determined by many aspects including the type of starch modification, the concentration of modifying agents, as well as the source of the starch used. Therefore, this work aimed to evaluate the barrier, mechanical, optical (color and opacity), and structural (FTIR) properties of films made with double modified yam starch and plasticized with glycerol.

2. Materials and methods

2.1. Raw materials

"Hawthorn" yam (*Dioscorea rotundata*) from the farm "El Raicero" (Corozal, Sucre, Colombia) was used. Yams were selected with a good physiological and microbiological condition. Analytical grade glycerol, sodium hypochlorite (NaOCl), and sodium trimethaphosphate (STMP) were used.

2.2. Extraction of starch

The process of extraction of starch from yam was carried out following the procedure described by Fu et al. [22], using a system of mucilage separation and starch extraction on a pilot scale, in which phase separation occurs due to the injection of air and the subsequent generation of mucilage-laden bubbles, thus allowing native starch to be obtained. The starch was dried in a forced convection oven at 40 °C for 16 h, to a humidity of approximately 10%; it was then macerated and passed through a 100-mesh sieve.

2.3. Modification of yam starch

2.3.1. Oxidized yam starch

The oxidation process of native starch was followed according to Wang and Wang [23] and Dias et al. [24], with some modifications. 200 g of yam starch was dispersed in 500 mL of distilled water in a 2000 mL beaker. The starch dispersion was heated at 35 °C and pH was adjusted to 9.5 using 2 N NaOH. Then NaClO with effective chlorine from 1.5% (relative to dry starch) was slowly added to the suspension and mixed for 30 min. The pH value of the mixture was maintained at 9.5 by adjusting with 1 N NaOH and finally was adjusted to 7 with 1 N H2SO4. The oxidizing process was terminated after 1.5 h. The product was washed several times to remove extra chemicals, then dried in a forced-air oven at 40 °C for 16 h to a water content of 10%, this was macerated and passed through a 100-mesh sieve.

2.3.2. Cross-linked yam starch

The cross-linking of yam starch with sodium trimetaphosphate (STMP) was carried out using the methodology described by Woo and Seib [25] and Liu et al. [26], with some modifications. The maximum concentration of the modifying agent allowed by the FDA for starches intended for the food industry (3% w/w of STMP with respect to the

weight of the starch) was used. A suspension was prepared using 100 g of starch (dry basis) in 150 mL of distilled water, 3% w/w of STMP was added until a complete mixture was achieved. Then the pH was adjusted to 10.0 by the addition of NaOH 1N with constant stirring. The suspension was heated to 45 °C for 3 h maintaining the agitation, the pH was adjusted to 6.5 with a 10% HCl solution. Then the starch was washed four times with an equal volume of distilled water and separated by centrifugation at 3000xg for 5 min. and then dried at 50 °C for 24 h, macerated, and passed through a 100-mesh sieve.

2.3.3. Dual modified yam starch

The dual modification of yam starch was carried out by first oxidation of native yam starch followed by cross-linking, according to the methodology described above.

2.4. Preparation of yam starch-based films

The filmogenic solutions were prepared according to the methodology described by [13], with some modifications. The amount of each type of starch (1 and 2%) and glycerol (5 and 15% w/w starch base) were added to 500mL of distilled water according to the experimental design. The suspensions were heated at 90 °C for 5 min until complete gelatinization of starch. The edible films were made by the casting method by spreading 60 g of the filmogenic solutions on square Teflon coated molds of approximately 210 cm^2 and then dried at a temperature of 25 °C for 24 h and stored in a desiccator at 25 °C and relative humidity of 52% for 48 h for further analysis.

2.5. Characterization of yam starch films

2.5.1. Film thickness

The thickness of the film samples was measured with a precision digital micrometer with an accuracy of 0.01 mm. Mean thickness values for each sample were calculated and used in water vapor permeability (WVP) and tensile strength (TS) calculations.

2.5.2. Optical properties of films

2.5.2.1. Color parameter. The color of the films was determined using a colorimeter (KONICA Minolta, Japan), and the D65 (daylight) CIELab scale was used to determine the parameters L* (L, from black (0) to white (100)), a* (a, from green (-128) to red (127)), and b* b, from blue (-128) to yellow (127)). The color of the film was expressed as the color difference (ΔE*) according to Eq. (1).

$$\Delta E = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \tag{1}$$

where ΔL*, Δa*, and Δb* are the differences between the sample color parameter and the white plate color standard (L* = 94.8, a* = -0.78, b* = 1.43), which is used as the background for determining the color film.

2.5.2.2. Opacity (%). Film opacity was determined according to ASTM D523 (1999). Opacity was calculated as the relationship between the opacity of the film superposed on the black standard (Op$_b$) and the film superposed on the white standard, Op$_w$ (Eq. 2).

$$Op_f = \frac{Op_b}{Op_w} \times 100 \tag{2}$$

2.5.3. Fourier Transform Infrared Spectroscopy, FTIR

The yam starch films were scanned in an infrared spectrometer (FTIR THERMO, Model NICOLE IS 5). The samples were measured in a glass cell with ZnSe. The spectra were performed in the regions 4000–400 cm^{-1}. The films were conditioned in a dryer with silica gel for 7 days at

room temperature. The crystalline and amorphous areas were determined by processing the spectra with the Omnic 9 program.

2.5.4. Mechanical properties of the films

An Instron Universal Testing Machine (Model 3400, Instron Corporation, Canton, MA, USA) was used to assess the mechanical properties of the film. The mechanical properties of the films were evaluated by determining the tensile strength (TS) and elongation at break (%). Before testing, films were conditioned for 4 days at 55% RH (saturated potassium carbonate solution), and 22 °C. Films were cut into 25 mm wide and 100 mm lengthwise strips. Film strips were then held between two clamps of the universal testing machine, with a grip-to-grip separation of 50 mm, and a crosshead speed of 1 mm/s. The TS was calculated by dividing the maximum breaking load by the cross-sectional area of the initial sample. The elongation was calculated by dividing the extension at break of the sample by the initial reference length of the sample and multiplying by 100.

2.5.5. Film barrier properties

Water vapor permeability (WVP) was determined gravimetrically at 22 °C according to the methodology described by Gontard et al. [27], with some modifications. Yam starch films without visual defects (no bubbles or fractures) were selected, cut to a set diameter, and placed in a glass cell containing distilled water. Silicone grease was used to seal the film to the cell. The cells were placed in a desiccator containing silica gel (~0% RH) and kept at 22 °C in a laboratory oven (DiES, model TH53). The cells were weighed on an analytical balance every 2 h for the first 8 h and then at 24 h. The water vapor transmission rate (WVTR) was defined as the slope (S) divided by the transfer area (At) and this was calculated by Eq. (3).

$$WVTR_m = \frac{S}{A_t} \qquad (3)$$

The existence of a layer of stagnant air inside and above the cell generates a significant resistance to water vapor transport; therefore, the WVP value was corrected according to the methodology proposed by Gennadios et al. [28], and this was determined according to Eq. (4).

$$WVP = 1.157 \times 10^{-5} \frac{WVTR_c * L}{\Delta P_a} \qquad (4)$$

where: WVTRc is the corrected water vapor transmission rate, L is the film thickness, ΔPa is the pressure drop between the above and below the film, and 1.157×10^{-5} is the conversion factor of the units.

Table 1. Matrix of factorial experimental design of modified yam starch-based films.

Treatment	Starch type	Yam starch, %	Glycerol, %
T1	Native	1	5
T2	Native	1	15
T3	Native	2	5
T4	Native	2	15
T5	Oxidized	1	5
T6	Oxidized	1	15
T7	Oxidized	2	5
T8	Oxidized	2	15
T9	Cross-linked	1	5
T10	Cross-linked	1	15
T11	Cross-linked	2	5
T12	Cross-linked	2	15
T13	Dual	1	5
T14	Dual	1	15
T15	Dual	2	5
T16	Dual	2	15

2.6. Experimental design and data analysis

The experiment was conducted under a completely randomized design and a $4 \times 2 \times 2$ factorial arrangement structure. The factors evaluated were: type of starch: native, oxidized, cross-linked, and dual-modification (oxidized/cross-linked); starch concentration: 1 and 2%, and glycerol concentration: 5 and 15% based on starch weight (Table 1). To establish whether there is an effect of the independent variables on the dependent variables, an analysis of variance (ANOVA) was applied at a significance level of 5%. Tukey's multiple range test was used to compare mean values, using the free version of the statistical package R 3.2.1. The experiments were performed in triplicate for each treatment.

3. Results and discussion

3.1. Optical properties of films

3.1.1. Film color parameters

Table 2 shows the values of the color parameters of edible films made from native and modified yam starch.

The luminosity (L*) of the yam starch films was between 94 and 95, very close to the values of the standard white plate where the sample was placed (L = 94.8), indicating that yam starch films tend to be transparent. Furthermore, these values are similar to those of oxidized potato starch films, 95.7–97.18 [29], and edible agar-based films reinforced with nano-bacterial cellulose, 96.59–96.94 [30].

The a* color parameter was between 1.17 and 1.41 (Table 2), which indicates that the films have a low intensity of red color, particularly the dual-modified starch (oxidized/cross-linked) which presented the lowest values of this parameter (1.17–1.22). These values are similar to those reported for edible films with tea polyphenols, 0.3–1.5 [31], but higher than the biodegradable films produced from *cordia myxa*, -1.76 and -0.63 [32], and oxidized potato starch films, -5.41 and -5.13 [29], which presented a green color tone. The values for parameter b* were between 6.54 and 7.02 (Table 2) indicating a low intensity of the yellow color shade. These results are similar to those reported for oxidized potato starch films, 7.7–7.23 [29], and edible films based on eggplant flour and corn starch, 7.3–7.9 [33].

The values for total color difference (ΔE*) of films made from native starch and modified yams were in the range of 0.70 and 1.59 (Table 2). These results indicate a clear coloration in all samples evaluated [34]. These values are similar to those obtained in oxidized potato starch films, 0.65–3.09 [29], and edible films based on agar reinforced with nano-bacterial cellulose, 0.29–0.79 [30].

The ANOVA shows that starch concentration (p = 0.001) and starch type (p = 0.0000) significantly affected the color parameter ΔE. The decrease in starch concentration causes a reduction in ΔE of 29.23%, due to the decrease of solids in the film-forming suspension [35]. Films made with dual-modified starch showed the lowest average value (ΔE = 0.88) and a decrease of approximately 25.4% with respect to native starch. This may be due to the effect of the modifying agents (NaOCl and STMP) on the amylose structure, preventing intermolecular or intramolecular association within the starch granules, leading to a light color of the films [35]. The color of the film is one important parameter since it has a direct impact on the appearance of the product and acceptance for consumers.

3.1.2. Opacity (%)

The opacity values (%) of films made with yam starch were between 10.26 and 12.33% (Table 2), which are similar to those reported for films of native wheat starch, 11.46% [36], oxidized potato starch film (11.38–11.93%) [29], and polysaccharide from *Anacardium occidentale* L [37]; but lower than those of modified corn starch films with beeswax (20.81–41.15%) [38], and films based on cassava starch and polyvinyl alcohol (23.8–42.9%) [39]. Opacity showed that starch type (p = 0.0000), starch concentration (p = 0.0000), and interaction between starch type and starch concentration (p =

Table 2. Color parameters of modified yam starch-based films.

Treatment	L*	a*	b*	ΔE*	Opacity, %
T1	94.46 ± 0.02[abcd]	1.37 ± 0.03[fg]	6.54 ± 0.05[a]	1.22 ± 0.02[bcdef]	10.26 ± 0.32[a]
T2	94.64 ± 0.11[bcde]	1.41 ± 0.02[g]	6.54 ± 0.05[a]	1.38 ± 0.09[cdef]	10.33 ± 0.25[ab]
T3	94.40 ± 0.03[abcd]	1.34 ± 0.02[defg]	6.94 ± 0.04[b]	1.03 ± 0.06[abcde]	12.33 ± 0.47[e]
T4	94.47 ± 0.06[abcd]	1.32 ± 0.02[def]	6.99 ± 0.04[b]	1.07 ± 0.06[abcde]	12.33 ± 0.51[e]
T5	94.79 ± 0.05[cde]	1.31 ± 0.02[cdef]	6.93 ± 0.01[b]	1.43 ± 0.07[ef]	10.60 ± 0.26[ab]
T6	94.68 ± 0.12[cde]	1.36 ± 0.02[efg]	7.01 ± 0.11[b]	1.28 ± 0.12[bcdef]	10.63 ± 0.15[ab]
T7	94.24 ± 0.08[ab]	1.28 ± 0.04[bcde]	6.98 ± 0.02[b]	0.86 ± 0.07[ab]	12.1 ± 0.36[de]
T8	94.37 ± 0.09[abc]	1.31 ± 0.02[cdef]	6.93 ± 0.01[b]	0.96 ± 0.08[abc]	12.2 ± 0.34[e]
T9	94.82 ± 0.05[de]	1.31 ± 0.02[cdef]	6.91 ± 0.04[b]	1.42 ± 0.05[def]	11.13 ± 0.25[abc]
T10	94.99 ± 0.40[e]	1.32 ± 0.02[def]	7.02 ± 0.04[b]	1.59 ± 0.40[f]	11.23 ± 0.15[bcd]
T11	94.36 ± 0.11[abc]	1.31 ± 0.02[cdef]	6.98 ± 0.09[b]	0.97 ± 0.09[abc]	12.0 ± 0.20[cde]
T12	94.47 ± 0.12[abcd]	1.29 ± 0.05[a]	6.96 ± 0.02[b]	1.09 ± 0.15[abcde]	12.23 ± 0.20[e]
T13	94.52 ± 0.19[abcd]	1.22 ± 0.02[ab]	6.94 ± 0.05[b]	1.12 ± 0.18[bcde]	10.9 ± 0.40[ab]
T14	94.40 ± 0.22[abcd]	1.23 ± 0.03[abc]	6.99 ± 0.02[b]	0.99 ± 0.22[abcd]	10.86 ± 0.20[ab]
T15	94.12 ± 0.04[a]	1.17 ± 0.03[a]	7.00 ± 0.07[b]	0.72 ± 0.04[a]	12.23 ± 0.20[e]
T16	94.09 ± 0.10[a]	1.26 ± 0.05[bcd]	7.02 ± 0.07[b]	0.70 ± 0.09[a]	12.1 ± 0.25[de]

Means in the same column with different letter are significantly different (Tukey's test, $p < 0.05$).

0.0260) significantly affect opacity. Increasing starch concentration (1–2%) increased opacity to 12.09, 13.68, and 14.44% for films of double modified, native, and oxidized starches, respectively, while for films of cross-linked starches the increase in opacity was only 8.34%. This increase is because the opacity of yam films depends on their thickness [40], and therefore on the percentage of starch, which led to more opaque films. The opacity of starch films is of great importance when they are used to display the packaged food to the consumer as food surface coatings.

3.2. Fourier Transform Infrared Spectroscopy

Figure 1 shows Fourier Transform Infrared Spectroscopy (FTIR) for yam starch films with different concentrations of starch and glycerol. In the region 500 to 4000 cm^{-1}, a variation in the stretch absorbance signals of all films made with modified starch was shown with respect to those made with native starch. In the region between 3000 and 3900 cm^{-1}, a peak was observed for all starch films indicating stretching in the absorbance of the hydroxyl group, attributable to a higher presence of
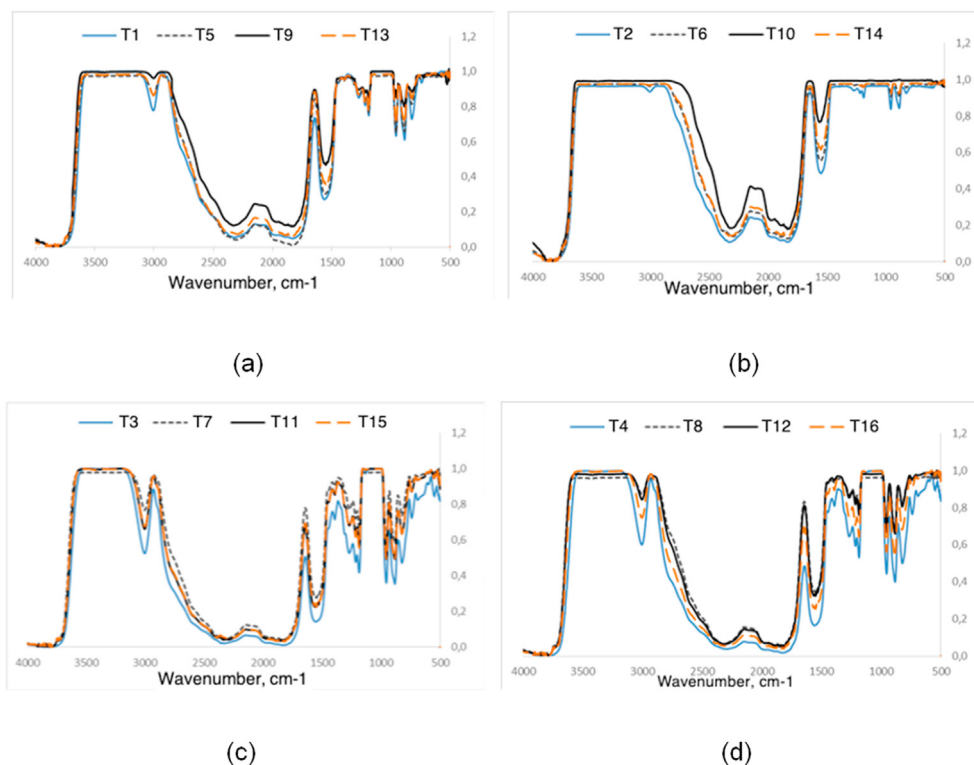

Figure 1. FTIR spectrum of modified yam starch-based films (T1 to T16 represent the different treatments). (a) Films with 1% yam starch and 5% glycerol, (b) films with 1% yam starch and 15% glycerol, (c) films with 2% yam starch and 5% glycerol, (d) films with 2% yam starch and 15% glycerol.

these groups by the incorporation of glycerol and water [41]. A peak located in the 2930 cm^{-1} band is related to the stretching of the C–H group of the glucopyranose ring. For the region between 900 – 1100 cm^{-1}, no differences were found in the position of the peaks (band lengthening) for each of the films made with native, oxidized, cross-linked, and dual-modification (oxidized/cross-linked) starches.

For films made from a mixture of 1% yam starch and 5% glycerol (Figure 1a), characteristic peaks of 932.3, 995.6, and 1151.8 cm^{-1} starch were observed, which can be attributed to the stretching of the C – O bond. The band between 991 and 1158 cm^{-1} can be said to be associated with crystalline and amorphous structures of native starch [42, 43]. Similar results were obtained for films made with banana oxidized starch [44]. For the region between 500 and 900 cm^{-1}, there was a difference with the disappearance of several peaks corresponding to 529 cm^{-1}, 575.6 cm^{-1}, and 582 cm^{-1} for the film of oxidized starch compared to that of native starch. This could be attributed to the formation of new functional groups (carbonyl) by the action of the modifying agent (NaOCl) [44], which is reflected in the increased absorbance for the peaks in the band from 900 – 1200 cm^{-1}.

Crosslinked and dual modified starch films showed the appearance of a peak in the 582.3 cm^{-1} bands attributed to the pyranoid ring [45]. For films made with a mixture of 1% yam starch and 15% glycerol (Figure 1b), changes were observed in the oxidized starch films with respect to native starch, with partial disappearance of the peaks located in the band from 500 – 763 cm^{-1} which could be attributed to increased absorbance of the peaks located in the band from 900 – 1250 cm^{-1} corresponding to the carbonyl group.

On the other hand, the crosslinked and dual modified starch films showed a partial disappearance in the values located in the band between 528 and 763 cm^{-1} with the films of native starch. This could be attributed to the formation of new functional groups by the action of the modifying agent (STMP) [45], which can be reflected in the increase in absorbance in the 1646.6 cm^{-1} bands corresponding to the bending of the O–H and C–O functional groups. Similarly, an increase in absorbance was noted for the values located in the band of 1366.6 cm^{-1}, this change can be attributed to the bending of the C–H functional group that could be generated by the effect of the modifying agent. In the band located between 900 and 1250 cm^{-1}, there was a variation in the signal at 1050 cm^{-1}, which may be caused by the stretching of the C–O–C group. For the double modified starch-based films, a change was noted in the region around 567.7 cm^{-1}, this value could be assigned to the vibration generated by the glucopyranose ring [45].

For the films made with a mixture of 2% oxidized and oxidized/cross-linked starch with 5 (Figure 1c) and 15% glycerol (Figure 1d), an increase in the absorbance values was observed in the peaks located in the wavelength of 3000 to 3900cm^{-1}, the peaks in the band of 2930, 1645, 1382 cm^{-1}, and the peaks located along with the band of 1250 to 500cm^{-1}, generated by the modifying agents (NaOCl and STMP). Also, the cross-linked starch films showed the highest values of absorbency along with the entire band from 3900 to 500cm^{-1}. Likewise, a disappearance of the characteristic peaks of starch in the region of the fingerprint (1250–500 cm^{-1}) was observed, this can be associated with the concentrations of starch and glycerol used for the treatments that correspond to the highest levels of both factors.

3.3. Mechanical properties of the films

Table 3 shows the tensile strength and elongation values of films made from yam starch. Tensile strength is between 2.18 and 6.09 MPa, while elongation is between 8.49 and 16.62%. These values are similar to those reported for sorghum-based [8], and dual-modified films and dual-modified corn starch-based films [17].

The ANOVA shows that starch type (p = 0.0000), starch concentration (p = 0.0000), glycerol concentration (p = 0.0000), and the interaction starch type–glycerol concentration (p = 0.0025) significantly affected the tensile strength of yam starch films. An increase in starch

concentration results in a 13.76% increase in tensile strength. This is because a higher concentration of solids generates a greater thickness of the film and therefore more strength is needed to break it.

An increase in the glycerol concentration produces a reduction in the tensile strength for starch films, which depends on the type of starch used. For cross-linked yam starch films this decrease was 3.15%, dual modified (oxidized/cross-linked) and native yam starch films were between 9.46 and 9.9%, while for oxidized yam starch films the reduction in tensile strength was 17.51%. This reduction in the oxidized starch films could be because during the processing of the films the crystalline structure of the starch was destroyed mainly by the high temperature and the shear force, becoming an amorphous phase that favors the penetration of glycerol (plasticizer) into the matrix [46].

The reduction in the tensile strength values of yam starch films with the increase of glycerol is because the plasticizer interferes in the association of the polymer chain facilitating its sliding and improving its flexibility as it decreases the rigidity of the net, producing a less ordered film structure and increasing the movement capacity. Furthermore, the addition of glycerol tends to provide additional water to the matrix due to its hygroscopic nature [47]. Similar results were obtained in films with pre-gelatinized corn starch [48].

The analysis of variance shows that the factors studied and the interaction starch concentration–glycerol concentration (p = 0.0034) significantly affected the elongation (%) of yam starch films. For films made with modified starches, there is a percentage of elongation that varies between 10.38 and 11.38%, while for native starch the value was 14.3%. The effect of the type of starch on elongation for modified starch films could be due to the incorporation and formation of functional groups. By analyzing the interaction, it can be established that for a low level starch concentration (1%), elongation of films made with yam starch has an increase of 17.03% when the glycerol concentration increases from 5 to 15%, while the same increase in glycerol concentration causes an increase of only 11.93% for a high level (2%) starch concentration. This could be because an increase in starch concentration generates a decrease in the interactions between starch and glycerol, making them more rigid [49].

3.4. Water vapor permeability

Table 4 shows the values for water vapor transfer rate (WVTR) and water vapor permeability (WVP). The average values of the measured water vapor transfer rate (WVTRm) and the corrected water vapor

Table 3. Tensile strength and elongation (%) of modified yam starch-based films.

Treatment	Tensile strength, MPa	Elongation, %
T1	2.52 ± 0.24^{ab}	13.91 ± 0.31^{h}
T2	2.21 ± 0.29^{a}	16.62 ± 0.65^{i}
T3	2.93 ± 0.12^{b}	13.02 ± 0.22^{gh}
T4	2.70 ± 0.22^{b}	13.88 ± 0.22^{h}
T5	5.42 ± 0.17^{g}	11.55 ± 0.19^{def}
T6	4.17 ± 0.24^{c}	13.33 ± 0.30^{gh}
T7	5.60 ± 0.29^{gh}	9.94 ± 0.31^{bc}
T8	4.92 ± 0.29^{de}	10.72 ± 0.42^{cd}
T9	5.64 ± 0.26^{gh}	10.36 ± 0.69^{bcd}
T10	5.39 ± 0.21^{fg}	12.41 ± 0.41^{efg}
T11	6.09 ± 0.31^{i}	8.49 ± 0.39^{a}
T12	5.97 ± 0.26^{hi}	10.25 ± 0.51^{bcd}
T13	4.98 ± 0.29^{ef}	11.19 ± 0.43^{cde}
T14	4.53 ± 0.26^{cd}	12.66 ± 0.47^{fgh}
T15	6.01 ± 0.24^{hi}	9.10 ± 0.15^{ab}
T16	5.42 ± 0.26^{g}	10.55 ± 0.71^{cd}

Means in the same column with different letter are significantly different (Tukey's test, p < 0.05).

Table 4. Water vapor permeability of modified yam starch-based films.

Trat.	WVTRm, g/m^2*día	WVTRc, g/m^2*día	Error, %	Thickness, μm	WVP, 10^{-10} (g/m*s*Pa)
T1	1080	2392.6	54.9	33 ± 0.84[fg]	9.16 ± 1.24[ef]
T2	877	1534.5	42.8	34 ± 0.94[gh]	6.63 ± 0.40[bcd]
T3	1080	2272.5	52.6	58 ± 0.70[b]	7.50 ± 0.43[bcd]
T4	1220	3219.0	62.2	60 ± 1.10[bc]	12.57 ± 0.47[fg]
T5	783	1298.3	39.7	36 ± 0.14[ef]	4.50 ± 0.62[a]
T6	949	1821.3	47.8	28 ± 0.58[a]	5.00 ± 0.26[ab]
T7	899	1628.9	44.8	62 ± 0.92[h]	10.26 ± 1.04[ef]
T8	1010	1991.3	49.1	55 ± 0.12[cd]	6.26 ± 0.25[bc]
T9	933	1699.3	45.1	35 ± 0.97[g]	6.78 ± 0.63[bcd]
T10	1210	3078.7	60.7	37 ± 0.43[j]	5.24 ± 0.21[ab]
T11	899	1648.1	45.4	59 ± 1.59[bc]	15.09 ± 0.33[g]
T12	1110	2435.7	54.3	98 ± 5.06[d]	14.07 ± 1.33[g]
T13	1050	2257.7	53.4	35 ± 1.05[i]	9.10 ± 0.97[ef]
T14	1100	2413.7	54.3	33 ± 0.86[e]	8.55 ± 1.64[cde]
T15	1190	3007.6	60.4	67 ± 0.72[bcd]	13.60 ± 1.09[g]
T16	1200	3004.2	60.1	55 ± 0.40[b]	10.61 ± 0.59[ef]

Means in the same column with different letter are significantly different (Tukey's test, p < 0.05).

transfer rate (WVTRc) show an error ranging from 39.7 to 62.2%. High error rates may be associated with the height of the air space within the capsule used for the permeability measurement. The higher the WVP rate through a film, the more important the air space resistance is, and the greater the error produced. The WVP of yam starch films was between 4.5×10^{-10} and 1.5×10^{-9} g/m*s*Pa, which is lower than reported for single and dual modified sorghum starch films of $1.1–2.5 \times 10^{-9}$ g/m*s*Pa [8], but higher than those reported for dual-modified corn starch films of 0.78–1.05 g*mm/m^2*h*kPa ($2.1–2.9 \times 10^{-10}$ g/m*s*Pa) [17], dual-modified cassava starch of 15.95–22.19 g*mm/m^2*day*kPa ($1.84–2.57 \times 10^{-10}$ g/m*s*Pa) [15], dual-modified rice starch films, 1.62–1.83 g*mm/m^2*day*kPa ($1.88–2.12 \times 10^{-11}$ g/m*s*Pa) [14], and films made from native and modified cush-cush yam and cassava starch ($1.8–3 \times 10^{-11}$ g/m*s*Pa) [50]. It should be noted that several of these studies do not report the correction of water vapor permeability due to stagnant air in the cell, which is about 50%.

The ANOVA shows that starch type (p = 0.0000), starch concentration (p = 0.0000), starch type–starch concentration interaction (p = 0.0000) and starch type–glycerol concentration interaction (p = 0.0015) significantly affected the WVP of yam starch films. The water vapor permeability of films was in the order of oxidized starch film < native starch film = cross-linked starch film = dual-modified starch film. The oxidation reduced the WVP of yam starch film by 51.5% compared to native starch film when 1% starch was used. These results were similar to those reported for the oxidized starch film from cassava [15] and oxidized starch film from sorghum [51]. The changes in water affinity resulting from starch oxidation can be explained by a replacement of hydrophilic hydroxyl groups by more hydrophobic aldehyde groups; therefore, the capacity of the film to absorb water vapor for oxidized starch film was reduced [15, 52].

An increase in starch concentration produces an increase in WVP of about 25% in native and dual modified starch films, while for cross-linked and oxidized starch films, the increase was about 50%. The increase in WVP with starch concentration has been reported for films made from native and modified sorghum starch [51]. This increase in WVP is related to the increase in film thickness [40, 53]. When the starch–glycerol concentration interaction is analyzed, when going from low (5%) to high (15%) in the glycerol concentration, there was a decrease in the WVP of about 15%, for dual starch films (oxidized/cross-linked), while for films of native starch it presented an increase of 13%. The increase in WVP of native yam starch films is because as the concentration of glycerol increases, the permeability also increases

due to the high degree of hygroscopicity of glycerol [54], in addition to the fact that the OH polar groups along the plasticizer chain develop hydrogen bridges between starch and glycerol [55]. While the reduction in WVP values of modified starch films is due to the incorporation of phosphate groups and the formation of carboxyl and carbonyl groups, they seek to replace functional OH groups by making the modified yam starch films less related to water molecules [23, 29, 56].

4. Conclusion

The type of starch, starch concentration, and glycerol concentration have a significant effect on the color, structural, mechanical, and water vapor permeability properties of films made from modified and native yam starches. Films made with native and modified yam starches show differences in the FTIR, due to the formation or incorporation of functional groups in different ways according to the type of modification and starch concentration used. The tensile strength of films made with native yam starches and modified with glycerol is reduced as the concentration of glycerol is increased because it interferes with the starch chains causing a decrease in the rigidity of the films which allows them to increase elongation. The water vapor permeability of edible films is affected by the relationship between starch modification, starch concentration, and glycerol concentration. A lower concentration of oxidized starch and glycerol causes the formation of functional groups that have no affinity with water, allowing a reduction in water vapor permeability, which is essential for food preservation.

Declarations

Author contribution statement

Germán Narváez-Gómez: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Jorge Figueroa-Flórez: Performed the experiments.

Jairo Salcedo-Mendoza: Contributed reagents, materials, analysis tools or data.

Carmen Pérez-Cervera: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ricardo Andrade-Pizarro: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

[1] S. Mali, M.V.E. Grossmann, M.A. García, M.N. Martino, N.E. Zaritzky, Mechanical and thermal properties of yam starch films, Food Hydrocoll. 19 (2005) 157–164.

[2] P. Cazón, G. Velazquez, J.A. Ramírez, M. Vázquez, Polysaccharide-based films and coatings for food packaging: a review, Food Hydrocoll. 68 (2017) 136–148.

[3] S.L.M. El Halal, R. Colussi, V.G. Deon, V.Z. Pinto, F.A. Villanova, N.L.V. Carreño, A.R.G. Dias, E. da R. Zavareze, Films based on oxidized starch and cellulose from barley, Carbohydr. Polym. 133 (2015) 644–653.

[4] C.A. Romero-Bastida, L.A. Bello-Pérez, M.A. García, M.N. Martino, J. Solorza-Feria, N.E. Zaritzky, Physicochemical and microstructural characterization of films prepared by thermal and cold gelatinization from non-conventional sources of starches, Carbohydr. Polym. 60 (2005) 235–244.

[5] S. Mali, M.V.E. Grossmann, M.A. García, M.N. Martino, N.E. Zaritzky, Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources, J. Food Eng. 75 (2006) 453–460.

[6] J. Zou, M. Xu, L. Wen, B. Yang, Structure and physicochemical properties of native starch and resistant starch in Chinese yam (Dioscorea opposita Thunb.), Carbohydr. Polym. 237 (2020) 116188.

[7] M. Rodríguez, J. Osés, K. Ziani, J.I. Maté, Combined effect of plasticizers and surfactants on the physical properties of starch based edible films, Food Res. Int. 39 (2006) 840–846.

[8] S. Mehboob, T.M. Ali, M. Sheikh, A. Hasnain, Effects of cross linking and/or acetylation on sorghum starch and film characteristics, Int. J. Biol. Macromol. 155 (2020) 786–794.

[9] S. Punia, K.S. Sandhu, S.B. Dhull, M. Kaur, Dynamic, shear and pasting behaviour of native and octenyl succinic anhydride (OSA) modified wheat starch and their utilization in preparation of edible films, Int. J. Biol. Macromol. 133 (2019) 110–116.

[10] J. Colivet, R.A. Carvalho, Hydrophilicity and physicochemical properties of chemically modified cassava starch films, Ind. Crop. Prod. 95 (2017) 599–607.

[11] A. Jansson, L. Järnström, Barrier and mechanical properties of modified starches, Cellulose 12 (2005) 423–433.

[12] T.J. Gutiérrez, N.J. Morales, M.S. Tapia, E. Pérez, L. Famá, Corn starch 80:20 "waxy":regular, "native" and phosphated, as bio-matrixes for edible films, Procedia Mater. Sci. 8 (2015) 304–310.

[13] L.M. Fonseca, J.R. Gonçalves, S.L.M. El Halal, V.Z. Pinto, A.R.G. Dias, A.C. Jacques, E. da R. Zavareze, Oxidation of potato starch with different sodium hypochlorite concentrations and its effect on biodegradable films, LWT - Food Sci. Technol. 60 (2015) 714–720.

[14] T. Woggum, P. Sirivongpaisal, T. Wittaya, Properties and characteristics of dual-modified rice starch based biodegradable films, Int. J. Biol. Macromol. 67 (2014) 490–502.

[15] Y. Tanetrungroj, J. Prachayawarakorn, Effect of dual modification on properties of biodegradable crosslinked-oxidized starch and oxidized-crosslinked starch films, Int. J. Biol. Macromol. 120 (2018) 1240–1246.

[16] R.A. González-Soto, M.C. Núñez-Santiago, L.A. Bello-Pérez, Preparation and partial characterization of films made with dual-modified (acetylation and crosslinking) potato starch, J. Sci. Food Agric. 99 (2019) 3134–3141.

[17] X. Hu, X. Jia, C. Zhi, Z. Jin, M. Miao, Improving properties of normal maize starch films using dual-modification: combination treatment of debranching and hydroxypropylation, Int. J. Biol. Macromol. 130 (2019) 197–202.

[18] W.R. Saman, I. Yuliasih, Sugiarto, Dual modification of sweet potato crosslinking-hydroxypropylation as biodegradable film materials, IOP Conf. Ser. Earth Environ. Sci. 399 (2019) 012060.

[19] Z.E. Cabrera Canales, M.L. Rodríguez Marín, C.A. Gómez Aldapa, G. Méndez Montealvo, M. Chávez Gutiérrez, G. Velazquez, Effect of dual chemical modification on the properties of biodegradable films from achira starch, J. Appl. Polym. Sci. 137 (45) (2020), 49411.

[20] S. Sukhija, S. Singh, C.S. Riar, Effect of oxidation, cross-linking and dual modification on physicochemical, crystallinity, morphological, pasting and thermal characteristics of elephant foot yam (Amorphophallus paeoniifolius) starch, Food Hydrocoll 55 (2016) 56–64.

[21] F. Zhou, Q. Liu, H. Zhang, Q. Chen, B. Kong, Potato starch oxidation induced by sodium hypochlorite and its effect on functional properties and digestibility, Int. J. Biol. Macromol. 84 (2016) 410–417.

[22] Y.C. Fu, P.Y. Huang, C.J. Chu, Use of continuous bubble separation process for separating and recovering starch and mucilage from yam (Dioscorea pseudojaponica yamamoto), LWT - Food Sci. Technol. 38 (2005) 735–744.

[23] Y.-J. Wang, L. Wang, Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite, Carbohydr. Polym. 52 (2003) 207–217.

[24] A.R.G. Dias, E. da R. Zavareze, E. Helbig, F.A. de Moura, C.G. Vargas, C.F. Ciacco, Oxidation of fermented cassava starch using hydrogen peroxide, Carbohydr. Polym. 86 (2011) 185–191.

[25] K. Woo, P.A. Seib, Cross-linking of wheat starch and hydroxypropylated wheat starch in alkaline slurry with sodium trimetaphosphate, Carbohydr. Polym. 33 (1997) 263–271.

[26] J. Liu, B. Wang, L. Lin, J. Zhang, W. Liu, J. Xie, Y. Ding, Functional, physicochemical properties and structure of cross-linked oxidized maize starch, Food Hydrocoll. 36 (2014) 45–52.

[27] N. Gontard, S. Guilbert, J.L. Cuq, Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film, J. Food Sci. 58 (1993) 206–211.

[28] A. Gennadios, C.L. Weller, C.H. Gooding, Measurement errors in water vapor permeability of highly permeable, hydrophilic edible films, J. Food Eng. 21 (1994) 395–409.

[29] E. da R. Zavareze, V.Z. Pinto, B. Klein, S.L.M. El Halal, M.C. Elias, C. Prentice-Hernández, A.R.G. Dias, Development of oxidised and heat–moisture treated potato starch film, Food Chem. 132 (2012) 344–350.

[30] X. Wang, C. Guo, W. Hao, N. Ullah, L. Chen, Z. Li, X. Feng, Development and characterization of agar-based edible films reinforced with nano-bacterial cellulose, Int. J. Biol. Macromol. 118 (2018) 722–730.

[31] L. Dou, B. Li, K. Zhang, X. Chu, H. Hou, Physical properties and antioxidant activity of gelatin-sodium alginate edible films with tea polyphenols, Int. J. Biol. Macromol. 118 (2018) 1377–1383.

[32] M.A. Haq, F.A. Jafri, A. Hasnain, Effects of plasticizers on sorption and optical properties of gum cordia based edible film, J. Food Sci. Technol. 53 (2016) 2606–2613.

[33] M. Nouraddini, M. Esmaiili, F. Mohtarami, Development and characterization of edible films based on eggplant flour and corn starch, Int. J. Biol. Macromol. 120 (2018) 1639–1645.

[34] T.J. Gutiérrez, N.J. Morales, E. Pérez, M.S. Tapia, L. Famá, Physico-chemical properties of edible films derived from native and phosphated cush-cush yam and cassava starches, Food Packag. Shelf Life 3 (2015) 1–8.

[35] L.A. Muñoz, J.M. Aguilera, L. Rodriguez-Turienzo, A. Cobos, O. Diaz, Characterization and microstructure of films made from mucilage of Salvia hispanica and whey protein concentrate, J. Food Eng. 111 (2012) 511–518.

[36] F.M. Fakhouri, S. Maria Martelli, L. Canhadas Bertan, F. Yamashita, L.H. Innocentini Mei, F.P. Collares Queiroz, Edible films made from blends of manioc starch and gelatin – influence of different types of plasticizer and different levels of macromolecules on their properties, LWT 49 (2012) 149–154.

[37] M.G. Carneiro-da-Cunha, M.A. Cerqueira, B.W.S. Souza, M.P. Souza, J.A. Teixeira, A.A. Vicente, Physical properties of edible coatings and films made with a polysaccharide from Anacardium occidentale L. J. Food Eng. 95 (2009) 379–385.

[38] T.A. Ochoa, B.E. García-Almendárez, A.A. Reyes, D.M.R. Pastrana, G.F.G. López, O.M. Belloso, C.R. González, Design and characterization of corn starch edible films including beeswax and natural antimicrobials, Food Bioprocess Technol. 10 (2017) 103–114.

[39] J. Zanela, J.B. Olivato, A.P. Dias, M.V.E. Grossmann, F. Yamashita, Mixture design applied for the development of films based on starch, polyvinyl alcohol, and glycerol, J. Appl. Polym. Sci. 132 (43) (2015), 42697.

[40] S. Mali, M.V.E. Grossmann, M.A. García, M.N. Martino, N.E. Zaritzky, Barrier, mechanical and optical properties of plasticized yam starch films, Carbohydr. Polym. 56 (2004) 129–135.

[41] E. Basiak, A. Lenart, F. Debeaufort, How glycerol and water contents affect the structural and functional properties of starch-based edible films, Polymers (Basel) 10 (2018) 412.

[42] O. Sevenou, S.E. Hill, I.A. Farhat, J.R. Mitchell, Organisation of the external region of the starch granule as determined by infrared spectroscopy, Int. J. Biol. Macromol. 31 (2002) 79–85.

[43] J.J.G. van Soest, H. Tournois, D. de Wit, J.F.G. Vliegenthart, Short-range structure in (partially) crystalline potato starch determined with attenuated total reflectance Fourier-transform IR spectroscopy, Carbohydr. Res. 279 (1995) 201–214.

[44] P.B. Zamudio-Flores, A. Vargas-Torres, J. Pérez-González, E. Bosquez-Molina, L.A. Bello-Pérez, Films prepared with oxidized banana starch: mechanical and barrier properties, Starch - Stärke 58 (2006) 274–282.

[45] H. Chi, K. Xu, D. Xue, C. Song, W. Zhang, P. Wang, Synthesis of dodecenyl succinic anhydride (DDSA) corn starch, Food Res. Int. 40 (2007) 232–238.

[46] L. Zhang, W. Xie, X. Zhao, Y. Liu, W. Gao, Study on the morphology, crystalline structure and thermal properties of yellow ginger starch acetates with different degrees of substitution, Thermochim. Acta 495 (2009) 57–62.

[47] S. Mali, L.S. Sakanaka, F. Yamashita, M.V.E. Grossmann, Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect, Carbohydr. Polym. 60 (2005) 283–289.

[48] G. Bonacucina, P. Di Martino, M. Piombetti, A. Colombo, F. Roversi, G.F. Palmieri, Effect of plasticizers on properties of pregelatinised starch acetate (Amprac 01) free films, Int. J. Pharm. 313 (2006) 72–77.

[49] S.P. Miranda, G. Cárdenas, D. López, A. V Lara, C.D.E. Películas, D.E.Q. Compuesto, E.N. Un, S.P. Miranda, G. Cárdenas, D. López, A.V. Lara-sagahon, Comportamiento

de películas de Quitosán compuesto en un modelo de almacenamiento de aguacate 47 (2003) 331–336.

[50] T.J. Gutiérrez, M.S. Tapia, E. Pérez, L. Famá, Structural and mechanical properties of edible films made from native and modified cush-cush yam and cassava starch, Food Hydrocoll. 45 (2015) 211–217.

[51] B. Biduski, F.T. da Silva, W.M. da Silva, S.L. de M. El Halal, V.Z. Pinto, A.R.G. Dias, E. da R. Zavareze, Impact of acid and oxidative modifications, single or dual, of sorghum starch on biodegradable films, Food Chem. 214 (2017) 53–60.

[52] S.-D. Zhang, Y.-R. Zhang, X.-L. Wang, Y.-Z. Wang, High carbonyl content oxidized starch prepared by hydrogen peroxide and its thermoplastic application, Starch - Stärke 61 (2009) 646–655.

[53] B. Cuq, N. Gontard, J.-L. Cuq, S. Guilbert, Functional properties of myofibrillar protein-based biopackaging as affected by film thickness, J. Food Sci. 61 (1996) 580–584.

[54] D. Muscat, B. Adhikari, R. Adhikari, D.S. Chaudhary, Comparative study of film forming behaviour of low and high amylose starches using glycerol and xylitol as plasticizers, J. Food Eng. 109 (2012) 189–201.

[55] L. Yang, A.T. Paulson, Mechanical and water vapour barrier properties of edible gellan films, Food Res. Int. 33 (2000) 563–570.

[56] R.L. Shogren, Rapid preparation of starch esters by high temperature/pressure reaction, Carbohydr. Polym. 52 (2003) 319–326.