



Structural and mechanical properties of edible films made from native and modified cush-cush yam and cassava starch



Tomy J. Gutiérrez^{a,*}, María Soledad Tapia^a, Elevina Pérez^a, Lucía Famá^b

^a Instituto de Ciencia y Tecnología de Alimentos, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 47097, Caracas 1041-A, Venezuela

^b LP&MC, IFIBA-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. 1, Buenos Aires, C1428EHA, Argentina

ARTICLE INFO

Article history:

Received 7 March 2014

Accepted 18 November 2014

Available online 3 December 2014

Keywords:

Starch

Cross-linking

Edible film

Structure

Uniaxial tensile strength

ABSTRACT

Several different hydrocolloids, such as starch, have been proposed as suitable base materials (matrices) for edible films in food packaging. Edible films from native and modified starch plasticized with glycerol were developed. Starches were obtained from dark cush-cush yam (*Dioscorea trifida*) and cassava (*Manihot esculenta* C.) from Venezuela, and chemically modified by cross-linking with sodium trimetaphosphate. The uniaxial tensile, microstructural and barrier properties of the films were then evaluated to determine their potential as a replacement for existing synthetic materials used in the food industry. The structure of the materials showed that the gelatinization process of cush-cush yam films was poorer than that of cassava. The glycerol–starch interaction (glycerol–amylose) was stronger in the films composed of modified starches and was more marked in cassava based films. All the films studied exhibited promising mechanical properties, with those derived from cush-cush yams showing the highest Young's modulus and resistivity values. Cassava based edible films and films derived from modified starch from both sources showed maximum flexibility, reinforcing the idea that the glycerol–starch interactions are stronger in these materials. Crosslinked films tended to be more permeable to water vapor due to their hydrophilic characteristics. The properties observed in these biodegradable materials highlight their potential as food packaging materials, thus enabling the replacement of synthetic materials that contaminate the environment.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Starch stands out as a potential biopolymer matrix for the manufacture of edible plastics due to its ubiquitous, cheap and biodegradable nature. Tropical roots and tubers are valuable sources of amylaceous materials from which starch-based edible films and coatings could be produced. Several studies have focused on the properties and manufacture of starch-based films derived from various botanical sources, showing that roots and tubers are promissory for these purposes (González & Pérez, 2003; Pérez, Borneo, Melito, & Tovar, 1999; Pérez, Gibert, Rolland-Sabaté, et al., 2011; Pérez, Gibert, Sabate, et al., 2011; Pérez, Schultz, & Pacheco, 2005; Pérez, Segovia, Tapia, & Schroeder, 2012; Tapia et al., 2012). In particular, white and purple *Dioscorea trifida* has been reported

as a new waxy yam starch with promising properties (Pérez, Gibert, Sabate, et al., 2011). However, the films made from this starch should be investigated more thoroughly due to its waxy nature (Tapia et al., 2012). Cassava starch has been extensively studied for its renewability, low cost, biodegradability and wide availability (Matos & Pérez, 2003; Pérez, Breene, & Bahanasey, 1998; Sívoli, Pérez, Rodríguez, De Abrisqueta, & Raymúndez, 2005). In recent years native starches from tropical crops have been used to prepare edible films (García, Martino, & Zaritzky, 2000) as coatings for the protection and enhancement of fruit products (Hernández, Emaldi, & Tovar, 2008; Rojas-Graü, Tapia, & Martín-Belloso, 2007). The amylaceous components are naturally packed in crystalline regions to form the granular semi-crystalline structure of the starch. As the waxy starches contain low amylose within the starch granule, this produces a higher relationship of crystallinity between amylopectin and amylose, easily producing a plastic structure.

The modification of starch by cross linking (Matos & Pérez, 2003; Sívoli et al., 2005) can improve the functional properties

* Corresponding author. Tel.: +58 212 7534403; fax: +58 212 7533971.

E-mail addresses: tomy.gutierrez@ciens.ucv.ve, tomy_gutierrez@yahoo.es (T.J. Gutiérrez).

not only of starch, but also of edible starch-based coatings, films and foams. Starch can be chemically modified by cross-linking with sodium trimetaphosphate which improves its functional properties leading to higher paste clarity and consistency, stability during freeze–thaw cycles and the ability to form an emulsion due to its polar nature (Lim & Seib, 1993; Whistler & Paschall, 1967; Wurzburg, 1986). Similarly, cassava starch phosphated has very high viscosity and low cohesiveness (Moorthy, 1994). Despite the large amount of research done on starch based films the ultrastructure and the mechanical properties of cross-linked thermoplastic starch materials has been little studied (Jiménez, Fabra, Talens, & Chiralt, 2012).

The aim of this study was to evaluate the ultrastructure, uniaxial tensile strength, water vapor permeability and color properties of edible films prepared from native and cross-linked cush-cush yam and cassava starches.

2. Experimental

2.1. Materials

Native starch from dark purple cush-cush yam (*D. trifida*) was obtained from a variety from the Venezuelan Amazon ($12 \pm 3\%$ apparent amylose) and cassava starch by extracting the starch from a variety of cassava (*Manihot esculenta* C.) ($21 \pm 3\%$ apparent amylose) on sale at a local market in Caracas, Venezuela (Gutiérrez, Pérez, Guzmán, Tapia, & Famá, 2014). The extraction of the starch from the cush-cush yam and cassava tubers was carried out using the methodology described by Pérez, Bahnassay, and Breene (1993), obtaining in both cases a yield of approximately 30% (Gutiérrez, Pérez, et al., 2014). Modified starches were prepared from native starches by cross-linking method (phosphating of the starches). The apparent amylose content of the modified dark purple cush-cush yam starch and the cassava starch was $\sim 11\%$ and $\sim 22\%$, respectively (Gutiérrez, Pérez, et al., 2014). The degrees of substitution (DS) of the starches were: $0.0006 \pm 0.0002\%$ and $0.017 \pm 0.009\%$ for native and modified dark purple cush-cush yam, respectively, and $0.0015 \pm 0.0002\%$ and $0.008 \pm 0.001\%$ for native and modified cassava, respectively (Gutiérrez, Pérez, et al., 2014). Glycerol from Prolabo, Sweden, was employed as plasticizer in the formation of the films.

2.2. Preparation of the modified starch

Phosphate-modified starch was prepared using sodium trimetaphosphate, following the methodology described by Kerr & Cleveland (1959), modified by Lim and Seib (1993). The maximum concentration of the modifying agent allowed by the FDA for starches intended for the food industry (3% W/W of sodium trimetaphosphate with respect to the weight of the starch) was used.

2.3. Film formation

Edible films were prepared from a film forming solution (FFS) made by mixing 2% W/V of starch and 1.9% W/V of glycerol in distilled water. The solution was then heated in a water bath with constant stirring at 90°C for 30 min to ensure starch gelatinization (Hernández, 2006). The gel was then degassed by applying a vacuum for 30 min, poured into stainless steel trays 40×30 cm, and dried in a Mitchell dehydrator (Model 645 159) for 24 h at 45°C . The resulting thermoplastic starch films: native cush-cush yam (TPS-NY), phosphated cush-cush yam (TPS-PY), native cassava (TPS-NC) and phosphated cassava (TPS-PC) were then carefully removed from the casting molds. Before characterization, the films were conditioned at $\sim 57\%$ relative humidity (RH) for a week.

2.4. Characterization

2.4.1. Light microscopy

Small pieces ($2\text{ cm} \times 1\text{ cm}$) of each film were mounted onto glass slides, examined using an optical microscope (Olympus BX60M, Japan) at $50\times$ and photographed with a video camera imaging system (Olympus IMAGE RS). At least three microphotographs of each system were taken.

2.4.2. Scanning electron microscopy (SEM)

The films were cryofractured by immersion in liquid nitrogen, mounted on bronze stubs and sputter coated with a thin layer of gold for 35 s. The fracture surface of each material was then analyzed using a Philips XL series 30 (Holanda) scanning electron microscopy (SEM).

2.4.3. Determination of film thickness

The thickness (e) of the films was determined following the methodology described by Rojas-Graü, Raybaudi-Massilia, et al. (2007) and Rojas-Graü, Tapia, Rodríguez, Carmona, and Martín-Belloso (2007). A digital micrometer (Micromaster[®]) with an accuracy of 0.001 mm was used. For each film a total of 18 measurements were taken at several randomly selected points and the mean thickness calculated. The results were used for the determination of water vapor permeability and tensile properties.

2.4.4. Water vapor permeability (WVP)

Water vapor permeability was measured following ASTM E96-00 (1999) and the correction method described by Gennadios, Weller, and Gooding (1994). Circular acrylic cells containing pieces of film (exposed area $\sim 15.2\text{ cm}^2$) were introduced into desiccators at ambient temperature with a relative humidity of $\sim 50\%$.

WVP values were calculated as:

$$\text{WVP} = \frac{G \times e}{S \times \text{RH} \times t \times A} \quad (1)$$

where G is the mass gained, e the thickness of the film, S the saturated vapor pressure at 25°C , RH the relative humidity, t time, and A the exposed area of each sample.

All assays were performed in triplicate, reporting the average and standard error in each case.

2.4.5. Color

The following color parameters of the films: L^* , (where $L^* = 0$ indicates black and $L^* = 100$ white), a^* (position between red and green) where negative values indicate green while positive values indicate magenta, and b^* (position between yellow and blue) where negative values indicate blue and positive values indicate yellow, were measured according to the standard test method (ASTM D-1925, 1995) using a Macbeth[®] colorimeter (Color-Eye 2445 model, illuminant D65 and 10° observer) standardized with a white reference plate ($L^* = 93.52$, $a^* = -0.81$ and $b^* = 1.58$). Color differences (ΔE), as measured by the magnitude of the resultant vector of the three components: brightness difference, ΔL , red-green chromaticity difference, Δa , and yellow-blue chromaticity difference, Δb (Valencia Rodríguez, 2001), were calculated by the following equation:

$$\Delta E = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2} \quad (2)$$

where $\Delta a = a_i - a$, $\Delta b = b_i - b$, y and $\Delta L = L_i - L$. The index i is the reference value of each parameter.

The yellowness index (YI) which, as its name suggests, determines the degree of yellowness of a substance, was calculated

according to ASTM D-1925 (MacFarlane, MacFarlane, & Billmeyer, 1936), using the CIELAB scale:

$$YI = \frac{100(1277X - 1067Z)}{Y} \quad (3)$$

2.4.6. Uniaxial tensile strength

At least ten pieces of each film, with an effective length of 10 mm and width 0.5 mm, were cut. Tests were performed at ambient temperature (25 °C) with an Instron dynamometer (Instron Ltd., High Wycombe, UK) (5 Lbs) at 0.02 in/s, according to ISO 527-2. The stress-strain behavior of the films was calculated from the force–time curves. Young's modulus (E), maximum stress (σ_m), strain at break (ϵ_b) and toughness (T) were reported.

The elastic modulus was determined from the slope of the linear regression of the stress-strain curves where the maximum stress value is the maximum point of each curve, and the strain at break corresponds to the maximum elongation of the samples before rupture. Toughness was determined as the area under the stress-strain curves.

At least 10 trials for each film system were performed. The mean and standard error are reported. An analysis of variance at a significance level of 5% ($p = 0.05$) was then performed. This is to determine possible statistically significant differences between the results obtained.

3. Results and discussion

3.1. Light microscopy observations

Fig. 1 shows the images of the films observed by optical microscopy. TPS-NY and TPS-PY (Fig. 1 a and b) contained small fragments identified as starch granules that failed to complete

disruption during the heating process, thus suggesting that cushion yam starches need higher temperatures to complete gelatinization (Gutiérrez, Pérez, et al., 2014). This was not observed for cassava starch-films (Fig. 1 c and d) which gelatinized at lower temperatures, completely disrupting the grains (Gutiérrez, Pérez, et al., 2014).

The incomplete disruption of the cushion yam grains resulted in a weaker interaction between the glycerol and starch. In contrast, the glycerol blocked the rearrangement of the starch segments in the cassava films, resulting in a stronger glycerol–starch interaction. The crystalline particles present may act as nuclei for inducing the recrystallization of amylaceous macromolecules during cooling and storage, producing brittle films (García, Famá, Dufresne, Aranguren, & Goyanes, 2009). These results are relevant to the discussion of the mechanical properties of TPS-NY and TPS-PY.

As regards to the phosphated starches, the stronger interaction between the gelatinized starch and the glycerol was observed. This inhibited the re-crystallization of the starch, producing less grainy films (Gutiérrez, 2013).

3.2. Scanning electron microscopy (SEM)

Fig. 2 shows the SEM images of the cryo-fracture surfaces of the different films. It can be seen that the films produced are non-porous. All the systems presented a compact structure, but this was far more marked in the films made from cassava starch (Fig. 2c and d), where the white strokes or lines that divide the dark areas seem to form dark regions closer (Kaláb, 2011). Similar structures have been reported in cassava starch-protein films by Saavedra and Algecira (2010) and by García et al. (2009) in their study of cassava-glycerol films. The pattern is probably produced by the high amount of amylose present in cassava starch systems (Miles, Morris, & Ring, 1985; Miles, Morris, Orford, & Ring, 1985; Noel, Ring, & Whittman, 1992).

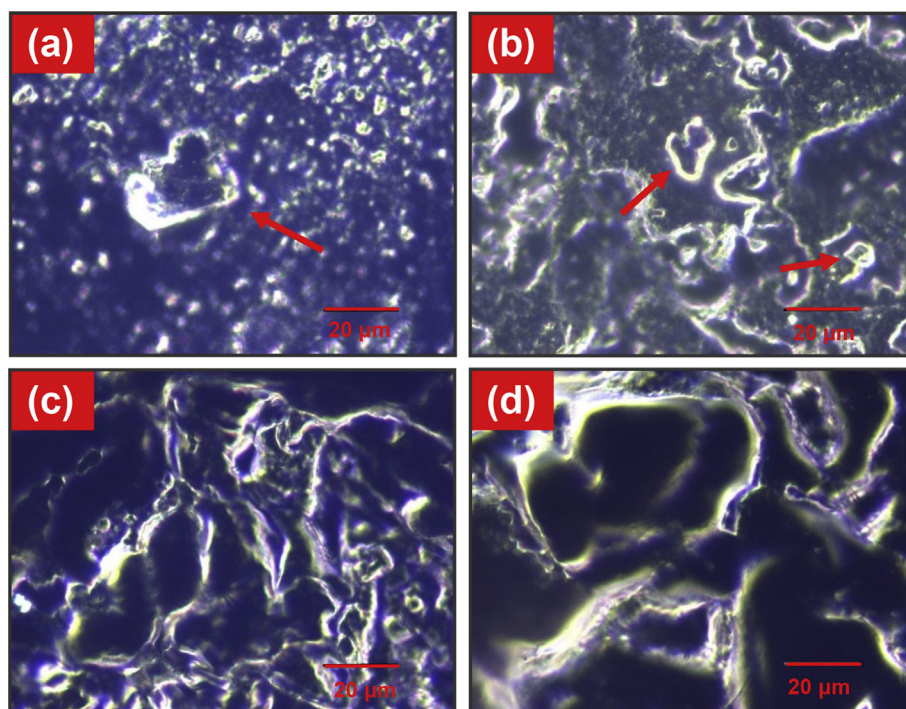


Fig. 1. Optical micrographs of the films based on: (a) native cushion yam (TPS-NY), (b) phosphated cushion yam (TPS-PY), (c) native cassava (TPS-NC) and (d) phosphated cassava (TPS-PC). At 50× of magnification. Red arrows indicate starch granules with incomplete disruption within edible films. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

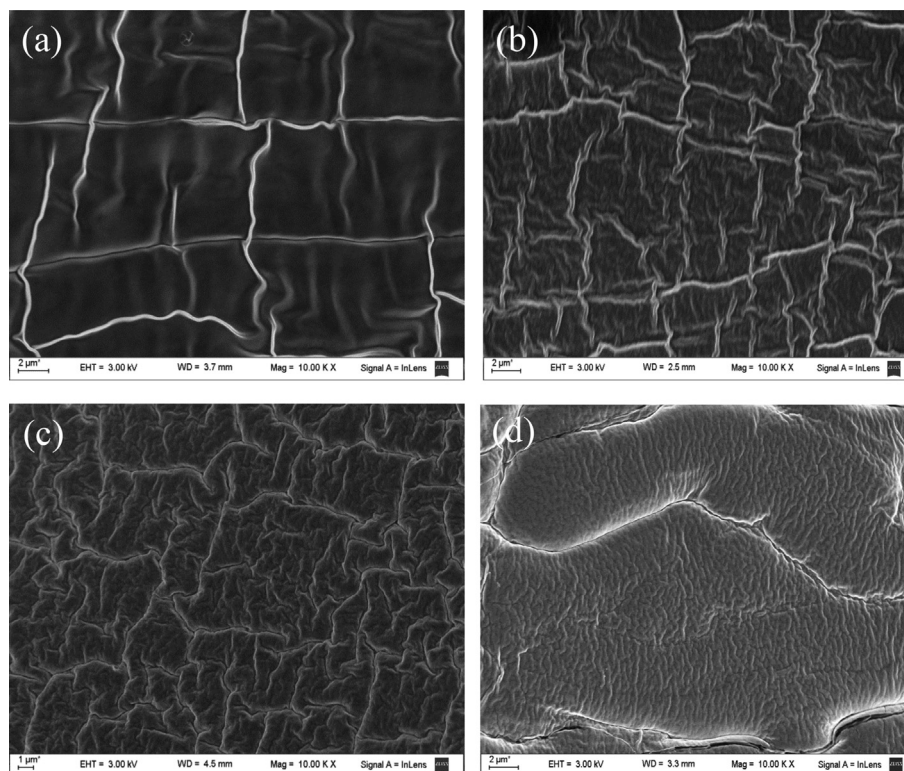


Fig. 2. SEM micrographs of the cryogenic fracture surface of the films based on: (a) native cush-cush yam (TPS-NY), (b) phosphatized cush-cush yam (TPS-PY), (c) native cassava (TPS-NC) and (d) phosphatized cassava (TPS-PC). At 10 k× of magnification.

3.3. Thickness

Thickness is an important characteristic of coatings because it affects barrier properties such as WVP and other gases. As the films studied are hydrophilic, thickness particularly affects water vapor permeability due to differences between the water vapor pressure and the buildup of moisture on the film–air interface (Melián, 2006).

Table 1 shows the thicknesses of the different systems studied. It can be observed that the modified cush-cush yam starch films were ~45% thicker than TPS-NY films. Pérez et al. (2012) reported a significant increase in the thickness of cross-linked starch-based films derived from *D. trifida*. Crosslinking apparently strengthens the internal bonds of the starch grains. The addition of phosphate groups also produces starch granules with a higher molar volume, which is manifested by an increase in their size (Gutiérrez, Pérez, et al., 2014; Sívoli et al., 2005). This factor, together with a greater interaction between the starch and the plasticizer during gelatinization, could result in thicker films (Gutiérrez, Morales, Tapia, Pérez, & Famá, 2014). These interactions appear to become less relevant when the amylose content in the starch is increased,

however, no statistically significant differences were observed in the thicknesses of the systems derived from cassava starch.

Thus, it seems that the high degree of substitution observed for the crosslinked cush-cush yam starch (Gutiérrez, Pérez, et al., 2014) has a positive effect on the glycerol–starch interactions that occur during the gelatinization process.

3.4. Water vapor permeability (WVP)

Water vapor permeability (WVP) is one of the most important properties of edible films, since one of the main functions of food packaging is to prevent or reduce the transfer of moisture from the surrounding environment to the food. WVP can be used to predict the loss or gain of water in the food covered by the film. WVP is affected by numerous factors such as the thickness of the films, a_w , humidity and the relative proportions of the components used in their formulation, among others.

Coatings and edible films made from polysaccharides are characterized by their limited capacity to prevent the transfer of water vapor due to their hydrophilic nature (García, Martino, & Zaritzky, 1998; Kester & Fennema, 1986; Mc Hugh & Krochta, 1994).

Table 1
Thickness (e), water vapor permeability (WVP) and color parameters of the different films.

Parameter	TPS-NY	TPS-PY	TPS-NC	TPS-PC
e (mm)	0.12 ± 0.01^a	0.17 ± 0.02^b	0.17 ± 0.02^b	$0.16 \pm 0.03^{a,b}$
WVP ($\times 10^{-11}$ g/m s Pa)	1.8 ± 0.4^a	$3 \pm 1^{a,b}$	2.1 ± 0.2^a	2.7 ± 0.1^b
L	16.48 ± 0.04^c	19.48 ± 0.03^d	11.0 ± 0.1^b	7.16 ± 0.09^a
a	0.0 ± 0.1^a	-0.1 ± 0.1^a	0.0 ± 0.4^a	-0.3 ± 0.4^a
b	-0.9 ± 0.1^b	-0.7 ± 0.1^b	-2.7 ± 0.3^a	-2.3 ± 0.2^a
Color differences (ΔE)	77.11 ± 0.04^b	74.10 ± 0.03^a	82.7 ± 0.1^c	86.5 ± 0.1^d
Whiteness index (WI)	16.47 ± 0.04^c	19.48 ± 0.03^d	10.9 ± 0.1^b	7.13 ± 0.09^a
Yellow index (YI)	-5.43 ± 0.02^a	-3.82 ± 0.02^b	-20.25 ± 0.02^c	-21.38 ± 0.02^d

Equal letters in the same row indicate no statistically significant differences ($p \leq 0.05$).

The WVP values for the systems studied are given in Table 1. No statistically significant differences ($p \leq 0.05$) were observed between TPS-NY and TPS-PY, however, the films derived from the latter showed slightly higher WVP values. Pérez et al. (2012) found similar patterns in the WVP of films made from native and modified white *D. trifida* starch.

Phosphated cassava starch film showed significantly higher WVP values in compared to films derived from native cassava starch. This effect is probably due to an increase in the acquired hydrophilicity by crosslinking (Gutiérrez, Morales, et al., 2014; Pérez et al., 2012). Considering the hydrophilic nature of these films, it was expected that the water vapor barrier would be weakened in the systems made from modified starches (Gutiérrez, Morales, et al., 2014; Kester & Fennema, 1986; Tapia et al., 2008).

Mali, Grossmann, García, Martino, and Zaritzk (2004) reported that the WVP of films derived from yam starch was affected by their thickness and concentrations of glycerol and starch. Mc Hugh, Avena-Bustillos, and Krochta (1993), studied the effect of thickness on the WVP of hydrophilic films. These authors concluded that an increase in the thickness of the film increases resistance to water transfer and consequently the equilibrium partial pressure of water on the inner surface of the films. Thus, in hydrophilic films water vapor permeability is positively correlated with film thickness, due to the changing conditions in the partial pressure of water vapor on the inside of the films. Thus, the lowest value of WVP observed for TPS-NY films could be explained by the fact that this was the thinnest of the film systems studied.

The water vapor permeability of cush-cush yam films was not significantly different to that of cassava derived films, however, cush-cush yam films tended to be less permeable. García et al. (2009) reported that the WVP of waxy starch films tended to be lower than that of films made from cassava; however, the wide dispersion of their results revealed that any differences were not significant. In our study, despite the fact that there were no significant differences between the thicknesses of TPS-NY and TPS-PC, there was a slight tendency towards an increase in the WVP of thicker edible films.

3.5. Color

Table 1 shows the results of the color parameters of the films studied. The TPS-PY film had a higher value of L compared to that of TPS-NY indicating that it tends to be whiter than the native cush-cush yam film. The opposite was observed for the cassava starch films: TPS-NC films exhibited higher values of L compared to TPS-PC films. However, overall, the lightness values for the systems made from cassava starch were whiter than those made from cush-cush yam starch. Nevertheless, it is important to note that all the films were fairly transparent according to their L values. Kim and Lee (2002) found that crosslinking altered the lightness of potato starch derived films, which is consistent with the findings of the present study.

All the films showed a values of around zero. Despite there being no significant differences observed ($p \leq 0.05$) for this parameter, the films derived from modified starches showed a slight tendency towards negative values, indicating that they tended towards a green color.

The parameter b indicates a tendency towards a blue coloration. This effect was more marked in cassava films (lower negative b values). No significant differences were observed between native and crosslinked starch films ($p \leq 0.05$).

The greatest differences in the color of the films, ΔE , were observed in the films made from cassava starch, reinforcing the idea that these films are whiter. This could be due to the higher amounts

of amylose present in cassava starch compared to yam starch (Gutiérrez, Pérez, et al., 2014).

The results of the yellowness index, YI , were consistent with those of the b parameter, being negative in all cases. The most negative values of YI were obtained for cassava starch films, indicating a lower degree of yellowness of this material.

3.6. Uniaxial tensile strength

The stress-strain curves of each film system studied are shown in Fig. 3. A small linear zone was observed followed by a nonlinear zone until breaking point, regardless of the starch used. A more marked brittle behavior was found for cush-cush yam starch films, accompanied by the highest Young's modulus and maximum stress values (Table 2). Similar results were reported by Tapia et al. (2012) for films made from *D. trifida* white starch. On the other hand, other authors (Alves, Mali, Beleia, & Grossmann, 2007; Lourdin, Valle, & Colonna, 1995) have reported the opposite, concluding that both Young's modulus and tensile strength, increase linearly with the amount of amylose. In our study, the increases in these parameters observed in TPS-NY and TPS-PY could be attributed to the starch grains present in these materials (Fig. 1 a and b). Generally, the permanence of crystalline particles act as nuclei for inducing the recrystallization (retrogradation) of starch macromolecules (Mina, Valadez, Herrera-Franco, & Toledano, 2009) leading to a more fragile material (García et al., 2009). Stiffness caused by retrogradation is a typical phenomenon of moisture plasticization. During gelatinization the water acts as a plasticizer resulting in a weaker glycerol–starch interaction. Gutiérrez (2013) recently reported that starch based films derived from cush-cush yam show moisture plasticization. As mentioned above, glycerol interacts more strongly with cassava than with cush-cush yam starch, probably due to the formation of hydrogen bonds between the glycerol and amylose molecules. This glycerol–amylose interaction would weaken the intra and intermolecular interactions between starch macromolecules leading to an increase in the movement and rearrangement of their chains and thus in the flexibility of TPS-NC and TPS-PC. This results in an increase in the strain at break values of cassava films; while decreased the maximum tensile strength (Hu, Chen, & Gao, 2009).

On the other hand, a stronger glycerol–amylose interaction limits the possible interaction between water and glycerol or starch, enabling that the water vapor to pass more easily through

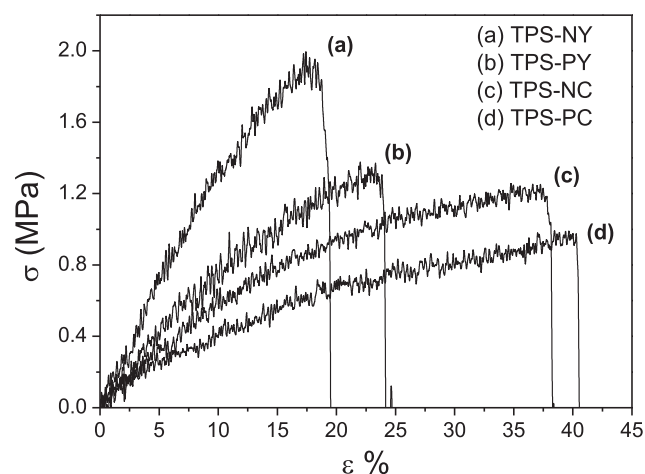


Fig. 3. Stress (σ) – strain (ϵ) curves of the films based on: (a) native cush-cush yam (TPS-NY), (b) phosphatized cush-cush yam (TPS-PY), (c) native cassava (TPS-NC) and (d) phosphatized cassava (TPS-PC).

Table 2

Parameters of the uniaxial tensile strength tests: Young's modulus (E), maximum stress (σ_m), strain at break (ϵ_b) and toughness (T).

Sample	E (MPa)	σ_m (MPa)	ϵ_b (%) [± 2]	T ($\times 10^5$ J/m ³)
TPS-NY	13.9 \pm 0.6 ^d	1.88 \pm 0.08 ^c	19 ^a	2.2 \pm 0.1 ^b
TPS-PY	8.5 \pm 0.7 ^c	1.21 \pm 0.06 ^b	24 ^b	1.9 \pm 0.1 ^a
TPS-NC	6.2 \pm 0.4 ^b	1.16 \pm 0.05 ^b	38 ^c	3.1 \pm 0.2 ^d
TPS-PC	3.9 \pm 0.3 ^a	0.95 \pm 0.02 ^a	40 ^c	2.5 \pm 0.1 ^c

Equal letters in the same column indicate no statistically significant difference ($p \leq 0.05$).

the films. This could explain the tendency of the WVP to increase in cassava starch films (Table 1).

Saavedra and Algecira (2010) proposed that cassava starch-protein films have higher elasticity values due to their more compact structure. This agrees with our results in which the SEM images we obtained for the cassava based films (Fig. 2) correspond to the greater elasticity observed.

The modification of both starches by crosslinking produced stronger hydrogen bonds between the phosphated starch and the plasticizer, thus leading to a decrease in Young's modulus, maximum stress and toughness, and an increase in the strain at break, consequently increasing the elasticity of the films (Table 2). According to Mina et al. (2009), these results indicate that glycerol plays a more effective role during the plasticization of the modified starch than during that of the native starch. This effect was more notable in cush-cush yam films, possibly because the crosslinking of cush-cush yam starch results in a higher degree of substitution than cassava starch (Gutiérrez, Pérez, et al., 2014) producing stronger starch–plasticizer interactions. In cassava films, the strain at break increased slightly in crosslinked starch films, but this difference was not significant ($p \leq 0.05$) (Gutiérrez, Pérez, et al., 2014).

Romero-Bastidas et al. (2005) studied the physicochemical and microstructural characteristics of edible films based on unconventional starch sources (banana, okenia, wild plant and mango). These authors suggested that differences in the structure of the starches due to the source material play an important role in the mechanical properties of coatings, and furthermore, that the smaller the sizes of the starch granules the poorer their physical properties for the manufacture of edible films. This is consistent with previous observations made by these authors of optical micrographs of all the starches used (Gutiérrez, Pérez, et al., 2014).

The mechanical properties of both types of film show that they could both be considered as coatings depending on the particular requirements of the product to be coated. Cush-cush yam starch based materials are recommended for coverings when a greater resistance is needed, and cassava starch based films for more flexible coatings.

4. Conclusions

The effects of different sources of starch and their chemical modification on the structure, tensile strength, water vapor permeability and color properties of biodegradable edible films were investigated.

The structure of films derived from cush-cush yam based films, in contrast to those made from cassava, contained small starch granules indicating that this starch did not have a complete disruption during the heating process, suggesting that cush-cush yam starches require higher temperatures for gelatinization. The incomplete disruption of the cush-cush yam granules resulted in a weaker interaction between the glycerol and the amylose molecules. Modification of the starches by crosslinking resulted in thicker, less grainy films indicating a strengthening of the glycerol–starch interaction.

No holes were observed in any of the films produced, but cush-cush yam systems tended to be less yellow and more transparent.

The water vapor permeability of films made from the cross-linked starches showed a tendency to increase due to their greater hydrophilicity after modification.

Cush-cush yam starch films were found to be brittle compared to cassava-based films, and also showed the highest Young's modulus and maximum stress values. In contrast, a flexible behavior was observed in the cassava films indicating a decrease in the intra and intermolecular interactions between starch macromolecules that increase the movement and rearrangement of their chains. A greater flexibility was also observed in modified starch films compared to native systems, suggesting that crosslinking results in an increase in the number of hydrogen bonds between the phosphate groups of modified starches and glycerol. These findings suggest that films derived from cassava have stronger glycerol–starch interaction that those made from cush-cush yam and that this interaction can be further strengthened by crosslinking.

Finally, the physicochemical properties evaluated in this study demonstrate the high potential of biodegradable films as packaging materials in the food industry, always considering the characteristics of the product to be packaged and the packaging requirements. Cush-cush yam starch based materials are recommended for coatings where greater resistance is required and cassava starch films for more flexible packaging.

Acknowledgements

The authors would like to thank the Fondo Nacional de Ciencia y Tecnología (FONACIT) of the Bolivarian Republic of Venezuela for co-financing this research project (grant S3-2012002114), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET PIP 2011–2014 Project 11220090100699), University of Buenos Aires (2010–2012 Project 20020090300055, UBACYT 2011–2014 Project 20020100100350, UBACYT 2012–2015 Project 20020110200196), PICT-2012-1093, and Dra. Silvia Goyanes.

References

- Alves, V. D., Mali, S., Beleia, A., & Grossmann, M. V. E. (2007). Effect of glycerol and amylose enrichment on cassava starch film properties. *Journal of Food Engineering*, 78, 941–946.
- ASTM. (1999). *Standard methods for water vapor transmission of materials (E96–00) Annual Book of ASTM Standards*. Philadelphia, PA: American Society for Testing and Materials.
- ASTM D-1925. (1995). *Standard test method for yellowness Index of plastics*. Philadelphia: American Society for Testing and Materials.
- García, N. L., Famá, L., Dufresne, A., Aranguren, M., & Goyanes, S. (2009). A comparison between the physico-chemical properties of tuber and cereal starches. *Food Research International*, 42, 976–982.
- García, M. A., Martino, M. N., & Zaritzky, N. E. (1998). Plasticizer effect on starch-based coatings applied to strawberries (*Fragaria ananassa*). *Journal Agriculture Food Chemistry*, 46, 3758–3767.
- García, A., Martino, M. N., & Zaritzky, N. E. (2000). Microstructural characterization of plasticized starch-based films. *Starch/Stärke*, 52(4), S118–S124.
- Gennadios, A., Weller, C. L., & Gooding, C. H. (1994). Measurement errors in water vapor permeability of highly permeable, hydrophilic edible films. *Journal of Food Engineering*, 21, 395–409.
- González, Z., & Pérez, E. (2003). Evaluación fisicoquímica y funcional de almidones de yuca (*Manihot esculenta* Crantz) pregelatinizados y calentados con microondas. *Acta Científica Venezolana*, 54, 127–137.
- Gutiérrez, T. J. (2013). *Propiedades físicas, químicas y microestructurales de películas comestibles a base de almidón de mapuey y yuca*. Trabajo de Grado. Universidad Central de Venezuela.
- Gutiérrez, T. J., Morales, N. J., Tapia, M. S., Pérez, E., & Famá, L. (2014). Corn starch 80: 20 “waxy:regular”, “native” and phosphated, as bio-matrixes for edible films. *Procedia Materials Science* (in press).
- Gutiérrez, T. J., Pérez, E., Guzmán, R., Tapia, M. S., & Famá, L. (2014). Functional properties of native and modified by crosslinking, dark-cush-cush yam and cassava starches. *Journal of Polymer and Biopolymer Physics Chemistry*, 2(1), 1–5.
- Hernández, O. (2006). *Películas y coberturas comestibles a base de diferentes almidones: Digestibilidad in vitro de películas y caracterización física de coberturas*.

- sobre fresas (*Fragaria ananassa*). Tesis de Grado. Universidad Central de Venezuela.
- Hernández, O., Emaldi, U., & Tovar, J. (2008). In vitro digestibility of edible films from various starch sources. *Carbohydrate Polymers*, 71, 648–655.
- Hu, G., Chen, J., & Gao, J. (2009). Preparation and characteristics of oxidized potato starch films. *Carbohydrate Polymers*, 76, 291–298.
- Jiménez, A., Fabra, M. A., Talens, P., & Chiralt, A. (2012). Edible and biodegradable starch films: a review. *Food and Bioprocess Technology*, 5(6), 2058–2076.
- Kaláb, M. (2011). Cheese: Development of structure. SCIMAT 2000–2011 <http://www.magma.ca/~scimat/Cheese.htm>.
- Kerr, R. W., & Cleveland, F. C., Jr (1959). Orthophosphate esters of starch U.S. patent 2,884,413. *Food Packaging and Shelf Life*, 3(2015), 1–8. <http://dx.doi.org/10.1016/j.fpsl.2014.09.002>.
- Kester, J. J., & Fennema, O. (1986). Edible films and coatings: a review. *Food Technology*, 36, 323–329.
- Kim, M., & Lee, S. J. (2002). Characteristics of crosslinked potato starch and starch-filled linear low-density polyethylene films. *Carbohydrate Polymers*, 50, 331–337.
- Lim, S., & Seib, A. P. (1993). Preparation and properties of wheat and corn starch phosphates. *Cereal Chemistry*, 70(2), 137–144.
- Lourdin, D., Valle, G. D., & Colonna, P. (1995). Influence of amylose content on starch films and foams. *Carbohydrate Polymers*, 27, 261–270.
- MacFarlane, D. S., MacFarlane, D. K., & Billmeyer, F. W. (1936). Method and instrument for selecting personal compatible colors. United States Patent 5313267. Available from: <http://www.freepatentsonline.com/5313267.html>.
- Mali, S., Grossmann, M. V., Garcia, M. A., Martino, M. N., & Zaritzky, N. E. (2004). Barrier, mechanical and optical properties of plasticized yam starch films. *Carbohydrate Polymers*, 56, 129–135.
- Matos, M. E., & Pérez, E. (2003). Characterization of native and modified cassava starches by scanning electron microscopy and X-ray diffraction techniques. *Cereal Food World*, 48(2), 78–81.
- Mc Hugh, T. H., Avena-Bustillos, & Krochta, J. M. (1993). Hydrophilic edible films: modified procedure for water vapor permeability and explanation of thickness effects. *Journal of Food Science*, 58(4), 899–903.
- Mc Hugh, T. H., & Krochta, J. M. (1994). Milk-protein-based edible films and coatings. *Food Technology*, 48, 97–103.
- Melián, D. (2006). *Desarrollo de una película comestible funcional a base de gelano incorporando componentes fisiológicamente activos*. Caracas, Venezuela: Universidad Central de Venezuela. Trabajo Especial de Grado.
- Miles, M. J., Morris, V. J., & Ring, S. G. (1985a). Gelation of amylose. *Carbohydrate Research*, 135(2), 257–269.
- Miles, M. J., Morris, V. J., Orford, P. D., & Ring, S. G. (1985b). The roles of amylose and amylopectin in the gelation and retrogradation of starch. *Carbohydrate Research*, 135(2), 271–281.
- Mina, J. H., Valadez, A., Herrera-Franco, P. J., & Toledano, T. (2009). Influencia del tiempo de almacenamiento en las propiedades estructurales de un almidón termoplástico de yuca (TPS). *Ingeniería y Competitividad*, 11(2), 95–106.
- Moorthy, S. N. (1994). Tuber crop starch. In *Tech bulletin series: 18* (p. 40). Kerala, India: Central Tuber Crops Research Institute.
- Noel, T. R., Ring, S. G., & Whittman, M. A. (1992). The structure and gelatinization of starch: a review. *Food Science Technology Today*, 6, 159.
- Pérez, E., Bahnassay, Y., & Breene, W. (1993). A simple laboratory scale method for isolation of amaranthus starch. *Starch/Stärke*, 45(6), 211–214.
- Pérez, E., Breene, W., & Bahanasey, Y. (1998). Variation in the gelatinization profiles of cassava, sagu and arrowroot native starches as measured by different thermal and mechanical methods. *Starch/Stärke*, 50, 70–72.
- Pérez, E. E., Borneo, R., Melito, C. G., & Tovar, J. (1999). Chemical, physical and morphometric properties of peruvian carrot (*Arracacia xanthorrhiza* B.) starch. *Acta Científica Venezolana*, 50, 240–244.
- Pérez, E., Gibert, O., Sabate, A., Jiménez, Y., Sánchez, T., Giraldo, A., et al. (2011). Physicochemical, functional and macromolecular properties of waxy yam starches discovered from "Mapuey" (*Dioscorea trifida*) genotypes in the Venezuelan Amazon. *Journal of Agricultural and Food Chemistry*, 59, 263–273. <http://pubs.acs.org/doi/pdf/10.1021/jf100418r>.
- Pérez, E., Gibert, O., Rolland-Sabaté, A., Segovia, X., Sánchez, T., Reynes, M., et al. (2011). Evaluation of the functional properties of promising *Dioscorea trifida* L waxy starches for food innovation. *International Journal of Carbohydrate Chemistry*, 7. <http://dx.doi.org/10.1155/2011/165638>. Article ID 165638 <http://www.hindawi.com/journals/ijcc/2011/165638/>.
- Pérez, E., Schultz, F., & Pacheco, E. (2005). Characterization of some properties of starches isolated from *Xanthosoma sagittifolium* (tannia) and *Colocasia esculenta* (taro). *Carbohydrate Polymers*, 60(2), 139–145.
- Pérez, E., Segovia, X., Tapia, M. A., & Schroeder, M. (2012). Native and cross-linked modified *Dioscorea trifida* (cush-cush yam) starches as bio-matrices for edible films. *Journal of Cellular Plastics*, 48(6), 545–556.
- Rojas-Graü, M. A., Raybaudi-Massilia, R. M., Soliva-Fortuny, R. C., Avena-Bustillos, R. J., McHugh, T. H., & Martín-Belloso, O. (2007). Apple puree-alginate edible coating as carrier of antimicrobial agents to prolong shelf-life of fresh-cut apples. *Postharvest Biology and Technology*, 45(2), 254–264.
- Rojas-Graü, M. A., Tapia, M. S., & Martín-Belloso, O. (2007). Empleo de recubrimientos comestibles en frutas frescas cortadas: nuevo enfoque de conservación y desarrollo de productos. *Alimentaria*, 38, 105–118.
- Rojas-Graü, M. A., Tapia, M. S., Rodríguez, F. J., Carmona, A., & Martín-Belloso, O. (2007). Alginate and gellan-based edible coating as carriers of antibrowning agents applied on fresh-cut Fuji apples. *Food Hydrocolloids*, 21, 118–127.
- Romero-Bastidas, C. A., Bello-Pérez, L. A., García, M. A., Martino, M. N., Solorza-Feria, J., & Zaritzky, N. E. (2005). Physicochemical and microstructural characterization of films prepared by thermal and cold gelatinization from non-conventional sources of starches. *Carbohydrate Polymers*, 60, 235–244.
- Saavedra, N., & Algecira, N. (2010). Evaluación de películas comestibles de almidón de yuca y proteína aislada de soja en la conservación de fresas. *NOVA-Publicación científica en ciencias biomédicas*, 8(14), 171–182, 1794–2470.
- Sívoli, L., Pérez, E., Rodríguez, P., De Abrisqueta, A., & Raymúndez, M. B. (2005). Cambios en la estructura granular durante el proceso de modificación química (fosfatado-acetilado) del almidón de yuca analizados por microscopía óptica y electrónica. *Acta Microscópica*, 14(1 y 2), 5–9.
- Tapia, M. S., Pérez, E., Rodríguez, P., Guzmán, R., Ducamp-Collin, M. N., Tran, T., et al. (2012). Some properties of starch and starch edible films from sub-utilized roots and tubers from the Venezuelan Amazons. *Journal of Cellular Plastics*, 48(6), 526–544.
- Tapia, M. S., Rojas-Graü, M. A., Carmona, A., Rodríguez, F. J., Soliva-Fortuny, R., & Martín-Belloso, O. (2008). Use of alginate-and gellan-based coatings for improving barrier, texture and nutritional properties of fresh-cut papaya. *Food Hydrocolloids*, 22(8), 1493–1503.
- Valencia Rodríguez, M. T. (2001). Efecto del tratamiento de preservación por depresión e la actividad acuosa en la calidad del alga. In *Tesis de Magister en Bromatología y Tecnología de la Industrialización de Alimentos*. Argentina: FCEN-UBA.
- Whistler, R., & Paschall, E. (1967). *Starch chemistry and technology* (Vol. II). New York and London: Academic Press.
- Wurburg, O. B. (1986). Forty years of industrial starch research. *Cereal Food World*, 31(12), 897–903.