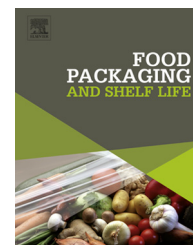


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# Physico-chemical properties of edible films derived from native and phosphated cush-cush yam and cassava starches

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## ABSTRACT

Edible, biodegradable films based on native and phosphated cush-cush yam and cassava starches plasticized with glycerol were developed by casting. The starches were chemically modified by cross-linking with sodium trimetaphosphate (STMP). The physicochemical properties of each of the different starch films were then evaluated and compared in order to determine their potential applications in the food industry. The amylose molecules in the cassava starch strongly interacted with glycerol resulting in an increase in the number of hydrogen bonds. This led to a slight shift upwards in the temperature required for the onset of the degradation of the cassava starch-based films, and even higher temperatures for degrading the films based on the modified starches. Films made from phosphated starches were more hydrophilic, producing an increase in solubility and crystallinity. Finally, the characteristics of the cassava films developed suggest that they would make good packaging materials, while films derived from cush-cush yam are more suitable as food coatings.

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## 1. Introduction

The growing consumer demand for healthier products that do not cause environmental pollution has led to a change in the approaches used for the manufacture of materials by the food packaging industry. Most of the synthetic products currently used are not degradable and their cost is rising steadily as they are produced from non-renewable resources such as oil (Yang & Paulson, 2000).

In the last 30 years several studies on edible films derived from natural biodegradable polymers such as cellulose, chitosan and starch have been undertaken (Chillo et al., 2008; Famá, Goyanes, & Gerschenson, 2007; Famá, Rojas, Goyanes, & Gerschenson, 2005; Flores, Famá, Rojas, Goyanes, & Gerschenson, 2007; Ghanbarzadeh, Almasi, Ali, & Entezami, 2010). In particular, starch has been the focus of a number of investigations due its biodegradable, renewable, inexpensive and edible nature as well as its wide availability (Lu, Tighzert, Berzin, & Rondot, 2005; Tharanathan, 2003).

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Molecularly, starch usually contains linear amylose and branched amylopectin. Although both components have the ability to form film, amylose is the most important (Romero-Bastidas et al., 2005). Starch from different sources has different amylose/amylopectin ratios, giving it specific properties depending on its origin (Famá, Bernal, & Goyanes, 2014; García, Famá, Dufresne, Aranguren, & Goyanes, 2009; Gutiérrez, Pérez, Guzmán, Tapia, & Famá, 2014; Krogars et al., 2003; Lawton, 1996).

Among the many naturally occurring starches, cush-cush yam (*Dioscorea trifida*) and cassava (*Manihot esculenta* C.) are very common in tropical latitudes and are used as food staples for some populations. A notable difference between these polysaccharides is their amylose content which is lower in cush-cush yam starches (Gutiérrez, Pérez, et al., 2014; Pérez et al., 2011). The molecular structure of native starches is often inefficient for the formation of films because of the invasive processes used in their extraction (Amani, Kamenan, Rolland-Sabaté, & Colonna, 2005; Bello-Pérez, Contreras, Romero, Solorza, & Jiménez, 2002; Kaur, Singh, & Singh, 2004). However, native cush-cush yam and cassava polysaccharides have shown promise for producing edible, biodegradable films (Gutiérrez, Pérez, et al., 2014; Pérez, Segovia, Tapia, & Schroeder, 2012). In addition, some native starch dispersions impart a cohesive rubbery texture to foods and are used as thickening agents (Wurzburg, 1986).

In order to overcome the limitations of native starches a number of techniques for their modification have been developed (Light, 1990; Swinkels, 1985, Chapter 8; Wurzburg & Szymanski, 1970). One common method is the cross-linking of the starch by phosphating which gives good results without generating large changes in its crystallinity or morphology (Matos & Pérez, 2003; Moorthy, 1994; Sívoli, 2009). This method can increase the tensile properties of starch films thus making them more adequate materials for, for example, food coatings (Hu, Chen, & Gao, 2009; Wurzburg, 1987). In addition, phosphating ensures that the films developed are actually edible and, consequently, considered safe by the FDA (2011).

Plasticizers are essential for the formation of many polysaccharide-based films and coatings (Krochta & De Mulder-Johnston, 1997). These components weaken the intermolecular interactions between adjacent polymer chains thus increasing film flexibility (Jongjareonrak, Benjakul, Visessanguan, Prodpran, & Tanaka, 2006; Sobral, dos Santos, & García, 2005).

One important and desirable feature of edible films and coatings is that they reduce moisture exchange between the product and its surrounding environment. The diffusivity and water solubility of these films are thus important characteristics which need to be controlled for their successful use as packaging materials (Gontard, Guilbert, & Cuq, 1993; Krochta, Baldwin, & Nisperos-Carriedo, 1994; McHugh & Krochta, 1994).

The aim of this study was to evaluate the stability, water content, water solubility and crystallinity of edible films prepared from cush-cush yam and cassava starches, and the effects of their modification by phosphating on these characteristics.

## 2. Experimental

### 2.1. Materials

Native starch was obtained from a variety of dark purple cush-cush yam (*D. trifida*) found in the Venezuelan Amazon ( $12 \pm 3\%$  apparent amylose) and from a variety of cassava (*M. esculenta* C.) ( $21 \pm 3\%$  apparent amylose) on sale at a local market in Caracas, Venezuela (Gutiérrez, Pérez, et al., 2014). The extraction of the starch from the cush-cush yam and cassava tubers was carried out using the methodology described by Pérez et al. (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 (phosphating 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  $0.0015 \pm 0.002\%$  and  $0.008 \pm 0.001\%$  for native and modified cassava, respectively (Gutiérrez, Pérez, et al., 2014). Glycerol from Prolabo, Sweden was employed as a plasticizer.

### 2.2. Modification of the starches

The starches were modified using sodium trimetaphosphate (STMP) according to the method described by Kerr and Cleveland (1959) with some small adjustments following (Lim & Seib, 1993). Native starch (300 g) and 15 g of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were suspended in 300 mL of distilled water, and the pH adjusted to 11 with 2.5% of NaOH solution. The slurry was then heated to  $45^\circ\text{C}$  and 2 g of STMP were added. The mixture was then shaken for 3 h and the pH adjusted every hour so that it remained at 11. After 3 h, the pH was lowered to 7 with 2.5% HCl solution. The slurry was then washed three times by suspension in distilled water, centrifuged at 1500 r/min for 15 min and dried at  $45^\circ\text{C}$ . The dried modified starch was milled and passed through a 60-mesh sieve. 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 preparation

Biodegradable films were prepared from each of the four starches using 2% (W/V) of starch, 1.9% (W/V) of glycerol and 500 mL of water. The films were heated for 30 min at  $90^\circ\text{C}$  in a water bath with constant stirring to ensure gelatinization (Hernández, 2006). After gelatinization the film-forming solutions (FFS) were degassed for 30 min by applying a vacuum. The FFS were then poured into  $40 \times 30$  cm stainless steel trays, maintaining a constant level and uniform thickness, and left in a tray dehydrator (Mitchell, USA, Model 645159) for 24 h at  $45^\circ\text{C}$ . Once dried the four thermoplastic starch film systems (TPS): native cush-cush yam (TPS-NY), phosphated cush-cush yam (TPS-PY), native cassava (TPS-NC) and phosphated cassava (TPS-PC) were peeled off the trays.

The resultant materials were conditioned with a saturated solution of NaBr ( $a_w \sim 0.575$  at 25 °C) for 7 days prior to each test.

## 2.4. Characterization of the films

### 2.4.1. Stability in acidic or alkaline solutions

In order to evaluate the stability of the films in acidic and alkaline solutions, 25 × 25 mm pieces were immersed in containers with 10 mL of standard solutions of hydrochloric acid (0.1 mol/L) or sodium hydroxide (0.1 mol/L). The containers were sealed and maintained at 25 °C for 24 days. The changes in the appearance of the samples were recorded with a Cyber-shot Sony camera, model DSC-H3 with 8.1 mega pixels.

### 2.4.2. Thermogravimetric analysis (TGA)

Thermogravimetric tests were performed using Shimadzu DTG-60. Samples between 4 mg and 10 mg were heated from room temperature to 550 °C at a rate of 10 °C/min and nitrogen flow 30 mL/min. The weight loss of the materials was recalculated on dry basis and the different degradation phases noted. Analyses were performed in triplicate to ensure repeatability.

### 2.4.3. Moisture content

The moisture content of the different systems was determined using standard methods of analysis according to the International Association of Official Analytical Chemistry (AOAC, 1990) and the following equation:

$$\% \text{ moisture} = \frac{m_w - m_d}{m_w} \times 100 \quad (1)$$

where  $m_w$  is the wet mass and  $m_d$  the dry mass of the film systems.

The dry mass was determined by heating a ~0.5 g sample of each film in a vacuum oven at 100 °C for 24 h. An analytical balance (Denver Instrument APX-200) was used to monitor the weight. Analyses were performed in triplicate and the average weight reported.

### 2.4.4. Water solubility

Water solubility was measured according to Romero-Bastidas et al. (2005) using the modification proposed by Hu et al. (2009), with the following equation:

$$\% \text{ solubility} = \frac{m_i - m_f}{m_i} \times 100 \quad (2)$$

where  $m_i$  is the initial dry mass and  $m_f$  the final dry mass.

### 2.4.5. Water activity ( $a_w$ )

The water activity ( $a_w$ ) of the films was determined using a psychrometric  $a_w$  meter Aqualab Cx-2 (Decagon Devices, Pullman, USA) previously calibrated with water at 25 °C. The average value of three measurements was reported.

### 2.4.6. X-ray diffraction (XRD)

X-ray diffraction tests on the different films were performed using a vertical goniometer X-ray diffractometer (Siemens D 5000) (radiation Cu K $\alpha$  = 1.5406 Å, 40 kV and 30 mA). Scattered radiation was detected in an angular range of 3–33° (2 $\theta$ ), at a

step size of 0.02° and scan speed of 2 s. The distances between the planes of the crystals  $d$  (Å) were calculated from the diffraction angles (°) measured from the X-ray pattern, according to Bragg's law. The thicknesses of the samples on the slides were ~200  $\mu$ m. Percent crystallinity was determined by measuring the relative intensity of the main peaks from the scattering spectrum according to Hermans and Weidinger (1961).

## 3. Results and discussion

### 3.1. Film stability in acidic or alkaline solutions

The aim of this study was to evaluate whether films derived from edible and biodegradable sources could be used in the food packaging industry. Since many food products are either slightly acidic or slightly alkaline it is important to determine whether the stability of the films used to wrap or coat them is affected by pH.

In order to study the stability of the starch based films samples of all the systems were immersed in either an acid or an alkali medium. Films derived from both starches left in the acidic solution (HCl) remained visually unchanged for at least 24 days, thus suggesting that they are stable in acid. All the films developed could therefore be used for packaging slightly acidic food products. Similar results were obtained by Hu et al. (2009) for thermoplastic polymer films derived from potato starch.

Fig. 1 shows the photographs of the films after 24 days in an alkaline solution. As can be observed the films made from phosphated starch (TPS-PY and TPS-PC) (Fig. 1b and d) were slightly less swollen than the native starch-based films (Fig. 1a and c), thus demonstrating greater stability in an alkaline medium. These results indicate that cross-linking gave the films increased stability.

The TPS-PY films were the most stable in the alkaline medium (Fig. 1b). It is possible that modified cushion yam starch is less susceptible to gelling than cassava starch because it contains higher concentrations of amylopectin (Gutiérrez, Pérez, et al., 2014).

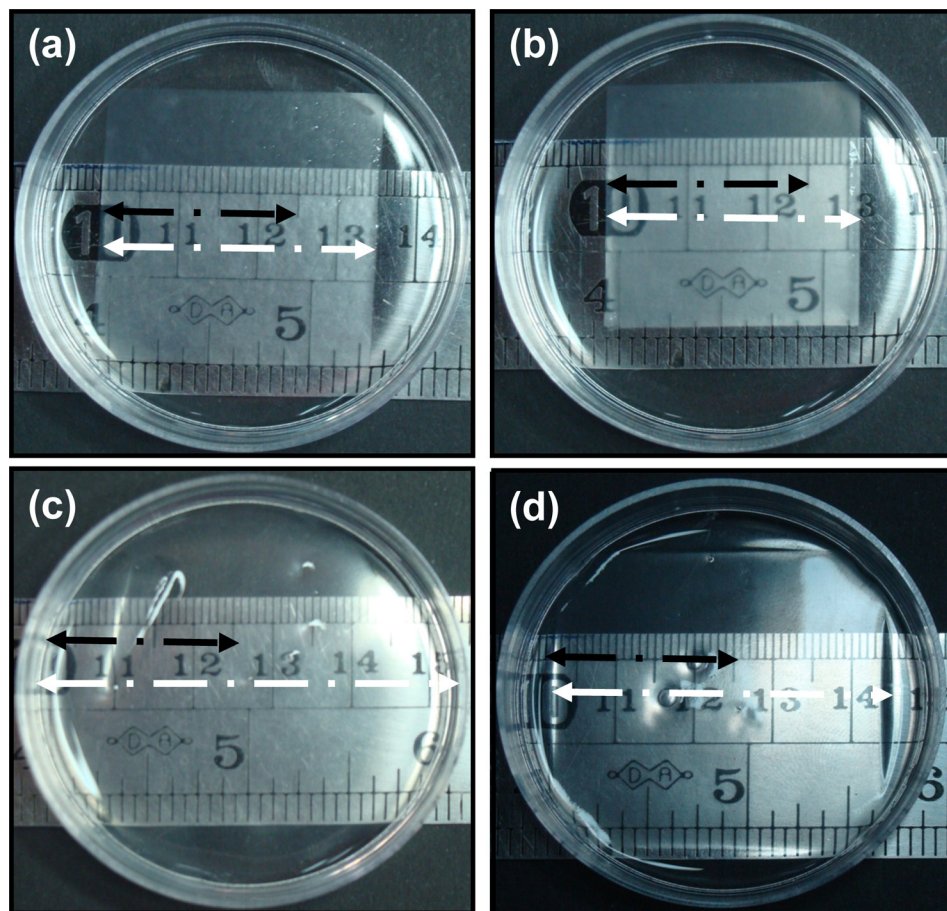
The disintegration and dissolution of the films in the alkaline medium could be due to the reaction of the sodium hydroxide with the hydroxyl groups of the starch molecules. This destroys and reduces hydrogen-bonding interactions and intra and intermolecular interactions between the starch macromolecules thus facilitating swelling and starch gelatinization. Furthermore, sodium ions may react with the carboxyl groups to form carboxylate groups which would increase the hydrophilicity and solubility of the starch (Hu et al., 2009).

It is important to note that all the systems studied showed greater stability in the alkaline medium than other TPS films reported in the literature (Hu et al., 2009; Medina, Pardo, & Ortiz, 2012).

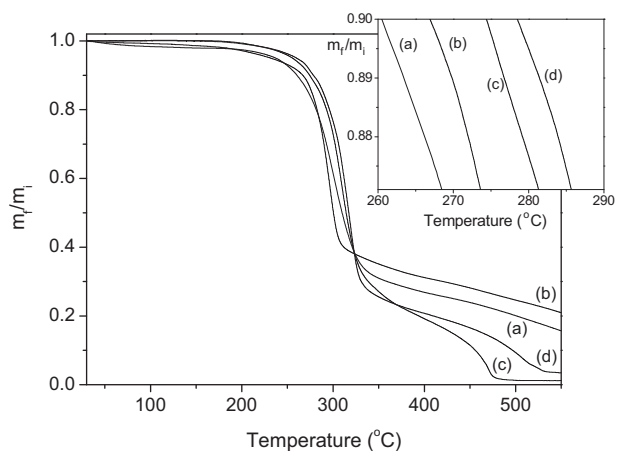
### 3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed in order to analyze the thermal stability of the four film systems (Fig. 2).





**Fig. 1** – Digital photographs of the thermoplastic starch films immersed in alkaline medium after 24 days: (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). Black line highlights initial length of the films. White line highlights final length of the films after 24 days immersed in alkaline medium.



**Fig. 2** – TGA curves of the different films studied: (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), in dry basis.

According to the literature, the thermal decomposition of glycerol-starch biofilms occurs in three main stages (García et al., 2009; Jiang, Qiao, & Sun, 2006; Rajan, Prasad, & Abraham, 2006; Rath & Singh, 1998; Wilhelm, Sierakowski, Souza, & Wypych, 2003). In the first stage water is lost; the second sees the onset of the decomposition of the glycerol-rich phase which also contains starch, and in the third stage the partially decomposed starch undergoes oxidation (García et al., 2009; Wilhelm et al., 2003).

As can be seen from Fig. 2, the highest rates of thermal degradation occurred in the temperature range between 200 °C and 330 °C during the decomposition of the glycerol-rich phase (García et al., 2009). The addition of glycerol decreases intra and intermolecular interactions between starch-starch chains and strengthens hydrogen bonding interactions between the hydroxyl groups of the starch chains and the glycerol molecules (Cyras, Tolosa, & Vazquez, 2006). The TGA curves of the thermoplastic films derived from cush-cush yam starches showed that their thermal degradation occurred at around 290 °C, whereas for cassava materials this was close to 310 °C. It is well known that glycerol-amylopectin interactions are not the same as glycerol-amylose interactions: the highly branched

amylopectin does not interact as strongly with the glycerol as amylose (Cyras et al., 2006; García et al., 2009). In our films, cassava starch-based samples interacted strongly with glycerol due to an increase in the number of hydrogen bonding interactions with the amylose molecules. These differences in the strength of the interactions also meant that the onset of the thermal degradation of cassava starch films occurred at a higher temperature.

Fig. 2 also shows that the onset of the second stage of thermal degradation (decomposition of the glycerol) in the modified starch films was slightly higher than that of the native starch samples, thus leading us to conclude that phosphated starch produces films with a higher thermal resistance.

A further decomposition phase at around 475 °C was detected in the cassava based films (Fig. 2c and d). This was stronger in the TPS-PC films and is related to the presence of a cross-linked starch structure or aromatic ring formed by thermal decomposition (Ruiz, 2006).

### 3.3. Moisture content

Table 1 shows the moisture content of the different films studied. The films derived from cush-cush yam starch (TPS-NY and TPS-PY) showed a higher moisture content than the cassava starch-based films. This may be due to weak glycerol-amylopectin interactions which facilitate the absorption of water (Flores et al., 2007; Hu et al., 2009). This phenomenon typically occurs during moisture plasticization whereby water acts primarily as a plasticizer resulting in weak glycerol-starch interactions. Gutiérrez (2013) recently reported that cush-cush yam starch-based films show moisture plasticization. As mentioned above, the glycerol interacts more strongly with cassava starch than cush-cush yam starch, probably due to the formation of hydrogen bridge type bonds between the glycerol and amylose. This glycerol-amylose interaction leads to a decrease in the intra and intermolecular interactions between starch macromolecules thus increasing the movement and rearrangement of their chains.

No significant differences ( $p \geq 0.05$ ) were observed between the native and phosphated cassava starch based films, however, modification by phosphating seemed to decrease the moisture content of the films. These results agree with those reported by Cyras et al. (2006) in their study of films based on acetylated potato starch.

Furthermore, a higher moisture content was observed for TPS-NY compared to TPS-PY films. This suggests that the phosphorylation of the starches (both cassava and cush-cush

yam) strengthened the hydrogen bridge type bonds within them.

### 3.4. Water solubility

Table 1 shows the water solubility values of the different systems studied at 25 °C. It can be seen that the native starch films were significantly less water soluble ( $p \leq 0.05$ ) than the modified starch films. In a previous study, Gutiérrez, Morales, Tapia, Pérez, and Famá (2014) found that films made from cross-linked starch were more hydrophilic than native starch-based films. Thus, an increase in the degree of substitution leads to a rise in the solubility of the modified starch films. These results agree with the trend reported by Pérez et al. (2012) for native and phosphated *D. trifida* white starch based edible films.

The solubility of edible films provides an indication of their integrity in an aqueous medium, such that higher solubility values indicate a lower resistance to water (Romero-Bastidas et al., 2005).

The results of the water solubility of the films derived from the phosphated starches are promising – as stated by Sothornvit and Krochta (2000) after obtaining similar results – for their possible application as edible candy wrappers, since they easily dissolve and melt in the mouth.

### 3.5. Water activity ( $a_w$ )

The water activity of the films is reported in Table 1. As can be seen, the highest  $a_w$  value was obtained for the samples made from native cush-cush yam starch which were also the materials with the highest moisture content. Similar results have been found in the literature for potato starch based films (Rojas, 2008) and native and cross-linked white *D. trifida* edible coatings (Pérez et al., 2012). It is thus unlikely that edible films would suffer significant microbiological growth.

### 3.6. X-ray diffraction (XRD)

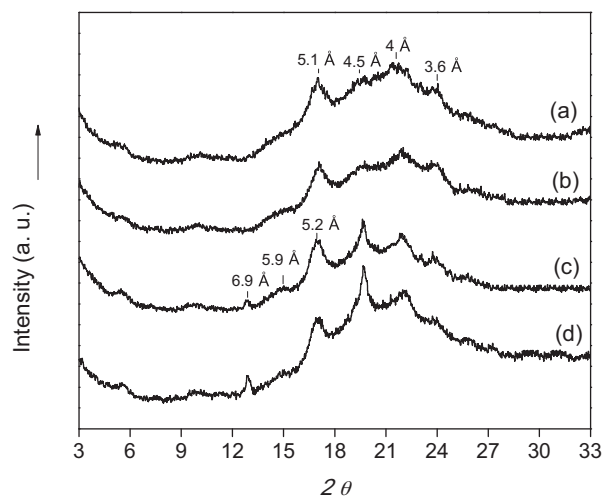
Fig. 3 shows the X-ray diffraction patterns of the films studied. As can be seen all the systems were composed principally of an amorphous phase with only a small crystalline fraction, thus agreeing with that previously reported for starch based films (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Famá et al., 2005, 2007; Famá, Flores, Gerschenson, & Goyanes, 2006; Flores et al., 2007; García et al., 2009; Kristo & Biliaderis, 2007).

In general, starches show A, B and C-type crystal structures. When glycerol is present the double helix

**Table 1 – Moisture content, water activity ( $a_w$ ), solubility and crystallinity of the different systems.**

Parameter	TPS-NY	TPS-PY	TPS-NC	TPS-PC
Moisture (%)	52 ± 2	37 ± 1 <sup>a</sup>	34 ± 5 <sup>a,b</sup>	32 ± 2 <sup>b</sup>
$a_w$	0.524 ± 0.007	0.501 ± 0.003	0.473 ± 0.001	0.492 ± 0.001
Solubility (%)	32 ± 2 <sup>c</sup>	47 ± 5	24 ± 1	36 ± 6 <sup>c</sup>
Crystallinity (%)	10 ± 1 <sup>d</sup>	10 ± 1 <sup>d</sup>	19 ± 2 <sup>e</sup>	20 ± 2 <sup>e</sup>

The values are the average of three determinations, similar letters in the same row indicates non-significant differences ( $n = 3$ ,  $p \leq 0.05$ ).



**Fig. 3 – X-ray diffraction pattern of the different films studied: (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).**

conformations are disrupted by the formation of stable single chain V-conformation helices resulting in the glycerol-amylose complex (Farhat, Oguntona, & Neale, 1999; Manzocco, Nicoli, & Labuza, 2003; Zobel, 1994). As can be seen in Fig. 3c and d the cassava starch films showed curves with diffraction peaks corresponding to the following  $d$ -spacings  $\approx 3.6$  Å,  $4.0$  Å,  $4.5$  Å,  $5.2$  Å,  $5.9$  Å and  $6.9$  Å (Famá et al., 2005; García et al., 2009; Tapia et al., 2012). Cush-cush yam starch films developed discreet conformations of A-type crystal structures with the most important peaks with  $d$ -spacings of  $\approx 3.6$  Å,  $4.0$  Å,  $4.5$  Å and  $5.1$  Å (Fig. 3a and b, TPS-NY and TPS-PY respectively). Angellier et al. (2006) and Mathew and Dufresne (2002) reported that waxy maize granules recrystallize in a B-type structure after complete disruption in water but afterwards develop into smooth A-type crystals. García et al. (2009) observed the same behavior in waxy starch films with peaks with  $d \approx 5.9$  Å,  $5.1$  Å and  $3.9$  Å, and similar results have also been reported by Primo-Martin, Van Nieuwenhuijzen, Hamer, and Van Vliet (2007) and Thielemans, Belgacem, and Dufresne (2006). The A-type patterns observed in TPS-NY and TPS-PY may be due to a local order generated by associated amylopectin chains. Pérez et al. (2012) and Tapia et al. (2012) suggested that the crystallinity of starch films is mainly associated with the amylose contained within them as it is almost linear compared to amylopectin which is highly branched. The presence of amylose, favoring strong interactions with glycerol, generates a type B X-ray diffraction pattern (García et al., 2009). In addition, the observation of a peak at  $4.5$  Å (Zobel, French, & Hinkle, 1967) suggests that there is an increase in the number of amylose-glycerol interactions. This corresponds to a type V crystal structure and is consistent with the results we obtained.

A slightly higher crystallinity was observed for the TPS-NC and TPS-PC samples (Fig. 3c and d), probably due to the higher amylose content present in cassava starches compared to cush-cush yam starches (Gutiérrez, Pérez, et al., 2014). The

values of the crystallinity percentages, calculated from the surface area under the curves, confirmed this (Table 1).

According to Osella, Sánchez, Carrara, de la Torre, and Buera (2005) the development of A or B-type X-ray diffraction patterns in starch films also depends on their water content. A decrease in moisture is highly correlated with an increase in the crystal phase of a semi-crystalline material (Chang, Chea, & Seow, 2000; Famá et al., 2005; Hu et al., 2009). Thus, the slight increase observed in the crystallinity of cassava starch films (Fig. 3c and d) agrees with the lower humidity values obtained for these materials.

## 4. Conclusions

In this study the physicochemical properties of films made from native and phosphated cush-cush yam and cassava starches were investigated.

Films derived from cassava starch showed more thermal stability than those made with cush-cush yam. This could be linked to an increase in the number of hydrogen bonding interactions between the amylose molecules of the cassava starch and the glycerol (Gutiérrez, Morales, et al., 2014; Gutiérrez, Tapia, Pérez, & Famá, 2014). In addition, the films made from cassava starch had a lower moisture content thus limiting microbial growth. Some food products such as candies or lollipops are intended to dissolve in the buccal pouch or beneath the tongue for absorption through the oral mucosa. Based on these primary results and taking into account that the raw materials used for the preparation of these films are edible and biodegradable, cush-cush yam starch films show more promise as wrappers (primary packaging) than cassava-based materials.

The technique used to chemically modify cush-cush yam and cassava starches by cross-linking was effective in developing more stable films.

The degradation temperatures corresponding to the glycerol-starch interactions were higher in the films made from the phosphated starches, making them more stable than those derived from native starches. In practice thermal stability is positively associated with the intramolecular forces between the starch and glycerol molecules. Consequently a higher thermal stability gives films with a higher integrability over time.

The films made from the cross-linked starches were more hydrophilic, thus increasing both the solubility and crystallinity of these materials.

Finally, the modification of the starches optimized the physicochemical properties of the edible films made from them, thus generating new materials with enhanced characteristics to be considered for their application in the food industry.

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