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Research Article

Pasting and Functional Properties of Chemically Modified Yam (*Dioscorea rotundata*) Starches

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Abstract: For the present study, we evaluated the effect of the concentration of modifying agents and reaction time on functional properties of yam (*Dioscorea rotundata* cv hawthorn) starch modified by oxidation and phosphatization. For oxidation was used a sodium hypochlorite concentration of 0.5 and 1.5 g/100 g starch (b.s.) and reaction time of 1 and 1.5 h; and for phosphating, sodium trimetaphosphate of 2 and 3 g/100 g starch (b. s.) and reaction time of 2 and 3 h. The pasting properties were determined during heating and cooling cycles (viscoamilograms) using a rotational rheometer (Anton Paar). The increase in modifying agent concentration and reaction time significantly reduces peak viscosity and setback by up to 98.53 and 95.62% respectively, while the pasting temperature decreases with both factors by up to 2.5% for both modifications. Functional properties such as swelling power, capacity and water absorption rate were affected over time in phosphating, but not in oxidation. Oxidation causes depolymerization and phosphating make starch granules more resistant to shearing, reducing viscosity when functional groups are introduced during modifications. The increased concentration of modifying agents and reaction time decrease the peak viscosity and setback of yam starch, but only time affects other properties, allowing its uses in the food industry to be extended.

Keywords: Oxidation, phosphating, rheometer, setback, swelling power, viscosity

INTRODUCTION

Starches are the source of reserve in the upper plants and are found in different parts of them as stem, fruits, roots and tubers (Gunaratne and Corke, 2007). It is a product used in food preparations due to its binding and thickening properties, which are very important for the food industry (Rengsutthi and Charoenrein, 2011); however, native starches have limitations due to their low thermal resistance, high viscosity and retrogradation and low solubility (Sukhija *et al*., 2016). This can be eliminated by modifying starch either by physical, chemical or enzymatic methods. Chemical modifications include acetylation, hydroxypropylation, oxidation and reticulation by phosphatization (Neelam *et al*., 2012).

Oxidation is carried out by modifying agents such as hydrogen peroxide, ozone and sodium hypochlorite and for phosphating it is used epichlorohydrin, Sodium Polyphosphate (SPP) and Sodium Trimetaphosphate (STMP) to reduce viscosity and retrogradation (Woo and Seib, 1997; Kaur *et al*., 2006; Sandhu *et al*., 2008; Zhou *et al*., 2016). The intensity of the changes in these properties is determined by the modifying agent concentration, reaction time and the starch source. Particularly, decreases of 13.2% (2753.5 to 2389 cP) in maximum viscosity have been reported in oxidized cassava starch with 0.5% active chlorine (Ascencio *et al*., 2016), 35.6% oxidized potato starch with 1.5% active chlorine (Fonseca *et al*., 2015) and 59.4% for oxidized barley starch with 2.0% active chlorine (El Halal *et al*., 2015) compared to the respective native starch.

For phosphate starches, peak viscosity reductions of 20.6% in elephant foot yam (*Amorphophallus paeoniifolius*) starch phosphate with 3% STMP compared to its native starch (Sukhija *et al*., 2016) were obtained. Regarding setback, reductions of 32.4% for bean starch (Vanier *et al*., 2012) and 50% for potato starch (Zhou *et al*., 2016) oxidized with active chlorine at 1.5 and 2.0%, respectively have been reported. It should be noted that modifications in native starches also cause changes in other functional properties. For example, the swelling power shows an 18% increase in cassava starch when the concentration of STMP is raised (Wongsagonsup *et al*., 2014), solubility decreases by 19.3% in phosphate corn starches with 2% STMP compared to native starches (Liu *et al*., 2014). In

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Corresponding Author: Narváez Germán J., University of Sucre, Sincelejo, Colombia this study, we evaluated the effect of the concentration of modifying agents and reaction time on functional properties of yam (*Dioscorea rotundata* cv hawthorn) starch modified by oxidation and phosphatization.

MATERIALS AND METHODS

Yam (*Dioscorea rotundata* cv hawthorn) from the market in the city of Sincelejo (Colombia) was used. Native yam starches were modified by oxidation using sodium hypochlorite (NaOCl, 13% active chlorine) and cross-linking by phosphatization using Sodium Trimetaphosphate (STMP).

Obtaining native yam starch: Yams (*Dioscorea rotundata* cv hawthorn) were selected according to good physiological and microbiological status. The starch extraction process was carried out at the Unitary Operations plant of the University of Sucre (Colombia) following the procedure described by Fu *et al*. (2005), using a bubbling system for the extraction of starch on a pilot scale. Once obtained, it was dried in a forced convection oven at 40°C for 16 h until a moisture of approximately 10%.

Modification of native yam starch: Once the yam starch was obtained and dried, it was passed through a sieve of 100 meshes to homogenize its granulometry and facilitate its modification by the following methods:

Native yam starch oxidation: The starch modification by oxidation was carried out according to the methodology described by Wang and Wang (2003) and Dias *et al*. (2011), with some modifications. For this procedure, 200 g of starch on a dry base was used in 500 mL of distilled water. The suspension was heated to 35°C and the pH adjusted to 9.5 using NaOH at 2N. Sodium hypochlorite (NaOCl) was then slowly added with an active chlorine concentration of 0.5 g/100 g of starch on a dry basis for 30 min, maintaining the pH at 9.5 with 1N H_2SO_4. Sodium hypochlorite was allowed to react for 60 min by adding 1N NaOH to stabilize the pH at 9.5 and finally, pH was adjusted to 7.0 with 1N H_2SO_4. The suspension was then filtered, centrifuged and washed with a double volume of distilled water and dried using a forced convection oven at 40°C for 16 h to a humidity of approximately 10%. The same procedure was applied using an active chlorine concentration of 1.5 g/100 g of starch (dry basis) and 90 min of reaction.

Phosphatization by reticulation of native yam starch: The phosphatization was carried out according to the methodology described by Woo and Seib (1997) and Liu *et al*. (2014), with some modifications. A suspension was prepared using 100 g of starch (dry basis) in 150 mL of distilled water, 2 g of STMP was added until complete mixing. The pH was then adjusted to 10.0 by addition of 1N NaOH and with continuous agitation. The suspension was heated to 45°C for 2 h and the pH set to 6.5 with a 10% (w/v) HCl solution. Then the starch was washed four times with an equal volume of distilled water, then centrifuged at 3000×g for 5 min and finally dried at 50°C for 24 h. The same procedure was repeated using 3 g of STMP and 3 h of reaction.

Pasting properties: The pasting properties of yam starches modified were determined using a rotational rheometer (Anton Paar, MCR 302, Austria). A 4% starch-water suspension was prepared and treated with a heating-cooling cycle. The samples were equilibrated at 50°C for 1 min, heated from 50 to 95°C at a heating rate of 6°C/min, then held at 95°C for 5 min. After the paste was cooled to 50°C at 6°C/min and kept at 50°C for 2 min. Paddle speed was set at 160 rpm in this analysis. The viscoamylogram described the various characteristics of the starch including peak temperature, peak viscosity, viscosity at 95°C after 5 min holding and the final viscosity at 50°C holding period. Other parameters including setback and breakdown were calculated from the above viscoamylogram characteristics. Three replicates of each sample were carried out. Data were processed using RheoCompass 1.12 software (Anton Paar, Austria).

Water absorption index, water solubility index and swelling power: These properties were determined according to the methodology reported by Aristizábal and Sánchez (2007). For this procedure, 1.0 g of starch was placed in a dry centrifuge tube, to which 25 mL of distilled water was added and preheated to 60°C. The system was installed in a 60°C water bath for 30 min, stirring the suspension 10 min after the heating was initiated. It was then centrifuged at 2700 rpm for 15 min. The supernatant (soluble starch) was extracted and the Volume (V) measured. An aliquot of 10 mL was taken and placed in a previously weighed petri dish. The supernatant was dried in an oven at 70°C for 12 h. The weight of the petri dish was recorded with the soluble part and the centrifuge tube containing the gel (insoluble starch). The Water Absorption Index (WAI), Water Solubility Index (WSI) and Swelling Power (SP) were determined according to Eq. (1), (2) and (3), respectively:

$$\text{WAI} = \frac{\text{gel weight (g)}}{\text{sample weight (g)}} \tag{1}$$

$$\text{WSI} = \frac{\text{soluble weight (g)} * V * 10}{\text{sample weight (g)}} \tag{2}$$

$$SP = \frac{\text{gel weight}}{\text{sample weight (g)} - \text{soluble weight (g)}} \quad (3)$$

Water absorption capacity: In a previously weighed centrifuge tube, 1.0 g of sample was deposited and 10 mL of distilled water was added, then it was gently stirred to homogenize the mixture, after which the suspension was centrifuged at 3500 rpm for 15 min. The supernatant liquid was decanted and the tube with the precipitate was drained for 10 min and then weighed. The mass gain is the water absorption capacity of the sample (AACC, 2012) and is determined according to Eq. (4):

$$\text{WAC (\%)} = \left[\frac{\text{Water mass retained(g)}}{\text{mass weight (g)}}\right] * 100 \quad (4)$$

Cold water solubility: This procedure was carried out according to the methodology proposed by Eastman and Moore (1984), with some modifications. First, 0.5 g of starch (dry basis) were deposited in a 50 mL test tube, 50 mL of distilled water were added and shaken manually for 30 sec. The mixture was homogenized at 5000 rpm for (2) min until the entire sample was solubilized. The tubes were then moved to centrifuge at 3500 rpm for 15 min. The supernatant was removed and a 10 mL of the sample were taken and transferred to a previously weighed petri dish. Finally, it was dried in a 110°C stove for 4 h and placed in a desiccator. The solubility of starches was estimated with Eq. (5):

$$\text{Solubility (\%)} = \frac{\text{solid in the supernatant (g)}*(5)}{\text{sample weight (g)}} * 100 \quad (5)$$

Statistical analysis: For each of the modifications of yam starches, a 2^2 experimental design was used, evaluating the following factors: Modifying agent concentration and reaction time. The response parameters were peak viscosity, trough viscosity, final viscosity, breakdown and setback, pasting temperature, swelling power, water absorption capacity, water absorption index, cold water solubility and water solubility index. ANOVA was performed at 95% confidence level ($p \leq 0.05$), data were processed by software R 3.2.1.

RESULTS AND DISCUSSION

The viscoamylograms for oxidized and phosphated yam starches are shown in Fig. 1a and 1b respectively, in which the viscosities of oxidized and phosphated starches decrease relative to native starch as the concentration of modifying agents and reaction times increase. This behaviour coincides with that reported for oxidized banana starches (Sánchez-Rivera *et al*., 2009), barley and corn (Chávez-Murillo *et al*., 2008); for cross-linked rice starches (Deetae *et al*., 2008), potato, pumpkin yam, lotus flower (*Nelumbo nucifera*) and modified sweet potato (Gunaratne and Corke, 2007), maize cross-linked with different agents (Hirsch and Kokini, 2002) and yam (*Dioscorea alata*) modified by alkaline treatment (Pacheco de Delahaye and Techeira, 2009).

Table 1 and 2 shows the pasting properties of oxidized, phosphatized and native yam starches. For oxidized yam starches, the maximum viscosity is between 32.7 and 2235.33 cP, while for the phosphatized it is between 29.1 and 1073.6 cP. In addition to the difference in peak viscosity between modified starches (oxidized and phosphatized), they have a lower peak viscosity than native yam starch (2608.6 cP). This is because of the modifying agents (NaOCl and STMP) affect the structure of the starch differently by forming covalent bonds and introducing carboxyl and carbonyl functional groups, which leads to a greater resistance of the granules to swelling, decreasing the resistance to the shear and viscosity (Jyothi *et al*., 2006; Ashogbon and Akintayo, 2014). Oxidized potato starches have peak viscosity values between 5800 and 7702 cP when the active chlorine concentration is top than 1.0% (Zhou *et al*., 2016), phosphated starches of cassava have peak viscosities between 3.0 and 159.3 RVU when the STMP is greater than 1.0% (Wongsagonsup *et al*., 2014). The peak viscosity of the native starch of yam *Dioscorea rotundata* is found in the range of native tuber starches, such as yam *Dioscorea alata* cv diamond 22, cassava and *Dioscorea* sp: 1792-2564 cP (Salcedo-Mendoza *et al*., 2016; Vargas-Aguilar and Hernández-Villalobos, 2013).

The trough viscosity of oxidized yam starches is between 49.6 and 2180 cP, whereas, for phosphated starches between 44.6 and 1408.3 cP, the majority of these values are lower than those found for native yam starch (2043 cP). This decrease about is because, during the modifications, functional groups are introduced which have an effect on the loss of viscosity during the final stage of the heating process (95°C). Phosphated cassava starches show values between 2.2 and 145.5 RVU (Wongsagonsup *et al*., 2014) when the concentration of STMP is changed. Native starches from other tubers show minimum viscosity values between 841.4 cP for cassava starch and 1500 cP yam (*Dioscorea alata*) starch (Salcedo-Mendoza *et al*., 2016).

For final viscosity, oxidized starches show values between 137.7 and 4196.3 cP, phosphated between 117.5 and 2405.3 cP and for the native, it was 3579.6 cP, which is higher compared to phosphated starch but slightly lower than the of oxidized starch with the lowest NaOCl concentration and reaction time. For this treatment, the structure of starch was not profoundly modified (partially disintegrated) which led to a further rearrangement of its molecules during the cooling stage, which influences the observed maximum viscosity (Wongsagonsup *et al*., 2014; Jyothi *et al*., 2006). The

Table 1: Pasting properties of starches: NS (Native Starch), OS (Oxidized Starch)

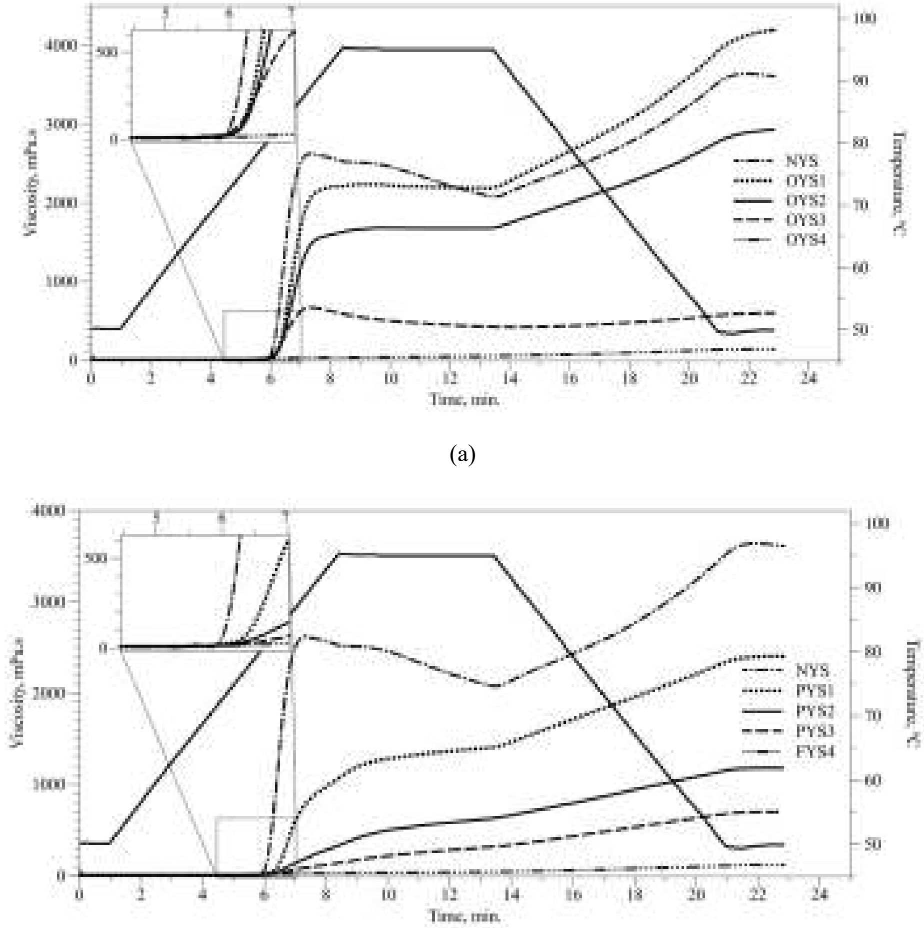
Starch	Peak viscosity (P), cP	Viscosity after 95°C holding (H), cP	Final viscosity after 50°C holding (F), cP	Breakdown (P-H), cP	Setback (F-H), cP	Pasting temperature, °C
NS	2608.6±42.8^{a}	2043.0±26.2^{b}	3579.6±6.8^{b}	565.6±53.2^{a}	1536.6±4.9^{b}	79.8±0.1^{b}
OS1 (0.5%-1 h)	2235.3±17.5^{b}	2180.0±21.6^{a}	4196.3±7.5^{a}	55.3±5.6^{c}	2016.3±4.6^{a}	80.3±0.1^{a}
OS2 (0.5%-1.5 h)	1684.6±35.1^{c}	1676.6±34.6^{c}	2927.6±4.3^{c}	8.0±1.7^{d}	1251.0±22.0^{c}	79.6±0.2^{b}
OS3 (1.5%-1 h)	6673.0±14.6^{d}	416.7±11.6^{d}	595.3±18.3^{d}	250.6±3.1^{b}	178.6±6.8^{d}	78.8±0.1^{c}
OS4 (1.5%-1.5 h)	32.7±1.2^{e}	49.6±0.5^{e}	137.7±0.9^{e}	16.8±0.8^{cd}	88.0±0.4^{e}	78.4±0.1^{d}

Means with different letters within the same column differ significantly ($p<0.05$)

Table 2: Pasting properties of starches: NS (Native Starch), FS (Phosphate Starch)

Starch	Peak viscosity (P), cP	Viscosity after 95°C holding (H), cP	Final viscosity after 50°C holding (F), cP	Breakdown (P-H), cP	Setback (F-H), cP	Pasting temperature, °C
NS	2608.6±42.8^{a}	2043.0±26.2a	3579.6±26.8^{a}	565.6±53.2^{a}	1536.6±4.9^{a}	79.8±0.1^{ab}
FS1 (2%2 h)	1073.6±7.6^{b}	1408.3±5.5^{b}	2405.3±19.5^{b}	334.6±5.5 ^{b}	997.0±19.7^{b}	80.1±0.2^{a}
FS2 (2%-3 h)	334.2±22.4^{c}	631.7±23.9^{c}	1178.5±25.5^{c}	297.5±2.0^{b}	546.7±1.5^{c}	78.6±0.1^{bc}
FS3 (3%-2 h)	139.9±22.5^{d}	319.1±23.0^{d}	700.0±22.7^{d}	179.1±0.5^{c}	380.8±0.2^{d}	77.8±0.7^{cd}
FS4 (3%-3 h)	29.1±3.2^{e}	44.6±9.1^{e}	117.5±9.9^{e}	15.5±6.0^{d}	72.9±0.9^{e}	77.2±1.0^{d}

Means with different letters within the same column differ significantly ($p<0.05$)



(a)

(b)

Fig. 1: Viscoamilograms of native yam starches modified by oxidation (a) NS (native); OS1 (oxidized 0.5%-1.0 h); OS2 (oxidized 0.5%-1.5 h); OS3 (oxidized 1.5%-1.0 h); OS4 (oxidized 1.5%-1.5 h) and phosphatation, (b) FS1 (phosphate 2%-2 h); FS2 (phosphate 2%-3 h); FS3 (phosphate 3% -2 h)

concentration of the modifying agent affects the final viscosity, e.g., for oxidized potato starches and phosphated cassava, changes in final viscosities occur between 3734 and 5321 cP (Zhou *et al*., 2016) and 3.7 and 282 RVU (Wongsagonsup *et al*., 2014), respectively. The final viscosity of native starch from other tubers presents values of 1925 cP for cassava starch, 2570 cP for yam (*Dioscorea alata* cv diamond 22) starch (Salcedo-Mendoza *et al*., 2016) and 7279 cP for potato starch (Zhou *et al*., 2016).

The breakdown is established as the difference between the peak and trough viscosity and shows the stability of the starch paste during heating. For oxidized yam starches, its value is between 8.0 and 250.6 cP, while for phosphatized yam starches its value is between 15.5 and 334.6 cP. These are lower than the of native starch (565.6 cP) because the modifying agents encourage the formation of cross-links that reinforce swollen granules against rupture under high temperature (95°C) and shear conditions. Also, low breakdown values are influenced by the observed peak viscosities (Jyothi *et al*., 2006). Oxidized potato starches have breakdown values between 5005 and 6106 cP when the active chlorine concentration is changed (Zhou *et al*., 2016), while phosphated cassava starches have values between 0.8 and 67.3 RVU when the STMP is modified (Wongsagonsup *et al*., 2014). Native starches have breakdown values of 292 cP for yam (*Dioscorea alata* cv diamond 22) starch and 1628.6 cP for cassava starch (Salcedo-Mendoza *et al*., 2016) and 7082 cP for potato starch (Zhou *et al*., 2016).

The setback is established as the difference between final viscosity and trough viscosity and shows the stability of the starch paste during cooling. For oxidized starches, it is between 88.0 and 2016.3 cP while for the phosphatized it is between 72.9 and 997 cP. The setback value for native starch was 1536.6 cP, which is higher compared to phosphated starches but lower than the one presented by oxidized starch with the lowest NaOCl concentration (0.5%) and reaction time (1 h). Note that for this treatment, the structure of starch was not profoundly modified (partially disintegrated) which led to a further reorganization of its molecules during the cooling stage (Wongsagonsup *et al*., 2014; Jyothi *et al*., 2006). Some studies show setback values for oxidized potato starches between 1184 and 2835 cP when the concentration of active chlorine (Zhou *et al*., 2016), while phosphated cassava starches have results between 1.5 and 136.5 RVU when the STMP is changed (Wongsagonsup *et al*., 2014). Native starch has values of 1023 cP for yam (*Dioscorea alata* cv diamond 22) starch, 965.6 cP for cassava starch (Salcedo-Mendoza *et al*., 2016) and 3511 cP for potato starch (Zhou *et al*., 2016).

The pasting temperature of oxidized starches is between 78.4 and 80.3°C and for the phosphated between 77.2 and 80.1°C. These values are similar to those reported in phosphated cassava starches with pasting temperatures between 66.7 and 72.7°C (Wongsagonsup *et al*., 2014) and oxidized corn starches between 69.2 and 70.5°C (Spier *et al*., 2013) when the concentration of modifying agent is changed. Native starch had a pasting temperature of 79.8°C, higher than those reported for native potato starches, 68.3°C (Zhou *et al*., 2016) and cassava, 68.8°C (Wongsagonsup *et al*., 2014); Similar to corn starch pasting temperature, 78.5°C (Spier *et al*., 2013), rice, 79.2°C (Xiao *et al*., 2012) and yam (*Dioscorea alata* cv diamond), 80.5°C (Figueroa-Flórez *et al*., 2016) and lower than the one reported for elephant foot yam (*Amorphophallus paeoniifolius*), 86.3°C (Sukhija *et al*., 2016).

For oxidized yam starch, ANOVA showed that the concentration of the modifying agent, reaction time and its interaction have significant effects on peak, trough, final and setback viscosities. For the low reaction time level (1 h) an increase in modifying agent concentration (NaOCl) results in a reduction in peak viscosity (70.14%), trough viscosity (80.88%), final (85.81%) and setback viscosities (91.14%). However, at the high level of reaction time (1.5 h), this same increase in NaOCl concentration causes a reduction in peak viscosity (98.05%), trough viscosity (97.04%), final (95.29%) and setback viscosities (92.95%). Comparing the treatment corresponding to a NaOCl concentration of 1.5% and reaction time of 1.5 h (selected for presenting lower value with native yam starch), this produces a reduction in peak viscosity of 98.7%, trough viscosity of 97.5%, final viscosity of 96.1% and setback viscosities of 94.2%. The setback reduction is important because it establishes that this starch has low backgradation offering a stability at low temperatures which helps when used in food products stored at room temperature. Reductions in viscosities occur because the increase in NaOCl concentration leads to depolymerization of starch chains, resulting in a substantial decrease in molecular weight and thus in shear strength (Kuakpetoon and Wang, 2001; Sandhu *et al*., 2008; Zhou *et al*., 2016). Similar results were reported for oxidized potato starches (Kuakpetoon and Wang, 2001; Zhou *et al*., 2016), bananas (Sanchez-Rivera *et al*., 2005) and barley and corn (Chávez-Murillo *et al*., 2008).

For oxidized yam starches, ANOVA showed that factors such as NaOCl concentration, reaction time and their interaction have a significant effect on the breakdown. For a concentration of 0.5% NaOCl, there is a reduction of 85.5% when the reaction time is increased from 1 to 1.5 h; while this same increase in time, causes a 93.2% reduction in the breakdown value when the NaOCl concentration is 1.5%. Also, there is a significant reduction of 98.5% with relation to native starch. This is because the modifying agent (NaOCl) reacts first with lipids, then promotes the depolymerization of the amylose and amylopectin molecule of the starch granule and finally forms the carboxyl and carbonyl groups (Thomas and Atwell, 1999; Wang and Wang, 2003; Kuakpetoon and Wang, 2001), therefore, an amount of modifying agent is consumed during the first minutes of reaction eliminating lipids and pigments, but after a while during the reaction time, the modification itself is established, facilitating the reduction of viscosities and breakdown, which indicates a better thermal stability (Sánchez-Rivera and Bello-Pérez, 2008; Dias *et al*., 2011; Zhou *et al*., 2016). Reduction breakdown results were reported for potato starches when modified by oxidation (Zhou *et al*., 2016).

The ANOVA for phosphated starch showed that the concentration of the modifying agent, reaction time and its interaction have a significant effect on the peak, trough, final, breakdown and setback viscosities. For a reaction time of 2 h, there is a decrease in peak viscosity (86.96%), trough viscosity (77.33%), final (70.89%), breakdown (46.46%) and setback (61.79%), with an increase in STMP concentration. However, for a reaction time of 3 h, this gain in STMP concentration produces a decrease in the evaluated variables: Peak viscosity (91.28%), trough viscosity (92.93%), final (90.02%), breakdown (94.77%) and setback (86.66%). Comparing the treatment corresponding to a STMP concentration of 3% and reaction time of 3 h (selected for having lower viscosity values), with the native starch, this produces a reduction in peak viscosity of 98%, trough viscosity of 97.8%, final viscosity of 96.7%, breakdown of 97.2% and setback of 95.2%. The reduction of viscosities could occur because by increasing the concentration of STMP, the bonds between starch chains are reinforced, which causes an increase in the density of cross-links, preventing swelling of the granules, which leads to a lower viscosity (Jyothi *et al*., 2006; Raina *et al*., 2007). Results of peak viscosity reduction, breakdown and setback results when STMP concentration is increased were reported (Gao *et al*., 2014).

The ANOVA showed that the modifying agent concentration and reaction time factors significantly affect the pasting temperature in both modifications. An increase in the concentration of the modifying agent (NaOCl or STMP) causes a 1.68% reduction in pasting temperature for oxidized starch and 2.47% for phosphatized yam starch. The above is because a higher concentration of modifying agent weakens and disintegrates the structure of starch, allowing a high sensitivity to temperature (Lawal, 2004). Similar results were presented for barley starch (El Halal *et al*., 2015) and cornstarch (Spier *et al*., 2013). However, they contrast with potato starch, where the increase in the concentration of the modifying agent (NaOCl) produces a 4.3% increase in pasting temperature (Zhou *et al*., 2016); This difference may be due to the different structure of starches. On the other hand, an increase in reaction time leads to a 0.69% reduction in pasting temperature for oxidized starch and 1.23% for phosphatized starch. An increase in reaction time allows more functional groups to be introduced when the modifications occur, which facilitates hydration and therefore the gelling at lower temperatures (Sangseethong *et al*., 2010). Results of pasting temperature reduction were replenished for cassava starch (Sangseethong *et al*., 2009; Salcedo-Mendoza *et al*., 2016) and yam (Salcedo-Mendoza *et al*., 2016).

Table 3 and 4 show the functional properties evaluated for yam starches: Water Absorption Capacity (WAC), Water Absorption Index (WAI), Water Solubility Index (WSI), Swelling Power (SP) and Cold Water Solubility (CWS). Oxidized yam starch had WAI, SP and CWS values similar to those of native yam starch. The results in WAC and WSI for oxidized yam starches are higher than native starch. Phosphated yam starch had WAI and SP values similar to those of native starch. The values in the WAC and WSI property for yam phosphated starches are higher than their native samples, but the results for CWS are lower. Studies report for native white and red malanga (*Colocasia esculenta*) starches present WAI values in 1.79 and 1.88, respectively and WSI values of 0.128 and 0.23 (Torres Rapelo *et al*., 2013). Yam (*Dioscorea alata*) starches have a CWS value of 0.071 (Pacheco de Delahaye and Techeira, 2009). On the other hand, the SP of native potato and bean starches at 90°C were 15.8 (Fonseca *et al*., 2015) and 8.94 (Vanier *et al*., 2012), respectively.

Table 3: Functional properties of oxidation-modified yam starch

Starch	WAC (%)	WAI	WSI	SP	CWS (%)
NS	104.7±3.3^{b}	191.2±0.2^{a}	0.005±0.001^{d}	1.900±0.020^{a}	0.36±0.03^{a}
OS 1 (0.5%-1 h)	185.9±6.1^{a}	192.5±5.4^{a}	0.087±0.006^{c}	1.927±0.053^{a}	0.32±0.08^{a}
OS 2 (0.5%-1.5 h)	185.5±3.8^{a}	184.8±0.9^{a}	0.119±0.024^{bc}	1.853±0.008^{a}	0.26±0.02^{a}
OS 3 (1.5%-1 h)	195.9±6.0^{a}	185.0±8.9^{a}	0.194±0.010^{a}	1.856±0.089^{a}	0.34±0.06^{a}
OS 4 (1.5%-1.5 h)	188.5±5.0^{a}	194.6±14.9^{a}	0.133±0.020^{b}	1.951±0.150^{a}	0.28±0.06^{a}

Means with different letters within the same column differ significantly ($p<0.05$)

Table 4: Functional properties of phosphatization-modified yam starch

Starch	WAC (%)	WAI	WSI	SP	CWS (%)
NS	104.7±3.3^{c}	191.2±0.2^{ab}	0.005±0.001^{b}	1.900±0.020^{ab}	0.36±0.03^{a}
FS 1 (2%-2 h)	184.9±5.1^{b}	184.2±0.2^{b}	0.079±0.009^{a}	1.844±0.002^{b}	0.20±0.10^{b}
FS 2 (2%-3 h)	192.0±4.4^{a}	195.4±3.2^{a}	0.033±0.008^{b}	1.955±0.032^{a}	0.12±0.08^{c}
FS 3 (3%-2 h)	184.8±8.6^{b}	190.6±3.8^{a}	0.035±0.025^{b}	1.907±0.038^{a}	0.18±0.03^{b}
FS 4 (3%-3 h)	193.9±2.5^{a}	193.5±5.5^{ab}	0.033±0.009^{b}	1.936±0.054^{ab}	0.06±0.04^{c}

Means with different letters within the same column differ significantly ($p<0.05$)

The ANOVA for the functional properties of oxidized cassava starch showed that no factors studied had any effect on WAC, WAI, SP and CWS. However, the Water Solubility Index (WSI) is affected by NaOCl concentration and the interaction between NaOCl concentration* reaction time. For the low level of the reaction time (1 h) there was an increase of 122.98% of the WSI when the NaOCl concentration was increased; but for a reaction time of 1.5 h, this same increase in the NaOCl only presented an increase of 11.76%. The increase in the water absorption capacity and water solubility index of oxidized yam starch compared to native yam starch is due to the depolymerization of yam starch chains, the penetration of the oxidizing agent in the amorphous region and the introduction of carboxyl groups (Forssel *et al.*, 1995; Sanchez-Rivera *et al.*, 2005; Lawal, 2004). Studies have reported increased solubility percentage of native starch in oxidized rice starches (Xiao *et al.*, 2012), bananas (Sanchez-Rivera *et al.*, 2005), malanga (*Colocasia esculenta*) (Lawal, 2004), corn (Liu *et al.*, 2014) and potato (Zhou *et al.*, 2016).

For phosphated yam starches the analysis of variance states that the properties WAC and CWS, are affected only by the reaction time factor. An increase in reaction time results in a 4.37% increase in WAC and a 51.72% decrease in CWS. All treatments showed an increase of 76% over native starch for WAC. For the WAI and SP properties, only the interaction between STMP concentration factors and reaction time was significant. For a reaction time of 2 h an increase in STMP concentration caused an increase in the WAI (5.02%) and SP (4.97%); however, for a reaction time of 3 h, caused a decrease of 2.48%. The high quantity of the modifying agent strengthens hydrogen bonds by penetrating into the starch granule, forming cross-links allowing the reduction of pH (Gao *et al.*, 2014). Similar results were reported for cross-linking of cassava starch and elephant foot yam (Sukhija *et al.*, 2016; Wongsagonsup *et al.*, 2014), but these results contrast with those reported for banana starch (Carmona-Garcia *et al.*, 2009).

The Water Solubility Index (WSI) is affected by STMP concentration, reaction time and its interaction, showing that at a 2 h reaction time there was a 55.69% decrease when the STMP quantity was increased, but at a 3 h reaction time, there was a 1.0% increase when the STMP concentration was increased. Decreased solubility is attributed to bonding and integrity of starch granules due to additional covalent bonds through phosphate groups that firmly hold starch granules together (Liu *et al.*, 2014). Results showing decreased solubility have been reported for corn-starch (Liu *et al.*, 2014), cassava (Wongsagonsup *et al.*, 2014), elephant foot yam (*Amorphophallus paeoniifolius*) (Sukhija *et al.*, 2016), rice (Xiao *et al.*, 2012) and banana (Carmona-Garcia *et al.*, 2009).

CONCLUSION

Modification by oxidation and reticulation by phosphatization of yam starch produces changes in pasting properties, significantly reducing the values of peak viscosity and retrogradation about native starch, which allows the use of this material in food matrices, making them more manageable and very stable. The pasting temperature decreases as the modifying agent's concentration and reaction times increase. Oxidation modification of yam starches does not affect functional properties such as IAA, PH and SAF. Oxidized and phosphated yam starches show increases in WAC, compared to native starch. The obtained characteristics, along with the modifications enable the use of this material to be extended in different food industries, such as the manufacture of edible coatings.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this study.

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