Influence of pH and hydrocolloids addition on yam (Dioscorea alata) starch pastes stability

S. Mali, C. Ferrero, V. Redigonda, A.P. Beleia, M.V.E. Grossmann, N.E. Zaritzky

Abstract

Yam tubers (Dioscorea alata) are a non-traditional starch source that could be used as food ingredient. The stability of yam starch pastes (6/100 g suspension) submitted to different pH conditions during gelatinization and the effect of hydrocolloids addition (guar and xanthan gums) on starch syneresis under refrigeration were analyzed. Changes in pH (3, 5, 6) or the addition of gums (0.1–0.5/100 g suspension) did not affect the starch gelatinization temperature nor the gelatinization enthalpy as determined by differential scanning calorimetry. Rheological behavior was characterized by amyllograph profiles and oscillatory rheometry. Amylograms showed that yam starch pastes maintained a high viscosity under heat treatment and mechanical stirring in neutral to slightly acidic conditions. Brabender viscosity increased when gums were added; the effect of guar gum on viscosity was more marked than that of xanthan gum. During refrigerated storage exudate production was observed of pastes without gums. Xanthan gum, at a concentration of 0.5/100 g suspension, showed higher effectiveness than guar gum to reduce exudate production during refrigerated storage. The addition of hydrocolloids could allow yam starch to be used in foods requiring low temperatures.

Keywords: Yam starch; Guar gum; Xanthan gum; Acidic conditions; Thermal stability; Refrigerated storage; DSC; Rheology

1. Introduction

Most of the starch employed by food industries is produced by extraction from corn, cassava, sweet potato, wheat or rice. Yam tubers (Dioscorea alata) are another potential starch source that could be used as food ingredient, but that has not been explored commercially (Valetudie, 1992). Several researchers have studied flour and starch obtained from yam tubers in order to find new food applications (Ciacco & D’Appolonia, 1978; Ige & Akinbutunde, 1981; Okaka & Anajekwu, 1990; Okaka, Okorie, & Ozo, 1991; Alves, 2000).

In food preparation, starch-based products can be submitted to different processing and storage conditions. Starch stability at different pH values is often a critical point. For wheat and corn starches peak viscosity decreases when increasing pH (Campbell, Porter Penfield, & Griswold, 1980; Dengate, 1988). When compared to starches from other sources yam starch pastes can maintain viscosity levels during thermal treatment. However, yam starch seems not to be adequate as a food ingredient when cold storage is required. This is because yam starch pastes show a marked tendency to retrogradation during storage, particularly on cooling, possibly on account of their relatively high amylose content (Alves, 2000). During refrigerated storage, retrogradation leads to a marked exudate production and increases gel firmness thus turning the product unacceptable. The instability of yam starch gels during storage is a limiting factor for the extensive use of this starch in food industry.

Starch-based formulations can be modified to have a higher viscosity and less syneresis by the use of small quantities of hydrocolloids. Guar and locust bean gums (galactomannans extracted from the seed endosperm of...
certain leguminous), alginates, carrageenans (polysaccharides extracted from brown and red seaweeds) and xanthan gum (polysaccharide produced by culturing the microorganism Xanthomonas campestris) are among the hydrocolloids most frequently employed as stabilizers.

In previous works the beneficial effects of using hydrocolloid to prevent textural changes in corn gelatinized starch–water systems has been demonstrated (Christianson, Hodge, Osborne, & Detroit, 1981; Ferrero, Martino, & Zaritzky, 1994; Ferrero & Zaritzky, 2000).

The objectives of the present work were: (i) to determine the stability of yam starch–water systems when they are submitted to different acidic conditions during gelatinization and (ii) to establish if the addition of hydrocolloids (guar and xanthan gums) can help prevent the negative textural effects during refrigerated storage.

2. Materials and methods

2.1. Materials

Yam starch was extracted from fresh yam tubers provided by local farmers (Londrina, Brazil) using a method previously described (Alves, Grossmann, & Silva, 1999).

Yam starch granules show a characteristic almond shape with a characteristic hilum located at the more acute pole. Their sizes ranged between 8–27 μm width and 12–33 μm length (Alves et al., 2002). Starch purity was 98.3/100g (d.b.); the other components were (on 100g, d.b.): 1.21g of non-starch carbohydrates, 0.16g of lipids, 0.18g of proteins and 0.15g of ashes. Amylose content in starch is close to 30% (Alves et al., 2002).

Xanthan and guar gums were tested as stabilizers. Xanthan gum (Lygomme KCT 50, provided by SKW Biosystems do Brasil Ltda) had the following specifications: viscosity of a 1/100g aqueous solution, 1800cP (measured in a Brookfield LVF viscometer, at 60rpm), pH in aqueous solution (1/100g)=7.0, loss on drying, less than 14/100g). Guar gum (provided by Kerry do Brasil Ltda) showed the following characteristics: viscosity of a 1/100g aqueous solution, 5200cP (measured in a Brookfield LVF viscometer at 12rpm), pH in aqueous solution (1/100g)=6.3, loss on drying, 9.8/100g.

2.2. Methods

Two series of experiments were done to analyse

(a) the effect of different pH values (3,5,6) on gelatinization, pasting properties and viscoelastic behavior of starch pastes without hydrocolloids,
(b) the effect of hydrocolloids (guar and xanthan gums) on starch gelatinization, rheological behavior and syneresis of yam pastes at pH = 6.

2.3. Thermal characterization by differential scanning calorimetry (DSC)

Gelatinization (onset, peak and conclusion) temperatures and enthalpies were determined by DSC using a Polymer equipment (Rheometric Laboratories, UK). Gelatinization was analyzed in:

(a) aqueous yam starch suspensions (6/100g suspension) of different pH (3, 5 and 6) that were attained by addition of different volumes of 0.15 N HCl to the yam starch suspension;
(b) aqueous yam starch systems (6/100g suspension) containing different levels of guar or xanthan gum (0, 0.1, 0.3 and 0.5/100g suspension).

In each case, 10g batches of starch suspensions were prepared under constant stirring and aliquots of 10–15mg were exactly weighed in coated aluminum pans and hermetically sealed. Scans were performed from 20°C to 120°C at a controlled constant rate of 10°C min⁻¹. After each test, pans were punctured and the exact dry weight of each sample was determined. Runs were performed in triplicates.

2.4. Pasting properties

Pasting properties of yam starch at different pH or at different starch–gum mixtures were evaluated under standardized conditions with a Brabender Viscograph (Pt 100 model, 700 cm g, Duisburg, Germany).

To study the effect of thermal treatment on starch pastes (without gums) in acidic conditions (pH=3, 5 and 6) 1.0 N HCl solution was added dropwise to the starch suspension (Shuey & Schmitz, 1980). The pH was monitored and remained constant during the test. For comparison, cassava (Manihot esculenta) starch pastes (6% w/w) at pH 3 and 6 were prepared and analyzed under the same conditions.

Samples were obtained from batches (450g) prepared with a constant concentration of yam starch (6/100g suspension) and different levels of guar or xanthan gums (0, 0.1, 0.3 and 0.5/100g suspension). Starch and gums were exactly weighed and dry mixed before adding to a previously weighed quantity of water. Solids were slowly added, under constant stirring to prevent lumping.

Once they were transferred to the Brabender Visco- graph bowl, samples were heated at 1.5°C/min from 30°C to 95°C, held at 95°C for 20 min and cooled down to 50°C at a rate of 1.5°C/min. Each analysis was done in duplicate.

2.5. Viscoelastic behavior

The rheological behavior of the gelatinized yam suspensions at different pH values and in systems...
containing xanthan or guar gums were studied in a Haake RV20 oscillatory rheometer (Haake, Germany) at 30°C using a plate–plate sensor system with 1 mm gap between plates. Data were analyzed using the Oscillation 2.0 Haake software. Two types of rheological tests were performed: (a) deformation sweeps at constant frequency to determine the maximum deformation attainable by a sample in the linear viscoelastic range \( (\gamma_{\text{lim}}) \) and (b) frequency sweeps at a constant deformation within the linear viscoelastic range. The mechanical spectra were obtained recording the dynamic moduli \( G' \) and \( G'' \) as a function of frequency. \( G' \) is the dynamic elastic or storage modulus, related to the material response as a solid. \( G'' \) is the viscous dynamic or loss modulus, related to the material response as a fluid. The complex modulus \( G^* \) defined as \( (G'^2 + G''^2)^{1/2} \) represents the global viscoelastic response of the system.

Pastes were prepared in batch (200 g) by addition of a weighed starch quantity to a previously weighed quantity of water to obtain 6/100 g suspension. The different values of pH were attained as previously described. Starch suspensions were gelatinized under constant stirring in a thermostatic bath at 95°C and once attained this final temperature, systems remained at 95°C during 20 min. The pH remained constant during heating. Samples were allowed to cool at room temperature in a controlled temperature cabinet (20°C), prior to performing the tests.

To determine the effect of hydrocolloids addition on the stability of yam starch pastes under refrigerated storage, batches were prepared as described for the determination of viscoelastic properties. As previously described, once an homogeneous system was obtained it was gelatinized (thermostatic bath at 95°C, held at 95°C for 20 min), divided into plastic tubes (2.5 cm diameter, 1.5 cm height), allowed to cool at room temperature (20°C) and stored in a controlled temperature chamber at 4°C for 0, 7 and 14 days. Part of these samples was used to determine exudate production.

2.6. Exudate determination

At different times (0, 7, 14 days) during refrigerated storage, starch systems were allowed to attain room temperature; exudate was decanted from the samples and weighed. Exudate was calculated as the weight of exudate per 100 g of sample. Three replicates were used.

2.7. Statistical analysis

Analysis of variance and comparison among treatments were carried out. Tukey’s test at 5% probability level determined differences among treatments. In the rheological experiments, means and standard errors were calculated with values obtained from different runs. Average amylographic curves are reproduced.

3. Results and discussion

3.1. Effect of pH on starch gelatinization parameters and rheological behavior

DSC results showed that samples at different pH conditions had the same initial, peak and final gelatinization temperatures (Table 1). Gelatinization enthalpies were not affected by the decrease in pH.

Shi and Seib (1992) found that waxy rice starch treated with acid (2.2 M HCl) up to 45 days showed a decrease in gelatinization temperature range and required less energy for gelatinization. In this high acidic condition the result was attributed to “corrosion” of amorphous regions of the granules caused by the acidic medium, facilitated by heating that promotes the exposition of the crystalline regions reducing the energy involved in the melting process (Wang & Wang, 2001).

In our case, neither gelatinization temperatures nor gelatinization enthalpies were affected, probably because the acidic treatment applied was not so drastic than that reported by Shi and Seib.

Pasting properties of yam starch were greatly affected by the pH of the medium as can be observed in the amylograph profiles (Fig. 1). Starch paste at pH 6, the usual pH of a well-washed native starch sample according to Rasper (1980), is highly stable to heat treatment. Amylograph patterns do not show the characteristic peak and paste viscosity increased during the period at constant temperature (95°C) and continued to increase during cooling. For comparison purposes, cassava starch pastes at the same concentration (6/100 g suspension) are also shown in Fig. 1. Cassava starch paste at pH = 6 showed a peak viscosity; afterwards viscosity decreased sharply. This behavior is characteristic of most starches since the granule breakdown produced along the amylograph test decreases the resistance to flow. When tested at pH = 5 yam starch showed the same pasting temperature than at pH 6 (80±1°C), but a higher increase of viscosity during heating, with a peak viscosity of 450 BU at 95°C. During the period at constant temperature (95°C) there was a sharp decrease of viscosity, which reflects less stability of the swollen granules against mechanical

<table>
<thead>
<tr>
<th>pH</th>
<th>( T_o ) (onset)</th>
<th>( T_p ) (peak)</th>
<th>( T_c ) (conclusion)</th>
<th>( \Delta H ) (J/g d.b.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>73.0^o (0.1)</td>
<td>76.0^o (0.1)</td>
<td>81.1^o (0.2)</td>
<td>14.4^o (1.2)</td>
</tr>
<tr>
<td>5</td>
<td>72.8^o (0.3)</td>
<td>76.2^o (0.1)</td>
<td>81.5^o (1.0)</td>
<td>13.9^o (1.0)</td>
</tr>
<tr>
<td>3</td>
<td>72.8^o (0.1)</td>
<td>76.8^o (0.5)</td>
<td>80.1^o (0.4)</td>
<td>9.7^o (0.7)</td>
</tr>
</tbody>
</table>

Standard errors are shown between parentheses. Values with the same letter are not statistically different (\( P < 0.05 \)). Runs were done in triplicate.
shear (Shuey & Schmitz, 1980). The cooling viscosity at pH = 5 was 100 BU lower than at pH 6. Starch gelatinized under higher acidic conditions (pH = 3) showed a lower peak viscosity at 84°C probably related to a more damaged granule structure. After this peak, the paste viscosity was drastically diminished, as a consequence of starch hydrolysis promoted by acidic heat treatment (Rogols, 1986). Severe acidic conditions also decreased the viscosity of the tapioca starch. However, yam starch paste at pH = 5 showed, during all the period at constant temperature and cooling stage, a higher viscosity than cassava starch at pH = 6. These results show that yam starch, as a thickener, would be more adequate than cassava starch at slight acidic conditions.

Oscillatory rheological assays demonstrated that the viscoelastic properties of gelatinized pastes were also affected by acidic conditions. Average $G^*$ values of the linear viscoelastic range (at 1 Hz) and standard errors were 1248 ± 90, 745 ± 57 and 479 ± 38 Pa for systems at pH = 6, 5 and 3, respectively. Frequency sweeps show differences in the complex modulus $G^*$ among the pastes gelatinized at pH 3, 5 and 6 (Fig. 2). Lower $G^*$ values were observed as pH decreased, particularly in the more acidic conditions. These results show the same tendency as those of Brabender amylographs.

3.2. Influence of hydrocolloid on starch gelatinization and pasting properties

Hydrocolloid addition up to 0.5/100 g suspension did not significantly ($P < 0.05$) affect gelatinization temperatures nor enthalpies (Table 2). Average value of gelatinization enthalpy was 14.4 J/g (SE = 1.2). Similar results were reported for other starch/gum systems (Ferrero, Martino, & Zaritzky, 1996; Biliaderis, Thessaloniki, Izidoriczky, & Prokpovich, 1997; Rojas, Rosell, & Barber, 1999).

Amylographic tests (Fig. 3a and b) showed evident differences comparing starch pastes with or without gums. The presence of gums did not affect pasting profiles (in all cases the absence of a peak indicates a similar behavior to that of yam starch pastes without gums), however higher viscosities were attained. Guar or xanthan gum tested alone (without starch) did not increase viscosity with temperature, even at the higher level (0.5%) (data not shown).

Yam starch pasting temperature (80 ± 1°C) decreased when guar or xanthan gums were added and this effect was directly dependent upon gum concentration. Pasting temperature was 75 ± 1°C for systems with 0.1/100 g guar or 0.1–0.3/100 g xanthan gum. For pastes with 0.3–0.5/100 g guar gum or 0.5/100 g xanthan gum pasting temperature was 70 ± 1°C (Fig. 3). Considering that gums did not produce changes in gelatinization temperatures measured by DSC, this decrease in pasting
temperature can be attributed to interactions between starch and gums as pointed out by Christianson et al. (1981) and Shi and BeMiller (2002).

The yam starch–gum mixtures showed higher hot paste viscosity during stirring at high temperatures than the starch alone and the effect was more pronounced when gum concentration increased. However the shape of the entire curves are similar to that of the yam starch. Guar was more effective than xanthan gum for viscosity and stability enhancement, in contrast with observations done by Rojas et al. (1999) for wheat flour. These gums interacting with the starch elements present in the hot

Table 2

<table>
<thead>
<tr>
<th>Gum type</th>
<th>Concentration (g/100 g suspension)</th>
<th>$T_o$</th>
<th>$T_p$</th>
<th>$T_c$</th>
<th>$\Delta H$ (J/g d.b.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>(without gum)</td>
<td>73.0° (0.1)</td>
<td>76.0° (0.1)</td>
<td>81.1° (0.2)</td>
<td>14.4° (1.2)</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>0.1</td>
<td>72.8° (0.1)</td>
<td>75.9° (0.1)</td>
<td>81.1° (0.5)</td>
<td>9.9° (1.4)</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>72.9° (0.2)</td>
<td>75.9° (0.1)</td>
<td>81.3° (0.4)</td>
<td>11.7° (1.4)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>72.9° (0.3)</td>
<td>76.1° (0.1)</td>
<td>81.0° (0.2)</td>
<td>12.4° (1.6)</td>
</tr>
<tr>
<td>Guar gum</td>
<td>0.1</td>
<td>73.0° (0.1)</td>
<td>76.1° (0.2)</td>
<td>81.3° (0.3)</td>
<td>13.9° (0.7)</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>72.9° (0.1)</td>
<td>75.9° (0.02)</td>
<td>81.3° (0.1)</td>
<td>13.7° (0.6)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>72.9° (0.2)</td>
<td>76.1° (0.3)</td>
<td>80.9° (0.4)</td>
<td>13.3° (0.8)</td>
</tr>
</tbody>
</table>

Standard errors are shown between parentheses.
Values with the same letter are not statistically different ($P<0.05$).
Runs were done in triplicate.

Fig. 3. Average amylographic patterns of yam starch pastes (6 g/100 g suspension): (a) with xanthan gum: ■ 0.1%; ▲ 0.3% and ● 0.5%. (b) With guar gum □ 0.1%; △ 0.3% and ○ 0.5%. ---- paste without gums. Temperature profile is shown as a function of time (temperature scale on right axis). Mean standard error = 15 UB.
paste (swollen granules, fragmented swollen granules, dispersed starch molecules) produced a viscosity increase during the cooling period (Fig. 3a and b). This increase is normally explained in starch systems as the tendency of the elements (mainly amylose molecules) to associate or retrograde with the temperature decrease (Rasper, 1980). In starch/gums mixtures the cold paste viscosity increase can be attributed to the gum–amylose and amylose–amylose interactions favored by cooling. According to our results, guar gum imparted higher cold viscosity to yam starch paste than xanthan gum; the opposite was reported by Sudhakar, Singhal, and Kulkarni (1995) for corn starch pastes. Shi and BeMiller (2002) demonstrated that a synergistic action exists on viscosity between starch and some gums and that guar or xanthan gums can be more or less effective depending on starch source (size and structure of the granule) analyzed.

3.3. Starch stability in hydrocolloid added systems under refrigerated storage

During refrigerated storage at 4°C, pronounced textural changes and exudate production were observed in systems without hydrocolloids. As shown in Fig. 4, exudate of yam starch increased up to 45 g exudate/100 g paste after 14 days of storage, however most of this exudate (84.4%) was released during the first 24 h of storage. Syneresis of the gel and amylose retrogradation led to hardened systems, of unacceptable texture. The addition of a hydrocolloid (xanthan or guar gums) up to 0.3/100 g suspension did not avoid exudate production but systems with xanthan gum released less exudate than systems with guar gum. However, a level of xanthan gum of 0.5/100 g suspension helped to prevent textural changes and syneresis was minimized.

Oscillatory rheological assays could not be performed in yam starch systems without hydrocolloids because of the marked syneresis and the firmness of the samples. In Fig. 5, $G'$ (elastic modulus) as a function of storage time (14 days) for yam starch systems with xanthan or guar gum are shown. In both systems, $G'$ markedly increased after 24 h of storage due to the development of a more firm structure attributed to starch retrogradation (Miles, Morris, Orford, & Ring, 1985). After this increase, $G'$ remained practically constant in pastes with xanthan gum during the rest of the storage period. Guar gum was less effective in preventing amylose retrogradation since $G'$ increased during the first week of storage and then remained constant. These results agree with the increase of exudate production (Fig. 4). Xanthan gum was more effective for maintaining the original texture in gelatinized yam systems. Ferrero and Zaritzky (2000) did similar observations for corn starch–sucrose systems.
added with several hydrocolloids and submitted to frozen storage.

The effect of xanthan and guar gums on preventing exudate production and textural changes associated to amylose retrogradation could be related to the capacity of these gums to avoid or minimize amylose–amylose interactions as well as to their hydrophilic character that prevents water separation.

4. Conclusions

Changes in pH (3, 5, 6) nor the addition of xanthan or guar gums (0.1 to 0.5 g/100 g suspension) did not affect yam starch gelatinization (temperature and enthalpy) as determined by DSC.

Yam starch pastes maintained high viscosities during heat treatment and mechanical stirring in neutral or slightly acidic conditions. This fact makes yam starch interesting as a potential ingredient in low acidic foods submitted to thermal treatment conditions.

The yam starch–gum mixtures showed higher hot paste viscosity during stirring at high temperatures than the starch alone and the effect was more pronounced when gum concentration increased.

Yam starch pastes are not stable during refrigerated storage, showing a marked tendency to syneresis and textural changes due to amylose retrogradation.

The addition of gums (xanthan or guar gum) to yam paste was effective in minimizing exudate release under refrigerated conditions. Xanthan gum at a level of 0.5/100 g prevented exudate production. Hydrocolloids also helped to prevent a marked increase in gel firmness characteristic of yam starch pastes. Thus, gums could allow the use of yam starch in foods that require refrigerated storage avoiding the undesirable effects of low temperatures on textural quality of these systems.

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