Carbohydrate Polymers 104 (2014) 66–72

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Rheological and biochemical properties of *Solanum lycocarpum* starch

Maria Carolina B. Di-Medeiros[a], Aline M. Pascoal[a,b], Karla A. Batista[a], Priscila Z. Bassinello[c], Luciano M. Lião[d], Maria Inês G. Leles[e], Kátia F. Fernandes[a,*]

[a] *Laboratório de Química de Proteínas, Departamento de Bioquímica e Biologia Molecular, Instituto de Ciências Biológicas – ICB II, Universidade Federal de Goiás, PB 131, Goiânia, GO, Brazil*
[b] *Instituto Federal de Educação, Ciência e Tecnologia de Goiás, Goiânia, GO, Brazil*
[c] *Embrapa – Centro Nacional de Pesquisa Arroz e Feijão, Laboratório de Grãos e Subprodutos, C. Postal 179, Santo Antônio de Goiás, GO, Brazil*
[d] *Instituto de Química, Universidade Federal de Goiás, PB 131, Goiânia, GO, Brazil*
[e] *Laboratório de Métodos de Extração e Separação LAMES – Instituto de Química, Universidade Federal de Goiás, CP 131, Goiânia, GO, Brazil*

ARTICLE INFO

Article history:
Received 12 November 2013
Received in revised form 6 January 2014
Accepted 7 January 2014
Available online 16 January 2014

Keywords:
Pasting properties
Retrogradation
Crystallinity
Thermal properties
Resistant starch
Digestibility

ABSTRACT

This study was conducted to evaluate the rheological and physicochemical properties of *Solanum lycocarpum* starch. The thermogravimetric analysis of *S. lycocarpum* starch showed a typical three-step weight loss pattern. Microscopy revealed significant changes in the granule morphology after hydrothermal treatment. Samples hydrothermally treated at 50 °C for 10 min lost 52% of their crystallinity, which was recovered after storage for 7 days at 4 °C. However, samples hydrothermally treated at 65 °C were totally amorphous. This treatment was sufficient to completely disrupt the starch granule, as evidenced by the absence of an endothermic peak in the DSC thermogram. The RVA of *S. lycocarpum* starch revealed 4440.7 cP peak viscosity, 2660.5 cP breakdown viscosity, 2414.1 cP final viscosity, 834.3 cP setback viscosity, and a pasting temperature of 49.6 °C. The low content of resistant starch (10.25%) and high content of digestible starch (89.78%) in *S. lycocarpum* suggest that this starch may be a good source for the production of hydrolysates, such as glucose syrup and its derivatives.

1. Introduction

Starch is a low-cost, renewable and biodegradable polymer produced by several plants. It is the most important vegetable storage polysaccharide and the main source of glucose in the human diet. Additionally, this polysaccharide is widely used in the food, textile, paper, chemical, pharmaceutical and biotechnological industries (Buléon et al., 1997; Falade & Okafor, 2013; Schirmer, Höchstötter, Jekle, Arendt, & Becker, 2013). The structure and the content of amylose and amylopectin vary depending on the source of the starch, and they determine the starch's functional and physicochemical properties.

Solanum lycocarpum St. Hill (Solanaceae) is a common and abundant plant in the Brazilian Cerrado. It was demonstrated in a previous work that *S. lycocarpum* fruits are a good source of starch, with a yield of 51% by dry weight. This yield is very high compared to those obtained from other traditional sources (Pascoal et al., 2013). In addition, the continuous expansion of this market demands new sources for starches with novel properties that will permit additional applications.

To determine the potential application of a starch, it is important to know its rheological and thermal properties, which drive the gelatinisation process.

The rheological knowledge of a starch is essential to better control its processing and to produce high-quality final products (Létang, Piau, & Verdier, 1999). Moreover, the gelatinisation of a starch is greatly affected by the molecular structure and the amylose/amylopectin ration (Simi & Abraham, 2008). Similarly, the molecular structure and amylose/amylopectin ratio determines the retrogradation degree of a starch during gelling. In foods, the gelatinisation and retrogradation of a starch during processing or storage greatly affect the product's texture, stability, quality, digestibility and functionality (Mutungi, Passauer, Onyango, Jaros, & Rohm, 2012).

Therefore, this study was conducted to better understand the thermal and rheological properties of the *S. lycocarpum* starch and thus the potential applications of this material.

2. Materials and methods

2.1. Materials

Unripe *S. lycocarpum* fruits used in this study were collected from the farm of the Universidade Federal de Goiás (Goiânia-GO, Brazil).

* Corresponding author. Tel.: +55 62 3521 1492; fax: +55 62 3521 1190.
E-mail addresses: kfernandes.lqp@gmail.com, katia@icb.ufg.br, katiaffernandes@hotmail.com (K.F. Fernandes).

0144-8617/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2014.01.023

2.2. Extraction of starch

S. lycocarpum starch was extracted as described by Pascoal et al. (2013). Briefly, the pulp was milled in the presence of 0.8% (w/v) citric acid solution. This material was deposited in a sieve (32 mesh) and washed successively with 0.05 mol L^{-1} NaOH and ethanol. The precipitated starch was dried in an air-forced oven at 45 °C until the weight was constant.

This methodology was also employed to extract the cassava and corn starches used in the pasting tests.

2.3. Thermogravimetric analysis (TG)

The thermal properties of the starch samples were measured with a SHIMADZU DTG-60/60 H thermal analyser with the temperature ranging from room temperature to 500 °C and increasing at 10 °C min^{-1}. The test was conducted under nitrogen atmosphere using a platinum pan. The initial weight of the sample was 17.6 mg.

2.4. Scanning electron microscopy (SEM) of heat-treated starch granules

The behaviour of the starch granules during hydrothermal treatment was examined in a JEOL JSM 6610 scanning electron microscope using a secondary electron detector with 15 kV of acceleration. Hydrothermal treatment consisted of incubating a sample containing 0.5 mg of starch in 10 mL of distilled water for 10 min in a bath pre-heated to 40, 50, 60 or 70 °C. After incubation, the samples were maintained at room temperature until completely dried. The samples were pulverised, and the powder was used in the SEM analysis.

2.5. Solubility and swelling power

The swelling power and the solubility of starches were determined at temperatures of 60, 70, 80 and 90 °C, as described (Leach, McCowen, & Schoch, 1959). The measurements were made by adding 1 g of starch and 50 mL of distilled water to pre-weighed tubes. The suspension was heated in a water bath for 30 min, and then the supernatant was collected and dried to a constant weight in an oven to quantify the soluble fraction. The tubes containing the swollen starch granules were weighed to determine the swelling power. The solubility and swelling power were calculated as described in the following equations:

$$\text{Solubility}(\%) = \frac{\text{soluble mass starch}}{\text{initial mass starch}} \times 100$$

$$\text{Swelling power}\,(g\,g^{-1}) = \frac{\text{final mass swollen of strach}}{\text{initail mass strach}}$$

2.6. X-ray diffractometry of hydrothermally treated starch granules

The X-ray diffractometry analysis was performed in samples of hydrothermally treated starch granules with a Shimadzu XRD-6000 X-ray diffractometer operating with the following conditions: tube Cu Kα radiation, 40 kV and 100 mA, scan ranging from 10,000 to 80,000.

Hydrothermal treatment consisted of incubating a sample containing 1.0 g of starch in 3 mL of distilled water for 10 min in a bath pre-heated to 50 °C or 60 °C. The samples were then left to dry at room temperature in a desiccator until analysis. To evaluate whether *S. lycocarpum* starch recovered its crystallinity after retrogradation, hydrothermally treated samples were stored at 4 °C for 7 days and then left to dry at room temperature in a desiccator until analysis.

The degree of crystallinity was estimated following the method of Nara and Komiy (1983). The crystallinity was expressed through the mathematical calculation of the peak area under the curve in the X-ray diffraction pattern. The degree of crystallinity was calculated according to the following equation:

$$D_c(\%) = \frac{A_c}{A_c + A_a} \times 100$$

where D_c refers to the degree of crystallinity, A_c refers to the crystallised area on the X-ray diffractogram, and A_a refers to the amorphous area on the X-ray diffractogram.

2.7. Differential scanning calorimetry (DSC)

The thermal characteristics of *S. lycocarpum* starch were studied with a Mettler Toledo model 822^e differential scanning calorimeter. Samples (3.5 mg) were weighed into aluminium pans, and deionised water (8 μL) was added. The pans were hermetically sealed and kept at room temperature for 1 h before analysis. The samples were heated from 25 to 120 °C at a rate of 10 °C min^{-1}. An empty aluminium pan was used as a reference. From the curve, the enthalpy of gelatinisation (ΔH) and the onset (*To*), peak (Tp), and end (Tc) temperatures were obtained using the data-processing software supplied with the DSC instrument (Kim, Wiesenborn, & Grant, 1997).

Hydrothermal treatment consisted of incubating a sample containing 1.0 g of starch in 3 mL of distilled water for 10 min in a bath pre-heated at 50 °C or 65 °C. The samples were then left to dry at room temperature in a desiccator until analysis.

To characterise the extent of the loss of crystallinity and retrogradation, a second DSC scan was performed using samples pre-treated at 50 °C or 65 °C and stored for 7 days at 4 °C. During the second DSC scan, the samples were heated at the same temperature interval used for assessing gelatinisation properties (Ovando-Martínez, Osorio-Díaz, Whitney, Bello-Pérez, & Simsek, 2011).

2.8. Pasting properties (RVA)

The pasting properties of *S. lycocarpum* starch were evaluated using a Rapid Visco Analyzer (RVA4, New Port Scientific Pty). Briefly, 3 g (dry) of starch was dispersed in 25 mL distilled water. A programmed heating and cooling cycle was employed at constant shear rate; the sample was held at 50 °C for 1 min, heated to 95 °C at a rate of 9.5 °C min^{-1}, and then held at 95 °C for 2.5 min. The samples were cooled subsequently to 50 °C at a rate of 11.842 °C min^{-1}. The parameters recorded were pasting temperature, peak viscosity, trough viscosity (minimum viscosity at 95 °C), final viscosity (viscosity at 50 °C), breakdown viscosity (peak – trough viscosity) and setback viscosity (final – trough viscosity). Pasting temperature is the temperature at the onset of a rise in viscosity.

2.9. Resistant starch (RS) and digestibility

Resistant starch was measured according to the methodology of Goni, Garia-Alinos, Manas, and Saura-Calixto (1997). Briefly, to remove protein and digestible starch, samples were incubated with pepsin for 1 h at 40 °C, pH 1.5 and then with α-amylase for 16 h at 37 °C, pH 6.9. The samples were centrifuged at 1430 g, the supernatant was removed, and the residue was treated with 2 mol L^{-1} KOH solution for 30 min. The samples were then incubated with amyloglycosidase for 45 min at 60 °C, pH 4.75 and centrifuged at 1430 × *g*. The residue was precipitated and dried in an air-forced

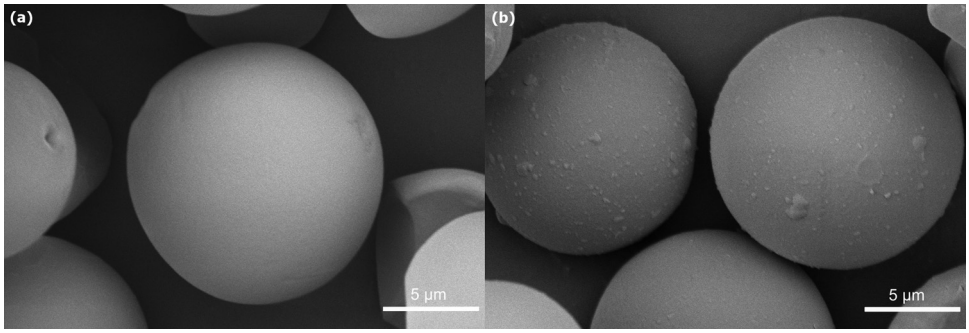

Fig. 1. SEM microstructures of (a) native and (b) hydrothermally treated (40 °C, 10 min) *S. lycocarpum* starch.

oven at 45 °C until the weight was constant. The percentage of resistant starch and total digestible starch were calculated according to the equations:

$$\mathrm{RS}(\%) = \frac{W_i(\mathrm{starch}) - W_f(\mathrm{starch})}{W_i(\mathrm{starch})} \times 100$$

$$\mathrm{DS} = W_i - \mathrm{RS}$$

where *RS* is the percentage of resistant starch, W_i is the initial weight of starch, W_f is the final weight of starch, and DS is the digestible starch.

3. Results and discussion

3.1. Thermogravimetric analysis (TG)

The thermal gravimetric analysis of *S. lycocarpum* starch showed a typical three-step weight loss pattern. In the first weight-loss step, which occurred in the range from 55 to 106.5 °C, a 15.1% weight loss was observed, corresponding to the vaporisation of volatile compounds, especially water molecules adsorbed to the starch granules.

A plateau was then observed until the temperature reached approximately 300 °C, when the second step related to the decomposition of the carbon backbone began. This second and main step of weight loss occurred in a sharp interval between 302.1 and 328.3 °C and represented a 62.4% weight loss. The sharp interval of weight loss indicates the presence of large amounts of compounds with very similar thermal properties, which is characteristic of homopolysaccharides such as starches. Similar to what occurs with starches from other sources, it is expected that the main decomposition step (from 300 to 350 °C) consists of a rapid dehydration and decomposition of the hydroxyl groups from glucose residues to form water molecules. Finally, the third step of weight loss ($T > 330$ °C) leads to the accumulation of carbon.

3.2. Scanning electron microscopy (SEM) of hydrothermally treated starch granules

The effect of the hydrothermal treatment of *S. lycocarpum* starch can be observed in the SEM images of the granules. Hydrothermal treatment at 40 °C resulted in a slight modification in the surface of the granule (Fig. 1b). The hydrothermal treatment for 10 min at 50 °C resulted in morphological changes and enhancement in the size of the starch granules from approximately 10–14 μm (Fig. 1) to 150–300 μm (Fig. 2a). Starch granules hydrothermally treated at 60 °C presented disordered and swelled structures (Fig. 2b), and a completely disordered and vitreous morphology was observed after hydrothermal treatment at 70 °C for 10 min (Fig. 2c).

3.3. Swelling power and starch solubility

The swelling power and solubility were studied to understand the nature of intra-granular bonds. Differences in swelling and solubility profiles indicate differences in the bonding forces within the starch granules. These bonds relax with increases in thermal agitation, which causes the starch granules to take up water, swell, and to release solubilised amylose into the aqueous medium (Balagopalan, Padmaja, Nanda, & Moorthy, 1988).

The swelling behaviour of *S. lycocarpum*, cassava and corn starches were investigated over temperatures ranging from 60 °C to 90 °C (Fig. 3a).

In general, the swelling power of the studied starches was found to increase as the temperature increased. However, the swelling profile of the studied starches was different. The swelling power of the *S. lycocarpum* starch showed a linear relationship with temperature ($r^2 = 0.98$), whereas cassava starch presented an exponential relationship ($r^2 = 0.95$). For corn starch, the swelling power increased until the temperature reached 80 °C and then remained stable.

This result can be explained by differences in the pattern and degree of association of the polysaccharide molecules in the amorphous areas of the granules, which leads to the different swelling

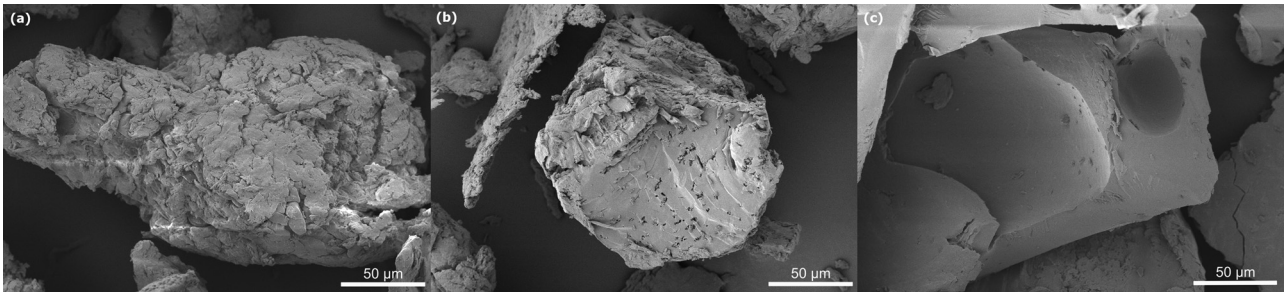

Fig. 2. SEM microstructures of starches from *S. lycocarpum* hydrothermally treated at (a) 50 °C, (b) 60 °C and (c) 70 °C for 10 min.

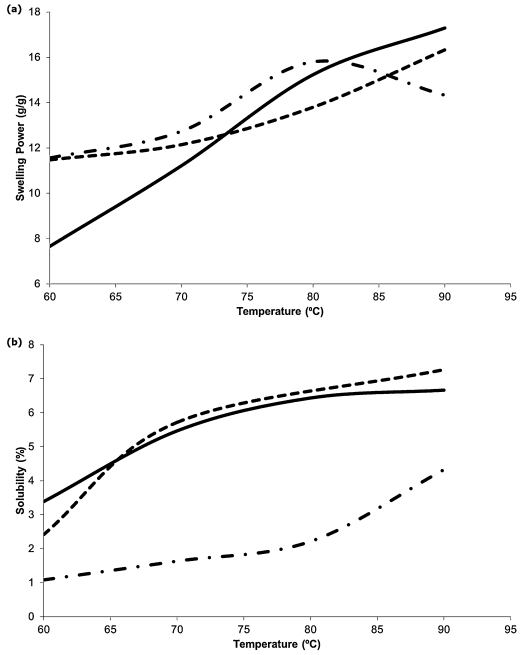

Fig. 3. Swelling power (a) and solubility (b) of the studied starches. (—) *Solanum lycocarpum*; (– –) cassava; and (– · –) corn.

behaviour in the studied starches (Joshi et al., 2013; Leach et al., 1959).

The starch solubility is a parameter that reflects the disintegration of the granules and the release of low molecular-weight compounds, primarily amylose. With the increasing temperature, water gradually swells the granules of starch and disrupts some of intermolecular and intramolecular hydrogen bonds among starch molecules (Ma, Jian, Chang, & Yu, 2008). At this time, the crystalline structure is destroyed, and an amorphous structure forms.

The studied starches showed an increased solubility as a function of temperature (Fig. 3b). The solubility of *S. lycocarpum* and cassava starches was similar, showing a two-step curve with increasing solubility up to 68 °C, above which there was a plateau. In contrast, the solubility of corn starch slowly increased as the temperature was raised to 78 °C, above which the solubility increased more rapidly. This difference in the solubility behaviour may be explained by the thermal properties and composition of the studied starches.

The hydration, swelling and solubility of starch during heating reflect the magnitude of the interaction between the starch chains within the amorphous and crystalline domains (Liu, Yu, Chen, & Li, 2007). The amylose to amylopectin ratio and the molecular weight and distribution of amylose and amylopectin may affect the extent of this interaction, resulting in variation in the swelling power and solubility of the starch.

3.4. X-ray diffractometry of hydrothermally treated starch

The heat treatment of starch in the presence of water results in the disruption of its crystalline structure. Factors such as the source, amylose content, chain length, and especially temperature of the hydrothermal treatment highly influence the loss of the crystallinity.

To examine the effect of hydrothermal treatment on the crystalline structure of *S. lycocarpum* starch, X-ray studies were conducted using samples heated at 50 °C or 65 °C for 10 min (Fig. 4).

Hydrothermal treatment at 50 °C resulted in several changes in *S. lycocarpum* starch. As previously reported, native *S. lycocarpum* starch is a C-type polymorph with strong reflection at 2θ of approximately 15.3°, 17.2°, 19.6°, 24.4°, 26.3° and a broad peak at 2θ of approximately 22.2°. As can be observed in Fig. 4a, the hydrothermal treatment caused the disappearance of the reflections at 2θ of approximately 24.4° and 26.3°. The pattern of the hydrothermally treated *S. lycocarpum* starch became very similar to the A-type polymorph.

The alteration observed in the diffractogram pattern was most likely caused by the close-packed arrangement assumed by amylopectin chains after the leaching of amylose from the starch granule, which is the initial event during gelatinisation. In this sense, it is possible that the reflections at 2θ of approximately 24.4° and 26.3° are related to a pattern produced by the interaction among the amylose chains or the amylose and amylopectin chains in the crystalline region of the intact starch granule. Similar results were obtained by Reddy, Suriya, and Haripriya (2013) working with starch from *Phaseolus vulgaris*.

Although the peaks at 2θ of approximately 15°, 17°, 20° and 22° remained strongly visible in the diffractogram, the crystallinity was reduced from 38% (Pascoal et al., 2013) in the native starch to 18% in the hydrothermally treated sample.

In contrast, the hydrothermal treatment at 65 °C for 10 min was sufficient to disrupt the internal forces that maintain the crystalline structure of the *S. lycocarpum* starch granule, making it totally amorphous (Fig. 4b).

3.5. Retrogradation studies

Retrogradation is a phenomenon involving the interaction among amylose and amylopectin chains to allow helical aggregation and an increase in crystalline order after gelatinisation. The structural arrangement of the starch chains within the amorphous and crystalline regions of the granule influence the extent of granule breakdown (Perera & Hoover, 1999). Therefore, the retrogradation property of a starch gel is influenced by its structural characteristics that drive the interactions among starch chains during gel storage. The retrogradation profile influences the quality, acceptability and shelf-life of starch-containing foods (Cozzolino, Roumeliotis, & Eglinton, 2013).

In this study, the retrogradation of *S. lycocarpum* starch gels was assessed by X-ray diffractometry and DSC. Fig. 5 shows the diffractogram of *S. lycocarpum* starch gels obtained by heating starch at 50 or 65 °C and then storing it at 4 °C for 7 days.

The diffractogram of the sample hydrothermally heated at 50 °C (Fig. 5a) is very similar to that of the native *S. lycocarpum* starch, which is compatible with a C-type polymorph (Pascoal et al., 2013). This result confirms that under the conditions employed in this hydrothermal treatment, the starch granule was only partially disrupted and may totally recover its structural order during storage at 4 °C for 7 days. Another piece of evidence for the structural reordering of this sample was the increase in the crystallinity degree, which increased from 18.24% immediately after hydrothermal treatment to 38.03% after 7 days storage, a value that is very close to that of the native starch (Pascoal et al., 2013).

However, the hydrothermal treatment at 65 °C seems to be effective in disrupting the internal interactions of amylose and amylopectin in the starch granule. The diffractogram of the sample stored at 4 °C for 7 days (Fig. 5b) shows a reflection peak at 2θ of approximately 17.0°. The reordering of the crystalline structure was low; the crystallinity degree was approximately 13.5%.

Several authors have reported that the A-type polymorph is mainly related to starches containing short-chain and close-packed amylopectin molecules (Cheetham & Tao, 1998; Hizukuri, 1985; Hizukuri, Kaneko, & Takeda, 1983; Xie et al., 2009). According to Yu and Christie (2005), the phase transition during the gelatinisation of these short-chain amylopectin-containing starches is

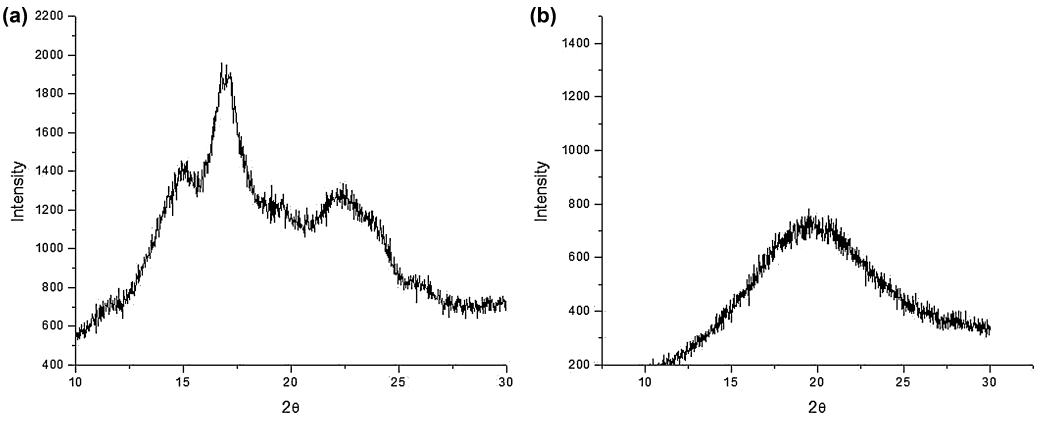

Fig. 4. X-ray diffraction spectra of the *Solanum lycocarpum* starch after hydrothermal treatment at (a) 50 °C and (b) 60 °C for 10 min.

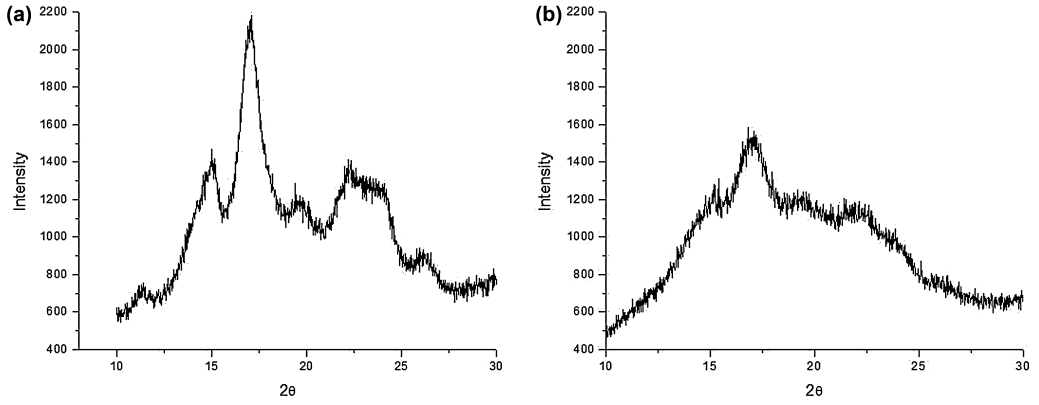

Fig. 5. X-ray diffraction spectra of the *Solanum lycocarpum* starch after hydrothermal treatment at (a) 50 °C and (b) 60 °C for 10 min, stored at 4 °C for 7 days.

characterised by the distancing of the helices without the loss of the primary structure, which they named a gel-ball structure. These gel-ball structures retain the "memory" of a regular pattern even after gelatinisation. These gel-ball structures need less energy to move than long-chain structures, especially in the presence of water, and starches containing these structures recover part of their crystallinity even after gelatinisation.

Considering these reports and the data obtained from the X-ray analysis of the hydrothermally treated *S. lycocarpum* starch, it is possible to suggest the presence of short-chain amylopectin in its composition. This inference is supported by the change from a C-type to A-type polymorph and the recovery of the crystallinity after storage for 7 days, which was complete after hydrothermal treatment at 50 °C and partial after the higher temperature treatment (65 °C).

In a previous study, the differential scanning calorimetry (DSC) of *S. lycocarpum* starch showed that the temperature of thermal transition (Tp) was 65 °C (Pascoal et al., 2013). In this study, hydrothermally treated samples were examined by DSC to evaluate the extension of the retrogradation process (Fig. 6).

The presence of an endothermic peak at 65 °C was observed in the thermogram of the sample hydrothermally treated at 50 °C. This endothermic peak shifts to 68 °C when the sample treated at 50 °C was stored at 4 °C for 7 days (Fig. 6a). These peaks are indicative of the presence of intact or partially gelatinised granules. This observation is in agreement with SEM and X-ray data (Figs. 2a, 4a and 5a).

However, the hydrothermal treatment at 65 °C, independently of whether it was followed by storage at 4 °C for 7 days, was sufficient to completely disrupt the starch granule, as evidenced by the absence of an endothermic peak in the thermogram (Fig. 6b). The recovery of the structural order of the *S. lycocarpum* starch after heat hydrothermal treatment at 65 °C was not sufficient to result in an endothermic peak in the DSC curve.

3.6. Pasting properties

Pasting properties are greatly affected by the granule size, the molecular structure of amylopectin, the amylose/amylopectin ratio, the extent of lipid/amylose complexes, and the thermal process employed to induce starch gelatinisation (Simi & Abraham, 2008; Tester, 1997).

Heating causes the disruption of internal ordered structure, and amylose starts to leach from the granules. Due to the heating and plasticisation effect of water, hydrogen bonds stabilising the crystalline structure in the amylopectin are destabilised, and water forms hydrogen bonds with amylopectin, leading to hydration and swelling. The starch granules become increasingly susceptible to shear disintegration due to swelling. The phase transition in starch was monitored by a viscometric method using a Rapid Visco Analyzer (RVA). The Rapid Visco Analyzer is an effective instrument for measuring the viscous properties of starches relating functionality to structural properties. The pasting characteristics of cassava, corn and *S. lycocarpum* starches were evaluated and are presented in Table 1.

As can be observed, the pasting temperature was similar for all studied starches. Pasting temperature reveals the minimum temperature required to cook, as well as the temperature at which the viscosity begins to increase during the heating process.

Among these starches, cassava starch exhibited the highest peak (4967.4 cP) and trough viscosity (2455.2 cP), followed by *S. lycocarpum* (4440.7 cP and 1779.72 cP). Lower values of peak and trough

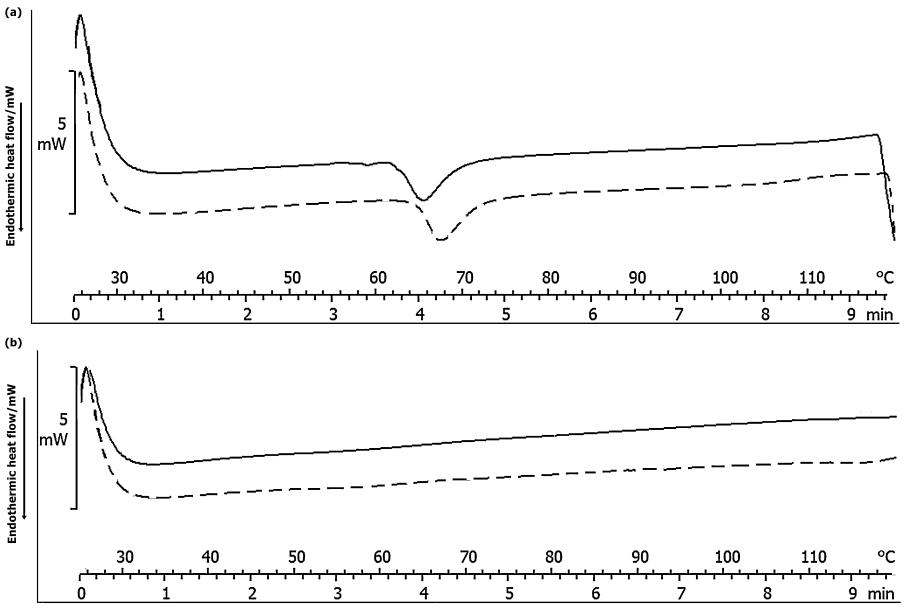

Fig. 6. DSC curve obtained for hydrothermally treated starch from *Solanum lycocarpum* at (a) 50 °C and (b) 65 °C. Dashed lines correspond to starch that was stored at 4 °C for 7 days after hydrothermal treatment.

Table 1
Pasting properties of the starches from *S. lycocarpum*, cassava and corn determined by RVA.

Starch	Pasting temperature (°C)	Peak (cP)	Trough (cP)	Breakdown (cP)	Final viscosity (cP)	Setback (cP)
S. lycocarpum	49.6 ± 0.1	4440.7 ± 40.9	1779.7 ± 28.2	2660.5 ± 69.2	2414.1 ± 256.3	834.3 ± 9.1
Cassava	49.1 ± 0.2	4967.4 ± 136.2	2455.2 ± 13.6	2512.2 ± 149.1	3296.7 ± 84.5	841.5 ± 97.9
Corn	49.6 ± 0.1	2071.3 ± 75.1	1275.4 ± 54.2	795.8 ± 100.7	3308.4 ± 9.9	2033.0 ± 61.1

Results are the mean ± standard deviation of three determinations.

viscosity were observed for corn (2071.3 cP and 1275.4 cP). Peak viscosity is related to the maximum swelling of the starch granule prior to disintegration and has also been described as the equilibrium point between the swelling and rupture of the granules (Liu, Yu, Xie, & Chen, 2006). Hoover (2001) stated that granules with high peak viscosity have weaker cohesive forces within the granules than those with lower values and would disintegrate more easily.

The high value of peak viscosity observed for *S. lycocarpum* starch indicates that, in spite of its high degree of crystallinity (38%) and high amylose content (34.7%) (Pascoal et al., 2013), the forces of interaction among the polymers that constitute the granule are weak. It is possible that *S. lycocarpum* starch contains short- or intermediate-chain amylose that easily moves out to the bulk, allowing the entrance of water molecules into the granule, contributing to the equilibration of the dynamic forces involved in the granule swelling.

Breakdown viscosity is indicative of the paste stability and results from the rupture of the swollen starch granules. The breakdown values showed that the paste of *S. lycocarpum* (2660.5 cP) and cassava (2512.2 cP) presents thermal stability. However, these pastes were less stable than corn starch (795.8 cP).

After granule rupture, when the system is cooled, the amylose chains that leached into the aqueous phase begin to associate and gradually form a gel. The gel formation leads to the final equilibrium viscosity. In this study, the highest final viscosity was observed for corn starch (3308.4 cP), followed by cassava (3296.7 cP) and *S. lycocarpum* starch (2414.1 cP).

Some factors must be considered to explain the final viscosity obtained for *S. lycocarpum* starch. The high value of peak viscosity associated with the high values of swelling power evidenced the weak forces that maintain the structure of the granule. In addition, the low value of trough viscosity and high value of breakdown viscosity confirmed the complete failure of the granule structure and leaching of amylose and amylopectin into the bulk. The disintegration of the starch granule leads to the high value of solubility obtained for *S. lycocarpum* starch.

In this scenario, a high final viscosity was expected, considering the important role that amylose plays in the gel network formation during gelling. However, the final viscosity was only intermediate. An explanation for this finding may be the presence of short-chain amyloses.

Finally, the setback viscosity is generally used as a measure of the gelling ability or retrogradation tendency upon the cooling of cooked starch pastes (Simi & Abraham, 2008). As can be observed in Table 1, *S. lycocarpum* starch presented a low setback value, thus signalling a reduced tendency to retrogradate. Therefore, its inclusion in foodstuffs may contribute to the final product's stabilisation.

3.7. Resistant starch (RS) and digestibility

The *in vitro* digestibility is an important parameter to be evaluated when proposing applications for a starch from a new source. The digestibility will determine the availability of glucose, and hence, the glycaemic index, the caloric value, the fermentability and several other important chemical and nutritional characteristics of the starch.

The digestibility of a starch depends on the portion of molecules susceptible to hydrolytic activity and the structural characteristics of the starch grain. In this sense, the presence of high amounts of amylose will facilitate hydrolysis, whereas the presence of a crystalline structure protects the glucosidic bonds against amylase activity.

The test for the *in vitro* digestibility of *S. lycocarpum* starch showed 89.8% hydrolysis, a higher value than that obtained for cassava (82.1%) or corn (78%). *S. lycocarpum* also presented the lowest amount of resistant starch (10.3%), compared to cassava (17.9%) and corn (22%). The lower content of resistant starch and high amount of digestible starch in *S. lycocarpum* suggest that this starch is a good source for the production of hydrolysates, such as glucose syrup and its derivatives.

4. Conclusion

In this study, the morphological, physicochemical, rheological and biochemical properties of *S. lycocarpum* starch were investigated. SEM analysis showed that hydrothermal treatment above 40 °C results in morphological changes, culminating in the starch granule rupture. The hydrothermal treatment at 50 °C for 10 min partially destroys the crystalline structure, which is completely recovered after storage at 4 °C for 7 days. In contrast, hydrothermal treatment at 65 °C for 10 min results in the complete disordering of the *S. lycocarpum* starch, which was evidenced by X-ray and DSC analysis. The pasting properties of *S. lycocarpum* starch revealed that this starch is a good source for inclusion in foodstuffs, because it presents a low setback value. *S. lycocarpum* starch presented high swelling power and solubility compared to starches from cassava and corn. In addition, *in vitro* starch digestibility revealed this material as a valuable source of glucose, due to its high digestibility and low amount of resistant starch.

Acknowledgments

Aline M. Pascoal thanks FAPEG for fellowship support. Karla A. Batista and Maria Carolina B. Di-Medeiros thank CAPES for fellowship support.

References

Balagopalan, C., Padmaja, G., Nanda, S. K., & Moorthy, S. N. (1988). *Cassava in food, feed and industry*. Boca Raton/Florida: CRC Press Inc.

Buléon, A., Pontoire, B., Riekel, C., Chanzy, H., Helbert, W., & Vuong, R. (1997). Crystalline ultrastructure of starch granules revealed by synchrotron radiation microdiffraction mapping. *Macromolecules*, *30*, 3952–3954.

Cheetham, N. W. H., & Tao, L. (1998). Variation in crystalline type with amylose content in maize starch granules: An X-ray powder diffraction study. *Carbohydrate Polymers*, *36*, 277–284.

Cozzolino, D., Roumeliotis, S., & Eglinton, J. (2013). Relationships between starch pasting properties, free fatty acids and amylose content in barley. *Food Research International*, *51*, 444–449.

Falade, K. O., & Okafor, C. A. (2013). Physicochemical properties of five cocoyam (*Colocasia esculenta* and *Xanthosoma sagitifolium*) starches. *Food Hydrocolloids*, *30*, 173–181.

Goni, I., Garia-Alinos, A., Manas, E., & Saura-Calixto, F. (1997). A starch hydrolysis procedure to estimate glycemic index. *Nutrition Research*, *17*, 427–437.

Hizukuri, S. (1985). Relationship between the distribution of the chain length of amylopectin and the crystalline structure of starch granules. *Carbohydrate Polymers*, *141*, 295–306.

Hizukuri, S., Kaneko, T., & Takeda, Y. (1983). Measurement of the chain length of amylopectin and its relevance to the origin of crystalline polymorphism of starch granules. *Biochimica et Biophysica Acta*, *760*, 188–191.

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: A review. *Carbohydrate Polymers*, *45*, 253–267.

Joshi, M., Aldred, P., McKnight, S., Panozzo, J. F., Kasapis, S., Adhikari, R., et al. (2013). Physicochemical and functional characteristics of lentil starch. *Carbohydrate Polymers*, *92*, 1484–1496.

Kim, Y. S., Wiesenborn, D. P., & Grant, L. A. (1997). Pasting and thermal properties of potato and bean starches. *Starch*, *49*, 97–102.

Leach, H. W., McCowen, L. D., & Schoch, T. J. (1959). Structure of the starch granule. I. Swelling and solubility patterns of various starches. *Cereal Chemistry*, *36*, 534–544.

Létang, C., Piau, M., & Verdier, C. (1999). Characterization of wheat flour-water doughs. I. Rheometry and microstructure. *Journal of Food Engineering*, *41*, 121–132.

Liu, H., Yu, L., Chen, L., & Li, L. (2007). Retrogradation of corn starch after thermal treatment at different temperatures. *Carbohydrate Polymers*, *69*, 756–762.

Liu, H., Yu, L., Xie, F., & Chen, L. (2006). Gelatinization of cornstarch with different amylose/amylopectin content. *Carbohydrate Polymers*, *65*, 357–363.

Ma, X. F., Jian, R. J., Chang, P. R., & Yu, J. G. (2008). Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites. *Biomacromolecules*, *9*, 3314–3320.

Mutungi, C., Passauer, L., Onyango, C., Jaros, D., & Rohm, H. (2012). Debranched cassava starch crystallinity determination by Raman spectroscopy: Correlation of features in Raman spectra with X-ray diffraction and 13C CP/MAS NMR spectroscopy. *Carbohydrate Polymers*, *87*, 598–606.

Nara, S., & Komiy, T. (1983). Studied on the relationship between water-saturated state and crystallinity by the diffraction method for moistened potato starch. *Starch*, *35*, 407–410.

Ovando-Martínez, M., Osorio-Díaz, P., Whitney, K., Bello-Pérez, L. A., & Simsek, S. (2011). Effect of the cooking on physicochemical and starch digestibility properties of two varieties of common bean (*Phaseolus vulgaris* L.) grown under different water regimes. *Food Chemistry*, *129*, 358–365.

Pascoal, A. M., Di-Medeiros, M. C. B., Batista, K. A., Leles, M. G. I., Lião, L. M., & Fernandes, K. F. (2013). Extraction and chemical characterization of starch from *S. lycocarpum* fruits. *Carbohydrate Polymers*, *98*, 1304–1310.

Perera, C., & Hoover, R. (1999). Influence of hydroxypropylation on retrogradation properties of native, defatted and heat–moisture treated potato starches. *Food Chemistry*, *64*, 361–375.

Reddy, C. K., Suriya, M., & Haripriya, S. (2013). Physico-chemical and functional properties of resistant starch prepared from red kidney beans (*Phaseolus vulgaris* L.) starch by enzymatic method. *Carbohydrate Polymers*, *95*, 220–226.

Schirmer, M., Höchstötter, A., Jekle, M., Arendt, E., & Becker, T. (2013). Physicochemical and morphological characterization of different starches with variable amylose/amylopectin ratio. *Food Hydrocolloids*, *32*, 52–63.

Simi, C. K., & Abraham, T. E. (2008). Physicochemical, rheological and thermal properties of Njvara rice (*Oryza sativa*) starch. *Journal of Agricultural and Food Chemistry*, *56*, 12105–12113.

Tester, R. F. (1997). Starch: The polyssacharide fractions. In P. J. Frazier, P. Richmond, & A. M. Donald (Eds.), *Starch structure and functionality* (pp. 163–171). Cambridge, UK: Royal Society of Chemistry.

Xie, F., Yu, L., Su, B., Liu, P., Wang, J., Liu, H., et al. (2009). Rheological properties of starches with different amylose/amylopectin ratios. *Journal of Cereal Science*, *49*, 371–377.

Yu, L., & Christie, G. (2005). Microstructure and mechanical properties of orientated thermoplastic starches. *Journal of Materials Science*, *40*, 111–116.