International Journal of Biological Macromolecules 117 (2018) 1029–1038

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: http://www.elsevier.com/locate/ijbiomac

Structure and properties of starches from Arracacha (*Arracacia xanthorrhiza*) roots

Nanci Castanha [a], James Villar [b], Manoel Divino da Matta Junior [a], Carlota Boralli Prudente dos Anjos [a], Pedro Esteves Duarte Augusto [a,*]

[a] Department of Agri-food Industry, Food and Nutrition (LAN), Luiz de Queiroz College of Agriculture (ESALQ), University of São Paulo (USP), Piracicaba, SP, Brazil
[b] Departamento de Ingeniería de Alimentos y Productos Agropecuarios, Facultad de Industrias Alimentarias, Universidad Nacional Agraria La Molina (UNALM), Lima, Peru

ARTICLE INFO

Article history:
Received 29 March 2018
Received in revised form 28 May 2018
Accepted 4 June 2018
Available online 05 June 2018

Keywords:
Arracacha
Arracacia xanthorrhiza Bancroft
Starch

ABSTRACT

Arracacha (*Arracacia xanthorrhiza* Bancroft) is an underexplored Andean root with a high starch content. In this work, starches from two different varieties of Peruvian arracacha were evaluated and characterized in relation to their granule morphology, molecular structure and properties. The starches presented round or polygonal shapes, with a mean diameter of ~20 μm and B-type granules. They were rich in amylopectin molecules with long chain lengths (with the ability to complex iodine) and some with intermediate sizes (indicating a defective crystalline structure). The starches presented low gelatinization temperature, enthalpy of gelatinization and tendency to retrogradation and high peak apparent viscosity and swelling capacity, even at moderate temperatures (60 °C), characteristics of high interest for industrial purposes. Besides, the starches presented a smooth and elastic gel and a high paste clarity. Overall, the arracacha roots presented attractive properties and can be used as an alternative botanical source for starch extraction.

1. Introduction

Starches are biomolecules with many industrial applications and relevant economic importance. They are used in many industries, for food (human and animal), pharmaceuticals, cosmetics, chemicals, petrochemicals and textiles, among others. Consequently, different properties are demanded, highlighting the importance of characterizing new natural sources.

Arracacia Bancroft is a genus of about 30 species, *Arracacia xanthorrhiza* being the only one cultivated [1]. The *Arracacia xanthorrhiza* Bancroft is possibly one of the oldest cultivated plants in the Andes, earlier even than the domestication of the potato (*Solanum tuberosum*) [2, 3]. The name "arracacha" is derived from the Quechua word "*racacha*" [4], and has been accepted as a standard term in several literatures, including in English. According to Hermann [1], other terms for the arracacha, such as the "Peruvian carrot" or "Peruvian parsnip", should be avoided to prevent misunderstandings. Currently, this root is cultivated in areas from Mexico to South America [1].

If compared to other popular root crops, like cassava and carrots, arracacha can be considered high perishable, a characteristic that constrains its commercial exploitation *in natura* [5]. In contrast to its current low consumption, commercialization and industrialization, which make this "underutilized", the arracacha is an Andean crop adapted to a wide climatic range in Peru [6], if compared with high-altitude species such as oca, olluco, maca or mashua, with a narrow ecological range [1]. Consequently, industrial applications for this root are highly relevant in order to boost its commercial importance and thus allow its cultivation.

An alternative for the best use of arracacha would be for starch extraction, since this root has a high starch content that is relatively simple to extract. In fact, there are some works with very promising results regarding the content and characterization of starch from arracacha varieties from Brazil [7–11], Venezuela [12] and Colombia [13]. However, although the Peruvian germplasm bank is very broad regarding the arracacha [14], as far as we know, no studies have been published about starches from the Peruvian varieties. Starch characteristics, such as granule and molecular size distribution, shape and composition, are largely influenced by its botanical origin [15], leading to different properties and possible applications.

Consequently, this work aims to characterize and evaluate starches from two different varieties of Peruvian arracacha ("arracacha morada" and "arracacha amarilla"), describing their structure, properties and possible applications.

2. Material and methods

2.1. Material

The starches were extracted from arracacha roots (*Arracacia xanthorrhiza* Bancroft), purchased from farmers in Peru. Two different

* Corresponding author at: Avenida Pádua Dias, 11, Piracicaba, SP 13418-900, Brazil.
E-mail address: pedro.ed.augusto@usp.br (P.E.D. Augusto).

https://doi.org/10.1016/j.ijbiomac.2018.06.015
0141-8130/

varieties were evaluated in the present work: "arracacha morada" ("morada" = purple) and "arracacha amarilla" ("amarilla" = yellow). The roots were collected and transported to the "*Universidad Nacional Agraria La Molina*" in Lima (Peru), and starch extraction was performed immediately.

The arracacha morada was cropped in *Huaraz* (Peru) and the arracacha amarilla was harvested in two different parts of the *Huánuco* region ("arracacha amarilla A" = valley region; "arracacha amarilla B" = high altitude region). It is important to mention that the effect of the planting site on the starch properties was not focus of the present study.

Furthermore, starches from other sources were used for comparison: potato starch (extracted, characterized as described by Castanha et al. [16]), maize starch (Argo CS 3400), high-amylose maize starch (i.e., a starch source with ~72% of amylose - Hylon VII), waxy maize starch (i.e., a starch source with ~98% of amylopectin - Amisol 4000) and cassava starch (kindly provided by "Ingredion Brasil Ingredientes Ltda"). The purpose of analysing these samples, in the same conditions of analysis used for the arracacha starches, was to provide data from common and widely known commercial starches, allowing a direct correlation among their properties.

All the chemicals were of analytical grade and used without further purification.

2.2. Starch extraction

The arracacha roots (composition shown in Table S1, supplementary material) were washed and cut into slices approximately 5 cm thick and immediately crushed in a laboratory scale blender for 3 min. The starch extraction was then performed according to the process described by Castanha et al. [16]. The starch obtained was dried in an air circulation oven at 35 °C to a moisture content of approximately 13%. The dried starch was ground in a mortar and sieved (250 μm) for further analysis. The proximal composition of the obtained starch is shown in Table S1 (supplementary material).

2.3. Roots and starch chemical composition

The protein and ash contents from the arracacha roots and starches were analysed using the methods described in AOAC [17]: the nitrogen content (for the crude protein content) was determined by the micro-Kjeldahl method using factor 6.25, and the ash content was determined in a muffle furnace at 550 °C until complete calcination.

The starch content of the roots was determined using a total starch determination kit (Code K-TSTA, Megazyme, Ireland), consisting of the enzymatic (α-amylase/amyloglucosidase) breakdown of the starch and subsequent colorimetric evaluation of the remaining glucose. This kit is based on the AOAC 996.11 [17] and AACC 76-13.01 [18] methods.

The mineral content was determined using an energy dispersive X-ray fluorescence spectrometer (Shimadzu EDX-720, Japan), according to Tezotto et al. [19].

The pH of a 10% (m/m) starch slurry was determined in a calibrated potentiometer (Tecnal, TEC-5 mode, Piracicaba, Brazil), under constant stirring, according to Adolfo Lutz Institute [20].

2.4. Starch characterization

2.4.1. Granule morphology: particle size distribution, scanning electron microscopy (SEM), light microscopy and polarized light microscopy

The size distribution of the starch granules (particles) was determined using a Laser Analyser (Partica LA-950V2 Laser Particle Size Analyser HORIBA, Japan) and the LA-950 software for Windows (HORIBA, Japan). The samples were dispersed in ethanol (99.5%). The volume-based mean diameter (D [3, 4], Eq. (1)) and the area-based mean diameter (D [2, 3], Eq. (2)) were evaluated, as was the distribution. Both area and volume equivalent diameters were evaluated since the D [3, 4] is more influenced by large particles, whereas the D [2, 3] is influenced by the smaller ones [21, 22].

$$D[4,3] = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3} \quad (1)$$

$$D[3,2] = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (2)$$

Scanning electron microscopy (LEO 435 VP, Leo Electron Microscopy Ltd., Cambridge, England) was used to evaluate the starch granule morphology and general appearance. The microscope was operated at an acceleration voltage of 20 kV. Dry starch was sprinkled onto double-sided adhesive tape placed in the middle of circular stubs. The stubs were coated with a 30-nm gold layer and then evaluated in the microscope.

A light microscope (model L1000, Bioval, Curitiba, Brazil) with a 20-W halogen lamp was used to evaluate the shape and surface of the starch granules. A 1% dispersion of starch in distilled water was prepared and immediately observed in the microscope. To better distinguish the granules, a drop of Lugol solution (I_2 and KI in ethanol) was mixed with a drop of the starch dispersion onto the glass slide, which was covered by a glass cover slip. The magnification used was 400× and a 1.3-megapixel portable camera was used to obtain the images. To observe the Maltese crosses of the starch samples, a polarized light filter was coupled to the same microscope, and the same starch dispersion was used but without the Lugol solution.

2.4.2. Molecular size distribution

The molecular size distribution profile of the starch molecules was determined by gel permeation chromatography (GPC), according to Song and Jane [23], with small modifications. A glass column (2.6 cm diameter and 70 cm high) packed with Sepharose CL-2B gel (Sigma, Sweden) was used. 0.1 g of starch was mixed with 10 mL of Dimethylsulfoxide (DMSO; 90%, Labsynth, Brazil) and heated in a bath of boiling water for 1 h and then kept at 25 °C for 24 h under constant stirring. An aliquot of 3 mL of this solution was mixed with 10 mL of absolute ethanol and then centrifuged for 30 min at 3000 *g*. The precipitated starch was dissolved in 9 mL of boiling distilled water and placed in a bath of boiling water for 30 min. An aliquot of 4 mL was then upwardly eluted in the chromatographic column, with an eluent solution (25 $mmol \cdot L^{-1}$ of NaCl and 1 $mmol \cdot L^{-1}$ of NaOH), at a rate of 60 $mL \cdot h^{-1}$. A fraction collector (Gilson, model FC203B, Middleton, England) was used to separate the sample into 4-mL portions, and these were then analysed for total carbohydrate content at 490 nm by the phenol-sulfuric [24] and blue value at 620 nm [25] methods, using a microplate reader (Asys Expert plus, Biochron, England). A glucose sample was used as a marker to indicate the end of the analysis.

2.4.3. Apparent amylose content

The apparent amylose content was determined according to the ISO methodology [26]. A reference curve was firstly made using standard amylopectin (A8515) and amylose (A0512 type III) from Sigma-Aldrich Pty Ltd. (Castle Hill, NSW, Australia). Starch grains were dispersed in ethanol 95% and NaOH 1 $mol \cdot L^{-1}$, and then gelatinized in a boiling water bath for 10 min. An aliquot of 18 mL was mixed with 2 mL of NaOH 0.09 $mol \cdot L^{-1}$. Then, an aliquot of 5 mL of this solution was transferred to a volumetric flask of 100 mL with 1 $mol \cdot L^{-1}$ acetic acid and iodine solution (0.2% I_2, 2% KI), forming a complex of blue colour, which was quantified by spectrophotometry at a wavelength of 620 nm (spectrometer Femto, Model 600S, São Paulo, Brazil).

2.4.4. X-ray diffraction patterns

The starch samples were maintained in a desiccator containing saturated $BaCl_2$ solution (25 °C, $a_w = 0.900$) for 10 days, to ensure a constant activity of water. An X-ray diffractometer (Shimadzu XRD 7000, Tokyo, Japan) with copper radiation was used at an angle 2θ ranging from 3 to 40°, using the following working conditions: scan rate of $2°\cdot min^{-1}$, 40 kV and 30 mA. The curves obtained were smoothed using the Origin software, version 9.1 (Microcal Inc., Northampton, MA, USA).

2.4.5. Thermal properties

The thermal properties (gelatinization and retrogradation) were evaluated using a Differential Scanning Calorimeter (DSC 2010, TA Instruments, New Castle, DE, USA), operating with the Thermal Advantage V 1.1A software (1999, TA Instruments). The Universal Analysis 2000 V 4.2E (TA Instruments) software was used to analyse the data. For the gelatinization study, 3 mg of starch (dry basis) was mixed with 7 μL of deionized water and placed in a hermetically sealed aluminium pan. The samples were kept at room temperature for 1 h before the measurement. The scanning temperature was from 30 °C to 100 °C and the heating rate was $10\ °C\cdot min^{-1}$. An empty pan was used as the reference. The onset, peak and conclusion temperatures and enthalpy of gelatinization (ΔH), on a dry basis, were obtained. In sequence, the pans with the gelatinized starch samples were stored for 7 days at 5 ± 2 °C for the retrogradation studies. Then, the same protocol mentioned above was applied to evaluate the thermal properties after retrogradation.

2.4.6. Pasting properties

Rapid Visco Analyser equipment (RVA-4, Newport Scientific Pvt. Ltd., Australia) using the Thermocline for Windows software (version 3.0) was used to determine the pasting properties of the starch samples. A suspension of 3 g (14% moisture basis) of starch in 25 g of distilled water was homogenized (for 10 s at 960 RPM) and then analysed under a constant shear (160 RPM), under 2 different heating protocols. In the first one, the suspension was initially held at 50 °C for 1 min, then heated to 95 °C at a rate of $6\ °C\cdot min^{-1}$, then kept at 95 °C for 5 min, followed by cooling to 50 °C at a rate of $6\ °C\cdot min^{-1}$, and finally holding it at 50 °C for 2 min. In the second protocol, the suspension was first held at 30 °C for 1 min, then heated to 95 °C at a rate of $9\ °C\cdot min^{-1}$, then kept at 95 °C for 5 min, followed by cooling to 30 °C at a rate of $9\ °C\cdot min^{-1}$, and finally holding it at 30 °C for 2 min.

2.4.7. Gel firmness

The firmness of the starch gel was determined by instrumental texture, using a Texture Analyser (TA.XT Plus, Stable Micro Systems Ltd., Surrey, UK) with a load cell of 50 kgf (490.3 N). After the RVA analysis, the gels obtained were stored in plastic cups (40 mm diameter × 20 mm height) for 24 h at 5 ± 2 °C before texture evaluation. To ensure uniform moisture of the samples and avoid drying, they were kept in a desiccator with water at the bottom. The samples were penetrated using a 0.5-cm cylindrical probe (P/0.5R) at $1\ mm\cdot s^{-1}$. The force measured by the equipment as a function of the penetration depth was then used to evaluate the gel firmness.

2.4.8. Water absorption index (WAI) and water solubility index (WSI)

The water absorption and solubility indexes were evaluated according to the procedure described by Anderson et al. [27], with minor modifications. 0.5 g of starch (dry basis) and 6 mL of distilled water were mixed in pre-weighed centrifuge tubes. The tubes were then placed in a thermal bath with stirring for 30 min at different temperatures (30, 40, 50, 55 and 60 °C) and then centrifuged at 3000 *g* for 10 min. The supernatant was dried and weighed (DS), and the precipitated retained in the tube was also weighed (PT). The WAI (Eq. (3)) and the WSI (Eq. (4)) were then calculated considering MS as the mass of the sample, on a dry basis.

$$WAI\left(\frac{g\ water}{g\ starch}\right) = \frac{PT-(MS-DS)}{(MS-DS)} \tag{3}$$

$$WSI\ (\%) = \frac{DS}{MS}\cdot 100 \tag{4}$$

2.4.9. Paste clarity

The paste clarity of the starches was evaluated by measuring the transmittance (T%) of the samples as described by Craig et al. [28] and modified by Aplevicz and Demiate [29]. 0.2 g of starch was mixed with 20 mL of distilled water in test tubes with screw caps. The tubes were then placed in a thermal bath with boiling water for 30 min and stirred individually every 5 min. The tubes were then cooled to room temperature and evaluated in a spectrometer at a 650 nm wavelength (Femto, Model 600S, São Paulo, Brazil).

2.5. Experimental design

The starch samples were extracted from one batch of arracacha (for both the starches and roots characterized in this work, Table S1, supplementary material). Each analysis was repeated at least twice, and each repetition was done at least in duplicate.

3. Results and discussions

3.1. Arracacha starch structure

3.1.1. Roots and starch proximal composition

Both the proximal composition (Table S1) and mineral content (Table S2) of the arracacha roots and their respective starches are provided in the supplementary material.

Considering the arracacha roots, it is possible to observe that they are a rich source of starch (more than 50% of the dry material).

The arracacha starch phosphorus content (~200–270 $mg\cdot kg^{-1}$) is relatively low if compared to the potato (*Solanum tuberosum*) starch, a rich source with a phosphorus content of approximately 800 $mg\cdot kg^{-1}$ [16]. However, Hoover [30] compared the organic phosphorus content reported in different works, and the arracacha starch phosphorus content is higher than the content in the starches from 12 other roots and tubers evaluated (except the potato). It is important to highlight that phosphorus is a component that, in general, increases paste viscosity and paste lightness and decreases retrogradation rates of starches [30, 31].

3.1.2. Morphology of the granules

The arracacha starch particle size distribution is presented in Fig. 1.

In general, the arracacha starches granules was around 20 μm (Fig. 1-C). If compared to starches from different sources (Fig. 1-D), the distribution of the size of the arracacha is similar to that observed for cassava starch. Maize starch has a higher granular population around 30 μm, while, with larger granules, most of those in potato starch appear in the 50 μm range. The volume-based mean particle diameter of the arracacha morada sample is higher than the one observed in the arracacha amarilla starches (Fig. 1-B), indicating that the diameter of the granules in this sample is larger than those of the arracacha amarilla.

Fig. 2 shows the general aspect of the arracacha roots and their respective starch granules under different views (light microscopy, polarized light microscopy and scanning electron microscopy). A complementary figure, containing only the SEM images of the starch samples, is available in the Supplementary material (Fig. S1).

Considering the morphology of the starch granules (Fig. 2), in general, they are round-shaped, with smaller ones with irregular

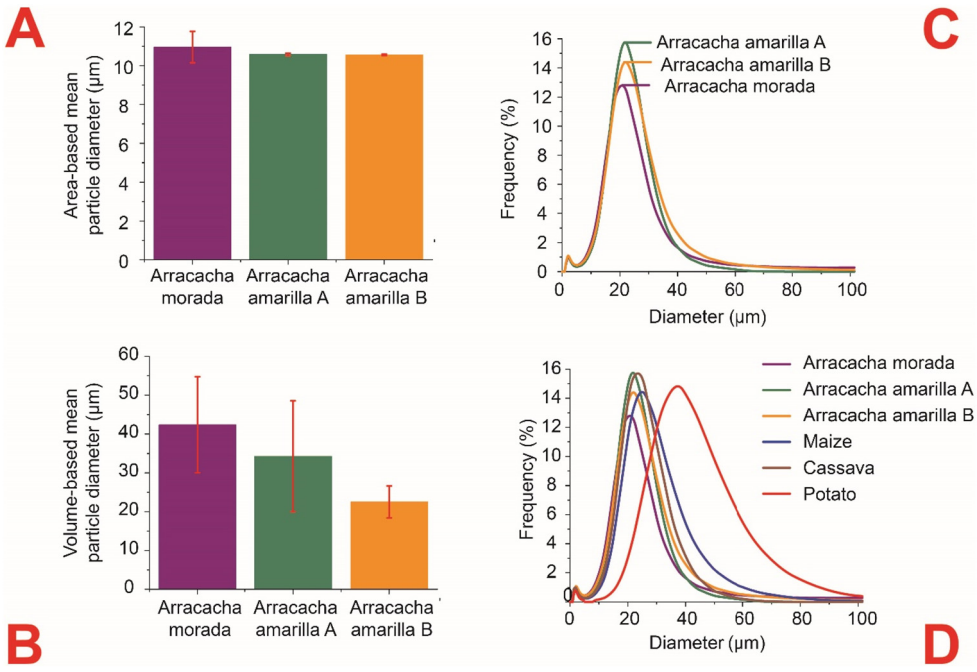

Fig. 1. Particle size distribution of the arracacha starches. (A) Area-based mean particle diameter; (B) volume-based mean particle diameter; (C) size distribution of the arracacha starches; (D) comparison among the size distribution of arracacha starches and starches from maize, cassava and potato starches. Vertical red bars represent the standard deviation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(polygonal) shapes, the granules of the morada variety being the most irregular. Besides, some granules in all samples had cracks and fissures on their surfaces, probably due to being closely packed in the cells of the arracacha roots in a "Lego-like" conformation, as proposed and demonstrated for arracacha starches from Colombia by Londoño-Restrepo et al. [13] (this compactness of the granules can be better observed in the electron microscopy images in Fig. 2 and in Fig. S1).

In fact, Alonso-Gomez et al. [32] presented SEM images of native cassava starches inside the cells and isolated, and it was possible to observe that the starch granules were "compressed", presenting a similar format to those observed in this work.

Furthermore, while studying arracacha starch from Brazilian roots (*Arracacia xanthorrhiza*, "Amarela de Senador Amaral" variety), Rocha et al. [11] also observed round and irregular-shaped granules, with a tendency to separate and crack, and some depressions on their surfaces - being consistent with the Peruvian roots.

Pérez et al. [33] argued that, on a macromolecular scale, the surface of starches can differ significantly between different botanical sources. The authors also commented that channels and pores can be found in starch granules affected by plant metabolic activities, such as its growth. This can be the case here studied.

3.1.3. X-ray diffraction

The X-ray diffraction patterns of the arracacha starches are presented in Fig. 3-E.

Starches were proved to be a crystalline material by P. Scherrer, almost 100 years ago [34]. Since then, studies regarding the starch crystallinity have been performed using the X-ray analysis. Several of these studies classifies the X-ray diffraction patterns of different starch samples into 3 different types: "A", "B" or "C" [34, 35]. According to this classification, the three varieties of arracacha starch can be classified as presenting a B-type pattern, typical of tubers and roots [34].

However, recent studies [13, 32, 36, 37] have been using a new approach to analyse the X-ray patterns of different starch samples, which are based on the comparison of the obtained patterns with standards from a database of Powder Diffraction Files (PDF-4) [38]. According to this approach, the X-ray diffraction patterns must be compared to standard patterns of "pure" amylose and amylopectin samples and with the peaks based on the α-amylose database (PDF 43–1858). It worth be mentioned that the amylopectin PDF database is still under study, as well as the amylose source used as reference is different from ours [32, 37].

In this way, when comparing our results with the amylose and amylopectin diffraction patterns obtained by Londoño-Restrepo et al. [37], we can observe some interesting results. In the arracacha samples, the peaks located at ~17°, 20°, 22.5° and 24° are correspondent to the amylose crystalline structure, while the ~5.5° peak was not observed in the PDF database. Alonso-Gomez et al. [32] believe that the 5.5° peak corresponds to nanocrystals.

However, despite using standards, the comparisons and the conclusions must be carefully evaluated, since the moisture content and the amount and conditions of the amylose and amylopectin molecules greatly influence the X-ray patterns [35]. In fact, as precisely stated by Londoño-Restrepo et al. [13], the crystalline structure of starches are far from been completely understood, and requires further studies.

3.1.4. Molecular size distribution and apparent amylose content

The apparent amylose content and the molecular size distribution of the arracacha starches are shown in Fig. 3.

The apparent amylose content obtained was high for starches of arracacha morada (39.0 ± 1.5%), amarilla A (35.8 ± 0.7%) and amarilla B (35.7 ± 0.7%). Works in the literature report much smaller amylose contents than those obtained in this work, with values from 18 to 20% from the Brazilian [9, 11] and Venezuelan [12] varieties.

However, the limitations of the analytical method and the interpretation of the results must be highlighted once again.

The amylose content obtained by this colorimetric analysis with iodine is considered "apparent", since long chains of amylopectin can also develop the characteristic blue colour of the amylose-iodine complex, leading to an "overestimated" amylose value [39–41]. Jane et al. [39] compared the absolute and apparent amylose values obtained for different starch sources and observed that, in some cases, the difference could be over 20%. This overestimation took place especially for the B-

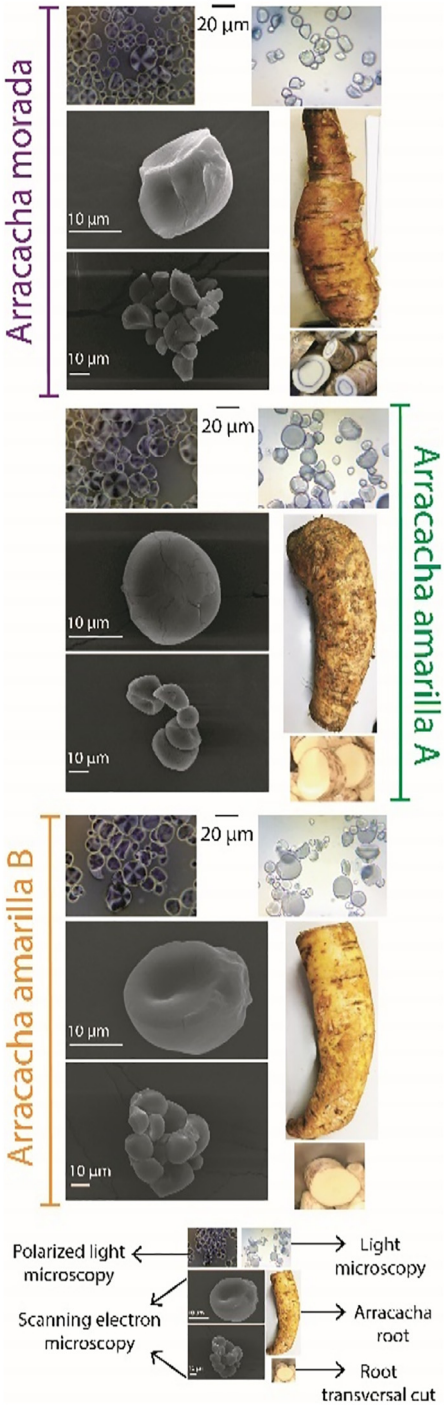

Fig. 2. General aspect of the arracacha roots and their respective starches.

type starches - as is the case of arracacha starches, as shown in Fig. 3-E. In fact, Rocha et al. [11] observed a high amylopectin-iodine affinity while studying starch from a Brazilian arracacha, concluding that the amylopectin in the samples could contribute to the blue colour observed in the apparent amylose analysis.

In such a way, the amylose content based on the iodine complex could lead to a false interpretation of the amylose value. So, a gel permeation chromatography (GPC) analysis was performed to elucidate better the proportion and chain length of both amylose and amylopectin in the arracacha starches.

The GPC analysis consists basically of the separation of the starch fractions based on their molecular sizes. Thus, the molecules with higher chain lengths elute first, since they are not able to penetrate the gel pores. On the other hand, the lower chain-length molecules are retained in the column and elute later [42].

Normally, the amylopectin molecules are described as being large and highly branched [42]. Therefore, they are supposed to be mainly contained in the first fraction, forming the first chromatogram peak, while the following portions are normally related to the amylose molecules. However, the starch molecules cannot be simply divided into only two fractions, since a number of small molecules of amylopectin may elute in the later fraction, or long chains of amylose may elute in the first. Therefore, the amylose and the amylopectin fractions are not sharply separated, but blend into each other through intermediate fractions [41, 42].

Considering this, the arracacha starches were evaluated using two different techniques in the GPC: the total carbohydrate method (based on a phenol-sulfuric colorimetric method) and the blue value method (also based on the starch-iodine complex). Once more, maize, high amylose and waxy commercial starches were used for comparison purposes.

Analysing the results (Fig. 3-A and -B), it is possible to observe that in some cases the amylopectin molecules can form the blue complex with iodine, as discussed by Jane et al. [39]. For example, while analysing the results of the blue value (Fig. 3-B), it is clear that waxy starch (which presents about 98% of amylopectin, thus should not form an intense blue colour with iodine) presented a distinct peak in the "amylopectin elution area", showing that these molecules were coloured by the iodine in the analysis. Similarly, when analysing the results of the blue value for the arracacha starches, the first peak is more pronounced when compared to the first peak in the other samples, indicating high chain-length molecules (probably amylopectin) that can form the iodine complex. In fact, when comparing the graphs of the total carbohydrate (Fig. 3-A) and blue value (Fig. 3-B), it is possible to observe that the arracacha starches do not follow the same patterns as maize starch, for example. A first peak in the total carbohydrate analysis for maize starch was higher than the one observed for the arracacha starches, but lower in the blue value analysis, confirming the theory that the amylopectin chains of the arracacha starches are being complexed with iodine.

Another important aspect that can be observed in the GPC results is the presence of a "shoulder" after the first peak in the chromatogram of the total carbohydrate results (Fig. 3-A), which is not present with maize starch (with a thin and well-delimited first peak). This can indicate a proportion of molecules (probably amylopectin) with "intermediate" sizes, suggesting an imperfect crystalline structure [39], which did not necessarily affect the RC of the starch samples (Fig. 3-F).

To sum up, considering the results shown in Fig. 3 and the literature [9, 11, 12, 39–41], it is possible to state that the arracacha starches are not amylose-rich, as could be assumed if considered only the apparent amylose analysis. Rather, they have amylopectin with long chain lengths, with the ability to complex the iodine. Also, there are intermediate-sized molecules that can indicate a defective crystalline structure.

In fact, this assumption is corroborated by other results in the present work: the gelatinization temperatures are low (DSC analysis, Table 1), the retrogradation tendency is low (DSC analysis, Table 1, and RVA analysis, Table 2), there was no syneresis even after 30 days of refrigerated storage (data not shown), the apparent viscosity peaks are high (RVA, Table 2) and, even at low temperatures (60 °C), these starches present a remarkable water absorption capacity (Fig. 4-E). Besides, the gels obtained after the gelatinization are elastic (not brittle, as can be seen in Fig. 4-C and D) and present a high paste clarity (discussed in the item 3.2.5). These characteristics give the obtained starches interesting properties, especially from an industrial perspective, as described below.

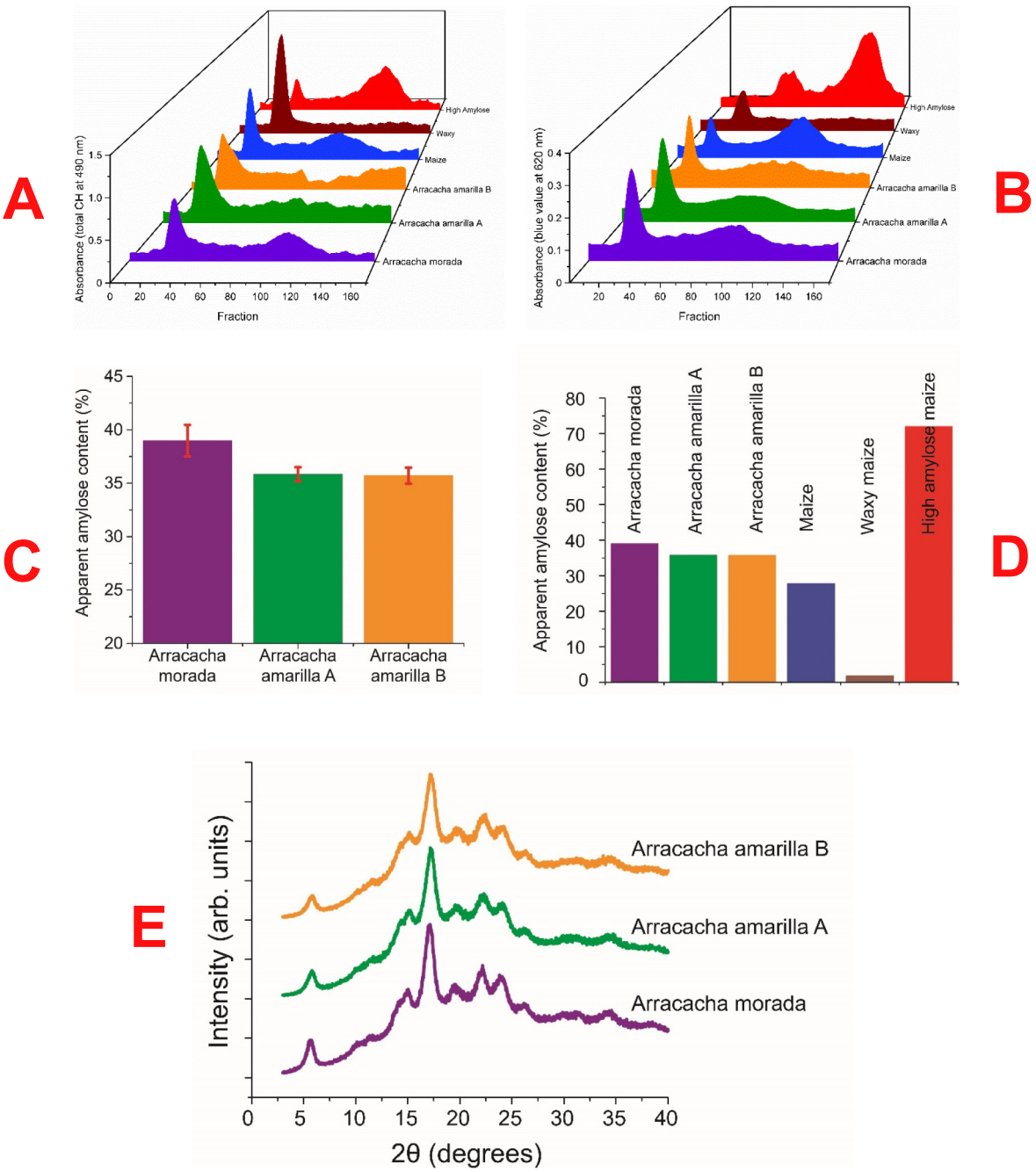

Fig. 3. Molecular size distribution (A, B) and apparent amylose content (C, D) of the arracacha starches and of three varieties of maize starch (normal, waxy and high amylose), and X-ray diffraction patterns and relative crystallinity (E, F) of the arracacha starches. (A) Total carbohydrates chromatogram; (B) Blue value chromatogram; (C) apparent amylose content of arracacha starches; (D) Apparent amylose content comparison among different sources; (E) X-ray diffraction patterns. Red bars represent the standard deviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Gelatinization and retrogradation properties of the arracacha starch samples. Average ± standard deviations. The percentage retrogradation (%R) was calculated by [($\Delta H_{retrogradation}$/$\Delta H_{gelatinization}$)·100].

Samples	Onset temperature (°C)	Peak temperature (°C)	Conclusion temperature (°C)	Enthalpy (J/g)	%R (%)
Gelatinization					
Morada	53.0 ± 0.6	57.8 ± 0.6	70.4 ± 0.6	6.1 ± 0.9	–
Amarilla A	55.0 ± 0.5	58.9 ± 0.8	71.9 ± 1.8	7.1 ± 0.8	–
Amarilla B	54.9 ± 0.5	59.1 ± 0.4	73.9 ± 0.2	8.8 ± 1.3	–
Retrogradation					
Morada	47.2 ± 0.1	57.5 ± 1.0	66.5 ± 0.2	0.56 ± 0.04	9.2
Amarilla A	48.4 ± 0.5	59.1 ± 0.1	67.5 ± 0.1	0.66 ± 0.01	9.3
Amarilla B	51.8 ± 0.0	59.5 ± 0.2	69.2 ± 2.4	0.56 ± 0.05	6.3

Table 2
RVA parameters of the arracacha starch samples. AV = Apparent Viscosity. Average ± standard deviations.

Test conditions	Sample	Peak AV (mPa·s)	Trough AV (mPa·s)	Breakdown (mPa·s)	Final AV (mPa·s)	Setback (mPa·s)	Pasting temperature (°C)
30-95-30 °C	Arracacha morada	10,708 ± 95	2135 ± 12	8573 ± 83	5155 ± 147	3021 ± 159	57.6 ± 0.8
	Arracacha amarilla A	10,833 ± 33	1942 ± 45	8891 ± 11	4631 ± 12	2689 ± 57	58.8 ± 0.0
	Arracacha amarilla B	10,429 ± 221	1898 ± 91	8532 ± 129	4344 ± 57	2446 ± 148	59.1 ± 0.4
50-95-50 °C	Arracacha morada	10,684 ± 136	2016 ± 6	8668 ± 130	3346 ± 99	1331 ± 93	56.5 ± 0.3
	Arracacha amarilla A	10,720 ± 74	1851 ± 18	8869 ± 92	3015 ± 21	1164 ± 2	57.5 ± 0.1
	Arracacha amarilla B	10,989 ± 84	1789 ± 62	9200 ± 23	2904 ± 29	1115 ± 33	58.4 ± 0.0

3.2. Arracacha starches structure-properties relationship

The properties of the starch are closely related to the structure of the starch molecules. The properties of the arracacha starches are described in the next item and illustrated in Fig. 4. Furthermore, whenever possible, they are related to the structure of the starches described in the previous section.

3.2.1. Thermal properties

The gelatinization and retrogradation properties of the arracacha starches are shown in the Table 1 and illustrated in Fig. S2 (supplementary material).

Starch gelatinization is a complex phenomenon that occurs in the presence of sufficient amounts of heat and water, following some steps: the intermolecular bonds of the starch molecules are weakened

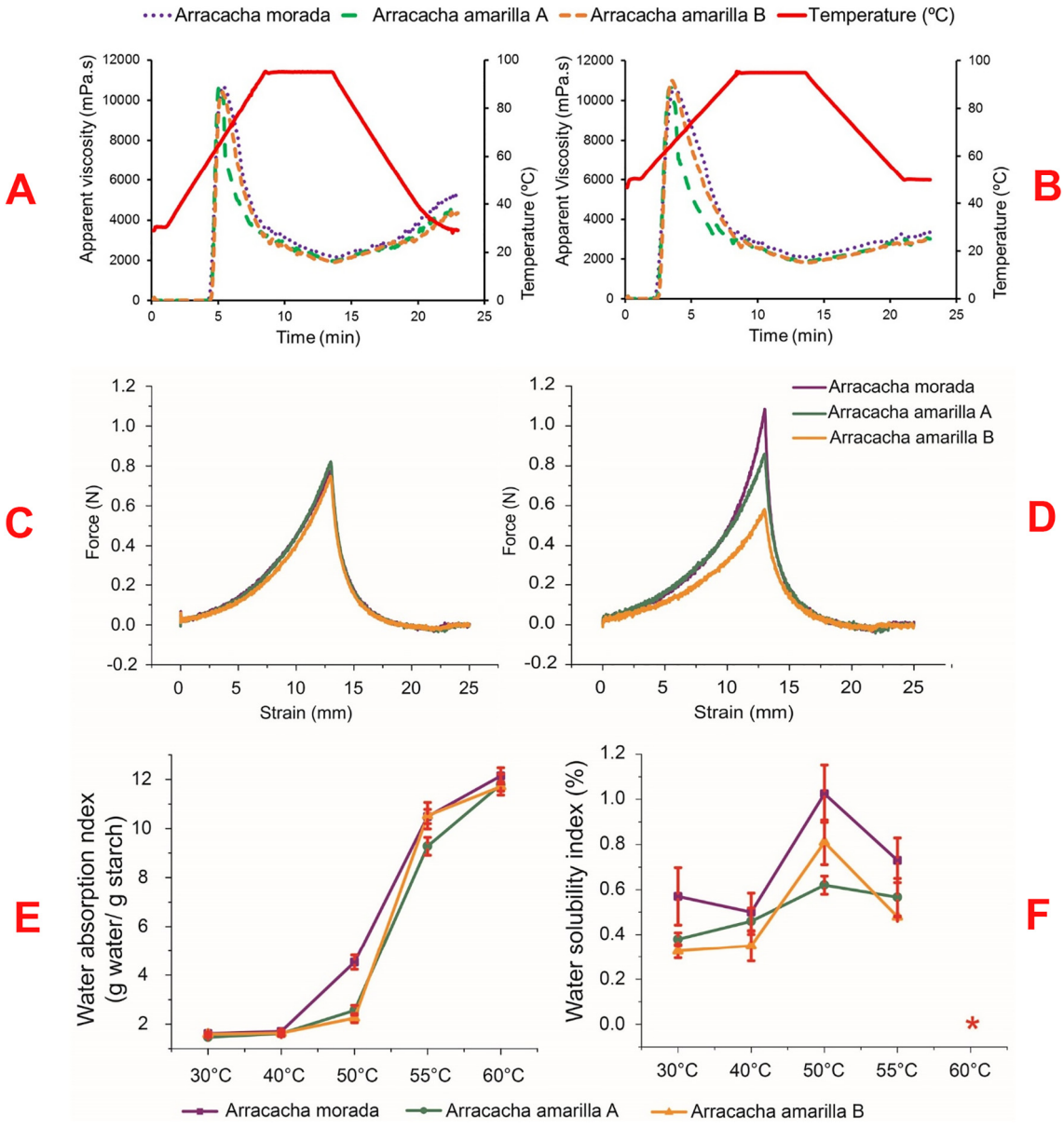

Fig. 4. RVA curves of the arracacha starch samples (A, B), strength of the arracacha starch gel samples (C, D) and Water absorption index and water solubility index of the arracacha starches in different temperatures (30, 40, 50, 55 and 60 °C) (E, F). (A) RVA at the heating program: 30 °C - 95 °C - 30 °C; (B) RVA at the heating program: 50 °C - 95 °C - 50 °C; (C) Gel obtained after the RVA heating cycle illustrated in A; (D) Gel obtained after the RVA heating cycle illustrated in B; (E) Water absorption index; (F) water solubility index. The red * symbol indicates no detectable value. Vertical red bars represent the standard deviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and water penetrates the starch granules, being able to bond with the molecular hydroxyl groups. In this process, the starch granules swell and lose their birefringence, becoming more and more fragile until they disintegrate [43]. Therefore, if the starch structure is naturally less compact (more "fragile"), less energy (heat) is necessary to cause a bond weakening.

In fact, the arracacha starches present a low onset temperature (approx. 53 to 55 °C) and a low enthalpy of gelatinization (approx. 6 to 9 J/g) if compared to other starch samples, such as potato (58.2 °C; 15.8 J/g), normal maize (64.1 °C; 12.3 J/g), waxy maize (64.2 °C; 15.4 J/g) and cassava (64.3 °C; 14.7 J/g) starches [39]. This result is in accordance with the imperfect crystalline structure of their granules (as discussed in the 3.1.3). Besides, the arracacha starch granules present cracks and fissures on their surfaces (Fig. 2), which may facilitate the uptake of water in their structure and, consequently, their gelatinization at lower temperatures.

The observed percentage retrogradation values were small, being close to those observed by Jane et al. [39] for waxy rice (5%) and waxy amaranth (5.2%) starches. Other starch samples showed higher retrogradation values, including potato (43.4%), tapioca (25.3%) or even waxy maize (61.6%) [39]. It clearly indicates that not only the amylose/amylopectin proportion, but also their chain lengths, may influence the retrogradation properties of the starch samples. In the case of the arracacha starches, the large amount of long-branched chains of amylopectin, which also have a heterogeneous distribution of size, may hinder to some extent the molecular reassociation after cooling, contributing to the low retrogradation tendency of the arracacha starches. Besides, to a degree, the phosphate groups may influence the low retrogradation tendency, since electronegative groups also hinder molecular reassociation [28].

Summarizing, when compared with common industrial sources, the arracacha starch thermal properties are characterized by low gelatinization temperatures, gelatinization with a small amount of energy and low retrogradation and syneresis. Consequently, the arracacha starches show a behavior of high industrial interest (especially for applications where refrigeration is used).

3.2.2. Pasting properties

The pasting properties of the arracacha starch samples are given in Table 2 (AV = apparent viscosity), and their relative curves are represented in Fig. 4-A and B.

In the RVA analysis, a sequence of events occurs. First, the starch granules swell until their maximum capacity (reaching the peak AV), followed by a leaching of polymers from the granules and a granular disruption. The leached polymers then suffer an alignment with consequent apparent decrease in viscosity (reaching the trough AV) and, after cooling, there is a reassociation of the molecules with an increase in the apparent viscosity of the system (reaching the final AV). The difference between the peak and trough AVs is known as breakdown and indicates, in a simplified way, the resistance of the starch granules to disruption. The difference between the final and trough AVs is known as setback, and indicates the tendency for re-association of the starch amylose molecules [40].

The RVA analysis was performed in two different heating programs, starting and ending at 50 °C (standard analysis) and at 30 °C. The latter temperature was selected because the gelatinization temperatures of the arracacha starches range between 55 and 60 °C (Table 2). Therefore, a cooling temperature close to 50 °C could be too high to evaluate the possible retrogradation tendency (setback) of these starches. In any case, the setback values of the starches were lower than those observed in samples with a high retrogradation tendency, such as maize and rice starches [44]. In fact, the low retrogradation tendency of the arracacha starches was also observed in the DSC analysis.

Two other characteristics that can be emphasized in relation to the pasting properties of the arracacha starches are their low gelatinization temperature (as discussed in the DSC analysis) and their high Peak AV (with values ranging between 10,500 and 11,000 mPa·s, as shown in Table 2). The Peak AV values are almost as expressive as those observed in potato starches (~12,500 mPA·s, Castanha et al. [16]), a source that is known for its high Peak AV. This expressive Peak AV is heavily influenced by the amylopectin content of the granules, which contributes to granule swelling [45]. Further, the phosphorus content of the arracacha starches, although not as expressive as in potato starch (as previously discussed), may also influence this result.

To sum up, considering the arracacha starch pasting properties, besides the low gelatinization temperatures and low retrogradation and syneresis (discussed in the DSC analysis), they presented a high Peak AV, which can be useful in applications where a highly viscous paste is interesting – for example, instant soups.

3.2.3. Water absorption and solubility indexes

The water absorption (WAI) and water solubility (WSI) indexes of the arracacha starches are presented in Fig. 4-E and F.

At room temperature, the WAI of the starches is related to the amorphous regions of the granules, since the crystalline regions are too compact to permit the entry of water [40], this condition being altered at the beginning of the gelatinization process.

The WAI is an indirect measure of the swelling capacity of the starch granules. At 30 and 40 °C, the WAI in the granules was negligible, indicating that, at these temperatures (below the onset temperatures measured in the DSC analysis), the starch granules were not able to absorb and/or retain any water. At 50 °C, which is slightly higher than the onset temperature of the samples, it was possible to observe an increase in the WAI, especially for the arracacha morada starch sample (which also had the lowest onset temperature). After this "changing-point", the WAI of the starches grew sharply, reaching its peak at 60 °C under the conditions studied.

Considering the solubility results, at 30 and 40 °C the soluble portion of the samples did not present large variations. The WSI presented a slight increase with increasing temperature (50 °C), which can be explained by the amylose fractions that may have leached from the granules at this temperature. However, as discussed earlier, as the temperature increased, the WAI of the starch samples also increased. Consequently, at 55 °C there was less available water in the system and, therefore, there was a lower soluble portion at this temperature if compared to 50 °C, explaining the lower WSI. Similarly, at 60 °C all water available for gelatinization was completely absorbed by the granules, and there was no soluble part to evaluate. For this reason, under these analysis conditions (0.5 g of starch in 6 mL of water), the samples were evaluated until 60 °C.

For comparison, we evaluated potato starch under the same conditions: the water absorption capacity of potato starch was below 4 g water/g starch until 60 °C, reaching a value of 8.4 g water/g starch at 95 °C. Consequently, the potato starch water absorption capacity at 95 °C is significantly below the capacity of the arracacha starch even at 60 °C (approx. 12 g water/g starch, or 100% of the available water), highlighting this property in arracacha starch.

To resume, the arracacha starches presented a high water absorption capacity even at low temperatures (60 °C) which, combined with their low retrogradation tendency, may confer desirable characteristics for industrial applications. For example, we consider products where a high incorporation of water is desirable, without affecting texture – which is the case of many commercial food products, such as meat products.

3.2.4. Gel texture properties

The gel strength of the arracacha starch samples is shown in Fig. 4-C and D.

The gels obtained after the RVA analysis were stored for 24 h at 5 ± 2 °C for reassociation of the starch molecules (especially amylose) and consequent stabilization of the gel. After that, a puncture assay was used to evaluate their texture. In general, the gels of all the samples

were smooth and elastic (not brittle). It is possible to observe that there was no difference in the gel strength of the arracacha starch samples obtained in the first heating cycle (30–95 °C). On the other hand, the gel from the arracacha morada sample was slight harder than the others in the standard heating cycle (50–95 °C).

Considering the other analysis, it is possible to observe that the apparent amylose content of the arracacha morada is higher than the arracacha amarilla (Fig. 3-C), and at 50 °C, the morada sample presented a higher soluble fraction (Fig. 4-F). As discussed, the apparent amylose content must be interpreted with caution. However, the analysis may still be used as an indicator for the order of magnitude of the amylose values among the arracacha starch samples. Considering all the information, arracacha morada may have a higher amylose fraction, which leached from the granule at 50 °C (but not at 30 °C) and, therefore, presents a higher reassociation after cooling, forming a more rigid gel if compared to the other arracacha starch samples.

However, if compared to other starch samples analysed under the same conditions, we observe that the gels from arracacha starches are softer than those from maize starch, (which required more than 3 N to be fully penetrated), or potato starch (demanded almost 2 N), but harder than those from cassava starch (requiring 0.4 N).

In short, for products where a non-brittle, soft and minimally consistent (with shaping capacity) gel is required, arracacha starch may be a good choice. Examples can be many refrigerated deserts, such as puddings (especially considering the other cited properties).

3.2.5. Paste clarity

The clarity of the arracacha starch pastes was over 90% of transmittance (100% being the equivalent of the transmittance of distilled water) for all samples: 96.1 ± 0.1% for arracacha morada, 92.8 ± 2.8% for the arracacha armilla A and 93.4 ± 2.9% for the arracacha amarilla B.

These results indicate a high paste clarity. In fact, the clarity of the paste from arracacha starches is comparable to potato starch paste (approx. 94%, Castanha et al. [16]), one of the clearest pastes for a native starch.

This high paste clarity can be attributed to different factors, including the high swelling capacity (WAI, Fig. 4-E), repulsion between negatively changed molecules (phosphate groups, Table S1) and low retrogradation tendency (DSC, Table 1 and RVA, Table 2) [28].

Considering the applications of starch, these are promising results, especially for the food, paper and textile industries, where a high paste clarity may be highly desirable. Furthermore, a clear paste obtained through a native (non-modified) starch can also increase the "natural" claim for the products where it is applied.

4. Conclusion

Considering the starch characteristics, both arracacha varieties (morada and amarilla) have an intermediate phosphorus content, and granules with an average size of about 20 μm, round-shaped (with smaller granules with polygonal shapes) and with some cracks and fissures on their surface. Also, the granules present a B-type pattern (typical of tubers and roots).

The apparent amylose content (based on iodine affinity) observed in the arracacha starch sample was high. However, the size-exclusion chromatography demonstrated amylopectin molecules with long chains with the ability to complex the iodine. Also, intermediate-sized molecules of amylopectin were observed, indicating a defective crystalline structure.

Considering the properties of the arracacha starches, they presented a low gelatinization temperature, a low enthalpy of gelatinization, a low retrogradation tendency and a high Peak apparent viscosity. These results were described based on the starch structure, and they are very interesting from an industrial perspective.

The water absorption and water solubility indexes indicated a high swelling capacity of the arracacha starches even at moderate temperatures (60 °C). Besides, the arracacha starch gels presented a smooth and "elastic" (not brittle) texture and a high paste clarity.

By comparing the characteristics of the two arracacha varieties studied in this paper, as well as by comparing the two starch samples from the "amarilla" variety, no expressive differences were observed among them.

Summarizing, the most relevant aspects of the arracacha starches were their low gelatinization temperature, low retrogradation tendency, high water absorption capacity and high paste clarity. From the industrial point of view, all these aspects being present in a non-modified starch may be desirable for many applications, especially for the food industry, since the native starches give a "natural" claim to processed foods.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2018.06.015.

Acknowledgements

The authors are grateful to:

- The São Paulo research foundation (FAPESP, Brazil) for funding the project n° 2016/18052-5;
- The National Council for Scientific and Technological Development (CNPq, Brazil) for funding the project n° 401004/2014-7 and the productivity grants of P.E.D. Augusto (306557/2017-7)
- The Coordination for the Improvement of Higher Education Personnel (CAPES, Brazil) for the N. Castanha PhD scholarship;
- The "Ministerio de Educación" (MINEDU, Peru) for the J. Villar research fellowship at USP (Resolución 292-2017-R-UNALM);
- The Technology Center of Cereal and Chocolate from the Food Technology Institute (ITAL), in the name of Dr. Izabela Dutra Alvim, for the particle size distribution analysis;
- The "Núcleo de Apoio à Pesquisa em Microscopia Eletrônica Aplicada a Pesquisa Agropecuária" (NAP/MEPA-ESALQ/USP) for the support and facilities of Electron Microscopy;
- The Laboratory of Soil Mineralogy (LSO-ESALQ/USP), in the name of Prof. Dr. Antonio Carlos Azevedo and Leandro Luís Góia, for the X-ray analysis;
- Mr. Caio Cesar de Lima Silva and Dr. Debora Nascimento e Santos, for general support;
- The anonymous Reviewer, by the excellent discussion (in special regarding crystallography) and improvements.

References

[1] M. Hermann, Arracacha (*Arracacia xanthorrhiza* Bancroft), in: M. Hermann, J. Heller (Eds.),Andean Roots Tubers Ahipa, Arracacha, Maca Yacon, International Plant Genetic Resources Institute, Rome - Italy 1997, pp. 75–173.
[2] S.M. Bukasov, The cultivated plants of Mexico, Guatemala and Colombia. Suppl. 47, Bull. Appl. Bot. Genet. Plant Breed. (Leningrad) 192 (Suppl. 58) (1930) 1–553.
[3] J.E.H. Bermejo, J. León, Neglected Crops: 1492 From a Different Perspective, Food & Agriculture Org., 1994
[4] J. Alvarez, Diccionario de peruanismos, Librería Studium Ediciones, Lima - Peru, 1990.
[5] E.K.R.P. de M. Buso, E. Clemente, K.R.F.S. Estrada, N.A.H. Zárate, J.S.B. Oliveira, Comportamento pós-colheita de mandioquinha-salsa revestida com quitosana, Rev. Ciênc. Agron. 45 (2014) 850–855, https://doi.org/10.1590/S1806-66902014000400024.
[6] R. Blas, M. Hermann, J.P. Baudoin, Analysis of the geographic distribution and relationships among Peruvian wild species of *Arracacia*, Genet. Resour. Crop. Evol. 55 (2008) 643–655, https://doi.org/10.1007/s10722-007-9267-9.
[7] K.M. Albano, C.M.L. Franco, V.R.N. Telis, Rheological behavior of Peruvian carrot starch gels as affected by temperature and concentration, Food Hydrocoll. 40 (2014) 30–43, https://doi.org/10.1016/j.foodhyd.2014.02.003.
[8] M. Leonel, M.P. Cereda, Caracterização físico-química de algumas tuberosas amiláceas, Cienc. Tecnol. Aliment. 22 (2002) 65–69, https://doi.org/10.1590/S0101-20612002000100012.
[9] J. Moraes, R.S. Branzani, C.M.L. Franco, Behavior of Peruvian carrot (*Arracacia xanthorrhiza*) and cassava (*Manihot esculenta*) starches subjected to heat-moisture treatment, Starch-Starke 66 (2014) 645–654, https://doi.org/10.1002/star.201300207.

[10] T.S. Rocha, I.M. Demiate, C.M.L. Franco, Características estruturais e físico-químicas de amidos de mandioquinha-salsa (*Arracacia xanthorrhiza*), Cienc. Tecnol. Aliment. 28 (2008) 620–628, https://doi.org/10.1590/S0101-20612008000300018.
[11] T.S. Rocha, V.A.G.G. Cunha, J.L. Jane, C.M.L.L. Franco, Structural characterization of peruvian carrot (*Arracacia xanthorrhiza*) starch and the effect of annealing on its semi-crystalline structure, J. Agric. Food Chem. 59 (2011) 4208–4216, https://doi.org/10.1021/jf104923m.
[12] M.S. Tapia, E. Pérez, P.E. Rodríguez, R. Guzmán, M.-N. Ducamp-Collin, T. Tran, A. Rolland-Sabaté, Some properties of starch and starch edible films from under-utilized roots and tubers from the Venezuelan Amazons, J. Cell. Plast. 48 (2012) 526–544, https://doi.org/10.1177/0021955X12445291.
[13] S.M. Londoño-Restrepo, N. Rincón-Londoño, M. Contreras-Padilla, B.M. Millan-Malo, M.E. Rodriguez-Garcia, Morphological, structural, thermal, compositional, vibrational, and pasting characterization of white, yellow, and purple Arracacha Lego-like starches and flours (*Arracacia xanthorrhiza*), Int. J. Biol. Macromol. 113 (2018) 1188–1197, https://doi.org/10.1016/j.ijbiomac.2018.03.021.
[14] J. Seminario, Raíces andinas: contribuciones al conocimiento ya la capacitación, International Potato Center, 2004.
[15] R.F. Tester, J. Karkalas, X. Qi, Starch - composition, fine structure and architecture, J. Cereal Sci. 39 (2004) 151–165, https://doi.org/10.1016/j.jcs.2003.12.001.
[16] N. Castanha, M.D. Matta Junior, P.E.D. Augusto, Potato starch modification using the ozone technology, Food Hydrocoll. 66 (2017) 343–356, https://doi.org/10.1016/j.foodhyd.2016.12.001.
[17] AOAC International, Official Methods of Analysis, 2006.
[18] AACC, "Approved Methods of the AACC". Method 76–11, 1976.
[19] T. Tezotto, J.L. Favarin, A. Paula Neto, P.L. Gratão, R.A. Azevedo, P. Mazzafera, Simple procedure for nutrient analysis of coffee plant with energy dispersive X-ray fluorescence spectrometry (EDXRF), Sci. Agric. 70 (2013) 263–267, https://doi.org/10.1590/S0103-90162013000400007.
[20] Adolfo Lutz Institute, Normas analíticas do Instituto Adolfo Lutz: Métodos físicos e químicos para análises de alimentos, 2008 1020.
[21] H. Bengtsson, E. Tornberg, Physicochemical characterization of fruit and vegetable fiber suspensions. I: effect of homogenization, J. Texture Stud. 42 (2011) 268–280, https://doi.org/10.1111/j.1745-4603.2010.00275.x.
[22] P. Lopez-Sanchez, J. Nijsse, H.C.G. Blonk, L. Bialek, S. Schumm, M. Langton, Effect of mechanical and thermal treatments on the microstructure and rheological properties of carrot, broccoli and tomato dispersions, J. Sci. Food Agric. 91 (2011) 207–217, https://doi.org/10.1002/jsfa.4168.
[23] Y. Song, J. Jane, Characterization of barley starches of waxy, normal, and high amylose varieties, Carbohydr. Polym. 41 (2000) 365–377, https://doi.org/10.1016/S0144-8617(99)00098-3.
[24] M. DuBois, K.A. Gilles, J.K. Hamilton, P.A. Rebers, F. Smith, Colorimetric method for determination of sugars and related substances, Anal. Chem. 28 (1956) 350–356, https://doi.org/10.1021/ac60111a017.
[25] B.O. Juliano, A simplified assay for milled-rice amylose, Cereal Sci. Today 16 (1971) 334–340 (doi:0009-0360).
[26] International organization for standarization - ISO, Determination de La teneur em amylose. Norme ISO 6647, 1987.
[27] R.A. Anderson, H.F. Conway, A.J. Peplinski, Gelatinization of corn grits by roll cooking, extrusion cooking and steaming, Starch-Starke 22 (1970) 130–135, https://doi.org/10.1002/star.19700220408.
[28] S.S.A. Craig, C.C. Maningat, P.A. Seib, R.C. Hoseney, Starch paste clarity, Cereal Chem. 66 (1989) 173–182.
[29] K.S. Aplevicz, I.M. Demiate, Caracterização de amidos de mandioca nativos e modificados e utilização em produtos panificados, Cienc. Tecnol. Aliment. 27 (2007) 478–484, https://doi.org/10.1590/S0101-20612007000300009.
[30] R. Hoover, Composition, molecular structure, and physicochemical properties of tuber and root starches: a review, Carbohydr. Polym. 45 (2001) 253–267, https://doi.org/10.1016/S0144-8617(00)00260-5.
[31] J.L. Jane, T. Kasemsuwan, J.F. Chen, Phosphorus in rice and other starches, Cereal Foods World. 41 (1996) 827–832.
[32] L. Alonso-Gomez, A.M. Niño-López, A.M. Romero-Garzón, P. Pineda-Gomez, A. del Real-Lopez, M.E. Rodriguez-Garcia, Physicochemical transformation of cassava starch during fermentation for production of sour starch in Colombia, Starch/Staerke 68 (2016) 1139–1147, https://doi.org/10.1002/star.201600059.
[33] S. Pérez, P.M. Baldwin, D.J. Gallant, Structural features of starch granules I, in: J.N. BeMiller, R.L. Whistler (Eds.), Starch Chem. Technol, 3rd ed.Academic Press, Amsterdam 2009, pp. 149–192.
[34] H.F. Zobel, Starch crystal transformations and their industrial importance, Starch-Starke 40 (1988) 1–7, https://doi.org/10.1002/star.19880400102.
[35] N.W.H. Cheetham, L. Tao, Variation in crystalline type with amylose content in maize starch granules: an X-ray powder diffraction study, Carbohydr. Polym. 36 (1998) 277–284, https://doi.org/10.1016/S0144-8617(98)00007-1.
[36] N. Rincón-Londoño, B. Millan-Malo, M.E. Rodríguez-García, Analysis of thermal pasting profile in corn starch rich in amylose and amylopectin: physicochemical transformations, part II, Int. J. Biol. Macromol. 89 (2016) 43–53, https://doi.org/10.1016/j.ijbiomac.2016.04.057.
[37] S.M. Londoño-Restrepo, N. Rincón-Londoño, M. Contreras-Padilla, A.A. Acosta-Osorio, L.A. Bello-Pérez, J.C. Lucas-Aguirre, V.D. Quintero, P. Pineda-Gómez, A. del Real-López, M.E. Rodríguez-García, Physicochemical, morphological, and rheological characterization of *Xanthosoma robustum* Lego-like starch, Int. J. Biol. Macromol. 65 (2014) 222–228, https://doi.org/10.1016/j.ijbiomac.2014.01.035.
[38] J. Faber, T. Fawcett, The powder diffraction file: present and future, Acta Crystallogr. Sect. B: Struct. Sci. 58 (2002) 325–332, https://doi.org/10.1107/S0108768102003312.
[39] J. Jane, Y.Y. Chen, L.F. Lee, A.E. McPherson, K.S. Wong, M. Radosavljevic, T. Kasemsuwan, Effects of amylopectin branch chain-length and amylose content on the gelatinization and pasting properties of starch, Cereal Chem. 52 (1999) 555, https://doi.org/10.1094/CCHEM.1999.76.5.629.
[40] Q. Liu, Understanding starches and their role in foods, in: S.W. Cui (Ed.), Food Carbohydrates Chem. Phys. Prop. Appl, 1st ed.CRC Press, Boca Raton, FL 2005, pp. 309–355.
[41] J.C. Shannon, D.L. Garwood, C.D. Boyer, Genetics and physiology of starch development, in: J.N. BeMiller, R.L. Whistler (Eds.), Starch Chem. Technol, 3rd ed.Academic Press, London, UK 2009, pp. 23–82.
[42] S. Hizukuri, J. Abe, I. Hanashiro, Starch: analytical aspects, in: A. Eliasson (Ed.), Carbohydrates Food, 2nd ed.CRC Press, Boca Raton, FL 2006, pp. 305–390.
[43] F. Xie, H. Liu, P. Chen, T. Xue, L. Chen, L. Yu, P. Corrigan, Starch gelatinization under shearless and shear conditions, Int. J. Food Eng. 2 (2007)https://doi.org/10.2202/1556-3758.1162.
[44] C.G. Biliaderis, Structural transitions and related physical properties of starch, in: J. BeMiller, R. Whistler (Eds.), Starch Chem. Technol, 3rd ed.Academic Press, New York 2009, pp. 293–359.
[45] R.F. Tester, W.R. Morrison, Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose, and lipids, Cereal Chem. 67 (1990) 551–557.