Starch

PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION OF ANDEAN TUBER STARCHES: POTATO (Solanum tuberosum ssp. Andigenum), OCA (Oxalis tuberosa Molina) AND PAPALISA (Ullucus tuberosus Caldas).

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Complete List of Authors:	Cruz, Gonzalo; Centro de Investigación y Transferencia de Santiago del Estero Ribotta, Pablo; Instituto de Ciencia y Tecnologia de Alimentos - Universidad Nacional de Córdoba Ferrero, Cristina; Centro de Investigacion y Desarrollo en Criotecnologia de Alimentos Iturriaga, Laura; Universidad Nacional de Santiago del Estero, CITSE
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Gonzalo Cruz[1], Pablo Ribotta[3], Cristina Ferrero[2], Laura Iturriaga[1]

[1] Centro de Investigación y Transferencia Santiago del Estero (CITSE) – CONICET-UNSE. Villa El Zanjón (4206), Argentina.

[2] Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA) – CCT-CONICET-LA PLATA – La Plata (1900), Argentina.

[3] Instituto de Ciencia y Tecnología de Alimentos Córdoba (ICYTAC) (CONICET-UNC). Córdoba (5000), Argentina.

Corresponding author

Laura Iturriaga

Av. Belgrano (S) 1912

Santiago del Estero (4200), Argentina.

e-mail: laura.iturriaga@gmail.com

fax: +54 0385 450 9500

Abbreviations:

AM: amylose

AP: amylopectin

C.A.U.Que.Va.:Cooperativa Agropecuaria y ArtesanalUnión Quebrada y Valles

D[4,3]: De Brouckere mean diameter (µm)

CD: crystallinity degree

SF: swelling factor

Tp: gelatinization temperature (°C)

K:consistency coefficient (Pa.s^{-n})

n: flow behavior index

G’: storage modulus (Pa)

G”: loss modulus (Pa)

tan δ: loss factor $tan\left(\frac{G"}{G'}\right)$

RVA: rapid visco analyzer

PT: peak temperature (°C)

PV: peak viscosity (cP)

FV: final viscosity (cP)

BD: breakdown (cP)

SB: setback (cP)

PCA: principal component analysis

I_C: integrated intensity of the crystalline phase

I_A: integrated intensity of the amorphous phase

τ: shear stress (Pa)

$\dot{\gamma}$: shear rate (s^{-1})

LVR: linear viscoelasticity region

ANOVA: analysis of variance

LSD: least significant difference

Keywords: Andean tuber starch, pasting properties, rheological properties, thermal properties

Abstract

The physicochemical and rheological properties of starches from four landraces of Andean potato (Cuarentona, Rosadita, Imilla and Waycha), and Oca and Papalisa tubers were investigated and compared against conventional potato starch. Proximate composition studies showed that the protein content in the studied starches varied between 0.29 % and 1.18 % (w/w), the ash content between 0.24 % and 1.14 % (w/w), and the lipid content between 0.14 % and 0.34 % (w/w). Scanning electron microscopy investigations showed differences in shape of the granules of Andean potatoes and Oca and Papalisa. The mean size D[4,3] of the granules ranged between 23.3 and 48.11 µm. Papalisa was the starch with the lowest AM content (20.4 %, w/w) and Rosadita had the greatest (28.03 %, w/w). The gelatinization enthalpy ranged from 18.7 to 14.8 J/g and the gelatinization temperature between 65.5 and 60.8 °C. Viscograms of starch pastes showed that Cuarentona was the sample with the greatest peak viscosity (3152 cP) and presented the greatest final viscosity (3222 cP). The Andean potato and tuber starches exhibited low breakdown values. The relationship between physicochemical and rheological properties was analyzed by PCA. Results indicated that Oca and Papalisa starches were different from the Andean potato starches. Cuarentona starch showed the greatest K, G', peak viscosity, final viscosity, and Oca starch the lowest ones. The protein content affected the peak viscosity and setback of the samples. Results suggest that these starches have similar properties to those of conventional potato starch.

1. INTRODUCTION

Andean tubers cover a group of starchy roots that grow up in highlands (above 3000 m of altitude) in the Andean region, which in Argentina is confined to the Quebrada de Humahuaca, Puna, and high valleys of the provinces of Jujuy and Salta. They have been consumed for more than 3000 years by Andean people such as Incas, Quechuas and Aymaras[1]. Among them, the most widespread are Andean potato (*Solanum tuberosum* ssp. Andigenum), Oca (*Oxalis tuberosa* Molina) and Papalisa (*Ullucus tuberosus* Caldas).

Nowadays, C.A.U.Que.Va.gathers a group of farmers from 25 locations including the regions of Tumbaya, Tilcara, Humahuaca, and Iruya who cultivate a very small fraction of ground, about 1.25 ha each. The production of native potatoes and Oca is 5321.25 tons and 387 tons, respectively, during the harvest season from January to May. These products are commercialized under different forms with a variable degree of processing. Some of the industrial applications are: packed fresh potatoes, purée from Andean potatoes dehydrated with solar energy, vacuum-packed precooked potatoes, and potato candies from glazed Oca variety, among others (http://www.cauqueva.org.ar/). Andean potatoes have been planted for thousands of years, and stocks include many varieties with different physiognomic and organoleptic characteristics. Some studies on the nutritional value and rusticity of Andean tubers confirm that they can be usedas alternatives to meet the increasing demand for human and animal food, and industrial applications [2]. In spite of this increasing insertion in the market, other ways of processing and potential uses have not been explored enough. Isolated potato starches from these Andean varieties could be of potential interest if they can provide a different functionality with respect to conventional starches.

Starch is a low-price and abundant polysaccharide used in foods and is the main component of these tubers. It improves the organoleptic characteristics and textural properties of the meals since it acts as thickening and gelling agent. These functional properties depend mainly on the AM:AP ratio, granule size and distribution, and concentration of starch, among others.

Potato starch differs significantly from those of other plant sources. Economic and performance factors make potato starch the best choice for food applications [3] because its pastes have good clarity and a neutral flavor [4]. Being the main component, it is possible to assume that the gelatinization properties of starch will strongly influence the cooked tuber properties. On the other hand, physicochemical characterization studies would help to identify the industrial applications of these starches.

Opportunities for improving the potential value and, in turn, the production of these crops are possible if their utilization can be expanded, e.g., as a source of industrial raw material for starch production. Studies supporting their utilization should consider improving production, and for downstream processes, characterizing this raw material in terms of starch properties. While in the literature the information about the physicochemical and functional properties of potato starch is abundant, there is still little knowledge about the physicochemical and functional properties of Andean tuber starches.

The objective of this work was to study the physicochemical and rheological properties of starches extracted from two Andean tubers: Oca and Papalisa, and from four Andean potatoes: Waycha, Imilla, Cuarentona and Rosadita.

2. MATHERIAL AND METHODS

2.1. Materials

Samples of four Andean potato varieties (*Solanum tuberosum* ssp. Andigenum) Cuarentona, Imilla, Rosadita and Waycha, and two of Andean tubers, Oca (*Oxalis tuberosa* M.) and Papalisa (*Ullucus tuberosus* C.) were purchased from a cooperative from Jujuy,Argentina, C.A.U.Que.Va. (2013 harvest). The Andean potatoes were cultivated in the region called Quebrada de Humahuaca, province of Jujuy (North 22° 35' 32" S, 65° 21' 22" W; South 24° 01' 41" S, 65° 26' 20" W; East 23° 09' 24" S, 65° 02' 45" W, and West 23° 08' 39" S, 65° 43' 39" W; from 1350 m to 3340 m above sea level). Oca and Papalisa were cultivated in Iruya, province of Salta (22° 47′ 30″ S, 65° 12′ 59″ W; 2780 m above sea level), Argentina. Potato starch S-4251 from Sigma Chemical Company was used as control.

2.2. Isolation of starchand chemical composition

The starches from tubers were isolated according to the method described by Lu et al. [5] and a centrifugation step suggested by Djabali et al. [6]. Tubers were washed, peeled, cut into 2–3 cm pieces, and soaked for 2 h in distilled water containing 20 mM sodium bisulfite and 10 mM citric acid. The pieces were processed using a centrifugal juice extractor. The starchy milk collected was filtered through a 150 µm sieve. The starch suspension filtered was allowed to sediment for a minimum of 30 min, after which the sediment was removed and suspended in distilled water. Finally, they were centrifuged at 2800 *g* for 10 min in a refrigerated centrifuge Z326K (HermleLabortechnik GmbH, Wehingen, Germany). After centrifugation, the upper layer was separated. The starch was dried at 40 °C for 48 h in an oven.

The moisture, ash, protein, and lipid content of isolated starch samples was determined according to Association of Official Analytical Chemists (AOAC) standard methods (925.10, 923.03, 920.87, and 922.06, respectively) [7].

2.3. Morphological characterization

The starch granules were observed using SEM SUPRA 55VP (ZEISS, Germany). The starch samples were sprinkled on a double-sided tape mounted on a stub, coated with gold (20 nm thick) in an ion sputter chamber JFC-1100 (Jeol, Japan). The starch samples were placed in the SEM chamber and were examined at 22 kV [8, 9]. Starch birefringence was examined with an optical microscope CME (Leica, Buffalo, USA) with a polarized filter. Images were captured with a digital camera DSC-W200 (Sony, Japan) attached to the microscope.

2.4. Particle size analysis

The granule size distribution of starch samples was determined by laser light scattering Mastersizer 2000E with a dispersing unit Hydro 2000MU measured with a He-Ne laser (633 nm) (Malvern Instruments, Worcestershire, UK). Among the parameters measured by the instrument, the D[4,3] and span were selected for the analysis. Diagrams of the volume mean diameter distribution of the particles were obtained as well. All these parameters were calculated assuming that the granules are spherical particles [10].

2.5. Amylose content

The AM content was determined by an enzymatic AM/ AP assay procedure utilizing commercial K-Amyl kit (Megazyme International, Ltd) according to the procedure described by Gibson et al. [11]. The amylose content was measured as the ratio of the glucose derived from the supernatant after treatement with concanavalin A and the glucose derived from the total starch solution, expressed as a percentage [11].

2.6. Swelling factor

The pasting procedure for this experiment was designed in order to avoid or reduce the bursting of the granules [12]. Therefore, 0.1 g of starch was weighed in 10 mL conical screw cap PP tubes, and the necessary quantity of water was added to reach a final weight of 2 g. Suspensions at a concentration of 5 % (w:w) were immersed in a boiling water bath for 5 min, under gentle agitation. Once the pasting times were reached, the tubes were immediately placed in a 25 °C water bath and left to stand for at least 2 h.

The SF, defined as the equilibrium volume of 1 g of dry starch after swelling under specified conditions, was determined by pasting the samples prepared as was previously described, centrifuging them at 1500 *g* for 10 min and removing the supernatant. The SF was calculated with Eq. 1:

$$SF = \frac{Mass\ of\ swollen\ sample(g)}{Initial\ mass(0.1g)} \quad (1)$$

2.7. X-ray diffraction (XRD)

The assay was performed in a powder diffractometer X-PertPro (PANanalytical, Almelo, Netherlands), equipped with exit beam crystalline graphite monochromator, Kα radiation of Cu, λ = 1.5418 Å, 40 kV voltage and 20 mA current, 0.25º divergence slit. Data were collected in the range 2° ≤ 2Θ ≤ 45º at 2 Θ/min run velocity. The XRD pattern was used to determine the area of the amorphous and crystalline phases of each sample,since levels of crystallinity in granular starch can be determined by the separation and integration of the areas under the crystalline X-ray diffraction peaks and amorphous area [13]. The crystallinity degree (CD) was determined as in Eq. 2, in which the area of the crystalline fraction is divided by the crystalline fraction plus the amorphous fraction [14].

$$CD = \frac{I_C}{I_C+I_A} \tag{2}$$

Crystalline and amorphous areas were quantified using PeakFit v4.12 software (SeaSolve Software Inc., San Jose, CA, USA).

2.8. Thermal properties

The gelatinization temperature and enthalpy were analyzed by DSC using a DSC Q100 device (TA Instruments- Waters LLC, New Castle, DE, USA). Hermetic aluminum pans were used to prepare 10 mg samples with 10:90 starch:water (w:w). Sealed pans placed in tubes were homogenized in a vortex and left torest for at least 2 h before beginning the assay. Temperature scanning from 10 to 130°C at a rate of 10 °C/min was used. An empty pan (air) and indium were used as a reference and calibration standard, respectively. The gelatinization peak temperature (Tp), To and ΔH of each sample were then determined from the thermograms using the Universal Analysis 2000 v4.3E software (TA Instruments-Waters LLC, New Castle, DE, USA) and normalized to the mass of dry matter.

2.9. Determination of pasting properties

A Rapid Visco-Analyzer instrument RVA 4500 (Perten Instrument AB, Hägersten, Sweden) was used to prepare the samples and obtain their apparent viscosity profile as a function of temperature and time. Andean potato starch (2.00 ± 0.01 g, 14 % moisture basis) and 25 mL of distilled water were placed inside the aluminum canister. The RVA Potato Starch Pasting Method (RVA Method 7.04) was applied as follows: the automatic stirring action was set at 960 rpm for 10 sec and then, slowed down to 160 rpm. The sample was equilibrated at 50 °C for 1 min, heated to 95 °C in 4 min 42 sec, held at 95 °C for 2 min 30 sec, cooled to 50 °C over 3 min 48 sec, and then held at 50 °C for 2 min. Viscosity and temperature were recorded over time; data gathering and analysis were performed using Thermocline for Windows software, provided by the instrument manufacturer; PT, PV, FV, BD, and SB were obtained from the viscograms [15].

2.10. Rheological properties

Rheological measurements were performed with arheometer AR 1000 (TA Instruments-Waters LLC, New Castle, DE, USA) at 25 °C. Data were analyzed by Rheology Advantage Data Analysis software V5.2.18 (TA Instruments Ltd-Waters LLC, New Castle, DE, USA). Samples at 5 % (w:w) were prepared as described in 2.6.

2.10.1. Flow behavior

Flow assays were evaluated using steel cone geometry of 40 mm diameter, 2° angle and 0.053 mm truncation gap.The shear rate was accelerated uniformly from 0 to 300 sec^{-1} in 3 min, and the maximum shear rate was kept constant for 2 min. Afterwards, the shear rate was decelerated uniformly to 0 sec^{-1} in 3 min. The descending flow curves were modeled using the power-law model, Eq. 3:

$$\tau = K \cdot (\dot{\gamma})^n \quad (3)$$

whereτ is the shear stress (Pa), K is the consistency coefficient ($Pa.sec^{-n}$), $\dot{\gamma}$ is the shear rate (sec^{-1}) and n is the flow behavior index (dimensionless).

2.10.2. Dynamic measurement

The dynamic rheological properties, such as storage modulus (G'), loss modulus (G'') and loss factor (tan δ), were determined by employing stainless steel smooth parallel plate geometry (diameter = 40 mm) with 1mm gap. A solvent trap system was used to minimize evaporation losses. Stress sweeps at a frequency of 1 Hz were carried out to find the linear viscoelasticity region (LVR), after which, frequency sweep rheograms at 1.0 Pa of oscillatory stress were obtained.

2.11. Statistical

The data were statistically treated by analysis of variance (ANOVA), the means were compared by the LSD Fisher test at a significance level of 0.05 using Infostat Statistical Software (UNC, Córdoba, Argentina) [16]. All the measurements were carried out in triplicate.

2.11.1. Principal component analysis (PCA)

A PCA of 21 measured starch properties was carried out to provide a ready means of visualizing the differences and similarities among these samples [8]. The PCA score plot and loading was built from the first two principal components [17]. Data analysis was performed with Infostat Statistical Software (UNC, Córdoba, Argentina) [16].

3. RESULTS AND DISCUSSION

3.1. Chemical composition of the starches

To verify the purity of the extracted starches, the proximate analysis was done, and the results are listed in Table 1. The moisture content varied between 14.0 % and 16.3 % (w:w) among the Andean starches. It was lower than in the Control potato starch that showed 19.5 % (w:w), which is normal for commercial potato starch. The ash content of all the starches showed significant differences and was greater than that of the Control potato starch. All commercial starches from cereal or tuber sources contain minor or trace quantities of uncombined inorganic materials, which normally originate in the crop from which the starch is isolated and from the water used to process the starch [18].

The lipid content was low for all the samples and in the same order of or lower than the Control starch. Papalisa, Rosadita and Control starches presented the greatest lipid content and Oca starch, the lowest. The protein content varied between the samples: Cuarentona, Oca and Papalisa starches showed the lower contents and Imilla,Rosadita and Waycha, the greatest. The Control potato starch protein content was negligible. Based on this composition, the purity of theses samples ranged from 97.46 % to 99.31 % for Rosadita and Control starches, respectively.

Rosadita, Waycha and Imilla were the samples with lower purity. Cuarentona, Oca and Papalisa presented the greatest purity. This purity can be considered high and indicates a proper extraction process.

3.2. Morphological characterization and particle size analysis

SEM observations revealed some differences in starch granule shapes (Figure 1). The granules of Andean potato starches such as those from Rosadita, Imilla, Cuarentona and Waycha were large, oval-shaped, irregular, nonporous, and presented an eccentric hilum typical of the potato starch [18, 19]. As was expected since it is a starch from another genotype, Papalisa granules showed a rounded and enlarged shape like a "comma" with a protuberance in one of their extremes. Oca granules were different as well and had an elliptic shape. The SEM micrographs also showed that the surface of all the granules appeared to be smooth with some thin layers similar to scales, which could give some evidence of the presence of a granular membrane [21]. Table 2 shows that all the starches presented differences in the D[4,3] values, which ranged from 23.3 to 48.11 µm. The samples with the largest particle size were Waycha, Rosadita, Cuarentona and Imilla, while Papalisa and Oca had the smallestone. The former four samples had a mean size of the same order as that of the Control starch. Besides, a wide range in size was observed since the span index was from 1.21 to 1.51 for Andean potato starches and from 0.91 to 1.16 for Oca and Papalisa starches. As is shown in Figure 2, Oca, Papalisa, Imilla and Control starch exhibited a monomodal distribution with particle sizes between 10 and 100 µm. Rosadita and Waycha starches presented a bimodal distribution with a main peak that ranged from 10 to 100 µm in particle size and a smaller peak between 100 and 1000 µm, which may be due to the presence of aggregates since the starches were filtered with an ASTM 150 µm sieve. Cuarentona showed a bimodal distribution but with a smaller peak between 1 and 10µm. Mean sizes of the major peak in the range of 10 to 100 µm were reported for potato starches [22].

3.4. Amylose content

The AM content of the starches is listed in Table 2. Rosadita, Imilla, Cuarentona and Waycha varieties exhibited greater AM contents (26.2 % to 28.3 %) than Oca and Papalisa (22.4 % and

20.4 %, respectively). The AM content of the Andean potato starches was greater than that informed for Indian potato starches [22]. These results are in the range reported for normal potato starch [23] and Oca starch [24].

3.5. Swelling factor

The results listed in Table 2 indicate that Papalisa starch showed the greatest SF; Waycha, Rosadita, Imilla and Control starch presented intermediate values and Cuarentona, the lowest one. It is widely accepted that waxy starches or those with low amylose content exhibit high swelling degrees because this property is associated with the AP content [25].The correlation between AM content and SFwas not significant, suggesting that SF would depend on other properties than the AM content, such as the internal organization or the strength of association between AM and AP in the granule [26]. Nevertheless, the presence of small granules in Cuarentona (1-10 µm) could also have an effect on the lowest swelling factor in this sample.

3.6. X-ray diffraction

All the starches exhibited X-ray B patterns with peaks at 2θ Bragg angles: 5.6°, 15°, 17°, 19°, 22° and 24° (diffraction patterns not shown). This kind of pattern is typical of most of the roots and tubers like potato, where the starch chains and water molecules are organized in a hexagonal packing [8]. Similar results were found by Santacruz et al. [9] in Andean starches from *Arracacha xanthorriza, Canna edulis and Oxalis tuberosa*. Some reports assign the presence of the three overlapped peaks at 2θ = 19° to the location of water molecules in the starch crystal [13].

XRD also measures the crystallinity degree of the starches as the ratio between the area enclosed by the peaks and the area under the curve (or amorphous area) [12]. The results shown in Table 2 indicate differences in crystallinity among the starches that ranged from 18.1 % to 24.6 %. It is accepted that there is anegative correlation between the AM content and the CD since amylopectin is the predominant crystalline component in granules, with the short-branched chains forming local organizations compatible with cluster models [27]. However, it was not possible to find such correlation among these samples, probably because AM contents were not different enough among the varieties toproduce differences in crystallinity. The CD values were the greatest in Cuarentona, Rosadita, Waycha and Control starchand intermediate in Imilla. Papalisa was the sample with the lowest CD even though it showed the lowest AM content. Starch potato crystallinity values slightly greater than those found in this work were reported [27, 28].

3.7. Thermal properties

When starch granules are heated in the presence of water, some endothermic events occur, which can be followed by DSC. Parameters such us To, Tp, ΔH have technological importance since they are a measure of the thermal energy that must be applied for gelatinization. The results obtained are given in Table 2. The gelatinization temperature for Andean tuber starches ranged from 60.8 °C for Oca starch to 65.5 °C for Rosadita starch, and they were lower than 66.1°C for the Control potato starch. The onset temperatures of the peak showed significant differences among the samples andvaried in a pattern similar to that of Tp confirmed by the Pearson correlation coefficient of 0.98 (Table 4). Significant differences between ΔH for all the samples were found. They ranged from 14.8 to 19.7 J/g for Waycha and Control starches, respectively. The thermal properties of potato and other tuber starches differ widely in the bibliography [8, 17, 21, 25, 29] since they depend on the degree of crystallinity, the granule size, the AM/AP ratio and the microstructure of the granule, which in turn depend on the climatic and soil conditions where the tubers grow up. No significant correlations between thermal properties and the AM content, CD and D[4,3] were found in this study.

3.8. Rheological properties

The dynamic properties of the systems at 5% w:w are listed in Table 3. Mean values of three replicates of G' and G", taken from the rheograms at a frequency of 1 Hz,are included. The results showed significant differences among the samples. Cuarentona sample had the greatest G' (170.2 Pa) and Oca, the lowest (76.2 Pa). The rest of the samples presented G' values that ranged from 110.1 to 139.9 Pa. Considering G", Cuarentona was the sample with the greatest value (55.3 Pa) and Papalisa had the lowest (13.4 Pa). The rest of the samples presented G" values that ranged from 15.2 to 39.8 Pa.The parameter that relates the viscous and the elastic behavior is tan δ,which was greater than 0.1 for all the systems.The greatest tan δ value was for Cuarentona starch (0.32) and the lowest for Papalisa (0.11). The rest of the samples presented tan δ values that ranged from 0.19 to 0.29.These results describe an elastic behavior since G' was greater than G" in the range of frequency applied. However, the tan δ values indicate that the systems are not able to store the dynamic energy applied, which is partly lost, so they do not form strong gels at the concentration studied. In the experimental conditions, moduli showed a dependence on frequency, as can be seen in Figure 3.

Starch gels can be considered as systems where swollen granules, enriched in amylopectin, are embedded in and reinforced by interpenetrating amylose gel matrix [31]. Depending on the starch concentration and the AM content, the gel obtained can be classified as strong or weak. At the concentration of the systems studied, a closed packed system was reached after gelatinization since the volumetric fraction (ϕ) wasgreaterthan 0.7 for all samples. The volume fraction was calculated by applying Eq.4 (data not shown) [32]

$$\Phi = c \,.\, SF \qquad (4)$$

where "c" is the concentration of starch suspension % (w:w) and SF, the swelling factor, dimensionless.

The critical AM concentration necessary to form gels was reported as C*=1.5 % [31], below which the gel is not totally formed. The mechanical dynamic spectra allow identifying these differences. While strong gels present a G' independent of frequency and tan δ values < 0.1, weak gels show some dependence and tan δ values > 0.1 [33].

Based on these criteria, the results shown in Figure3 would indicate that the starch suspensionsin general behaved as weak gels.However, Papalisa presented the more elastic gel and Cuarentona, the less elastic one.

Regarding the flow properties, the values of *K* and *n* corresponding to aqueous suspensions of gelatinized starch at 5 % w:wconcentration are summarized in Table 3. At this point, it is important to remark that the power law model to obtain K and n was applied to the down curve after having eliminated the time dependence behavior. It is well known that the gelatinized starch systems exhibit a typical thixotropic behavior. The results obtained indicate that *n* values were lower than 1 for all of the samples exhibiting a pseudoplastic behavior (data not shown). Cuarentona starch presented the greatest value of consistency coefficient *K* (16.7 Pa.s) and Oca starch showed the lowest (6.0 Pa.s). Papalisa presented a K value in the order of that of Imilla and Waycha, being the starch with the smallest granule size and the lowest AM content. The rest of the samples presented differences in K values that ranged between 8.0 and 13.3 (Pa.s). Despite the lack of correlation of these fundamental rheological parameters with the AM content or the D[4,3], there was a significant positive Pearson correlation of 0.75 between K and G'.

3.9. Pasting properties

The results of the RVA for the starches are summarized in Table 3 and in the RVA viscograms in Figure 4. Pasting temperature presented significant differences and ranged from 65.3 °C to 70.3 °C, the lowest for Oca and the greatest for Rosadita starches. By comparing PT with thermal properties, it was possible to find a good and significant correlation (0.76) with To from the DSC analysis (Table 4), PT being almost 10°C greater than To due to the difference in the concentration of starch.

Cuarentona sample had the greatest PV (3152 cP) among the Andean starches and Oca, the lowest one (1602 cP). The Control starch presented the greatest PV (4895 cP) among the tested samples but also showed themost pronounced BD (3132 cP), indicating less stability. In contrast, Andean potato and tuber starches showed significantly lower values of BD (364-577 cP) than control starch, which would suggest that these starches are more resistant to disruption by shear during gelatinization. Although the AM is the fraction that confers better granular integrity, no correlation between BD and the AM content was found. However, Papalisa presented the greatest BD (577 cP) after Control starch, in line with the lowest AM content found in this sample.

The FV differed significantly among all the samples, and the greatest value was for Cuarentona (3222 cP) and the lowest for Oca (1586 cP). All the Andean potato samples showed greater FV than the Control starch (2050 cP), probably because of the more marked granular disruption of the Control potato sample. Final viscosity is affected by the AM content as well, and this may explain why Oca and Papalisa were the samples with the lowest FV (1586 and 1865 cP, respectively). Good positive correlations (0.83, 0.90 and 0.77) between FV and G', G" and tan δ were found (Table 4), showing that in this case, the behavior of the samples presented the same tendency in empirical and fundamental measurements.

3.10 Principal component analysis (PCA)

The PCA was applied in order to detect differences and similarities between the starches. The results obtained are shown in Figure5. The first and second principal components (PC1 and PC2) explained the 41.1 % and 22.6 % of the overall variation, respectively. Considering the correlation with the original variables, the variability enclosed in PC1 is mainly due to the mean size D[4,3], the AM content, To, Tp, FV, K, G" and tan δ. Regarding PC2, the properties that contribute to the variability are ΔH, PV, BD, SB, and ash and protein content.

The score plot shown in Figure 5 indicates that Oca and Papalisa had the largest negative scores in PC1 and were located on the left of the plot. On the other hand, the rest of the samples presented positive scores in PC1 and were located on the right in the plot. Control starch presented the largest negative score in PC2, followed by Cuarentona, and both were located below, on the right of the plot. Imilla, Waycha and Rosadita were located on the right and upper side of the plot. Besides, Imilla and Rosadita differed slightly in the positive scores in PC1.

These results indicate that Oca and Papalisa were different from the rest of the samples, especially in the variables that are related to the PC1 axis. In fact, D[4,3], the AM content, To, Tp, FV and G" values of Imilla, Waycha, Rosadita, Cuarentona and the Control starch were greater and significantly different from those of Oca and Papalisa, as shown in Tables 2 and 3.

Among the Andean potato starches, the PCA biplot differentiates Cuarentona from Imilla, Rosadita and Waycha in the properties that define the variability in PC2, such as ash and protein content, PV, ΔH and SB. In fact, the former presented lower ash and protein contents and SB, and greater PV, BD and ΔH among the Andean potatoes. In this context, the protein content appears as a variable significantly affecting the PV and consequently the BD, since the greater the PV, the greater the BD. This correlation is evident in the varieties with the lowest protein content such as Cuarentona and the Control starch. On the other hand, in line with this observation, Imilla, Rosadita and Waycha exhibited lower PV than Cuarentona and the Control starch, and lower BD. However, the Pearson coefficients indicated that there is no correlation between the protein content with either K or G' (Table 4), which could be explained by the different experimental conditions and type of rheological measurement.

A similar analysis was done with the ash content, where no significant correlation was found with any variable studied (Table 4).

4. CONCLUSIONS

This research has led to new and relevant information on the physicochemical properties of these starches. The morphological studies revealed that the starches from Andean potato have similar characteristics and granule mean size to those of conventional potato starch, and Papalisa and Oca have specific shapes and lower granule mean size.

PCA showed that the behavior of starches extracted from tubers (not potatoes), Oca and Papalisa, was different from that of Andean potato starches and the Control starch. These differences could be mainly related to their lower mean size and AM content. Despite these characteristics, Papalisa formed more elastic gels than the rest of the samples, and Cuarentona was the starch with the greatest values of G', K and FV. All samples presented high stability at shearing since the BD was much lower than that of the Control potato starch.

No effects of ash or lipid contents on the physical properties of the starches were found, under the conditions of this study. However, the protein content seems to affect the PV and BD parameters in RVA.

This study indicates that starch can be satisfactorily extracted from Andean potatoes and tubers. The starches exhibit interesting thermal and rheological properties and could be applied in food formulation. Further studies exploring the behavior of Andean starches in real food matrices could confirm the potentiality of these alternative sources of starch.

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628 Table 1. Proximate analysis of starches expressed in (%, w:w).

Sample	moisture [1]	ash [2]	lipid [2]	protein [2]	Purity [3]
Papalisa	16.2 [b]	0.71 [d]	0.32 [b]	0.52 [c]	98.45
Oca	14.0 [a]	0.24 [a]	0.15 [a]	0.58 [c]	99.03
Cuarentona	16.3 [b]	0.48 [b]	0.24 [ab]	0.29 [b]	98.99
Imilla	14.1 [a]	0.61 [c]	0.25 [ab]	1.18 [e]	97.96
Rosadita	14.3 [ab]	1.06 [e]	0.34 [b]	1.13 [e]	97.47
Waycha	15.5 [ab]	1.14 [e]	0.21 [ab]	0.9 [d]	97.83
Control	19.5 [c]	0.33 [a]	0.32 [b]	0.04 [a]	99.31

629 Values within each column with the same superscript letters are not significantly different

630 ($p>0.05$). [1] wet basis. [2] dry basis (db). [3]Purity= [100 % (db) - (ash % + lipid % + protein %).

Table 2. Characteristic parameters of particle size analysis, AM content, SF, CD and DSC parameters.

Sample	D[4,3] [1] (µm)	specific surface area (m^2/g)	Span	AM (%)	SF [2],*	CD (%)	To (°C)	Tp (°C)	ΔH* (J/g)
Papalisa	23.30^{a}	0.307^{b}	1.161^{a}	20.4^{a}	19.3 ^{c}	18.1 ^{a}	58.3 ^{b}	62.7 ^{b}	18.0 ^{bc}
Oca	29.90^{b}	0.225^{a}	0.912^{d}	22.4^{b}	18.0 ^{bc}	23.8 ^{c}	55.9 ^{a}	60.8 ^{a}	17.7 ^{ab}
Cuarentona	42.82^{d}	0.206^{c}	1.285^{b}	27.6^{d,e}	17.3 ^{ab}	24.0 ^{c}	58.3 ^{b}	63.2 ^{bc}	18.7 ^{bc}
Imilla	39.29^{c}	0.185^{b}	1.214^{c}	26.8^{c,de}	17.6 ^{bc}	21.9 ^{b}	59.9 ^{cd}	64.4 ^{d}	15.2 ^{a}
Rosadita	43.91^{e}	0.201^{d}	1.310^{f}	28.03^{cd}	18.3 ^{bc}	24.6 ^{c}	60.3 ^{d}	65.5 ^{e}	18.6 ^{bc}
Waycha	48.11^{g}	0.188^{e}	1.518^{e}	26.2^{e}	18.8 ^{bc}	24.4 ^{c}	59.4 ^{c}	63.7 ^{c}	14.8 ^{a}
Control	46.43^{f}	0.163^{c}	1.333^{f}	26.2^{c}	18.2 ^{bc}	23.8 ^{c}	61.0 ^{e}	66.1 ^{e}	19.7 ^{c}

* Values expressed on dry basis (db)

Values within each column with the same superscript letters are not significantly different ($p>0.05$).

[1] D[4,3] standard deviation ranged from 0.03 to 1.21 µm.

[2] SF: 5 min in boiling water bath.

636 Table 3.Rheological properties and RVA parameters of starch pastes.

Sample	G' (Pa) [1]	G" (Pa) [1]	Tan δ	K (Pa.s)	n	PT (°C)	PV (cP)	BD (cP)	FV (cP)	SB (cP)
Papalisa	122.1 [cd]	13.4 [a]	0.110 [a]	8.8 [c]	0.479 [a]	68,7 [cd]	2037 [cd]	577 [b]	1865 [b]	405 [b]
Oca	76.2 [a]	15.2 [a]	0.199 [c]	6.0 [a]	0.532 [d]	65.3 [a]	1602 [a]	443 [ab]	1586 [a]	426 [b]
Cuarentona	170.2 [f]	55.3 [e]	0.325 [e]	16.7 [f]	0.474 [a]	68.7 [cd]	3152 [e]	497 [ab]	3222 [g]	568 [c]
Imilla	113.9 [bc]	32.8 [c]	0.288 [d]	8.0 [b]	0.514 [c]	69.4 [d]	1902 [bc]	376 [ab]	2698 [e]	1172 [e]
Rosadita	110.1 [b]	22.9 [b]	0.208 [c]	12.6 [d]	0.476 [a]	70.6 [e]	1741 [ab]	368 [ab]	2216 [d]	844 [d]
Waycha	139.8 [e]	39.8 [d]	0.285 [d]	9.5 [c]	0.523 [c]	67.9 [b]	2198 [d]	364 [a]	3107 [f]	1273 [f]
Control	119.2 [bcd]	32.4 [c]	0.272 [d]	13.3 [e]	0.504 [b]	68.3 [bc]	4895 [f]	3132 [c]	2050 [c]	288 [a]

637 Values within each column with the same superscript letters are not significantly different ($p>0.05$).

638 [1] Mean values of G' and G" that were taken from rheograms at frequency = 1 Hz.

Table 4: Pearson correlation coefficients for the properties of Andean potato and tuber starches

	D[4,3]	Span	AM	SF	CD	To	Tp	ΔH	PT	PV	BD	FV	SB	K	Area	G'	G''	Tan δ	ash	protein	lipid
D[4,3]	1.00																				
Span	0.78	1.00																			
AM	0.90*	0.62	1.00																		
SF	-0.35	0.17	-0.58	1.00																	
CD	0.78*	0.30	0.71	-0.51	1.00																
To	0.66	0.74	0.63	0.04	0.15	1.00															
Tp	0.68	0.67	0.67	-0.04	0.25	0.98*	1.00														
ΔH	-0.08	-0.23	-0.04	-0.09	0.05	0.05	0.20	1.00													
PT	0.34	0.54	0.56	-2.1E-4	-0.09	0.76*	0.74	0.06	1.00												
PV	0.45	0.35	0.27	-0.17	0.19	0.49	0.54	0.54	0.04	1.00											
BD	0.30	0.17	0.08	0.01	0.11	0.48	0.54	0.55	-0.04	0.91*	1.00										
FV	0.63	0.70	0.67	-0.36	0.33	0.30	0.23	-0.43	0.36	0.10	-0.26	1.00									
SB	0.45	0.52	0.48	-0.05	0.24	0.29	0.18	-0.86*	0.33	-0.46	-0.53	0.63	1.00								
K	0.55	0.51	0.63	-0.36	0.35	0.44	0.52	0.55	0.50	0.61	0.32	0.50	-0.19	1.00							
Area	-0.89*	-0.45	-0.81*	0.57	-0.81*	-0.52	-0.57	0.10	-0.10	-0.44	-0.39	-0.41	-0.35	-0.31	1.00						
G'	0.43	0.66	0.44	-0.17	0.06	0.30	0.24	3.8E-4	0.41	0.37	-0.02	0.83*	0.18	0.75*	-0.10	1.00					
G''	0.70	0.59	0.71	-0.58	0.47	0.28	0.27	-0.10	0.21	0.43	0.05	0.90*	0.30	0.70	-0.55	0.84	1.00				
Tan δ	0.80*	0.48	0.80*	-0.72	0.66	0.32	0.33	-0.21	0.09	0.41	0.15	0.77*	0.40	0.49	-0.83	0.53	0.90	1.00			

ash	0.33	0.67	0.30	0.47	0.07	0.40	0.31	-0.46	0.56	-0.40	-0.44	0.41	0.70	0.04	0.02	0.26	0.06	-0.06	1.00		
protein	0.07	0.10	0.24	0.04	0.05	0.12	0.06	-0.68	0.38	-0.78*	-0.69	0.18	0.81*	-0.42	-0.06	-0.24	-0.18	-0.05	0.65	1.00	
lipid	0.09	0.36	0.18	0.32	-0.30	0.72	0.74	0.47	0.80*	0.33	0.38	-0.13	-0.19	0.45	0.11	0.18	-0.13	-0.28	0.29	-0.05	1.00

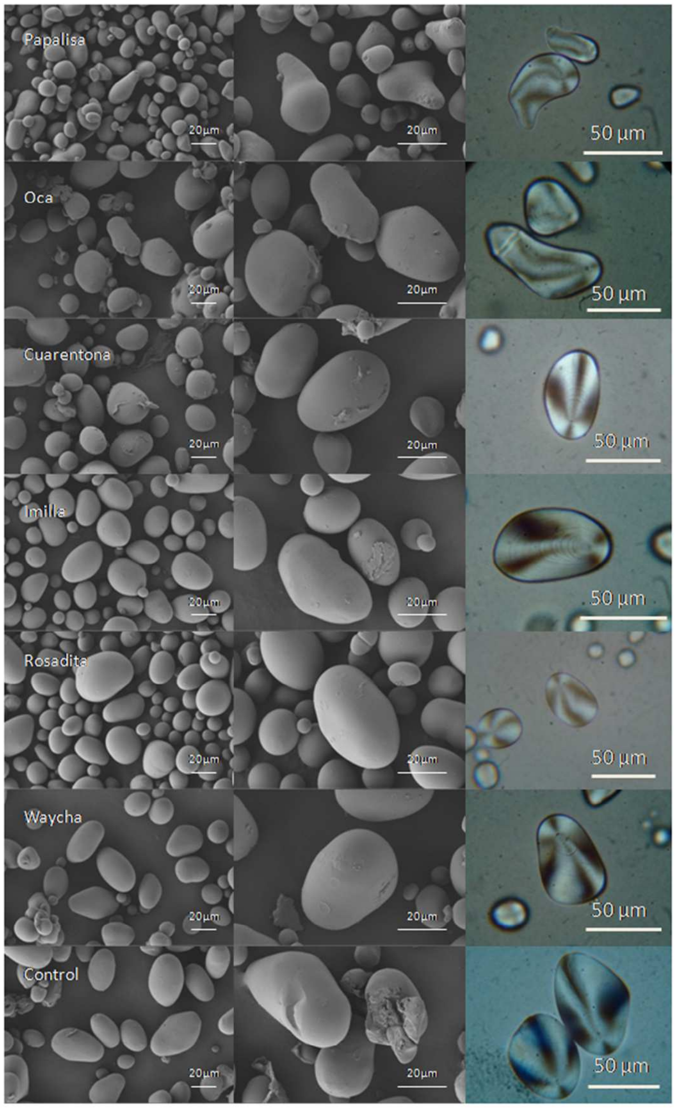

Figure 1: SEM and optical micrographs of isolated starches from Andean potatoes and tubers and the Control starch. From the left, the first two are SEM images at 600x and 1500x; the third image was taken under polarized light at 1000x magnification.
190x275mm (96 x 96 DPI)

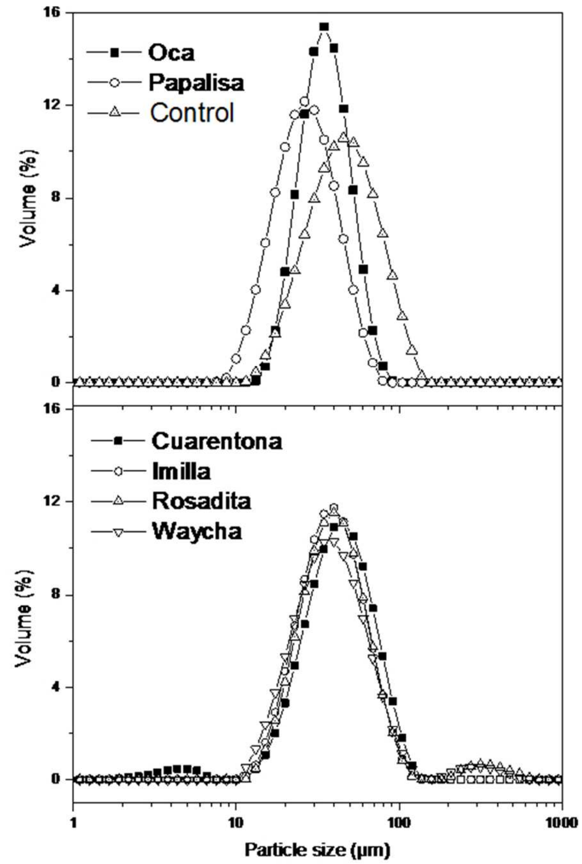

Figure 2: Granule size distribution of starches suspended in water measured by laser light scattering.
190x275mm (96 x 96 DPI)

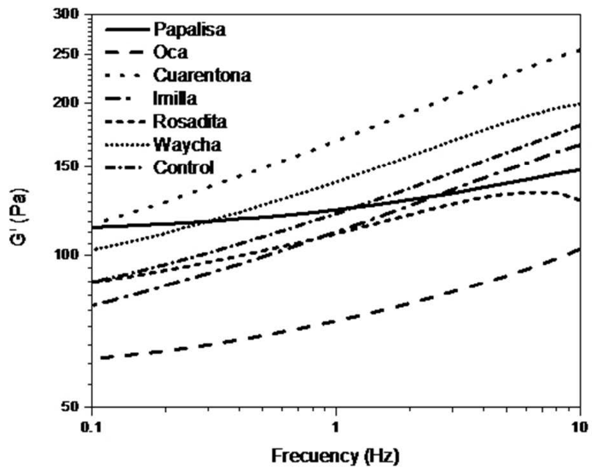

Figure 3: G’ vs. frequency of gelatinized starch suspensions at 5 % w:w.
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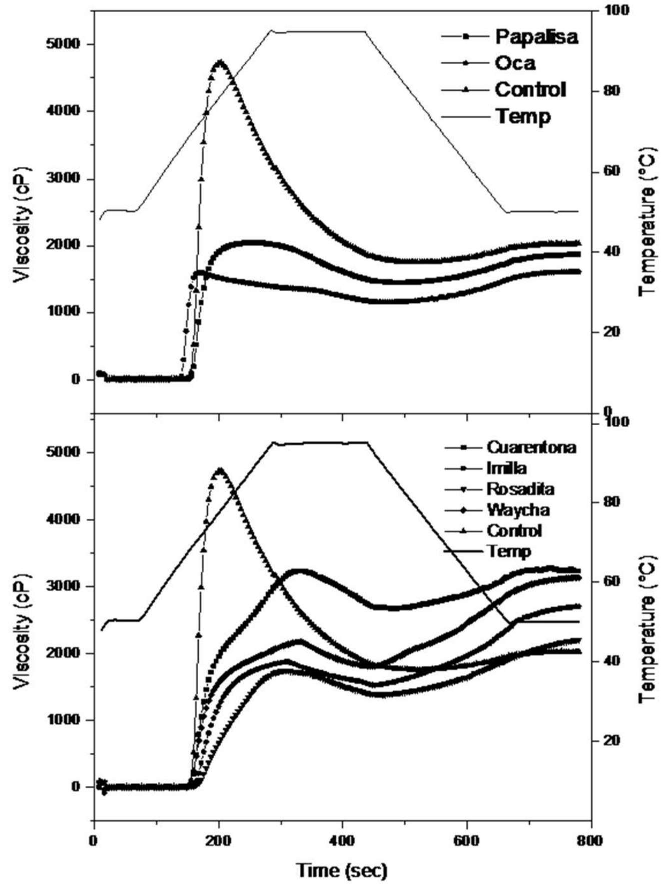

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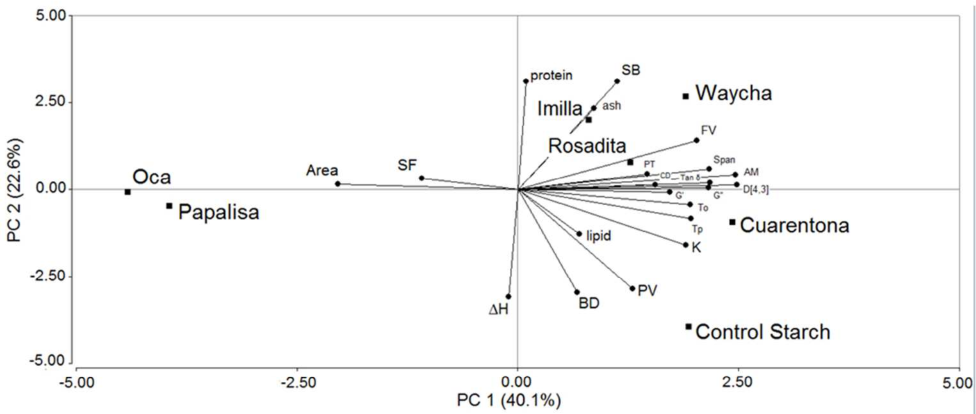

Figure 5: PCA: score and loading plot of PC1 and PC2 describing the overall variation among the Andean tuber starches.
275x190mm (96 x 96 DPI)