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Study of Physicochemical, Morphological, Functional, Rheological and Thermal Properties of Native Andean Potato Starch and its Application in Biobased Materials

Estudio de las propiedades fisicoquímicas, morfológicas, funcionales, reológicas y térmicas de almidón de papas nativas andinas y su aplicación en materiales biobasados

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Abstract

Starch is the most widely used biopolymer for packaging production. Starch obtained from native potatoes (*Solanum phureja*) may represent an alternative for the development of packaging materials due to its biodegradable nature, providing a potential use that may encourage the cultivation and valorization of these varieties. The objective of this study was to characterize starch from the potato varieties Curiquinga, Ratona Roja (*Solanum phureja*), and Diacol Capiro (*Solanum tuberosum),* and to evaluate the mechanical properties of starch-based films produced from these starches. The methodology consisted of determining moisture content and functional indices by gravimetry, granule size and morphology by scanning electron microscopy, amylose content by spectrophotometry, the amylographic profile by rapid viscosity analysis, and thermal properties by thermogravimetry and differential scanning calorimetry. The films were prepared using the casting method. The results showed that the amylose content of Ratona Roja and Diacol Capiro starches was 2% higher than that of Curiquinga starch, possibly due to their larger granule size. Ratona Roja starch exhibited lower water absorption index, swelling power, and maximum viscosity; however, its water solubility index and final viscosity were higher compared with the other varieties. The mechanical properties of films prepared with Ratona Roja starch showed greater elongation at maximum force (%) and Young's modulus (MPa), whereas tensile strength (MPa) was higher in films prepared with Diacol Capiro potato starch. It is concluded that the functional indices, viscosity profile, and thermal properties may be associated with amylose content and granule size, and these properties determine their potential applications. Starches from native potatoes may be an alternative biopolymer for the production of biodegradable materials.

Keywords

Biomaterial, biopolymers, food packaging, mechanical properties, potato starch.

Resumen

El almidón es el biopolímero más usado para la elaboración de empaques. El almidón obtenido de papas nativas (*Solanum phureja*) puede ser una alternativa para el desarrollo de empaques debido a su naturaleza biodegradable, generando una alternativa de uso que incentive el cultivo y su aprovechamiento. El objetivo del articulo consistió en caracterizar el almidón de las variedades de papas Curiquinga, Ratona Roja (*Solanum phureja)* y Diacol Capiro (*Solanum tuberosum*), y evaluar las propiedades mecánicas de biopelículas elaboradas con estos almidones. La metodología consistió en determinar el contenido de humedad e índices funcionales mediante gravimetría, el tamaño y forma del gránulo mediante microscopia electrónica de barrido, el contenido de amilosa mediante espectrofotometría, el perfil amilográfico mediante análisis rápido de viscosidad, y las propiedades térmicas usando termogravimetría y calorimetría diferencial de barrido. Las películas se elaboraron con el método "casting". Los resultados indicaron que el contenido de amilosa en las variedades Ratona Roja y Diacol Capiro fueron 2 % más altos que en la variedad Curiquinga, posiblemente por un tamaño de gránulo mayor. El almidón de la variedad Ratona Roja presentó un índice de absorción de agua, poder de hinchamiento y viscosidad máxima menores; sin embargo, el índice de solubilidad en agua y la viscosidad final fueron mayores en comparación con las otras variedades. Las propiedades mecánicas de las películas con almidón variedad Ratona Roja presentaron mayor elongación a la fuerza máxima (%) y módulo de Young (MPa), mientras la resistencia a la tracción (MPa) fue mayor en la película con almidón de papa Diacol Capiro. Se concluye que los índices funcionales, el perfil de viscosidad y las propiedades térmicas pueden estar relacionadas con el contenido de amilosa y tamaño de gránulo, estas propiedades determinan sus posibles usos. Los almidones de papas nativas puede ser un biopolímero alternativo para la elaboración de materiales biodegradables.

Palabras clave

Biomaterial, biopolímeros, , empaques de alimentos, propiedades mecánicas, almidón de papa.

1. INTRODUCTION

Potato (*Solanum tuberosum*) is a crop that constitutes a fundamental pillar of the economy of Colombia. More than 100 000 producers are engaged in potato cultivation; this activity generates over 350 000 direct and indirect jobs and is estimated to account for approximately 20 million labor-days per year. In Colombia, 90% of the potato-growing area is concentrated in four departments: Cundinamarca (36%), Boyacá (27%), Nariño (22%), and Antioquia (5%) [1]. According to FEDEPAPA, national production reached 2 526 330 t in 2022 [2]. In this context, the department of Nariño has considerable agro-industrial potential within the potato production chain, and starch extraction may represent a viable alternative.

Of total national potato production, 6.8% corresponds to a wide diversity of native potatoes (*Solanum phureja*). However, these tubers show a clear tendency toward disappearance due to low demand, limited technological innovation, and the absence of industrial processing for transformation and preservation [3]. The agro-industrialization of other potato varieties, particularly native varieties, may open new opportunities for the use of these Andean tubers in both food and non-food applications; extracting starch from native potato varieties increases their added value [4]. The department of Nariño is a center of native potato biodiversity, among which the Ratona Roja and Curiquinga varieties stand out. Therefore, extracting and characterizing starch from these varieties may encourage their use and production, thereby contributing to the preservation of regional biodiversity.

The importance of starch is due to its wide application in food and non-food sectors [5]. It provides texture and consistency in foods and is also used in the manufacture of products such as paper, adhesives, and biodegradable packaging [6]. Given the current pollution crisis associated with petrochemical packaging materials and microplastic generation, particularly in the food industry, the development of new materials has become increasingly important. Certain residues may migrate from packaging materials into food depending on the type of packaging material, the composition of the food, and storage conditions [7]. By contrast, starch-based films do not generate microplastics and may therefore be used in food-packaging applications. Starch is the most widely used biopolymer in the production of edible films and biodegradable packaging. Starch-based films have strong potential to replace plastics in the packaging sector because they combine flexibility and resistance [8]-[10].

The properties of starches extracted from different botanical sources, together with compositional differences, determine the properties of films produced from this biopolymer [8], [11]-[13]. Non-conventional starches obtained from native potato varieties from southwestern Colombia have been little studied. Understanding these starches makes it possible to establish processing parameters and anticipate the potential characteristics of materials produced from these raw materials. Amylose content and granule size are key determinants of rheological and thermal behavior, as well as solubility and water absorption capacity. It has been reported that native potato starches exhibit distinctive characteristics, including low gelatinization temperatures and high viscosities, due to their high amylose contents [5], [14], [15]. Likewise, differences in the composition and properties of native potato starches influence the characteristics of the resulting films [16], [17]. Therefore, the objective of this study was to characterize the starch extracted from two native potato varieties, Curiquinga and Ratona Roja (*Solanum phureja*), and from the commercial potato variety Diacol Capiro (*Solanum tuberosum),* and to compare the mechanical properties of films produced from the extracted starches.

2. MATERIALS AND METHODS

2.1 Raw material and starch extraction

Two native potato varieties, Curiquinga and Ratona Roja (*Solanum phureja*), and one commercial potato variety, Diacol Capiro (*Solanum tuberosum*), cultivated in the department of Nariño, Colombia, were selected. The tubers were sorted, washed, and disinfected. Starch extraction was carried out using the wet-milling method, with 1% sodium bisulfite added to prevent enzymatic browning. The extracted starch was dried at 45 °C for 24 h in a convection dryer (Industrias Químicas FIQ). Subsequently, the dried starch was milled, sieved through a No. 100 mesh, and stored in resealable bags under ambient conditions (T: 18 ± 2 °C; RH: 60 ± 5%) until further use.

2.2 Yield, moisture content, amylose content, granule size and shape

The extraction yield (%) was calculated as the amount of starch extracted (g) per amount of processed potato (g). Moisture content (%) was determined by gravimetry using a drying oven (Thermolab TH53) at 100 °C for 24 hours. Amylose content was determined by the amylose-iodine colorimetric method, using a UV-VIS spectrophotometer (Mapada P4). The shape and size of the starch granules were analyzed by Scanning Electron Microscopy (Quanta 200), the micrographs were analyzed using ImageJ software.

2.3 Pasting properties

The amylographic profile was determined by rapid viscosity analysis using a rotational rheometer (TA Instruments AR1500EX) according to the methodology reported by [18], for this purpose starch solutions were prepared (4 g in 100 mL). The analysis started at a temperature of 50 °C, then, heating began with an increase of 10 °C/min until reaching 90 °C, maintaining this temperature for 5 minutes, after that, the temperature was decreased to 50 °C, maintaining this temperature for 2 minutes. From the graph the following were determined: pasting temperature (PT), maximum viscosity (MV), final viscosity (FV), rupture viscosity (RV) and setback viscosity (SV).

2.4 Functional properties

The functional properties that were calculated were: the Water Absorption Index (WAI), Water Solubility Index (WSI) and Swelling Power (SP), using equations (1), (2) and (3), following the methodology described by [13] and [4] with some modifications.

Solutions were prepared by adding 1 g of starch (W_0) in 25 mL of distilled water, heated in a water bath at different temperatures (60, 70, 80 and 90 °C) for 10 min, then cooled to up to 25 °C using an ice bath, the samples were shaken in a centrifuge (Dynamica 18R) at 4900 rpm for 30 minutes. Then, the supernatant was separated and its volume (mL) measured, the centrifuge tube was weighed and the weight of the gel (W_1) was calculated; A 2 ml aliquot was taken from the supernatant and placed in a Petri dish to be dried at 70°C for 4 hours in a forced air dryer oven (Biobase BOV-V45F), The amount of soluble starch was weighed and the weight of the total soluble (W_2) was calculated with respect to the total volume of the supernatant.

$$\mathrm{WAI} = \frac{W_1\ (\mathrm{g})}{W_0(\mathrm{g})} \tag{1}$$

$$\mathrm{WSI} = \frac{\mathrm{W}_2\ (\mathrm{g})}{\mathrm{W}_0\ (\mathrm{g})} x\ 100 \tag{2}$$

$$\mathrm{SP} = \frac{\mathrm{W}_1\ (\mathrm{g})}{W_0\ (\mathrm{g}) - \mathrm{W}_2\ (\mathrm{g})} \tag{3}$$

Where:
W_0 is the weight (g) of the starch sample on a dry basis (D.B)
W_1 is the weight (g) of the starch gel gelatinized at different temperatures
W_2 is the weight (g) of soluble starch in the supernatant

2.5 Thermal properties

The thermal properties of the starches were determined by thermogravimetric analysis and differential scanning calorimetry (TA Instruments SDT-Q600). From the thermograms, the following were determined: degradation stages (%), residual mass (%), peak gelatinization temperature (T_p – °C) and maximum degradation temperature (T_{max} – °C).

2.6 Production and mechanical evaluation of bioplastic films

The films were prepared according to the Casting method or solvent evaporation described by some authors [19], [20]. Solutions (4 g of starch in 100 mL of distilled water) of starch from different varieties Capiro, Ratona Roja and Curiquinga were prepared. The solution was heated to 90 °C and maintained for 10 minutes, then cooled to 70 °C and glycerol was added (30% with respect to the amount of starch D.B). The solution was poured into a laminator equipment (Ceirobot PB4.8) equipped with a Teflon surface, molded and dried at 60°C for 1.5 hours, the films were stored under conditions (T:18 ± 2 °C and R.H: 60 ± 5%). The mechanical evaluation of the films was carried out according to the international technical standard ASTM D882-18 [21] using a texturometer (Lloyds-LS1) with gripping jaws and a 1 kN load cell, at a preload speed of 10 mm/min and a test speed of 12.5 mm/min, specimens of 125 mm by 25 mm were used. The mechanical properties measured were Percentage of total elongation at maximum force (%), tensile strength (MPa) and Young's modulus (MPa). Moisture content (%) was measured using a moisture balance (KERN DBS) and thickness with a micrometer (mm).

2.7 Statistical analysis

A completely randomized design was used and an analysis of variance (ANOVA) with Fisher's LSD test at 95% confidence level was performed to identify significant differences among the properties of each starch type. The results were reported as mean ± standard deviation. In the case of functional properties, temperature was included as a covariate in the analysis. To evaluate the mechanical properties of the films, the same statistical analysis was applied, comparing the different starch types. The number of replicates (n) is indicated in the results tables for each variable. The denomination of the extracted starches is: Ratona Roja variety – RRS, Curiquinga variety – CQS and Diacol Capiro variety – DCS.

3. RESULTS AND DISCUSSION

The results of the chemical, physical, pasting, functional and thermal properties of the starches extracted from the native potato varieties RRS and CQS and the commercial variety DCS are presented below.

3.1 Extraction yield, moisture content and amylose content of starches from three potato varieties

The yield (%) in starch extraction for the native potato varieties was slightly higher than that obtained for the commercial potato variety (Table 1), however, there were no statistical differences among the varieties (see Table 1). Yield depends on several factors: the extraction parameters, the potato variety and the physiological condition of the tuber; at an advanced maturity stage, the available starch decreases due to hydrolysis processes; a wide range of yields has been reported, for sweet starch extracted from different native potato varieties between 9.63 – 14.99% [22], the starch yield of two native potato varieties 14.51% and 13.32% [14]; [17] reported lower yields in starch extraction for three Colombian potato varieties: 7.5; 9.3 and 10.2% for Criolla potato (*S. phureja*), Pastusa and Sabanera (*S. tuberosum*), respectively. [23] and [24] extracted starch from native potatoes in other regions of the world reporting yields between 12.0 – 12.7% and 12.95 – 16.30%, respectively. The yield of the extracted starch may exceed 50% of the dry matter of the tuber, therefore, native potatoes may be an important source for obtaining this biopolymer, which could be used as raw material in the production of biodegradable materials.

Table 1. Extraction yield (%), moisture content (%), amylose content (%) and granule diameters (μm) of starches extracted from different potato varieties*. Source: own elaboration.

Physical properties	Type of Starch		
	DCS	RRS	CQS
Yield (M.B) (%) (n=3)	10.21 ± 0.80 ^{a}	11.84 ± 1.78 ^{a}	11.65 ± 0.59 ^{a}
Moisture content (%) (n=9)	11.12 ± 0.79 ^{a}	11.76 ± 0.92 ^{a}	11.80 ± 0.89 ^{a}
Amylose content (%) (n=10)	33.09 ± 2.45 ^{b}	33.01 ± 1.13 ^{b}	31.25 ± 0.32 ^{a}
Average diameter of the major axis (μm) (n=250)	25.03 ± 15.51 ^{b}	22.63 ± 16.68 ^{b}	16.95 ± 15.88 ^{a}
Average diameter of the minor axis (μm) (n=250)	19.18 ± 9.70 ^{c}	16.70 ± 10.09 ^{b}	12.53 ± 10.00 ^{a}

*Data (mean ± SD) in the same row with different superscript letters indicates significant differences (P ≤ 0.05).

The moisture content of starch is important because it determines its storage stability, at higher moisture content starch is susceptible to microbial attack and loss of its properties. Some authors report a wide moisture range for starch obtained from Andean potato varieties (subsp. *Phureja*): between 14.15 – 15.62% [4], between 9.20 – 10.20% (subsp. *Andigena*) [25], between 10.20 – 15.79% (subsp. *Andigena*) [26], and moisture contents of 12.54 – 14.36% (subsp. *Andigena*) [14], lower starch moisture contents than those obtained between 7.95% and 9.35% for Colombian potato varieties [17]. The results obtained are within these ranges, with no differences among the varieties studied and are relatively low, which guarantees their microbiological and functional stability.

DCS and RRS have higher amylose content than CQS, possibly because larger granule size is associated with a higher amount of amylose [22], [27]. Lower amylose contents have been reported in some native potato varieties: 24.34 - 29.11% [4]; 16.10 - 23.47% [28]; 24.9 – 30.0% [25]; 21.58 – 26.50% [16]; 27.77 – 30.33% [22]. Meanwhile, other studies indicate amylose contents higher than those obtained, [26] reported values between 23.40 - 35.50%, [24] reported contents between 29.91 – 36.66% in Chinese native potatoes, [5] mentioned an amylose content of 33.90% for the Andina potato variety and 35.50% for the Ratona Blanca potato variety, [14] reported amylose contents of 42.09% and 43.56% in native potato starches, [15] reported amylose values for native potatoes between 36.29% and 43.96%. On the other hand, the potato starches obtained present higher amylose content than other starch sources: up to 30.73% in cassava [29], in rice between 19.73% and 21.53% [30] and in maize between 21.5% and 22.4% [5], [31].

Variations in amylose content may be due to several factors, cultivation conditions and harvest times, crop altitude (Andean zone), soil organic matter content, as well as factors associated with the genetics of each variety, amylose synthesis conditions and the physiological state of the plant. It is important to know the amylose-amylopectin content and ratio in starch to select a plant material that allows obtaining a biopolymer with functional characteristics for the production of biodegradable packaging, the amount of amylose determines the functional properties of starch and its capacity to generate a bioplastic material in combination with other ingredients. Amylose content provides mechanical strength in films, however, it makes starch more prone to retrogradation and susceptible to contact with water [8], [32]-[34], an important disadvantage to consider in packaging materials however, the amylopectin fraction also influences the properties of starch-based films because this branched structure provides elongation to the materials and greater water resistance [33], [32], as a limitation for this study the methodology used only the amylose standard.

3.2 Granule size and shape

In the results presented in Table 1, it is observed that the granule size of DCS and RRS are comparable, unlike the CQS granule which is relatively smaller (see Table 1). The microphotographs (Figure 1) show the shapes of the potato starch granules of the varieties DCS (a.), RRS (b.) and CQS (c.), a heterogeneous distribution in granule size is observed, generally with uniform smooth surfaces with very few protuberances and absence of pores, this type of surface reduces water absorption [11] most of the granules showed spherical or ellipsoidal shapes (See Figure 1).

Potato starch has a wide granule size distribution depending on the variety, but also on the previous conditioning processes; diameters between 12 µm to 72 µm have been reported for starch granules isolated from native potatoes from Peru [26], between 1 µm to 84 µm for native potatoes from southern Colombia [5], between 15 µm to 110 µm for native potatoes in China [27] and in potatoes from Indonesia average granule sizes between 32.98 µm and 35.04 µm have been reported [35]. The diameter of the varieties studied, compared with other authors, is relatively small, between 12 µm and 25 µm; these data are close to those reported by [15] in Peruvian native potatoes between 12 µm and 20 µm.

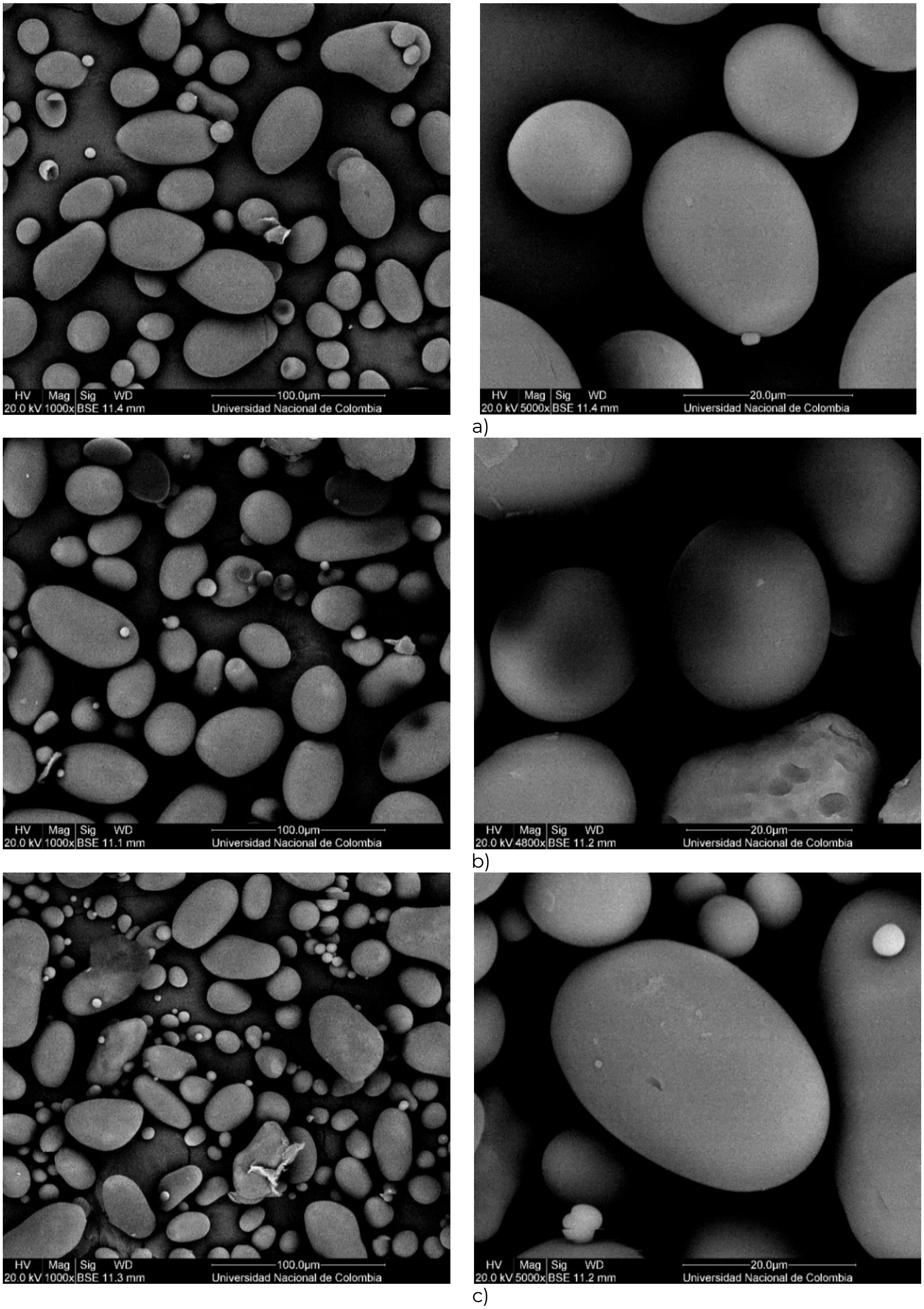

Figure 1. Micrographs of starch granules from different potato varieties at x1000 and x5000. a) DCS, b) RRS and c) CQS. Source: own elaboration.

The granule size of the native potato starches was relatively small due to the sieving processes, the main disadvantage of obtaining a small granule size lies in the energy requirements for its disintegration, since a smaller size indicates greater thermal stability [36], [37], the peak gelatinization temperatures Tp were relatively high for these starches, however, the pasting temperatures PT remained low, granule size also affects viscosity because size determines starch hydration and swelling during the hydrothermal process, however it depends on the concentration and crystalline structure of the granule [31], [38] The size and shape of the granule determine the starch processing conditions, the amount of energy required for complete gelatinization, the viscosity during mixing, its subsequent gelation, which are relevant in the molding and drying process, in general granule size affects the film production process by the solvent evaporation method or “Casting”.

3.3 Pasting properties

The analysis of the starches from the three potato varieties is presented in Figure 2. The PT was 63.9 °C; 64.5 °C and 66.6 °C for the DCS, CQS and RRS varieties, respectively. PT may vary depending on other components in the starch, according to [5] in native potatoes there is an inverse correlation between amylose content and PT, however, in this study this correlation was not observed possibly due to other compounds present in the starch such as phosphorus and protein content, and due to granule size; variations in granule size directly influence water absorption and viscosity development [35], the low pasting temperatures of the starches indicate that less energy is required in hydrothermal processing to begin granule hydration.

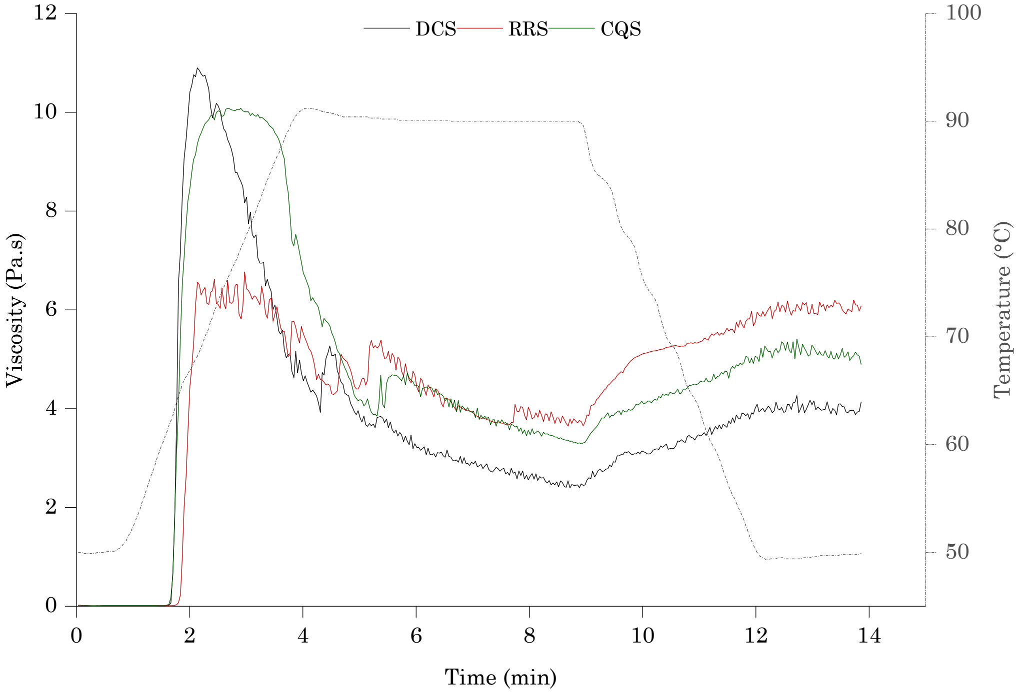

Figure 2. Pasting profile of DCS, RRS and CQS starches. Source: own elaboration.

A higher amylose content tends to generate a lower MV, since amylose tends to interact with lipids forming complexes that reduce granule swelling [11], [28], the presence of other compounds in the starch can affect the amylographic behavior, this could explain the high PT and low MV for RRS starch. High viscosities may be related to small granule sizes, since, due to their greater surface area with respect to volume they have greater swelling power [11], however, other authors differ from this interpretation, indicating a directly proportional relationship between granule size and viscosity [31], [38]; that is, other parameters such as composition, crystalline structure, porosity and measurement conditions affect viscosity. The low viscosity of RRS may be associated more with amylose content than with granule size and in the case of CQS the small granule size would explain its high viscosity. In native potato starches, MV values of 8.71 Pa.s (Andina Var.) and 6.15 Pa.s (Ratona Blanca Var.) have been reported [5]; 4.0 Pa.s (Amarilla Reyna Var.) and 12.0 Pa.s (Azul Helada Var.) [14] and other authors report higher viscosities between 14.58 – 19.45 Pa.s [15].

The RV was 8.46 Pa.s; 6.78 Pa.s and 3.05 Pa.s for DCS, CQS and RRS, respectively. The SV was 0.68; 5.19 and 6.96 for the RRS, CQS and DCS varieties. According to [5] RV represents the stability of the granules against shear and temperature, higher values of this parameter indicate lower stability; whereas SV is related to the ability of starch to generate retrogradation. Thus, DCS starch has lower processing stability and, on the other hand, greater retrogradation, this can be considered an advantage since starch may require lower energy consumption for its transformation (lower PT and Tp values) and form a material with differential rheological properties.

The FV was higher for RRS (6.08 Pa.s), followed by CQS (4.89 Pa.s) and the lowest was for DCS (3.94 Pa.s); FV refers to the capacity of starch to form viscous pastes, a positive correlation between amylose content and FV has been reported [5], this is evidenced in Ratona Roja potato starch, this biopolymer can form a more viscous film-forming solution that can affect the mechanical properties of the films. The FV results reported by other authors coincide with those obtained in this study, for native varieties FV of 5 Pa.s was found [14], and between 5.91 Pa.s and 4.57 Pa.s [15]. It is relevant to know the pasting behavior of starches used as bioplastic material, since it was observed that the viscosity of the film-forming solution is important both at the time of preparation, and at the time of molding and drying the film, a very high final viscosity does not allow adequate molding of the sheet, while a very low final viscosity does not allow adequate film formation, viscosity can also affect the water evaporation process during drying, a higher viscosity implies greater cohesion of the molecules that limit solvent evaporation, by having wetter films there is greater susceptibility to contact with water and this is considered a disadvantage for its application as food packaging material.

3.4 Functional properties

Table 2 presents the results of the functional properties Water Absorption Index (WAI), Water Solubility Index (WSI) and Swelling Power (SP) of two native potato varieties: RRS and CQS and the commercial variety DCS at different evaluation temperatures 60, 70, 80, 90 °C (see Table 2).

WAI and SP are characteristics that indicate the capacity of the starch granule to hydrate and incorporate water into its molecular structure, while WSI indicates the fraction of starch soluble in water; these properties are directly related to its structure, size and composition. The results indicate that these functional properties tend to increase proportionally with temperature, for any potato starch variety. This behavior coincides with that reported in other studies [4] and [16].

The crystalline structure of starch granules is altered when they are hydrated and subjected to high temperatures, water molecules form bonds with the exposed hydroxyl groups of amylose and the side chains of amylopectin, the increase in temperature weakens the internal associative forces that maintain the granular structure of native starches, facilitating hydration and swelling, thus the capacity of starch granules to retain water is influenced by amylose content, at lower amylose content a higher swelling power is exhibited [11], [32], [38]. RRS starch differs statistically from DCS and CQS starches, being the one that presents the lowest WAI and SP at all evaluated temperatures, this behavior may be due to its high amylose content.

Regarding water solubility, higher WSI is observed in RRS starch at 90°C, below this temperature CQS and DCS starches tend to be more soluble.

Table 2. Water Absorption Index (WAI), Water Solubility Index (WSI) and Swelling Power (SP) of different starches from potato varieties*. Source: own elaboration.

Functional properties	Evaluation temperature	Type of starch		
		DCS	RRS	CQS
WAI (g of water/g of starch)	60	10.46 ± 0.83 ^{b}	8.83 ± 0.26 ^{a}	11.21 ± 0.81 ^{c}
	70	14.29 ± 0.65 ^{c}	11.63 ± 0.25 ^{a}	13.51 ± 0.81 ^{b}
	80	15.50 ± 0.33 ^{c}	12.70 ± 0.44 ^{a}	14.82 ±0.67 ^{b}
	90	16.64 ± 0.96 ^{b}	15.48 ± 0.40 ^{a}	16.66 ± 1.12 ^{b}
WSI (g of soluble starch/g of starch - %)	60	0.68 ± 0.05 ^{b}	0.22 ± 0.03 ^{a}	0.66 ± 0.07 ^{b}
	70	1.19 ± 0.10 ^{b}	0.59 ± 0.07 ^{a}	1.09 ± 0.13 ^{b}
	80	1.65 ± 0.23 ^{b}	1.23 ± 0.17 ^{a}	1.40 ± 0.13 ^{a}
	90	1.62 ± 0.20 ^{b}	2.42 ± 0.24 ^{c}	1.42 ± 0.09 ^{a}
SP (g of gel/g of hydrated starch)	60	10.78 ± 1.00 ^{b}	8.69 ± 0.35 ^{a}	11.28 ± 0.80 ^{b}
	70	14.46 ± 0.34 ^{c}	11.59 ± 0.48 ^{a}	13.64 ± 0.79 ^{b}
	80	16.07 ± 0.35 ^{c}	12.85 ± 0.46 ^{a}	15.17 ± 0.59 ^{b}
	90	16.93 ± 0.96 ^{b}	15.85 ± 0.43 ^{a}	16.89 ± 1.17 ^{b}

*Data (mean ± SD) in the same row with different superscript letters indicate significant differences ($P \leq 0.05$). n=9.

Granule size can also influence the swelling power of starches. Small granule sizes tend to have a greater surface area and therefore faster and greater hydration [11], [27], [37], this trend could explain the behavior of WAI and SP for CQS potato starch. Unlike native potato starches, DCS starch does not have a clear trend that explains its high WAI and SP values, however, it is possible that it contains considerable amounts of other compounds; the presence of lipids, proteins and phosphorus in the starch granule has a significant effect on the physicochemical and functional properties of starch [39] in this way the presence of other compounds in starches can affect their water absorption capacity.

The results of the functional properties are within the ranges reported by other authors: [16], found between 55°C and 95°C, solubilities between 1 - 8% and SP between 4 - 25 g/g for different varieties of Andean native potatoes (Peru). On the other hand, some authors report considerably higher values, [24] reported for starches from some varieties of Chinese native potatoes, solubility between 7.5 - 13.5% and SP between 30 - 50 g/g evaluated at 90°C. In Peruvian native potato starches (subsp. Andigena) the technofunctional indices were evaluated between 50 °C and 90 °C, their results indicated an increase in WAI from 3.13 to 32.20 for the Azul Helada (AH) variety and from 3.4 to 49.56 for the Amarilla Reyna (AR) variety. SP increased from 3.96 to 46.6 and from 4.49 to 64.2 for the AH and AR varieties, respectively. Water solubility for the two native potato varieties was higher than 20% [14]. In other native potato varieties, solubility ranges between 3.48% and 7.39%, water absorption power between 11.14 (g/g) and 45.27 (g/g) and swelling power between 11.55 (g/g) and 47.45 (g/g), in the ranges between 60 °C and 80 °C [15], in potatoes from different altitudes swelling power of 18.53 and 19.11 (mL/g) and solubility of 2.59% and 3.03% were reported [35]; the differences in functional indices may be due to the methodology applied.

The functional indices are closely related to the amylographic behavior obtained for the potato varieties, in the production of starch-based sheets it is important to have low solubility indices, while at the same time an intermediate water absorption and swelling capacity that allow amylose release during gelatinization and water release during drying.

3.5 Thermal properties

In the thermogravimetric analysis shown in Figure 3, two degradation stages are observed for the three starches evaluated, the first corresponds to water evaporation and the second to depolymerization. Water evaporation was 14.19% (139.76 °C); 13.08% (111.27 °C) and 9.96% (131.44 °C) for RRS, DCS and CQS, respectively. Depolymerization was 64.13% (319.41 °C), 65.84% (322.01 °C) and 67.58% (331.45 °C) for DCS, RRS and CQS, respectively. The residual mass was 22.79; 22.47 and 19.97% for DCS, CQS, RRS starch, respectively.

The differential scanning calorimetry analysis shown in Figure 3, corresponds to an endothermic process, that is, heat energy is required for gelatinization, it is observed that Tp was 80.44; 81.68 and 91.87 °C for DCS, RRS and CQS, respectively. Tp indicates the maximum temperature at which the polysaccharide gelatinizes and the amylose content is completely released from the starch granule into the aqueous medium, this can generate interactions with other compounds, such as lipids and proteins favorable to film formation. [11] indicated that there is a direct relationship between amylose content and peak gelatinization temperature, who explained that this is because the double helices formed by amylose molecules are more stable and require more energy to be disorganized during gelatinization.

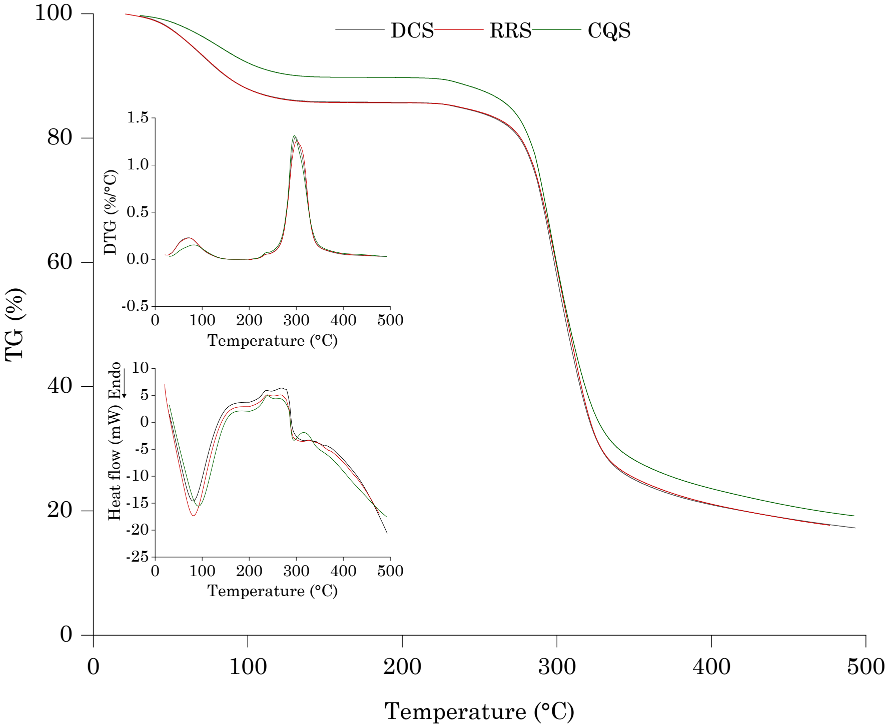

Figure 3. Thermogravimetry and differential scanning calorimetry analysis of starches from different potato varieties DCS, RRS, CQS. Source: own elaboration.

Higher Tp indicated greater thermal stability [27], [14], a smaller granule size confers a higher Tp [36], [37]. CQS starch is the one with the greatest thermal stability due to its small granule size and lower amylose content. Thermal properties influence the film manufacturing process and therefore can have an impact on the mechanical properties of the films. The aim is to reduce the energy cost in material production, for this reason low gelatinization temperatures Tp would be more convenient, DCS and RRS starches require less energy to be processed. Some authors report lower peak gelatinization temperatures in potato starches than those reported, between 57°C and 62°C [22] between 54.9 and 59.7°C [15], between 61.8 and 66.4 [14] and between 69.3 and 74.7 [35].

In the DTG curve shown in Figure 6, it is observed that Tmax was 295.64 °C; 298.15 °C and 301.71 °C for CQS, DCS and RRS starch, respectively; these results indicate that the polymers are possibly resistant to thermal processes such as extrusion for manufacturing packaging at industrial scale.

3.6 Mechanical properties of films based on native and commercial potato starches

The results of the mechanical evaluation of films made from RRS and CQS as native varieties and DCS as a commercial variety are presented in Table 3. The films did not show any variation in moisture content (M.B) between 10.80 ± 0.76; 10.72 ± 0.79 and 10.82 ± 0.83% (n = 9, P-value = 0.964) for DCS, RRS and CQS varieties, respectively.

Table 3. Total elongation at break (%), tensile strength (MPa), Young's modulus (MPa)*, and thickness (mm) of films based on potato starches from different varieties. Source: own elaboration.

Mechanical properties	Starch film		
	DCS	RRS	CQS
Total elongation at break (%)	2.16 ± 0.32 ^{a}	3.65 ± 0.54 ^{b}	2.16 ± 0.13 ^{a}
Tensile strength (MPa)	2.29 ± 0.42 ^{c}	2.02 ± 0.25 ^{b}	1.61 ± 0.26 ^{a}
Young's modulus (MPa)	190.66 ± 35.21 ^{b}	200.26 ± 39.68 ^{c}	158.43 ± 21.07 ^{a}
Thickness (mm)	0.61 ± 0.13 ^{a}	0.63 ± 0.17 ^{a}	0.77 ± 0.11 ^{b}

*Data (mean ± SD) in the same row with different superscript letters indicates significant differences ($P \leq 0.05$). n=15.

Films produced with RRS starch presented greater elongation (%) and Young’s modulus (MPa), with statistically significant differences compared with films produced with CQS and DCS starch. The highest tensile strength (MPa) was obtained by films produced with DCS starch.

The film-forming capacity of starches is directly related to amylose and amylopectin content. The composition of these components can influence the properties of starch-based films, films with higher amylose content usually have better mechanical strength characteristics [33], [34]. The molecular weight of amylose and amylopectin also plays an important role in determining the strength and elongation of the film; linear amylose chains have a greater capacity to establish hydrogen bonds between linear segments, in contrast, the highly branched structure of amylopectin limits the formation of a cohesive and resistant network, resulting in a more fragile and brittle material. [8], higher amylose content generates large crystalline domains, these crystalline domains are dispersed and could function as reinforcement to modify the amorphous structure of the matrix, thus improving the mechanical properties of the film [20], amylopectin chains also play an important role in the mechanical properties of films, since they reduce their water solubility and generate greater elongation, due to their branched distribution [33], [32].

Amylose-rich starches are characterized by their high gelling capacity [34], , which allows their molding as sheets and their structuring as packaging materials; in addition to amylose content, other starch characteristics can be indicators for obtaining desired mechanical properties, larger particle size and low swelling power generate greater mechanical strength [16], larger granule size generates films with greater thickness [20] and therefore the mechanical properties are affected, since the larger the film area, the lower the tensile strength.

Other authors have produced films with starches from different sources comparing their mechanical strength: [20] reported for potato starch films (20.5% amylose and thickness of 0.183 mm) tensile strength values higher than 6 MPa, Young’s modulus higher than 150 MPa and elongation at break percentage higher than 80%, these values were better than those for cereal starch films. Films produced with potato starch (*S. tuberosum* L.) with a thickness of 0.3 mm have better mechanical properties than other Andean tubers, the tensile strength was 21.6 MPa, Young's modulus of 1305 MPa, while elongation at break is close to 50%, the properties of these films depend on their chemical composition [12]. [16] produced very thin native potato starch-based films (thicknesses between 0.066 – 0.083 mm) and found that the mechanical properties are located within a wide range, tensile strength is between 2.38 MPa to 13.27 MPa, elongation at break between 2.43% to 23.49% and Young's modulus between 115.9 MPa to 1292.1 MPa. Films produced with Colombian potato starch present tensile strengths between 1.9 MPa and 2.4 MPa and elastic moduli between 11.8 MPa and 16.2 MPa [17]; differences in mechanical properties can be explained by moisture conditions, dimensions and the speed and stress parameters used in tensile tests.

The mechanical results indicate that films produced with RRS and DCS starches, which contain a higher percentage of amylose, have better mechanical behavior. The low swelling power and low maximum viscosity of RRS starch may influence the production of films with higher elastic modulus. The smaller granule size in CQS starch generated greater thickness that reduces tensile strength and therefore Young's modulus. In general, potato starch can be used for the production of bioplastics with similar or improved mechanical properties compared with other starch sources [40] however this depends both on the properties of the starch and on the type of processing used for its manufacture.

4. CONCLUSIONS

The characteristics of native potato starches RRS and CQS and commercial potato starch DCS presented different characteristics that may affect the production of biodegradable films. The pasting profile, functional properties and thermal properties may be related to amylose content and granule size. DCS and RRS potato starches presented statistically higher amylose content and granule size, compared with CQS potato starch, a smaller granule size provides greater thermal stability. RRS starch had low Water Absorption Index (WAI) and Swelling Power (SP), that is, the hydration and swelling capacity of the granule is reduced during the gelatinization process, in addition this starch presents a high Water Solubility Index (WSI) especially at 90°C. The low maximum viscosity MV of RRS starch may be due to the high amylose content, the final viscosity FV of RRS potato starch may alter drying and allow obtaining mechanically more resistant sheets. The mechanical properties of films produced with RRS potato starch presented greater elongation at maximum force (%) and Young's modulus (MPa), this starch may be an alternative biopolymer for the production of biodegradable materials that are resistant with adequate flexibility as food packaging material, however its functionality is conditioned by the resistance capacity to contact with water and permeability to water vapor and other gases, for which we suggest starch modification or the addition of compounds that increase the hydrophobicity of the biopolymer.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

AUTHORSHIP CONTRIBUTION

David Fernando López Enríquez: Conceptualization, Design, Research development, Writing, and Final revision of the manuscript.

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Oswaldo Osorio: Conceptualization, Design, and Final revision of the manuscript.

Alfredo Ayala: Conceptualization, Design, and Final revision of the manuscript.