



PHYSICOCHEMICAL, THERMAL AND RHEOLOGICAL PROPERTIES OF NATIVE STARCHES AND ACETYLATED DISTARCH ADIPATES FROM MAIZE AND CASSAVA

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ABSTRACT – The present work aimed to compare commercial native starches and acetylated distarch adipates according to their physicochemical, thermal, paste, textural and rheological properties. Native maize starch presented the highest value (59.9 °C) of onset temperature gelatinization (T_o), and modified cassava starch the lowest (53.1 %). Starches aqueous suspensions were submitted to conventional heating and their resulting gels were evaluated regarding their physical stability (stability to freeze-thaw cycles), paste, textural and rheological properties (steady state). Concerning physical stability, native maize starch gels showed the lowest syneresis. It also showed the lowest values of peak paste viscosity (μ_{max}), breakdown and setback that can be related to the gel stability. Regarding rheology data, the Power Law model had fitted all the samples. All the samples showed no time dependence, excepted for modified cassava starch, which showed rheopectic behavior.

KEYWORDS: starch, gel, texture, viscosity, stability.

1. INTRODUCTION

Starch is the most abundant storage reserve carbohydrate in plants. It is mostly compound by two macromolecules: amylose and amylopectin. Amylose is essentially linear, whereas amylopectin has a branched structure with 5 – 6 % α -(1,6) linkages. Starches can be employed in many applications in the food industry, as a thickener and gelling agents in a wide range of foods, such as yogurt preparations and ready-made desserts. However, native starches are hardly used, since they have a low water retention capacity, shear resistance, and thermal resistance, making the formulations more prone to phase separation (Singh, Kaur, & McCarthy, 2007). Starch modifications by physical, enzymatic, chemical or combined methods are used to improve the granule's structure. The chemical modification involves the introduction of functional groups into the starch molecule, resulting in markedly altered physicochemical properties (Damodaran, Parkin, & Fennema, 2010).

Cross-linking treatment is intended to add intra and inter-molecular bonds at a random location in the starch granule to enable the starch to resist process conditions, as low pH, high shear, and high temperatures (Vaclavik & Christian, 2008). Another modification is the stabilization, which starch acetates are obtained. They are commonly produced with acetic acid and acetic anhydride as starch esterification reagents. In this reaction part of hydroxyl groups on anhydrous-glucose units is substituted with acetyl groups and, consequently, esters are formed (Ackar et al., 2015). Stabilized starches are not appropriate for foods that require prolonged heating. However, starches may be modified by a combination of both crosslinking and stabilization treatments. These starches generally have lowered gelatinization and pasting temperatures, producing pastes with greater viscosity (Damodaran et al., 2010).

Nowadays, to the best of our knowledge, there are few reports comparing properties of native starches and acetylated distarch adipates. Mali & Grossmann (2001) evaluated acetylated, cross-linked and pre-gelatinized cassava starches produced in a single-screw extruder. They found that acetylation, cross-linking and pre-gelatinization steps increased the cold viscosity, water absorption index and gel hardness, and reduced the gel cohesiveness, paste clarity and retrogradation comparing to their native starches. So, the main objective of the present study was to compare commercial native and acetylated distarch adipates from maize and cassava according to their physicochemical, thermal, paste, textural and rheological properties.

2. MATERIAL AND METHODS

2.1 Material

Native maize (29 wt % of amylose, and 13.5 wt % of moisture) and native cassava (25.8 wt % of amylose, and 9.2 wt % of moisture) starches were provided by Delaware (RS, Brazil) and Fritz & Frida (RS, Brazil), respectively. A Brazilian company (PR, Brazil) provided modified starches from maize (29.3 wt % of amylose, and 10.9 wt % of moisture) and cassava (25.3 wt % of amylose, and 14.7 wt % of moisture, combination of cross-linking and stabilization treatments). According to the company, the starches were modified by reacting adipic acid with anhydride at alkaline pH, resulting in acetylated distarch adipates.

2.2. Thermal properties

The starch grains were thermally characterized by Differential Scanning Calorimetry (DSC 6000, Perkin Elmer, US) following the methodology proposed by Beninca et al. (2013). A mixture of 4:1 (water:starch, w/w) was prepared inside aluminum pans, and then sealed. Suspensions were left overnight to equilibrate the moisture content. The samples were heated from 25 to 100 °C at 10 °C·min⁻¹. Gelatinization enthalpy (ΔH_{gel}), onset (T_o), peak (T_p) and final (T_f) gelatinization temperatures were determined using Origin 6.0 software (Microcal, Malvern, UK), on a dry basis.

2.3. Pasting and textural properties

A Rapid Viscosity Analyzer (RVA, RVA-3D model, Newport Scientific, Australia) was used to determine the pasting properties according to the AACC International method (2010). A sample of 3 g and 25 ± 0.1 mL of distilled water (corrected for 14% of moisture) were placed in aluminum containers. The mixture was heated to 50°C and held at this temperature for 2 min, then it was heated to 95°C and held for 5 minutes. The objective of this method is to obtain a complete paste curve, including pasting temperature (T_{pasta}) (°C), maximum viscosity (μ_{max}) (cP), minimum viscosity (μ_{min}) (cP), breakdown (cP) (difference between μ_{max} and paste viscosity hold at 95 °C for 5 minutes), final viscosity (μ_f) (cP) and setback (cP) (difference between μ_f and paste viscosity hold at 50 °C for 2 min). The texture of the starch gels (12%, w/w; obtained in the RVA analysis) was analyzed in a Texturometer (TA.XT.plus, Stable Micro Systems, England), with cylindrical probe of aluminum P/20R (\varnothing = 40 mm), pre-test velocity = 1.0 mm.s⁻¹; test speed = 1.7 mm.s⁻¹; post-test velocity = 10.0 mm.s⁻¹ and compression force of 40%. The test follows the AACI Method 74-09.01 (2010), adapted for gel texture.

2.4. Physical stability

Gelatinization was performed by heating a starch solution at 5 % (w/w) under mechanical agitation (Fisatom, São Paulo, Brazil) in a jacketed beaker connected to a thermostatic bath (Lauda T, Germany) with water at 90 °C. After that, the solution was kept at 90 °C for 10 min to ensure sample uniformity. The stability of the starch gel to freezing and thawing cycles was performed as the method proposed by White et al. (1989). 20 g of starch gel (W_0) were subjected to 4 cycles of freezing (-20 °C) and thawing (30 °C) for 24 h and 1.5 h, respectively. In the end, the sample was centrifuged (6000 g, 30 min, 25 °C) and the supernatant weighed (SE). The percentage of the syneresis was expressed as a percentage of exudate water in relation to the initial mass. All tests were done in triplicate.

2.5. Steady rheological measurements

Gels were analyzed according to their rheological properties after 24h. Rheological measurements were carried out in a rotational rheometer (Ares, TA Instruments, New Castle, US), using cone-plate geometry (50 mm

in diameter, 0.391 radians, and GAP of 0.0533 mm). Vaseline oil was applied to cover the exposed gel surfaces to avoid sample drying during the analysis. All measurements were performed in triplicate at 25 ± 1 °C. Flow curves were determined by recording shear stress values when shearing the starch gels at increasing shear rates from 1 to 100 s^{-1} . The data were fitted to the rheological models of Ostwald-de-Waele (Power law, Eq.1) and Herschel-Bulkley (Eq.2).

$$\tau = K \cdot \dot{\gamma}^n \quad (1)$$

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \quad (2)$$

where τ represents the shear stress (Pa), $\dot{\gamma}$ the shear rate (s^{-1}), K the consistency index (Pa.s), n the flow index (dimensionless), and τ_0 the minimum shear stress (Pa) of the Herschel-Bulkley model.

2.6. Statistical analysis

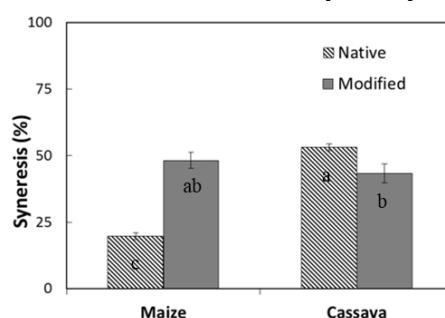
The results were analyzed statistically using Statistica 10.0 software (StatSoft, Tulsa, USA). One-way analysis of variance (ANOVA) and Tukey test were applied to establish significant differences. The rheological model's parameter estimation was accomplished by the least-square method.

3. RESULTS AND DISCUSSION

Gels physical stability are presented in Figure 1. Native maize starch gel showed the highest resistance to freeze/thawing (20 % of syneresis). The higher syneresis showed by cassava gels in the freeze-thaw cycles can be related to the amylopectin retrogradation that is slower than amylose. It is known that amylose is responsible for short-term retrogradation rate, although amylopectin systems proceed slowly over several weeks of storage and contribute to the long term retrogradation behavior (Eliasson, 2004). The retrogradation kinetics for amylopectin, under thermal stress, with high proportions of long chains were also accelerated as reported by other authors who had studied amylopectin kinetics (Lai, Lu, & Lii, 2000).

Syneresis in freeze/thawed gels is due to the increased molecular association between starch chains at reduced temperature excluding water from the gel structure. It was expected that modified starches reduce the potential for increased interchain bonding by limiting the movement of the chains. However, modified starches did not differ significantly from the native cassava starch gel. As commented before, depending on the botanical origin, starches the same source can present different chain length distribution and molecular size of branched molecules (Eliasson, 2004).

Figure 1 – Stability to the freezing and thawing cycles of native and modified starch gels from maize and cassava. Equal letters in the bars do not differ from each other by Tukey test at 5 % level of significance.



Thermal properties of the native and modified starches from maize and cassava are shown in Table 1. Based on the values of T_0 , native and modified maize starches need more energy to begin the gelatinization process. Beninca et al. (2013) and Li and Zhu (2018) found higher gelatinization range for native cassava starch (63.97 °C - 77.57 °C) and native maize starch (68.3 °C - 78.3 °C), respectively. Different temperature ranges can be related to sample composition, which includes granule size, amylose content, proportion, and kind of crystalline organization, the structure of starch granules, geographic origin and culture conditions (Gao et al., 2014). Singh et al. (2007) compared native and acetylated starch properties and detected a reduction in the gelatinization

temperature range for potato (57 - 66 °C → 48 - 67 °C), and maize (59 - 70 °C → 55 - 64 °C) starch, respectively. For Kapelko-Zeberska, Zieba, Szychaj, & Grysztyn (2015), acetylated potato starches also undergo phase transitions at lower temperatures than their native starches.

Table 1 – Thermal properties of the native and modified starches from maize and cassava.

Sample	ΔH_{gel} (J/g)	T_o (°C)	T_p (°C)	T_f (°C)
Native Maize	7.0 ± 0.9 ^{a*}	59.9 ± 1.3 ^a	65.9 ± 0.5 ^a	72.1 ± 0.4 ^a
Native Cassava	9.9 ± 1.8 ^a	56.9 ± 0.2 ^b	64.5 ± 0.7 ^a	72.3 ± 2.4 ^a
Modified Maize	10.5 ± 3.3 ^a	58.0 ± 0.9 ^a	65.6 ± 0.5 ^a	72.1 ± 0.7 ^a
Modified Cassava	9.9 ± 1.9 ^a	53.1 ± 0.2 ^c	60.1 ± 0.1 ^b	68.6 ± 0.4 ^b

* Equal letters in the column do not differ from each other by the Tukey test at 5% level of significance.

Table 2 presents the viscoamylographic data (pasting temperature (T_{paste}), peak viscosity (μ_{max}), breakdown, final viscosity (μ_f), setback, and peak time) obtained for each starch.

Table 2 – Pasting properties of native and modified starches from maize and cassava

Sample	T_{paste} (°C)	μ_{max} (cP)	Breakdown (cP)	μ_f (cP)	Setback (cP)
Native Maize	69.80 ± 0.44 ^{b*}	2257.67 ± 10.41 ^d	547.33 ± 10.50 ^d	2382.00 ± 12.29 ^c	671.67 ± 6.51 ^c
Native Cassava	66.20 ± 0.48 ^c	3520.67 ± 104.04 ^b	2197.33 ± 53.20 ^a	1980.67 ± 41.49 ^d	657.33 ± 31.50 ^c
Modified Maize	75.65 ± 0.97 ^a	3196.33 ± 35.73 ^c	632.67 ± 31.50 ^c	3777.67 ± 89.67 ^b	1214.00 ± 92.24 ^b
Modified Cassava	75.42 ± 0.05 ^a	4745.33 ± 84.88 ^a	1777.33 ± 34.43 ^b	4706.67 ± 113.78 ^a	1738.67 ± 7.23 ^a

* Equal letters in the column do not differ from each other by the Tukey test at 5% level of significance.

Pasting temperature represents the initial increase in viscosity as the granules begin to swell due to the beginning of gelatinization. Cassava starches presented lower T_{paste} than maize starches, indicating lower resistance to intramolecular H₂ bridges dissociation. According to Sandhu & Singh (2007), crosslinked starches have a higher paste temperature due to the additional bonds present in the chains, resulting in a granule more resistant to rupture than the original unmodified starch.

Cassava starches presented higher μ_{max} than maize starches. The paste viscosity is important in the sensory and quality evaluation of starch, and it must be known to designing equipment in food production lines. The peak viscosity that represents the maximum viscosity achieved after the heating was higher for modified starches than for native ones. This result can be associated with the reactions of stabilization and crosslinking, which increases the gel strength when shear forces (agitation) are applied.

The cassava starches presented a breakdown larger than the maize starches, i.e, the cassava granules showed a lower resistance at high temperatures under mechanical agitation. In other words, a larger drop represents a greater gel fragility. The setback is the process where reassociation of the molecules of cross-links occurs forming a network that holds water inside. The native samples showed a lower setback than the modified ones, indicating greater stability to retrogradation. These results can be attributed to the botanical variety (geographic origin and culture conditions) since all samples were commercial. During the cooling phase, the maize starches had their viscosities increased probably to the retrogradation of starch molecules. Differently from the cassava starches that showed final viscosity lower than the peak viscosity.

The differences between the modified starches can be related to the extension of each modification since crosslinked starches are not more tolerant to cold temperatures, different from the stabilized starch that are gelling tolerant in low temperatures. The level of crosslinking varies directly with the concentration of the crosslinking agent, time and temperature. The greater the degree of crosslinking, the smaller the granule volume. As a result, at the same concentration, the highly crosslinked starch shows lower peak viscosity than the lower crosslinked starch (Shah, Mewada, & Mehta, 2016).

Table 3 presents the textural properties (hardness, cohesiveness, and gumminess) of starch gels. Native maize starch gel presented higher values of hardness (898 g) in relation to the other starches. Starches which have higher amylose content and longer amylopectin chains, generally form hard gels (Mua & Jackson, 1997) due to recrystallization (Miles, Morris, Orford, & Ring, 1985). Although the native maize starch has a statistically equal

percentage of amylose to the modified maize starch, the modification by stabilization maintain the amylose chains attached after cooking, i.e., less removal of chains prevents retrogradation, resulting in a lower gel hardness. Besides the gel hardness, the guminess is also related to the starch composition (Sandhu & Singh, 2007). Again, native maize starch showed the highest guminess (368). According to Kälviäinen, Roininen, & Tuorila (2000), guminess is the necessary force to disintegrate the material. Teng, Chin, & Yusof (2013) also found higher guminess values for native maize starch gels (111) compared to the native ones (3,4). The difference was attributed to the higher amylose content of maize sample. The higher the amylose content, the higher the strength required to disintegrate the gel due to the stronger intermolecular interactions between the linear chains. Native cassava starch had the highest cohesiveness (0.7), which is the simulated force to break the gel internal bonds (Kälviäinen et al., 2000). Cohesiveness for a starch gel represents its resistance to the second deformation according to its behavior in the first deformation.

Table 3 – Textural properties of native and modified starch gels from maize and cassava

Sample	Hardness (g)	Cohesiveness	Guminess
Native Maize	898 ± 46 ^a	0.50 ± 0.04 ^c	368 ± 32 ^a
Native Cassava	128 ± 5 ^c	0.70 ± 0.02 ^a	89 ± 1 ^c
Modified Maize	123 ± 3 ^c	0.54 ± 0.02 ^c	66.6 ± 0.8 ^d
Modified Cassava	170 ± 8 ^b	0.62 ± 0.01 ^b	106 ± 4 ^b

* Equal letters in the column do not differ from each other by the Tukey test at 5% level of significance.

Table 4 summarizes the values of estimated parameters for Power Law and Herschel-Bulkley models. The high R² values and low percentages of ϵ demonstrating the good adjustment of the data to both proposed models. All the samples showed shear-thinning behavior.

Table 4 – Steady rheological parameters of native and modified starch gels from maize and cassava

Sample	Power law				Herschel-Bulkley				
	K (Pa.s)	n	R ²	ϵ (%)	τ_0 (Pa)	K (Pa.s)	n	R ²	ϵ (%)
Native Maize	8.8 ± 0.3 ^{a*}	0.19 ± 0.01 ^d	0.97	4.50	1.0 ± 0.9 ^a	7.97 ± 0.87 ^a	0.2 ± 0.0 ^b	0.97	4.43
Modified Maize	0.65 ± 0.02 ^d	0.6 ± 0.0 ^a	0.99	9.21	-0.7 ± 0.1 ^b	0.9 ± 0.1 ^d	0.6 ± 0.0 ^a	0.99	4.77
Native Cassava	2.6 ± 0.1 ^c	0.5 ± 0.0 ^b	0.99	5.38	-0.41 ± 0.39 ^b	2.8 ± 0.2 ^c	0.5 ± 0.0 ^a	0.99	5.15
Modified Cassava	4.3 ± 0.1 ^b	0.5 ± 0.0 ^c	0.99	1.50	1.25 ± 0.25 ^a	3.7 ± 0.1 ^b	0.5 ± 0.0 ^a	0.99	1.01

* Equal letters in the column do not differ from each other by the Tukey test at 5% level of significance

Power law and Herschel-Bulkley models provided a good fit (high value of R² and low value for ϵ) for all samples. Despite this, the τ_0 values were negative or near zero for the Herschel-Bulkley model, which means that this model is not adequate for these gels. Power law behavior has also been reported for several starch gels obtained under different (Kim, Yoo, Park, Shim, & Lee, 2012; Monroy, Rivero, & García, 2018). The consistency (K) and the flow behavior (n) indexes were significantly affected (p < 0.05) by the botanical source and the chemical modification. The values of K and n found for NCS (Table 5) are similar to those reported by Kim et al. (2012) (K = 3.53 and n = 0.53) for 4 % w/w cassava starch obtained from different sources and time/temperature process. Moreover, native and modified starch gels, and native cassava starch gel presented no time dependence. On the other hand, modified starch gel presented rheopetic behavior.

4. CONCLUSIONS

The native and modified starches from maize and cassava present significant differences on onset temperature of gelatinization (T_0), syneresis, paste temperature (T_{pasta}), hardness, guminess and consistency index (K). Cassava starches had higher μ_{max} values than maize starches because of the amylopectin structure, and modified starches had higher viscosities than native starches due to crosslinking modification. The Power law model presented the best fit of the experimental data. Different cultivars had a direct influence on the thermal, functional and rheological properties of the gels



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