

# Chemical and physical modification of corn starch and application in cupuassu

# and babassu dairy dessert

# Modificação química e física de amido de milho e aplicação em sobremesa

# láctea de cupuaçu e babaçu

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Natália Tolfo de Souza ORCID: https://orcid.org/0000-0002-7136-5096 Federal University of Rondônia, Brazil E-mail: nataliatolfos@gmail.com Geovanna Lemos Lima ORCID: https://orcid.org/0000-0002-0108-7078 Federal University of Rondônia, Brazil E-mail: gegeolemos@gmail.com Gabrieli Oliveira-Folador ORCID: https://orcid.org/ 0000-0001-9077-8737 Federal University of Rondônia, Brazil E-mail: gabrieli.oliveira@unir.br Gisele Teixeira de Souza Sora ORCID: https://orcid.org/0000-0001-5043-7620 Federal University of Rondônia, Brazil E-mail: giselesora@unir.br Ladyslene Chrístyns de Paula ORCID: https://orcid.org/ 0000-0001-6265-1237 Federal University of Rondônia, Brazil E-mail: ladyslene.paula@unir.br Luís Fernando Polesi ORCID: https://orcid.org/0000-0001-9513-7373 Federal University of Sergipe, Brazil E-mail: lfpolesi@academico.ufs.br

## Resumo

O amido de milho não é adequado para produtos que necessitam de armazenamento refrigerado, devido à alta sinérese. Para superar esta e outras limitações, podem ser utilizadas modificações químicas e físicas. Considerando a aplicação de frutas amazônicas em sobremesa láctea como forma de agregar valor aos produtos, este trabalho teve como objetivo modificar o amido de milho com tratamentos químicos e físicos, avaliar suas características físico-químicas, aplicar o amido modificado em sobremesa láctea de babaçu e cupuaçu e avaliar suas propriedades físico-químicas e sensoriais. Os amidos foram modificados quimicamente por peróxido de hidrogênio e hipoclorito de sódio a 1, 2 e 3% e fisicamente por HMT com 15, 20 e 25% de umidade e *annealing* à 50, 55 e 60 °C. A modificação pelo peróxido de hidrogênio causou uma diminuição considerável na liberação de água, com sinérese após 7 dias de 0%, por isso esse amido foi utilizado na sobremesa láctea. A análise de sinérese das sobremesas confirmou que a modificação do peróxido de hidrogênio foi capaz de reduzir consideravelmente a sinérese dos produtos lácteos. Os provadores

não sentiram diferença significativa entre as amostras com amido nativo e modificado nos testes sensoriais. A sobremesa mista láctea obteve boa aceitação e intenção de compra.

**Palavras-chave:** Amido de milho. Modificação química. Modificação física. *Theobroma grandiflorum. Attalea speciosa.* 

# Abstract

Corn starch is not suitable for products that require refrigerated storage, due to the high syneresis. To overcome this and other limitations, chemical and physical modifications can be used. Considering the application of Amazonian fruits in a dairy dessert as a way of adding value to the products, this work aimed to modify corn starch with chemical and physical treatments, evaluate its physical-chemical characteristics, apply the modified starch in babassu and cupuassu dairy dessert and evaluate their physical-chemical and sensory properties. The starches were chemically modified by hydrogen peroxide and sodium hypochlorite at 1, 2 and 3% and physically by HMT with 15, 20 and 25% of humidity and annealing at 50, 55 and 60 °C. The modification by hydrogen peroxide caused a considerable decrease in the release of water, with syneresis after 7 days of 0%, so this starch was used in the dairy dessert. The syneresis analysis of the desserts confirmed that the hydrogen peroxide modification was capable of considerably reducing the syneresis of dairy products. The tasters did not feel any significant difference between the samples with native and modified starch in the sensory tests. The mixed dairy dessert received good acceptance and purchase intention.

**Keywords:** Corn starch. Chemical modification. Physical modification. *Theobroma grandiflorum*. *Attalea speciosa*.

## **1. Introduction**

Dairy dessert is a ready-to-eat food with great acceptance by consumers. However, the use of native starch in its formulation can lead to defects during its cold storage, such as high syneresis.

Starch is a polysaccharide energy source for cereals, legumes, roots and tubers and is the main reserve substance in higher plants. Starch is used by industry as a caloric ingredient and as an enhancer of technological properties in food systems due to its low cost. It is used to alter or control various characteristics such as texture, appearance, moisture, consistency and stability in storage (Silva *et al.*, 2008).

The starch granules in contact with cold water show slight expansion (10-20%) due to the diffusion and absorption of water in the amorphous regions, but this expansion is a reversible process with drying. However, when the granules are heated in excess of water, they reach an irreversible point of expansion and lose the structural order due to the melting of the crystals. This process known as gelatinization can be defined as the rupture of the molecular order (breaking of hydrogen bonds) within the granule (Zavareze and Dias, 2011; Zhu and Xie, 2018).

The cooling of gelatinized starch causes the chains to be less energetic and have a strong tendency to re-associate by hydrogen bonds with adjacent molecules, forming a new ordered structure, this process is known as retrogradation. The storage of starch gel in cold temperatures can cause the starch chains to interact strongly with each other and expel water from the system, in a phenomenon known as syneresis (Zavareze and Dias, 2011; Zhu and Xie, 2018).

Native starches have some drawbacks, as some process conditions (temperature, pH, pressure) limit their use in industrial applications, as they have low shear resistance and high retrogradation and syneresis (Sánchez-Rivera *et al.*, 2005). In order to change the characteristics of starch that are not of industrial interest, the modification of starch is used to overcome these deficiencies.

Among the various forms of starch modifications, there are oxidative modifications by hydrogen peroxide and sodium hypochlorite, and physical modifications as heat moisture treatment - HMT (high temperature with low moisture) and annealing, which alter several properties of native starch.

The modification by oxidation is produced by the reaction of the starch with a specific amount of oxidizing reagent at controlled pH and temperature (Wang and Wang, 2003). Heat moisture modification is the treatment of starch at higher temperature and lower moisture level (<35%) while annealing is heating of the starch suspension above the glass transition temperature and below the onset gelatinization temperature with higher moisture level (Sudheesh *et al.*, 2020).

The oxidation of starch promotes molecular depolymerization and induces the formation of carbonyl and caboxyl groups. Oxidized starch has clearer pastes and lower tendency to retrograde (Kaur and Bhullar, 2016; Lima *et al.*, 2021).

Heat-moisture treatment (HMT) and annealing are physical modifications that change the physicochemical properties of starch without destroying its granular structure (Zavareze and Dias, 2011). Starches modified by these techniques have been extensively studied in recent years, however, the results obtained are variable, probably due to the starch source and process conditions (Sudheesh *et al.*, 2020; Wang *et al.*, 2014). HMT can reduce (Goel *et al.*, 2020; Sudheesh *et al.*, 2020) or increase retrogradation (Pepe *et al.*, 2015). Annealing increases retrogradation (Sudheesh *et al.*, 2020; Wang *et al.*, 2014).

In general, starches with greater retrogradation show greater syneresis. Therefore, modifications of starch that reduce retrogradation, may reduce syneresis. Modified starches that have low retrogradation and syneresis can be used in cold dairy desserts.

Cupuassu (*Theobroma grandiflorum*) and babassu (*Attalea speciosa*) are fruits found in the Amazon region and are little used in processed foods. Cupuassu is an acidic fruit, with an exotic and pleasant flavor, rich in volatile compounds, mineral salts, ascorbic acid and phenolic compounds. In addition, the pulp is composed of a large proportion of starch, pectin polysaccharides, and dietary fiber, mainly in the form of insoluble fibers, which improves the texture parameters of dairy products (Pereira *et al.*, 2018; Pompo *et al.*, 2020). Babassu flour is obtained from the fruit mesocarp, contains about 60% starch in addition to phenolic compounds that perform antioxidant activity. This flour is little used in processed foods, being its main destination feed and biomass (Silva *et al.*, 2019).

Thus, this work aimed to modify the native corn starch with chemical and physical treatments and to evaluate its applicability in cupuassu and babassu dairy dessert.

## 2. Materials and methods

Corn starch, babassu flour and cupuassu pulp were obtained from local market. The reagents used were of analytical grade.

### 2.1 Proximate composition of native starch

The moisture, protein, ash and lipid contents were evaluated according to the methodologies of the AOAC (2006). The moisture content was analyzed in an oven at 105 °C. The nitrogen content was determined by the micro Kjeldahl method, with a conversion factor for proteins of 6.25. The ash content was determined after calcination in a muffle at 550 °C. The lipid content was determined in a Soxleth extractor using hexane as solvent. The total carbohydrate content was calculated by difference.

### 2.2 Starch modifications

<u>Modification by hydrogen peroxide</u>: The modification by hydrogen peroxide was carried out according to the methodology described by Sangseethong, Termvejsayanom and Sriroth (2010), with modifications. Forty grams of native starch were weighed and kept in suspension in 60 mL of distilled water. The pH of the suspended starch was adjusted to 10 with 2 M NaOH, immediately afterwards, 0.04 g of copper sulfate was added. The sample was kept under constant agitation and hydrogen peroxide (1%, 2% or 3% based on starch) was added dropwise over a period of 15 min with stirring. During modification process, the pH of the sample was maintained at 10 with the addition of 2 M NaOH or 1 M H<sub>2</sub>SO<sub>4</sub>. After the addition of the oxidizing agent, the sample was kept under stirring in a thermal bath at 40 °C for 60 minutes. Then, the sample was neutralized with 1M

 $H_2SO_4$  to pH 7.0 to stop the modification. The modified starch was filtered under vacuum; suspended in 50 mL of 5% sodium bisulfite solution; vacuum filtered again; washed 4 times with 50 mL of distilled water and passed through 4 new vacuum filtrations. The sample was dried for 12 hours at 40 °C, ground, sieved (0.25 mm) and stored in airtight containers under refrigeration.

<u>Modification by sodium hypochlorite:</u> The modification by sodium hypochlorite was carried out according to the methodology described by Sangseethong, Termvejsayanom and Sriroth (2010), with modifications. Forty grams of native starch were weighed and kept in suspension in 60 mL of distilled water. The pH of the suspended starch was adjusted to 10 with 2M NaOH. In order for the modification to occur, the sample was kept in constant motion and sodium hypochlorite (1%, 2% or 3% based on starch) was added dropwise over a period of 15 min with stirring. During modification process, the pH of the sample was kept at 10 with the addition of 2 M NaOH or 1 M H<sub>2</sub>SO<sub>4</sub>. After the addition of the oxidizing agent, the sample was kept under agitation in a thermal bath at 40 °C for 60 minutes. Then, the sample was neutralized with 1M H<sub>2</sub>SO<sub>4</sub> to pH 7.0 to stop the modification. The modified starch was filtered under vacuum; suspended in 50 mL of 5% sodium bisulfite solution; vacuum filtered again; washed 4 times with 50 mL of distilled water and passed through 4 new vacuum filtrations. The sample was dried for 12 hours at 40 °C, ground, sieved (0.25 mm) and stored in airtight containers under refrigeration.

<u>HMT</u>: The modification by HMT was performed on 40 g of native starch added with distilled water to correct the humidity at 15, 20 and 25%. The samples were homogenized and kept in an airtight flask for 4 days at 4 °C. The samples were taken to an autoclave at 121 °C for 1 h. Then, the modified starch was dried for 12 hours at 40 °C, ground, sieved (0.25 mm) and stored in airtight containers under refrigeration.

<u>Annealing</u>: The modification by annealing method was carried out in 40 g of native starch suspended in 60 mL of distilled water. The samples remained in a thermal bath at 50, 55 or 60 °C with constant stirring for 24 hours. They were vacuum filtered, washed with 50 mL of distilled water, filtered again, dried for 12 hours at 40 °C, ground, sieved (0.25 mm) and stored in airtight containers under refrigeration.

## 2.3 Evaluation of modified and native starches

<u>Apparent amylose content:</u> The apparent amylose content was determined according to the ISO methodology (1987). The starch granules were dispersed with ethanol and gelatinized with sodium hydroxide. An aliquot was acidified and after the reaction with iodine the complex formed of blue color was quantified by spectrophotometry at 620 nm.

<u>Water absorption index (WAI) and water solubility index (WSI)</u>: WAI and WSI were determined according to Anderson *et al.* (1969) with modification. The sample (0.5 g) was mixed with 6 mL water in a centrifuge tube and continuously stirred for 30 min in a water bath at 30 °C. The suspension was centrifuged at  $3000 \times g$  for 10 min. The supernatant was dried at 105 °C for 4 h to obtain the dry solid weight, and the wet sediment was weighed. The indices were determined as:

WAI (g/g) = Weight of wet sediment / (Weight of dry sample – Weight of dry solids in supernatant)

WSI (%) = (Weight of dry solids in supernatant / Weight of dry sample)  $\times$  100.

<u>Syneresis</u>: The syneresis was measured according to Sodhi and Singh (2003), with adaptations. Starch suspension (5%, w/w) was heated in a boiling water bath for 15 min, with constant stirring. The samples were stored for 7 days at 4 °C. Syneresis was measured as % amount of water released after centrifugation at  $3000 \times g$  for 10 min.

<u>Gel transparency:</u> The gel transparency was analyzed according to Gani *et al.* (2012), with adaptations. An aqueous starch suspension (0,1 g/10 g dry weight basis) was prepared by heating in a boiling water bath for 30 min with vortexing every minute for the initial 5 minutes and every 5 minutes until the remaining 30 minutes were completed. The samples were cooled for 1 h at 30 °C and transmittance was measured in a spectrophotometer at 650 nm using distilled water as blank. They were stored for 6 days at 4 °C and transmittance was determined every 24 h as already described.

<u>Swelling factor</u>: The swelling factor was determined according to Tester and Morrison (1990), with adaptations. The starch sample (50 mg) was added into centrifuge tubes (15 mL) with water (5 mL) and heated at 50 °C, 70 °C and 90 °C for 30 min, with constant stirring, in the first 5 minutes the tubes were vortexed to avoid decanting the starch. The tubes were rapidly cooled to room temperature, and 0.5 mL of 0.5 mg/mL blue dextran solution was added. The tubes were gently inverted several times to homogenize the solution. After centrifugation at  $1500 \times g$  for 5 min, the absorbance of the supernatant was measured at 620 nm.

# 2.4 Preparation of dairy dessert

The formulation of the dairy dessert was developed in a previous work (Souza *et al.*, 2021). The dessert formulation of the cupuassu fraction was: 40% water, 40% cupuassu pulp, 8% sugar, 5.6% powdered milk and 6.4% native or modified corn starch (starch with less syneresis). The ingredients were weighed and mixed, with the exception of cupuassu pulp. The homogenized mixture was heated to complete starch gelatinization. With the mixture still hot, the cupuassu pulp was added and homogenized until a smooth, homogeneous texture was obtained, without any fragments of the pulp. The samples were cooled and stored at 4  $^{\circ}$ C.

The dessert formulation of the babassu fraction was: 43% UHT milk, 34.5% condensed milk, 17.3% milk cream, 2.6% cocoa powder and 2.6% babassu flour. The ingredients were weighed and mixed, with the exception of milk cream. The homogenized mixture was heated until the sample viscosity increased (gelatinization of the starch present in the babassu flour). The milk cream was added and homogenized. The samples were cooled and stored at 4 °C.

The desserts were assembled in the proportion 50% babassu and 50% cupuassu for final consumption.

## 2.5 Evaluation of dairy dessert

<u>Syneresis</u>: To evaluate the effect of syneresis (by starch retrogradation or by acid coagulation of milk), four samples were evaluated: two samples with cupuassu pulp (one with native starch and one with modified starch) and two samples without cupuassu pulp (one with native starch and one with modified starch). The syneresis was measured according to Sodhi and Singh (2003), as described for the starch samples. Babassu dessert was not evaluated for syneresis because it was not added starch in its formulation.

<u>Proximate composition</u>: The moisture, protein, ash and lipid contents were evaluated according to the methodologies of the AOAC (2006), and the carbohydrate by difference, as previously described. The total dietary fiber content was determined using the enzymatic gravimetric method AOAC 985.29 (AOAC, 2006).

<u>Microbiological evaluation</u>: The microbiological quality of the samples was analyzed for *Bacillus cereus, Staphylococcus Aureus*, molds and yeasts, *Salmonella* sp. and thermotolerant coliforms. The samples were evaluated according to the traditional methodology of counting in depth (Pour Plate), with the exception of the thermotolerant coliforms that were evaluated by the

method of multiple tubes. Specific culture media were used for each group of microorganisms, varying the incubation temperature (Silva *et al.*, 2010).

<u>Sensory analysis:</u> Before conducting sensory analyzes, the project was submitted to the Research Ethics Committee of the Federal University of Rondônia Foundation and was approved under number CAAE 90969318.6.0000.5300.

The triangular test was used in order to assess the sensory difference perceived by 40 untrained tasters in relation to the general aspects of the samples. The samples to be compared were dairy dessert with modified starch and dairy dessert with native starch after 1 and 7 days of manufacture. The test was carried out by presenting the tasters with 2 dessert samples using native starch and 1 sample prepared with modified starch, all samples being properly coded and served with a glass of mineral water for washing the taste buds. The taster was informed that between the samples, two were the same and one was different and required to point out on the sensory form the sample code that showed a difference between them.

A team of 34 untrained tasters assessed the acceptability of the mixed dairy dessert sample, using a 9-point verbal hedonic scale, ranging from "I liked extremely" to "I disliked extremely". The sample contained an average of 30 g each and were served coded with random three-digit numbers, accompanied by a glass of mineral water to be used by the taster between sample tastings. Formulation samples were evaluated for the global impression attribute.

The acceptability index was calculated as: (average grade obtained by the product / maximum score of the scale used to evaluate the product)  $\times$  100

Together with the acceptance test, the purchase intention test was applied, where the tasters were asked to purchase their intention in relation to dairy dessert, through the verbal scales presented in the form, constituting a scale of one (definitely would not buy) to five (definitely would buy) points.

#### 2.5 Statistical analysis

The experimental design used was completely randomized, with three replications. The results were subjected to analysis of variance (ANOVA) and Tukey's test (p < 0.05) to compare means using the ASSISTAT software (version 7.7 beta).

# 3. Results and discussion

### 3.1 Proximate composition of the native starch

The corn starch used showed moisture content (9.10%), lipids (0.01%), proteins (0.27%) and ash (0.01%) similar to those found by Pérez-Pacheco *et al.* (2014). Starches generally have up to 2% non-carbohydrate constituents. The starch used in this work showed a high degree of puree (<0.5% of constituents other than carbohydrates).

# 3.2 Apparent amylose content of the starches

The apparent amylose content found in native and modified starches are shown in Table 1. Starches chemically modified by hydrogen peroxide and sodium hypochlorite showed a reduction in the apparent amylose content. Similar results were found by Kaur and Bhullar (2016) in tamarind kernel starch oxidized by sodium hypochlorite. According to these authors the reduction in the apparent amylose content is not only due to decrease in molecular size of amylose but also the rupture of helical structure of amylose that reduces the ability of iodine to make a blue color inclusion complex with amylose.

Samples		Apparent amylose content (%)	
Native starch		$22.79\pm0.60\ b$	
	1%	$20.25 \pm 0.63$ c	
hydrogen peroxide	2%	$16.81 \pm 0.52 \; d$	
	3%	$17.08 \pm 0.60 \text{ d}$	
sodium hypochlorite	1%	$17.80 \pm 0.34 \text{ d}$	
	2%	$12.67 \pm 0.45 \text{ e}$	
	3%	$5.61 \pm 0.22 \; f$	
	15%	$22.72\pm0.85~b$	
HMT	20%	$26.28 \pm 0.77$ a	
	25%	$21.63 \pm 0.22$ bc	
Annealing	50 °C	$17.06 \pm 0.83 \text{ d}$	
	55 °C	$23.12\pm0.76~b$	
	60 °C	$23.58\pm1.18~b$	

Table 1 - Apparent amylose content of native and modified starches

Values are mean  $\pm$  SD (n = 3). Values followed by the same letter do not differ significantly according to Tukey's test (p<0.05).

The apparent amylose content for the HMT treatment showed an increase in the treatment with 20% humidity and without difference for the others. As HMT is a treatment that uses heat and humidity, the moisture content used in the treatment may produce different results. Hoover *et al.* (2010) justifies these differences by the structural changes in the starch granules after the modifications, which involve amylose-amylose and amylose-lipid interactions.

The annealing treatment at 50 °C showed a reduction in the apparent amylose content. The decreased amylose content of annealed starch could be attributed to amylose leaching or the weakened iodine binding to the amylose helix as a result of a change in amylose confirmation (helix to coil) and/or facilitated interaction between amylose-amylose and/or amylose-amylopectin during annealing (WANG *et al.*, 2014).

## 3.3 Water absorption index (WAI) and water solubility index (WSI) of the starches

WAI and WSI of the native and modified starches are shown in Table 2.

Samples		WAI (g.g <sup>-1</sup> )	WSI (%)
Native starch		$1.75 \pm 0.07 \; g$	$0.18 \pm 0.15 \text{ de}$
hydrogen peroxide	1%	$2.01\pm0.03def$	$0.38\pm0.08~cde$
	2%	$1.98 \pm 0.00 \text{ def}$	$0.27 \pm 0.20 \text{ de}$
	3%	$2.01 \pm 0.06 \text{ def}$	$0.36 \pm 0.17$ cde
sodium	1%	$1.98 \pm 0.07 \text{ ef}$	$0.64\pm0.05~c$
hypochlorite	2%	$2.12 \pm 0.02$ cde	$2.14\pm0.06\ b$
	3%	$2.20 \pm 0.02$ bcd	$7.14 \pm 0.02$ a
	15%	$2.16 \pm 0.05$ bcd	$0.21 \pm 0.03 \text{ de}$
HMT	20%	$2.32\pm0.13~b$	$0.44 \pm 0.14 \text{ cd}$
	25%	$2.59\pm0.04a$	$0.42 \pm 0.11 \text{ cd}$
	50 °C	$1.94 \pm 0.05 \; f$	$0.16 \pm 0.14 \text{ de}$
Annealing	55 °C	$2.02\pm0.01 cdef$	$0.07\pm0.02~e$
	60 °C	$2.74 \pm 0.09$ a	$0.06 \pm 0.04 \text{ e}$

Table 2 - Water absorption index (WAI) and water solubility index (WSI) of native and modified starches.

Values are mean  $\pm$  SD (n = 3). Values followed by the same letter do not differ significantly according to Tukey's test (p<0.05).

The absorption of water by starch granules at room temperature occurs due to the diffusion and absorption of water molecules in amorphous regions (Bello-Pérez; Montealvo; Acevedo, 2006). According to Wang, Li, and Zheng (2020), the damaged granules are able to absorb more water at room temperature, since the degradation of the granules exposes more hydroxyls within the double helices, which increases the interaction with the surrounding water molecules. Thus, the WAI was lower in native starch (without degradation) than in starches with modifications that suffered some type of "damage" to the granules, either chemically or physically.

Starches modified by hydrogen peroxide showed an increase in WAI, but not proportional to concentration. Starches modified by sodium hypochlorite, HMT and annealing increased WAI with increasing treatment intensity.

WSI is a parameter that reflects the degree of purity of a native starch or the degree of degradation of a modified starch. Starch is insoluble in cold water, so WSI represents the other constituents that accompany starch. When a starch is subjected to some treatment it can have its chains broken with increased solubility (Lima *et al.*, 2021; Polesi; Sarmento, 2011).

The treatments with hydrogen peroxide, HMT and annealing did not modify the solubility of native starch. Sodium hypochlorite increased the solubility of starch by increasing the concentration of the oxidizing agent, which characterizes breakage of the chains (Lima *et al.*, 2021).

# 3.4 Syneresis of the starches

The syneresis of native and modified starches is shown in Table 3. Starch submitted to oxidation treatment acquires properties such as resistance to retrogradation and consequent reduction in syneresis (Aplevicz; Demiate, 2007). The synthesis of the hydrogen peroxide treatment corroborates what has been exposed in the literature.

Oxidation can cause the decrease in syneresis to occur by two distinct mechanisms, the first being the degradation of long chain amylopectins, or even the amylose molecules of amorphous lamellae, which would produce dextrins with lengths less suitable for reassociation. The second mechanism is the formation of carboxyl or carbonyl groups, which would make it difficult for new associations between the chains, also reducing the tendency to retrograde (Kuakpetoon; Wang, 2006). However, for Sangseethong, Lertphanich and Sriroth (2009), these two mechanisms could take place simultaneously in the starch granules during the modification process, thus, the predominant mechanism would determine the predominant effect of oxidation on this property.

Samples		Syneresis (%)
Native starch		$11.03 \pm 1.33 \text{ d}$
	1%	$0.67 \pm 0.23 \ e$
hydrogen peroxide	2%	$0.00\pm0.00~e$
	3%	$0.00 \pm 0.00 \ e$
	1%	nd
sodium hypochlorite	2%	nd
	3%	nd
HMT	15%	$24.26\pm0.46~b$
	20%	$25.40\pm1.07~b$
	25%	$29.30 \pm 1.22$ a
Annealing	50 °C	$10.61 \pm 1.00 \text{ d}$
	55 °C	$11.67 \pm 1.28 \text{ d}$
	60 °C	$18.06 \pm 0.90 \ c$

 Table 3 - Syneresis of native and modified starches.

Values are mean  $\pm$  SD (n = 3). Values followed by the same letter do not differ significantly according to Tukey's test (p<0.05). nd = not detected.

In the treatments with sodium hypochlorite, it was not possible to detect the amount of syneresis produced, since the gels formed by starches presented extremely low viscosity.

Modification by HMT increased the syneresis of starch. Singh *et al.* (2011) found an increase in the gel hardness (consequently greater syneresis) in sorghum starch treated by HMT and justified such an increase in the cross-linking formed between the starch chains.

Starch modified by annealing at 60 °C increased syneresis in relation to native starch. According to Zavareze and Dias (2011), annealing causes an increase in crystalline perfection and a reduction in the volume of the gel, with a consequent increase in the gel hardness, which promotes greater syneresis.

### 3.5 Gel transparency of the starches

The gel transparency found in modified and native corn starches on day 0 and day 6 are shown in Table 4. The gel transparency is proportional to the transmittance. Oxidation treatments (hydrogen peroxide and sodium hypochlorite) made the starch gel more transparent. According to Lawal (2004) this is due to the formation of carboxylic and carbonyl groups in the molecules that causes an electrostatic repulsion, which reduces the reassociation of the molecules and favors the increase of transparency.

The gels of HMT starches showed less transparency than native starch. This proves a greater interaction between the starch molecules, corroborating the results of the syneresis. This same effect occurred in the starch treated by annealing at 60  $^{\circ}$ C.

With the exception of treatment with sodium hypochlorite, the other treatments reduced the transparency of the gel during storage, which indicates greater interaction between the molecules. According to Naknaen, Tobkaew and Chaichaleom (2017), the increase in turbidity during storage is due to the interactions between leached amylose and amylopectin chains that lead to the development of junction zones. These zones reflect or scatter a significant amount of light.

Samples		<b>Day 0 (%)</b>	Day 6 (%)
Native starch		$17.30 \pm 2.01 \text{ f}$	$12.37 \pm 1.10 \text{ e}$
hydrogen peroxide	1%	$36.83 \pm 0.72 \text{ d}$	$30.17 \pm 1.40 \text{ c}$
	2%	$32.97 \pm 0.85 \text{ e}$	$25.93 \pm 2.39 \text{ d}$
	3%	$39.87 \pm 0.93 \text{ c}$	$30.83 \pm 1.43$ c
sodium	1%	$84.57 \pm 1.27 \text{ b}$	$87.13\pm1.70~b$
hypochlorite	2%	$98.73 \pm 0.25$ a	$98.57 \pm 0.45$ a
	3%	$98.40 \pm 0.46$ a	$98.83 \pm 0.51$ a
	15%	$6.70 \pm 0.17 \; h$	$4.17\pm0.06\ f$
HMT	20%	$7.00\pm0.44~h$	$4.60\pm0.10~f$
	25%	$6.63 \pm 0.47 \text{ h}$	$4.50\pm0.10\;f$
Annealing	50 °C	$15.00 \pm 0.79 \; fg$	$11.43 \pm 0.60 \text{ e}$
	55 °C	$16.37 \pm 1.10 \text{ f}$	$12.17 \pm 1.16 \text{ e}$
	60 °C	$12.43 \pm 0.42$ g	$9.30 \pm 0.53 \text{ e}$

### Table 4 - Gel transparency (% of transmittance at 650 nm) of native and modified starches.

Values are mean  $\pm$  SD (n = 3). Values followed by the same letter do not differ significantly according to Tukey's test (p<0.05).

### 3.6 Swelling factor of the starches

The swelling factor of the granule quantifies the intragranular water of a starch suspension heated to a certain temperature, that is, how much water the granule absorbs without breaking. The expansion of starch granules was studied at 50, 70 and 90  $^{\circ}$ C and are shown in Table 5.

Samples	6	50 °C	70 °C	90 °C
Native starch		$1.92 \pm 0.46 e$	$10.38 \pm 0.80$ hi	$24.64 \pm 0.69 c$
hudrogan	1%	$5.37\pm0.40\ c$	$30.31 \pm 0.63$ b	$32.42 \pm 0.67$ b
hydrogen	2%	$2.47\pm0.91e$	$21.38 \pm 0.77 \ d$	$34.77 \pm 0.26$ a
peroxide	3%	$5.48\pm0.00\ c$	$23.90 \pm 0.77$ c	$34.77 \pm 0.69$ a
sodium	1%	$4.67 \pm 0.67 \text{ cd}$	$55.63 \pm 0.56$ a	$9.71\pm0.56~h$
	2%	$12.23 \pm 0.79 \text{ b}$	$8.54\pm0.78~i$	$3.47\pm0.66$ j
hypochlorite	3%	$29.82 \pm 0.67$ a	$2.82\pm0.91~j$	$7.08\pm0.91~i$
	15%	$5.54 \pm 0.63 \text{ c}$	$0.33\pm0.75~h$	$20.89 \pm 0.69  \mathrm{de}$
HMT	20%	$5.59\pm0.50\ c$	$0.34 \pm 0.96$ ef	$18.30 \pm 0.59 \; f$
	25%	$2.50\pm0.68~e$	$0.34\pm0.43~fg$	$15.96 \pm 0.80$ g
	50 °C	$2.77 \pm 0.88$ de	$18.37 \pm 0.67 \text{ e}$	$18.91 \pm 0.88$ ef
Annealing	55 °C	$3.35 \pm 0.26 \text{ de}$	$14.89\pm0.66~g$	$16.93 \pm 0.89 \text{ fg}$
-	60 °C	$3.18 \pm 0.44$ de	$8.93 \pm 0.61$ hi	$21.18 \pm 0.78$ d

 Table 5 - Swelling factor of the granule of native and modified starches.

Values are mean  $\pm$  SD (n = 3). Values followed by the same letter do not differ significantly according to Tukey's test (p<0.05).

Starches modified with hydrogen peroxide obtained an increasing swelling factor as temperature increased, showing greater swelling than granules of native starch. The modifications occurred in the starch structure may have resulted in greater resistance in its stability, causing the increase in expansion to be greater without breaking the starch granule, in addition to facilitating the entry of water due to possible damage caused.

The samples modified by sodium hypochlorite showed an increase in the swelling factor at 50 °C in relation to native corn starch, however, at 90 °C the swelling had a considerable decrease. This may be related to the fact that with more aggressive modifications, the chains that make up the starch are fragmented and form a disorganized structure that allows more water to enter the starch granule at a lower temperature, but fails to keep the granule structure intact in higher temperatures, causing the granule to break and the water to return to the medium. Kaur and Bhullar (2016) also observed a reduction in the expansion factor of tamarind kernel starch oxidized by sodium hypochlorite.

Starches treated by HMT and annealing showed less expansion compared to native starch. Sudheesh *et al.*, (2020) also observed similar behavior in kithul starch treated by HMT and annealing. The authors justified that these treatments increase the interactions between the starch chains, reducing the swelling factor.

## 3.7 Cupuassu dessert syneresis

Starch modified by hydrogen peroxide showed the least syneresis (Table 3), so it was chosen to be applied in cupuassu dessert.

Sample	Syneresis (%)
with cupuassu pulp and native starch	$6.98 \pm 0.32$ a
with cupuassu pulp and modified starch	$1.10 \pm 0.28 c$
without cupuassu pulp and native starch	$3.89\pm0.48~b$
without cupuassu pulp and modified starch	$0.73 \pm 0.47 \ c$

Table 6 - Syneresis (%) of the desserts.

Values are mean  $\pm$  SD (n = 3). Values followed by the same letter do not differ significantly according to Tukey's test (p<0.05).

As the concentration of hydrogen peroxide did not significantly affect the syneresis of starch gel, the lowest concentration (1%) was used. The syneresis results of the desserts added with native and modified starch (1% hydrogen peroxide) with and without cupuassu pulp is shown in Table 6.

The desserts with native starch showed greater syneresis than with modified starch. This result corroborates the results of the syneresis of the starch gel, presented above.

Dessert with cupuassu pulp and native starch showed the greatest syneresis. This sample may have exuded more water because in addition to the syneresis due to the starch retrogradation, syneresis also occurred due to the coagulation of milk (Summer *et al.*, 2002). According to Pompo, Medeiros and Pena (2020), the cupuassu pulp was high acidity (pH 3.46), thus causing the coagulation of milk proteins with increased syneresis.

Thus, the application of the modified starch was effective in reducing the syneresis of the dessert.

### 3.8 Proximate composition of mixed desserts

The proximate composition of mixed cupuassu and babassu desserts with native corn starch and hydrogen peroxide modified starch are shown in Table 7.

The proximate composition of the desserts is a result of the components present in the raw materials used in the formulation. The dietary fiber content is the most relevant result in the dessert, as it was higher in the sample with modified starch. This can be explained because the chemical modification of starch can reduce its digestibility (Fuentes-Zaragoza *et al.*, 2010) and, consequently, increase the dietary fiber content, since the chemical groups inserted in the starch structure hinder the action of digestive enzymes used in the analysis of quantification of dietary fiber.

### Table 7 - Proximate composition of mixed desserts.

Parameters	with native starch	with modified starch
Moisture (%)	$67.37 \pm 0.13$ a	$66.48\pm0.08~b$
Ashes (%)	$0.87 \pm 0.01 \ a$	$0.88 \pm 0.01 \ a$
Proteins (%)	$3.65 \pm 0.35$ a	$3.85 \pm 0.19$ a
Lipids (%)	$4.42\pm0.01~b$	$4.56 \pm 0.09$ a
Dietary fiber (%)	$3.77\pm0.06~b$	$4.1 \pm 0.1 \ a$
Carbohydrates (%)	$19.93 \pm 0.49$ a	$20.13 \pm 0.30$ a

Values are mean  $\pm$  SD (n = 3). Values followed by the same letter do not differ significantly according to Tukey's test (p<0.05).

### 3.9 Microbiological evaluation

The investigation of contaminating microorganisms revealed counts of less than  $1 \times 10^1$  CFU/g for *Bacillus cereus*, *Staphylococcus Aureus*, molds and yeasts, absence of *Salmonella* sp. in 25 g and less than 10 MPN/g for thermotolerant coliforms.

The samples showed excellent microbiological quality and offered no risk of contamination to the consumer. This result is possibly related to the use of quality raw materials, an adequate production process and the use of good manufacturing practices when handling products.

### 3.10 Sensory analysis

The triangular test was performed after 24 and 168 (7 days) hours of sample manufacture. In the two days of analysis there was no statistical difference between the samples, however the number of tasters who reported a difference after 7 days of storage of the desserts increased.

The average obtained in the sensory analysis of acceptance on a 9-point hedonic scale of the mixed dairy dessert, in relation to the global impression parameter for the dessert with native starch

and with modified starch was 7.93 and 8.06, respectively, and the acceptability index was 88.2% and 89.6%, respectively. According to Dutcosky (2007), the decision criterion for the index to be of good acceptance is equal to or greater than 70%, thus the mixed dairy desserts obtained excellent acceptance. Despite little difference, in the analysis discussed the tasters expressed greater acceptance of the sample with modified starch.

The purchase intention for mixed dairy desserts is shown in Figure 1. Both samples showed a high rate of purchase intention. For dessert with native starch 44% of the tasters "definitely would buy", 34% "probably would buy", 19% "maybe/maybe not", 3% "probably would not buy" and no answer for "definitely would not buy". For dessert with modified starch, 56% of the tasters "definitely would buy", 19% "probably would buy", 22% "maybe/maybe not", 3% "probably would not buy" and no answer for "definitely would not buy". Therefore, in case this product is launched on the market, it has great chances of being purchased.

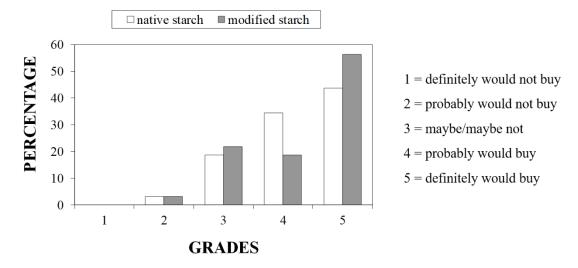


Figure 1 - Purchase intention for mixed dairy desserts

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