

Effect of hydrochloric acid in different concentrations and temperatures up to some properties of organic cassava starch

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Abstract

The main objective of the present work was to study the thermal properties and rheological behavior of natural and modified organic cassava starch with standard solutions of hydrochloric acid in concentrations 0.1 and 0.2 mol L⁻¹ and in temperatures 25 and 45°C, respectively, as well as verify the structural changes up to the surface of granules. The results allowed us to establish the relationship between the viscosity (RVA), the thermal properties (TG-DTA, DSC) and changes in the morphology of granules (NC-AFM). The major modifications in all the studied properties of the starch granules occurs in those treated with standard HCl at room temperature (25 °C), proportionally to higher concentrations.

Keywords: thermal analysis, modified starch, NC-AFM, RVA.

1. Introduction

Starch is a natural polymer, which has many and unique properties. It is a non-toxic, biocompatible, biodegradable and abundant polysaccharide; regenerated from carbon dioxide and water by photosynthesis in plants. Cassava (*Manihoc esculenta*, Crantz) is a species of the *Euphorbiaceae* family and one of the most important root crops in tropical regions in terms of food energy production [1, 2].

Tropical root and tuber are rich sources of starches, and vitamins and minerals (traces), and they serve as either subsidiary or subsistence food in parts of the tropical belt. Cassava (*Manihot esculenta*, Crantz) is an important vegetable crop in tropical regions, where on a food energy production basis; it ranks fourth after rice, wheat and corn as a source of complex carbohydrates. These root and tuber crops contain 70-80 % water, 16-24 % starch and small quantities (<4 %) of proteins and lipids and other substances [2 - 5].

Organic foods are produced using methods that do not involve modern synthetic inputs such as synthetic pesticides and chemical fertilisers: they do not contain genetic modifications and are not processed using irradiation, industrial solvents, or chemical food additives. Several countries require producers to obtain a special certification in order to market food as "organic" [2, 6, 7]. Organic starch is extracted following the same rules, and for this study it was kindly supplied by Tozan Co. Ltd., Ponta Grossa, PR, Brazil.

Starches are of great value for the food industry because they contribute greatly to the textural properties of many foods and are used in food and industrial applications

as a thickener, colloidal stabiliser, gelling agent, bulking agent and water retention agent [8].

Starch, in its native form, does not always have the physical or chemical properties appropriate for certain types of processing. Some of these constraints include, insolubility in cold water, low stability to freeze-thawing and syneresis, which in some cases makes them difficult to use. Starch modifications can be made by chemical, enzymatic and physical methods that promote specific functional properties for industrial purposes [9 - 11].

The main objective of the present work was to study the thermal, rheological and structural behaviour of natural and modified organic cassava starch with standard solutions of hydrochloric acid (0.1 and 0.2 mol L⁻¹) with controlled temperature (20 and 45 °C). The raw and the hydrolyzed organic cassava starches were submitted to thermal analysis, using the thermoanalytical techniques: simultaneous thermogravimetry and differential thermal analysis (TG-DTA); differential scanning calorimetry (DSC); the structural changes of granules by the non-contact atomic force microscopy (NC-AFM) and pasting properties by the rapid viscoamylographic analysis (RVA).

2. Materials and Methods

Cassava starch samples were supplied from Tozan Co. Ltd. (Ponta Grossa – PR – Brazil).

Five portions, each with twenty five grams of cassava starch were separated and identified as (a), (b), (c), (d) and (e). The untreated sample (a) was kept in a desiccator over anhydrous calcium chloride until constant mass.

The samples (b) and (d) were treated by one hour with 100 mL of standard HCl solutions 0.1 and 0.2 mol L⁻¹,

respectively, with continuous stirring and controlled temperature (45 °C).

The samples (c) and (e) were treated by one hour with 100 mL of standard HCl solutions 0.1 and 0.2 mol L⁻¹, respectively, with continuous stirring and controlled temperature (25 °C).

After this time, each suspension was filtered, washed with distilled water until complete elimination of chloride ions (test with H⁺/AgNO₃ solution), dried at room temperature and kept in a desiccator over anhydrous calcium chloride until constant mass.

TG and DTA curves were recorded using a simultaneous SDT 2960 System (TA Instruments) under a 100 mL min⁻¹ air flow purge gas, and a heating rate of 10 °C min⁻¹. The initial mass sample was about 7 mg. Alumina crucibles (sample and reference) were used for the TG and DTA experiments [11-13].

DSC curves were recorded using a DSC Q 200 System (TA Instruments) under an air flow of 50 mL min⁻¹, heating rate of 10 °C min⁻¹. A 4:1 (water:starch, w/w) slurry was prepared and maintained for one hour in order to equilibrate the moisture content. The aluminum crucibles were sealed with hermetic lid in order to study the gelatinization process [12, 13].

Atomic force microscopy non-contact method was performed with a SPM-9600 atomic force microscope (Shimadzu), which allows to be obtained surface images with high resolution. The NC-AFM measurements were performed at ambient conditions for each starch sample which were pressed using a hydraulic press and immobilized on the instrument sample holder [2, 5].

The micro-image in Figure 1 (resolution 20x20 μm) represents a group of some granules with resembles spherical or oval shapes. The instrument allows to perform measurements through several diameter particles and below the Figure they are depicted with irregularities in the surface. With the traced lines A-B, C-D by the equatorial regions it was possible to perform the measurements. On the other hand, several measurements with resolution 50x50 μm were carried out in different points of the tablets and the average diameters were calculated [2, 11].

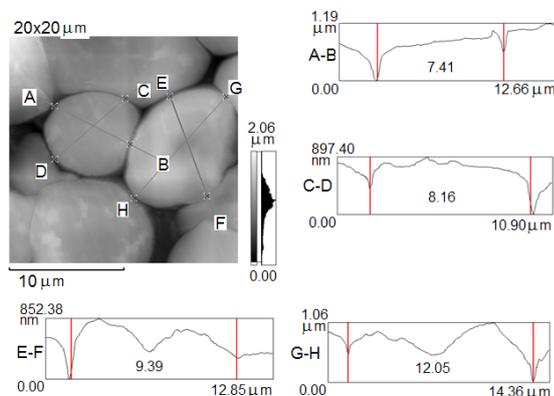


Figure 1. NC-AFM scheme for calculate average diameter of the granules.

The pasting properties were performed in an Rapid Viscoanalyzer RVA-4, (Newport Scientific) was used for studying the starch samples apparent viscosity profile during cooking in the presence of excess water (dispersions of starch at 10 % w/w, dry basis). The Standard analysis profile of the ThermoLine for Windows[®] software was employed for the analyses and the conditions involved increasing starch dispersion temperature from 50 to 95 °C in a 6 °C min⁻¹ rate, keeping at 95 °C for five minutes and then cooling until 50 °C at the same temperature rate. The apparent viscosity was expressed in centipoises (cP) [2, 14].

3. Results and Discussion

All the TG-DTA curves of the untreated and treated samples have shown similarity with mass loss (TG) in three main steps corresponding to endo or exothermic events (DTA). In the Figure 2 the TG-DTA curves of untreated organic cassava starch (a) are shown and summarized in the Table 1.

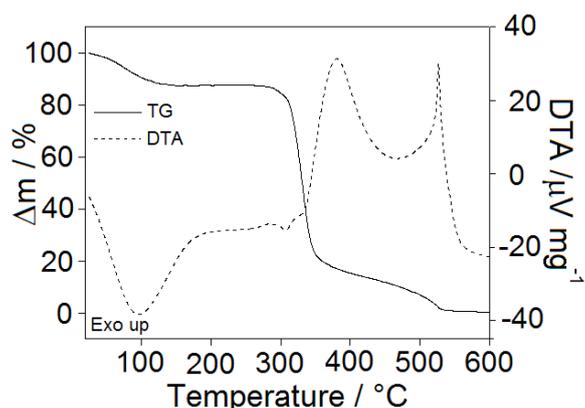


Figure 2. TG and DTA curves of untreated cassava starch, sample (a).

TG-DTA curves show the first mass loss attributed to dehydration, with corresponding endotherm, followed of stability. The second and third mass losses are due to decomposition of organic matter which begins with a little endotherm samples (a) and (c) attributed to depolymerization of the chains which occurs in an oxidizing atmosphere where are the formation of pyrodextrins [15-16], followed by two exothermic peaks, in an oxidizing atmosphere with ash formation. The little endothermic peaks after stability, not occurs in the thermal decomposition of the samples (b), (d) and (e). The ash content of each sample was: 0.14, 0.12, 0.12, 0.11 and 0.16 %, respectively.

Table 1. TG-DTA results of: (a) untreated cassava starch, (b) cassava starch treated with 0.1 mol L⁻¹ hydrochloric acid at 45 °C, (c) cassava starch treated with 0.1 mol L⁻¹ hydrochloric acid at room temperature, (d) cassava starch treated with 0.2 mol L⁻¹ hydrochloric acid at 45 °C, and (e) cassava starch treated with 0.2 mol L⁻¹ hydrochloric acid at room temperature.

Samples	Step	TG results mass loss / %	θ / °C	DTA results peak / °C
(a)	1 st	12.1	30-112	98 (endo)
	stability	-	112-308	-
	2 nd	68.1	308-345	308 (endo); 377 (exo)
	3 rd	19.7	345-554	554 (exo)
(b)	1 st	12.8	30-115	96 (endo)
	stability	-	115-297	-
	2 nd	62.5	297-349	302 (endo); 340 (exo)
	3 rd	24.6	349-588	565 (exo)
(c)	1 st	12.5	30-114	96 (endo)
	stability	-	114-289	-
	2 nd	58.7	289-343	329 (exo)
	3 rd	28.6	343-595	581 (exo)
(d)	1 st	8.8	30-116	92 (endo)
	stability	-	116-288	-
	2 nd	58.8	288-350	330 (exo)
	3 rd	32.1	350-597	580 (exo)
(e)	1 st	8.6	30-119	94 (endo)
	stability	-	119-289	-
	2 nd	57.2	289-345	332 (exo)
	3 rd	33.9	345-602	587 (exo)

(*) Δm mass loss (%), θ temperature range, T_p peak temperature

One of the important properties of the starch is the gelatinisation process. When starch is heated in excess water the amylopectin double helices dissociate, with accompanying loss of crystallinity, and the granules swell (by imbibing water). The starch granules can absorb water and an irreversible swelling takes place in this process. The data for this process are the “onset” or initial temperature (T_o), the “endset” or conclusion temperature (T_c), peak temperature (T_p) and gelatinization enthalpy (ΔH_{gel}), which were calculated and shown in the Figure 3.

These parameters as well as the viscosity are important for starch industry; they can reflect starch characteristics and play an important role in the application of the starches. All these parameters were obtained at the heating rate 10 °C min⁻¹, and are shown in the Table 2.

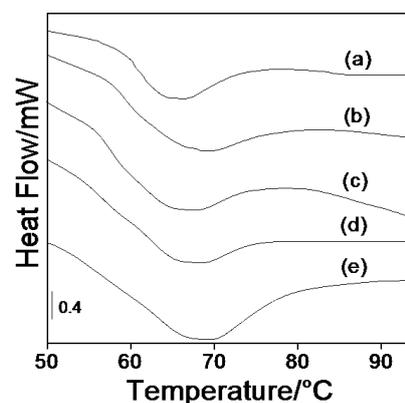


Figure 3. DSC gelatinisation curves: (a) native cassava starch, (b) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at 45 °C, (c) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at room temperature, (d) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at 45 °C, and (e) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at room temperature.

Table 2: DSC gelatinisation results: (a) native cassava starch, (b) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at 45 °C, (c) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at room temperature, (d) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at 45 °C, and (e) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at room temperature.

Samples	T _o /°C	T _p /°C	T _c /°C	ΔH _{gel} /Jg ⁻¹
(a)	58.91	64.56	74.97	9.63
(b)	56.96	66.70	75.66	5.79
(c)	55.47	65.01	75.42	6.47
(d)	54.30	65.55	75.79	5.40
(e)	54.82	67.62	78.52	8.34

(*) T_o “onset” initial temperature, T_p peak temperature, T_c “endset” final temperature, ΔH_{gel} gelatinization enthalpy.

All the obtained data were collected at same conditions, in duplicate and the values reflect the treatment conditions of each sample, as well as the instrument conditions.

In the Figure 4 the viscoamylographic profiles of the organic cassava starch samples are shown and differences are evident when considering viscosity peak, through and setback values.

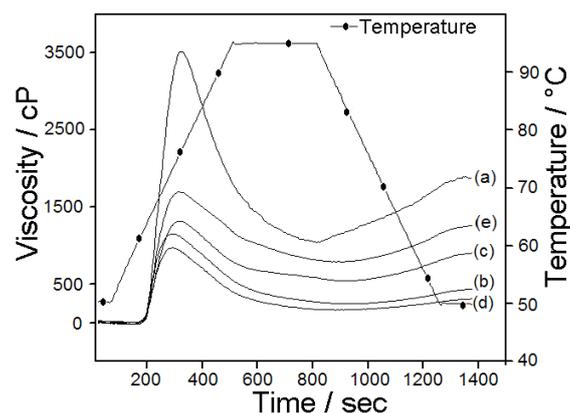


Figure 4. RVA profile of the organic cassava starch samples: (a) native cassava starch, (b) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at 45 °C, (c) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at room temperature, (d) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at 45 °C, and (e) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at room temperature.

It was possible to observe the typical native cassava starch cooking profile that includes a high viscosity peak followed by granule rupture and consequent cooking instability, ending with a moderate to low retrogradation tendency. In the case of the acid treatments, the viscosity values were inversely related with acid concentrations, as expected, but if one considers the behavior related with the temperature of reaction, with higher temperature (45 °C), the viscosity values were also higher than the reaction promoted at room temperature (25 °C). This was not expected as it is well known that temperature increase generally is related with higher reaction rate. In an attempt to explain this behavior, it may be speculated that reagent degradation could occur at higher temperatures.

Table 3. RVA and NC-AFM results: (a) native cassava starch, (b) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at 45 °C, (c) modified cassava starch with 0.1 mol L⁻¹ hydrochloric acid at room temperature, (d) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at 45 °C, and (e) modified cassava starch with 0.2 mol L⁻¹ hydrochloric acid at room temperature.

Samples	RVA					NC-AFM	
	Peak viscosity/ cP	Peak temperature /°C	Peak time / sec	Setback / cP	Break / cP	Final Viscosity / cP	d _a / μm
(a)	3500	78	315	890	2490	1900	14.43
(b)	1150	73	300	240	900	420	10.10
(c)	1300	76	306	470	720	980	10.23
(d)	990	73	298	30	750	270	11.01
(e)	1720	76	315	420	980	1250	10.25

(*) cP “centipoises”, sec “seconds”, Average diameter in μm

The non-contact atomic force microscopy technique (NC-AFM) was used to observe the surface of the untreated (Figure 5) and treated organic cassava starch granules, and allowed us to obtain micro-images with high resolution of each sample. The measurements were performed at ambient conditions and a pellet of each sample was fixed directly on an AFM sample holder, which was enough to immobilize the granules and prevent contamination of the starch surface.

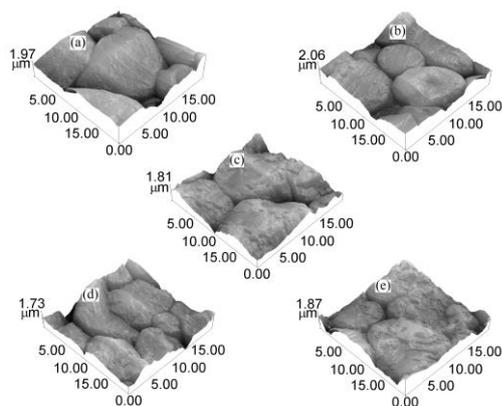


Figure 5: NC-AFM micro-images of: (a) native cassava starch, (b) modified cassava starch with 0.1 mol L^{-1} hydrochloric acid at $45 \text{ }^{\circ}\text{C}$, (c) modified cassava starch with 0.1 mol L^{-1} hydrochloric acid at room temperature, (d) modified cassava starch with 0.2 mol L^{-1} hydrochloric acid at $45 \text{ }^{\circ}\text{C}$, and (e) modified cassava starch with 0.2 mol L^{-1} hydrochloric acid at room temperature.

Based on the observations of atomic force microscopy (NC-AFM) results, it is possible to conclude that modifications on the surface of organic cassava starches were proportional to the HCl concentrations, although the acid added at $25 \text{ }^{\circ}\text{C}$ was more effective than at $45 \text{ }^{\circ}\text{C}$.

4. Conclusions

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) are techniques that allowed determining the hydration water, the main steps of decomposition and the ash content; all these results were in agreement with endo- or exothermic events and all the cassava starch show similar behaviour. Differential scanning calorimetry (DSC) was used in the study of the starch gelatinization process; the major gelatinization enthalpy was found for untreated sample (a), followed by those treated with HCl 0.2 mol l^{-1} at room temperature (e), HCl 0.1 mol l^{-1} at room temperature (c), HCl 0.1 mol l^{-1} at $45 \text{ }^{\circ}\text{C}$ (b) and HCl 0.2 mol l^{-1} at room temperature (d). The maximum viscosity of each sample showed the same sequence, according to the rapid viscoamylographic analysis (RVA), as well as the parts of smooth and protrusions, verified by atomic force microscopy (NC-AFM).

Acknowledgements

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