Thermoanalytical study on the action of nitric acid in the cassava starch granules

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Abstract

Modifications of starches can led to new products with new desirable properties and applications in several industrial fields as food, textile, paper and others. In this study samples of cassava starch were treated with standard nitric acid 0.1 and 0.2 mol L^{-1} at 25 and 45 ºC, respectively, by 60 minutes. After washed, dried and maintained in desiccator up to constant mass, the samples were analysed by TG/DTG whose technique allowed observing three main mass losses and the treated starches shown higher stability in the decomposition. When compared with the untreated cassava starch the gelatinization enthalpy (DSC) of the treated starches decreased mainly with the samples treated with acid at 0.2 mol L^{-1}. The increase of acid concentration and temperature show decrease in the relative crystallinity and low alterations in the average diameter of starch granules.

Keywords: Cassava starch, acid hydrolysis, thermal behaviour

1. Introduction

Starch is a raw material that can be from different botanical sources; is a semi-crystalline polymer and constituted by two polysaccharides: the amylose (mostly linear chain, with up to 3000 glucose molecules interconnected primarily by α-1,4 glycosidic linkages and few branched networks) and amylopectin (a large branched polymer with linkages of α-1,4 that serve as the backbone and α-1,6 bridges at the branching points. In its native form, starch has some technological constraints that need to be improved in order to make it possible and use it in industrial applications. Starches in the native form have some limitations in its applications thus the modified starches are largely used in several industries due to their different functionalities and new desirable properties [1-6].

The cassava (Manihot esculenta, Crantz) is a species from the Euphorbiaceous family and one of the most important root crops mainly in tropical countries that serve as subsistence food. These roots and tubers are good source of food energy production. It water content is around 70-80% and are rich in starch (16-24%) and low quantity of vitamins, minerals, proteins, lipids and other substances [1, 3, 7-9].

In agreement with the literature [10] the modified starches with acids (mainly HCl, H_2SO_4 and organic acids) are called "acid modified starches" or termed "acid-thinned starches" that diminishes the molar mass and increasing consequently the free aldehyde group content. The acid hydrolysis also decreases the viscosity of the slurry of starch granules.

In this investigation were made modifications in cassava starch granules with nitric acid in different concentrations and temperatures (this above the gelatinization enthalpy) and the effects upon the starch granules were analysed by thermoanalytical techniques (TG/DTG, DSC), the viscosity profile of starch slurry by RVA, and the structure of granules by atomic force microscopy (AFM) and X ray diffractometry (XRD).

2. Experimental

2.1. Material and Methods

The native cassava starch (500 g) for this study was bought in the local commerce of Ponta Grossa, PR, Brazil. The starch was divided in five parts of 100 g (dry basis). One of them was maintained as received, being the (A) sample, and the other samples were treated following the literature methodology [1, 8] with modifications: the cassava starches were treated with standard nitric acid solutions by 60 minutes 0.1 and 0.2 mol L^{-1} at 25 and 45 ºC, respectively. Then the modified samples were washed and filtered until complete elimination of NO_3^- ions, dried in room temperature and maintained in desiccator up to constant mass.

The TG curves were obtained with the thermal analysis system TGA-50 (Shimadzu, Japan), where the samples were heated from 35 ºC to 650 ºC using open alumina crucibles with approximately 5.0 mg of each sample under a synthetic air flow of 150 mL min^{-1} at a heating rate of 10 ºC min^{-1}. The instrument was preliminarily calibrated with standard weight and with standard calcium oxalate monohydrate. All mass loss percentages were determined using TA-60 WS data analysis software. The derivative

thermogravimetric curves (DTG), the first derivative of TG curves, were calculated [3, 4, 7, 11-17].

The DSC curves were obtained using the thermal analysis system model DSC-Q200 (TA-Instruments, USA) with the aim to investigate the gelatinization enthalpy. The DSC curves were recorded under an air flow of 50 mL min^{-1}, heating rate of 10 ℃ min^{-1} and samples weighing about 2.5 mg. A 4:1 (water:starch, m/m) mixture was prepared and maintained for 60 minutes in order to equilibrate the moisture content. The aluminum crucibles were sealed and then the curves were performed. The instrument was previously calibrated with Indium 99.99% purity, melting point with T_p. = 156.6 ℃, ΔH = 28.56 J g^{-1} [10-13].

The pasting properties of the samples were obtained by using the RVA-4 (Newport Sci., Australia) viscometer. A suspension of 3 g of starch in 25 g accurately distilled water underwent a controlled heating and cooling cycle under constant shear where it was held at 50 ℃ for two min, heated from 50 to 95 ℃ at 6 ℃ min^{-1}, and held at 95 ℃ for 5 min, cooled to 50 ℃ at 6 ℃ min^{-1} and maintained at 50 ℃ for 2 min [12-14].

X-ray diffraction powder patterns (XRD) were obtained by using an X-ray diffractometer mod. Ultima 4 (Rigaku, Japan), employing Cu Kα radiation (λ = 1.541 Å) and settings of 40 kV and 20 mA. The scattered radiation was detected in the angular range of 5 - 50º (2θ), with scanning speed of 8º min^{-1} and a step of 0.06º. The degree of relative crystallinity was quantitatively estimated using Equation 1 and following the method described in the literature [11, 15-19].

$$X_c = \frac{A_p}{(A_p + A_b)} \times 100 \qquad \text{Equation 1}$$

The micro-images of each sample with high resolution were observed using an atomic force microscope SPM-9600 (Shimadzu, Japan), by the non-contact method (NC-AFM). All the measurements were performed in triplicate and this technique allowed us to observe the surface of the studied starches and it was possible to calculate the average diameter and the average roughness of the samples [10, 11, 18].

All the results were studied and analysed its variance (ANOVA) with the Tukey test to compare sample means at 95% confidence level (p < 0.05) was performed using STATISTICA 7.0 software (StatSoft, Inc., Tulsa, OK, USA) [3, 11].

3. Results and Discussion

TG/DTG curves were performed and allowed to verify similar profile of each curve showing three main mass losses with distinct regions; the first, which begins in the room temperature up to around 189 ℃, was due to water evaporation. After dehydration each sample shows stability, followed by two steps of decomposition (2nd and 3rd mass losses) attributed to degradation and oxidation of organic matter (amylose and amylopectin), that occurs in oxidant atmosphere with formation of final residue (ash) that were, 0.98, 0.66, 0.56, 0.11 and 0.55% of initial mass,

respectively. All the TG/DTG curves are depicted in Figure 1 and the obtained results are shown in Table 1.
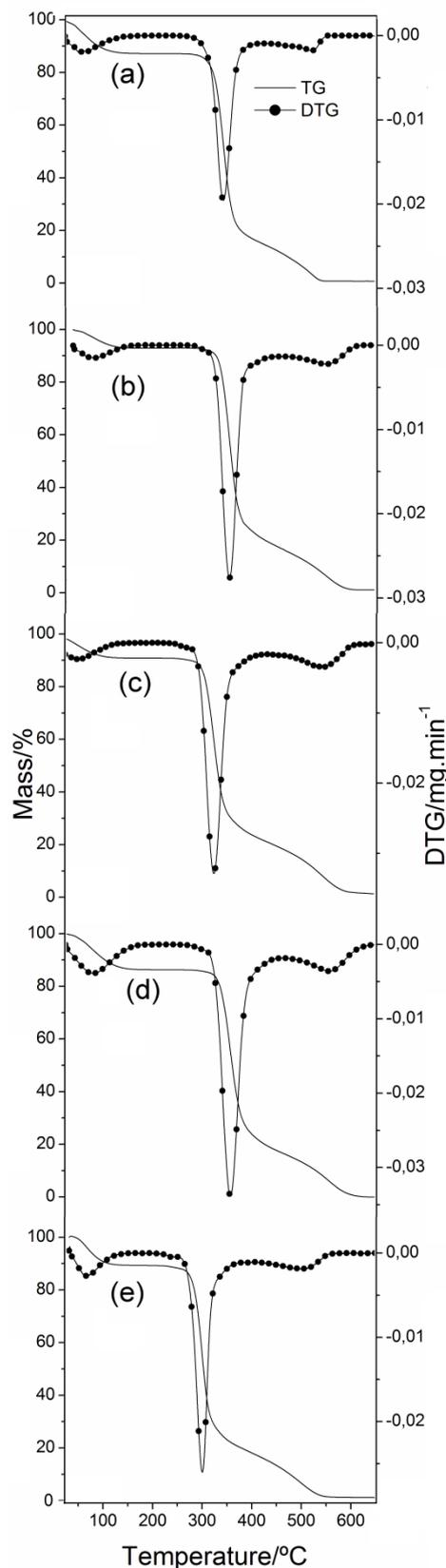

Figure 1: TG/DTG curves of: (a) untreated cassava starch; (b) cassava starch treated with HNO$_3$ 0,1mol L^{-1} at 25ºC, (c) cassava starch treated with HNO$_3$ 0,1mol L^{-1} at 45ºC; (d) cassava starch treated with HNO$_3$ 0,2mol L^{-1} at 25ºC; (e) cassava starch treated with HNO$_3$ 0,2mol L^{-1} at 45ºC.

In low acid concentrations (0.1 mol L⁻¹) the treated starches show increase in the final stability (TG) up to 616 and 619 ºC, respectively and the starch treated with acid at 0.2 mol L⁻¹ at 25 ºC up to 631 ºC. To the starch treated with HNO_3 0.2 mol L⁻¹ at 45 ºC this final stability was down up to 610 ºC. All the steps of decomposition with the obtained values of TG/DTG are gathered in Table 1.

Table 1: TG/DTG results of: (a) untreated cassava starch; (b) cassava starch treated with HNO_3 0,1mol L⁻¹ at 25ºC, (c) cassava starch treated with HNO_3 0,1mol L⁻¹ at 45ºC; (d) cassava starch treated with HNO_3 0,2mol L⁻¹ at 25ºC; (e) cassava starch treated with HNO_3 0,2mol L⁻¹ at 45ºC.

Samples	TG Results		DTG Results	
	Step	$\Delta m/\%$	$\theta/°C$	$T_p/°C$
(A)	1ˢᵗ	12.81	30-175	50.86
	stability	-	175-266	-
	2ⁿᵈ	71.52	266-416	341.80
	3ʳᵈ	14.69	416-594	521.17
(B)	1ˢᵗ	6.98	30-177	81.82
	stability	-	177-278	-
	2ⁿᵈ	74.54	278-444	353.45
	3ʳᵈ	17.82	444-616	550.03
(C)	1ˢᵗ	9.21	30-189	91.26
	stability	-	189-289	-
	2ⁿᵈ	70.30	289-444	348.43
	3ʳᵈ	19.93	444-619	549.77
(D)	1ˢᵗ	13.64	30-185	80.75
	stability	-	185-268	-
	2ⁿᵈ	69.39	268-459	356.75
	3ʳᵈ	16.86	459-631	548.25
(E)	1ˢᵗ	10.73	30-161	65.02
	stability	-	161-232	-
	2ⁿᵈ	70.58	232-387	300.73
	3ʳᵈ	18.14	387-610	494.95

*(θ)Temperature ranges, (T_p) peak temperatures and (Δm) mass losses

The DTG curves were calculated and the obtained results allowed us to determine the stability of each compound. As observed, with major acid concentration and major temperature the 2ⁿᵈ and 3ʳᵈ decomposition steps were shifted to higher temperatures, except to the sample treated with HNO_3 at 0.2 mol L⁻¹ and at 45 ºC.

The DSC curves were performed with the aim of calculate the gelatinization enthalpy. This is an endothermic phenomenon that occurs when water is added up to starch and heated; it occurs only in sealed crucibles and the energy required for the molecular order disrupter differs in the same botanical origin of starch and the way that it was treated. The characteristic of these transitions including "*on set*" and "*end set*" temperature (T_{on}, T_{end}), "*peak temperature*" (T_p) and "*gelatinization enthalpy*" (ΔH_{gel}) were calculated and are shown in Table 2. The shown DSC curves in Figure 2.
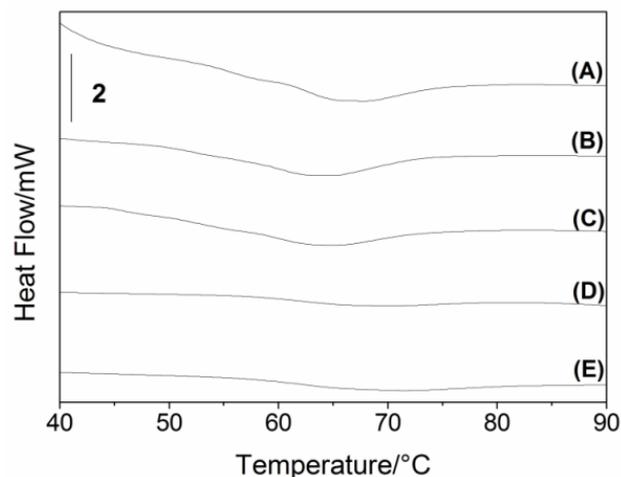

Figure 2: DSC curves of: (a) untreated cassava starch; (b) cassava starch treated with HNO_3 0,1mol L⁻¹ at 25ºC, (c) cassava starch treated with HNO_3 0,1mol L⁻¹ at 45ºC; (d) cassava starch treated with HNO_3 0,2mol L⁻¹ at 25ºC; (e) cassava starch treated with HNO_3 0,2mol L⁻¹ at 45ºC.

Although occurring in approximated temperatures the acid hydrolysis affect the gelatinization properties (ΔH) that were shifted to lower values, mainly with the increase of temperature and acid concentration. Similar behaviour was observed in previous studies of starches treated with different acids and concentrations [1, 3, 7, 8]. Other authors [12] found similar behaviour in study with corn starches treated with HCl solutions at 0.06, 0.14 and 1.0 N.

Table 2: DSC, AFM and XRD results of: (a) untreated cassava starch; (b) cassava starch treated with HNO_3 0,1mol L⁻¹ at 25ºC, (c) cassava starch treated with HNO_3 0,1mol L⁻¹ at 45ºC; (d) cassava starch treated with HNO_3 0,2mol L⁻¹ at 25ºC; (e) cassava starch treated with HNO_3 0,2mol L⁻¹ at 45ºC.

Samples	DSC gelatinization				AFM		XRD
	$T_{on}/°C$	$T_p/°C$	$T_{end}/°C$	$\Delta H_{gel}/J.g^{-1}$	$d_a/\mu m$	r_a/nm	Degree of relative cristallinity
(a)	58,76±0,26ᵃ	68,31±0,07ᵇ	71,28±0,01ᵇ	13,13±0,74ᵃ	9.99±3.49ᵇ	537.200	22.39±2.53ᵃ
(b)	52,42±0,08ᵈ	63,25±0,09ᵈ	65,61±0,06ᵉ	10,59±0,23ᵇ	12.52±4.30ᵃ	729.865	19.89±0.68ᵇ
(c)	50,61±0,13ᵉ	63,12±0,02ᵈ	66,01±0,04ᵈ	10,51±0,7ᵃ	9.76±2.33ᵇ	474.706	19.34±0.16ᵃᵇ
(d)	58,24±0,08ᵇ	66,79±0,02ᶜ	70,89±0,01ᶜ	5,15±0,32ᶜ	9.65±4.98ᵇ	374.304	16.15±0.75ᵇᶜ
(e)	57,25±0,21ᶜ	69,38±0,26ᵃ	72,52±0,15ᵃ	5,04±0,57ᶜ	8.95±6.55ᵇ	388.540	13.56±0.29ᶜ

(*) T_{on} onset temperature, T_p peak temperature, T_{end} endset temperature, ΔH_{gel} gelatinization enthalpy, (d_a) Average diameter, (r_a) Average roughness, the degree of crystallinity was calculated as a percentage, peaks are determined in 2θ.
(**)Averages followed by the same letters in the same column do not differ statistically by Tukey's test ($p < 0.05$).

The atomic force microscopy technique (AFM) turn it possible to observe the starch granules surface with high resolution and some effects of acid treatment at 25 and 45 °C. In Figure 3 we can verify that the granule structure was modified but not destroyed; the average diameter was maintained around 9-12 μm and the average roughness show slight alteration as few bulges in the surface. The results average roughness and the average diameter were calculated and the results are collected in Table 2.

In Figure 4 are shown the main X-ray diffractogram of the studied samples. The diffractograms are characteristic of starch from tuberous with no displacement in the main peaks at 2θ around 15, 17, 18 and 23°. According to the literature [8, 13] with the Equation 1, was calculated the relative crystallinity of untreated and modified starches and the results are depicted in Table 2.
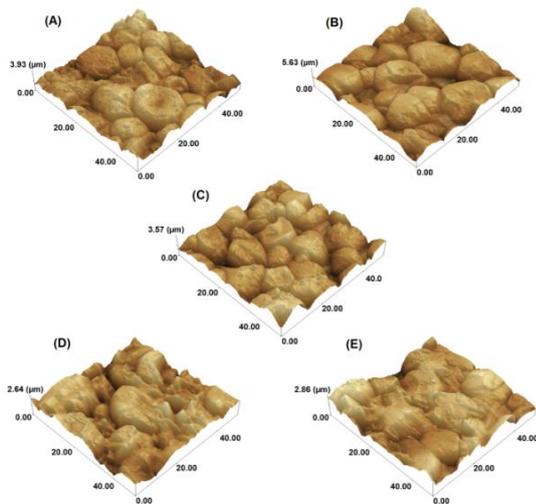

Figure 3: NC-AFM images of: (a) untreated cassava starch; (b) cassava starch treated with HNO_3 0,1mol L^{-1} at 25ºC, (c) cassava starch treated with HNO_3 0,1mol L^{-1} at 45ºC; (d) cassava starch treated with HNO_3 0,2mol L^{-1} at 25ºC; (e) cassava starch treated with HNO_3 0,2 mol L^{-1} at 45ºC.
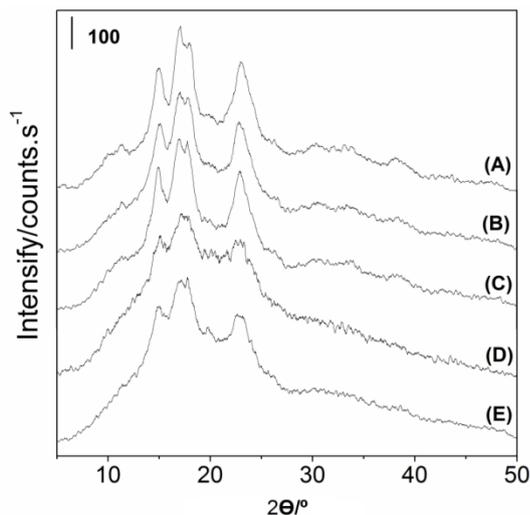

Figure 4: XRD diffractograms of: (a) untreated cassava starch; (b) cassava starch treated with HNO_3 0,1mol L^{-1} at 25ºC, (c) cassava starch treated with HNO_3 0,1mol L^{-1} at 45ºC; (d) cassava starch treated with HNO_3 0,2mol L^{-1} at 25ºC; (e) cassava starch treated with HNO_3 0,2mol L^{-1} at 45ºC.

The obtained results shown that some difference in relative crystallinity occurs in the starch granules mainly with those treated with acid at 45 ºC. The obtained values of relative crystallinity are collected in Table 2.
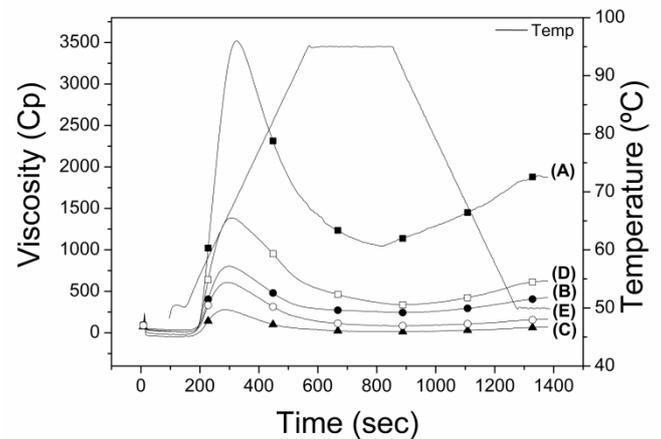

Figure 5: RVA viscograms of: (a) untreated cassava starch; (b) cassava starch treated with HNO_3 0,1mol L^{-1} at 25ºC, (c) cassava starch treated with HNO_3 0,1mol L^{-1} at 45ºC; (d) cassava starch treated with HNO_3 0,2mol L^{-1} at 25ºC; (e) cassava starch treated with HNO_3 0,2mol L^{-1} at 45ºC.

The viscograms (RVA) of untreated (a) and modified starches (b-e) are shown in Figure 5 and the results depicted in Table 3. As reported in literature [7, 8, 13], after the acid treatment of native starch the pasting properties can be shifted to higher temperatures and the acid action causes decrease in the viscosity of slurry with increase of temperature.

After reaching the maximum viscosity (at 95 ºC) all the samples lose this property that returns with lower intensity after cooling (final viscosity).

Table 3: RVA results of: (a) untreated cassava starch; (b) cassava starch treated with HNO_3 0,1mol L^{-1} at 25ºC, (c) cassava starch treated with HNO_3 0,1mol L^{-1} at 45ºC; (d) cassava starch treated with HNO_3 0,2mol L^{-1} at 25ºC; (e) cassava starch treated with HNO_3 0,2mol L^{-1} at 45ºC.

Samples	Pasting temperature/°C	Viscosity peak/cP	Peak time/sec	Setback/cP	Break/cP	Final viscosity/cP
(a)	63,45±1,13[a]	3516,00±2,83[a]	326,00±2,83[a]	827,00±8,49[a]	2442,00±14,14[a]	1874,5±3,54[a]
(b)	64,48±1,38[a]	800,00±2,83[c]	301,90±8,63[b]	178,50±0,71[c]	556,00±2,83[c]	422,50±0,71[c]
(c)	66,68±3,36[a]	277,00±2,69[e]	281,90±2,69[c]	52,00±2,83[e]	262,5±3,54[d]	66,50±0,71[e]
(d)	63,50±1,06[a]	1384,50±3,54[b]	307,90±0,14[ab]	288,00±2,83[b]	1046,50±6,36[b]	625,98±0,04[b]
(e)	64,75±1,77[a]	608,00±1,41[d]	296,10±5,52[bc]	81,50±4,95[d]	528,00±1,41[c]	163,50±2,12[d]

(*) cP "centipoises", sec "seconds".
(**) Averages followed by the same letters in the same column do not differ statistically by Tukey's test ($p < 0.05$).

4. Conclusions

The TG curves show characteristic steps of decomposition for untreated and modifies starches. DSC analysis was an important tool to determine the main gelatinization properties of starches. A reduction in ΔH_{gel} of the starches treated with nitric acid occurs in agreement with the treatment with other inorganic acids (HCl, H_2SO_4) that primarily attacks the amorphous regions and plays an important role in the thermodynamics and physicochemical properties without destroying its granule structure as it can be observed by atomic force microscopy. The relative crystallinity of starch granules decreased mainly in higher acid concentrations and temperatures.

Acknowledgements

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