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The thermal, rheological and structural properties of cassava starch granules modified with hydrochloric acid at different temperatures

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ABSTRACT

Starch is arguably one of the most actively investigated biopolymer in the world. In this study, the native (untreated) cassava starch granules (*Manihot esculenta*, Crantz) were hydrolyzed by standard hydrochloric acid solution at different temperatures (30 °C and 50 °C) and the hydrolytic transformations were investigated by the following techniques: simultaneous thermogravimetry–differential thermal analysis (TG–DTA), differential scanning calorimetry (DSC), as well as non-contact atomic force microscopy (NC-AFM), X-ray diffraction (XRD) powder patterns, and rapid viscoamylographic analysis (RVA). After the treatment with hydrochloric acid at different temperatures, the thermal stability, a gradual loss of pasting properties (viscosity), alterations in the gelatinization enthalpy (ΔH_{gel}), were observed. The use of NC-AFM and XRD allowed the observation of the surface morphology and topography of the starch granules and changes in crystallinity of the granules, respectively.

1. Introduction

Starch is a raw material of various botanical origins, and is the most important storage reserve carbohydrate in plants; it is used by the food, paper, chemical, pharmaceutical and textile industries, among many others. Starch, a semi-crystalline polymer, is composed of two polysaccharides: amylose and amylopectin. Amylose, a mostly linear chain, typically consists of up to 3000 glucose molecules interconnected primarily by α-1,4 glycosidic linkages and is reported to contain a few branched networks. Amylopectin is a large branched polymer with of α-1,4 linkages that serve as the backbone and α-1,6 bridges at the branching points. Unprocessed or native starches are structurally too weak and functionally too restricted for application in today's advanced technologies; processing is necessary to engender a range of functionality. The production of modified starches is an alternative that is in continuous development to surpass one or more of the limitations of native starches and thus to increase the utility of this polymer for industrial applications. The starch market has grown rapidly in the last few years, leading to the search for products with specific characteristics that support the requirements of the industry. Cassava (*Manihot esculenta*, Crantz) is an important vegetal crop in tropical regions, where, on a food energy production basis, it ranks fourth after rice, wheat and corn as source of complex carbohydrates. The main composition of these roots and tubers is: 70–80% water, 16–24% starch and small quantities <4% of proteins and lipids [1–5].

Chemical modifications bring about structural alterations and the introduction of new functional groups, thus affecting the physicochemical properties of the starches and making them fit for various industrial uses [6].

Starch can be modified by chemical, physical, genetic or enzymatic means. Acid modification is a chemical method and it is used to prepare thin boiling starches for food and non-food industrial applications. Acid-thinned modification is a type of hydrolysis using mineral acids at low concentration and at a temperature below gelatinization; it diminishes the molar mass, consequently increasing, the free aldehyde group content. It also decreases viscosity, increases the solubility of the granules and minimizes syneresis [6,7].

The selection of starch for industrial uses is made by considering its availability and also its physico-chemical characteristics that vary depending on the source. The growing demands for new starch products make it necessary to intensify studies about their structure, properties, modifications and applications [3–7].

For several years, many studies have been carried out with starches, flour starches, as well as modified starches and flours, using physico-chemical and instrumental methods [8–18].

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Due to the numerous issues involved, it becomes important to have a complete understanding of the properties of natural (untreated) and treated starches. The main objective of the present work was to study the thermal, rheological and structural behavior of untreated and treated cassava starch samples. The cassava starch granules were treated with standard hydrochloric acid solution at 0.15 mol L^{-1} for 8 h at 30 and 50 °C, respectively, and the main properties were described employing the techniques: simultaneous thermogravimetry–differential thermal analysis (TG–DTA), differential scanning calorimetry (DSC), rapid viscoamylographic analysis (RVA), X-ray diffraction (XRD) powder patterns and non-contact atomic force microscopy (NC-AFM).

2. Experimental

2.1. Materials

Commercial grade granular cassava starch was obtained from an industrial unit located in Ponta Grossa, PR, Brazil. Several samples were used and all analysis was performed in triplicate. All the chemical products used in this work were analytical grade.

2.2. Methods

2.2.1. Sample preparation

The acid thinned starches were prepared in the laboratory by following the procedure described in literature [19]: 100 g of native starch were added to 500 mL of hydrochloric acid solution 0.15 mol L^{-1} and maintained under continuous stirring for 8 h at 30 °C. After this time, the solution was filtered and washed with distilled water until complete elimination of chloride ions (test with Ag^+ solution), dried at room temperature and kept in a desiccator over anhydrous calcium chloride until constant mass.

The same procedure was followed for the other samples, while the temperature was maintained at 50 °C.

2.2.2. Thermal analysis

TG–DTA curves were recorded using a simultaneous TG 60 system (Shimadzu, Japan) under an air flow at 100 mL min^{-1} and at a heating rate of 10 °C min^{-1}. The initial mass sample was about 9 mg. Alumina crucibles were used for the TG–DTA experiments and the instrument was calibrated (mass and baseline) according to the instructions of the manufacturer. All mass loss percentages were determined by TA-60WS data analysis software.

DSC curves were recorded using a DSC 60 (Shimadzu, Japan) under an air flow at 100 mL min^{-1}, heating rate of 5 °C min^{-1}. A 4:1 (water:starch, w/w) mixture was prepared and left for 2 h in order to equilibrate the moisture content; 10 μL of each suspension was transferred to an aluminum crucible which was sealed, and tests were carried out in order to study the gelatinization. In order to obtain the DSC curves, the instrument was calibrated with indium 99.99% purity, m.p. = 156.6 °C, $\Delta H = 28.71$ J g^{-1}, and an empty aluminum crucible was used as reference.

2.2.3. Viscoamylographic behavior

The pasting properties of the starch samples [15,16] were determined using a RVA-4 Viscoamylograph (Newport Scientific Pvt. Ltd., Australia). A dispersion of 2.5 g (8% moisture) starch in 28 g of distilled water underwent a controlled heating and cooling cycle under constant stirring where it was held at 50 °C for 1 min, heated from 50 to 95 °C at 6 °C min^{-1}, and held at 95 °C for 5 min, cooled to 50 °C at 6 °C min^{-1}, and held at 50 °C for 2 min [1,2,6,19].

2.2.4. Structural analysis

The non-contact atomic force microscopy method NC-AFM (Shimadzu, Japan) was used to observe the surface of the starch granules. According to the literature [16–18], this method allowed us to obtain micro-images with high resolution of each sample, with no pretreatment, and it was possible to observe the structural changes in the surface of the granules as well as calculate the average roughness and average size of the particles. The measurements were performed at ambient conditions for the starch samples and then spread directly onto a sticking tape fixed on the AFM sample holder, which was enough to immobilize the granules and prevent surface contamination.

X-ray diffraction (XRD) powder patterns were obtained by using a D-5000 X ray diffractometer (Siemens, Germany), with Cu Kα radiation ($\lambda = 1.544$ Å) and a setting of 40 kV and 20 mA [14,19] to show alterations in the crystallinity. The degree of the relative crystallinity was calculated according to the literature [20], considering the region 10–50° for calculating the degree of crystallinity by having the most intense peaks.

For the DSC, RVA NC-AFM results the statistical significance was determined by Tukey's test ($p < 0.05$).

3. Results and discussion

The main physico-chemical properties of native and acid thinned starches are summarized below. According to the literature [11], thermogravimetry (TG) can be helpful to show the behavior of starch granules, when heating around 300 °C leads to depolymerization. TG–DTA curves of the samples are shown in Fig. 1.

The profile of the TG curves was similar, showing mass losses in three main steps; the first due to dehydration, with a corresponding endothermic peak in the DTA curve. When anhydrous, each sample was stable up to 280 °C. The second and third mass losses occured consecutively and are attributed to the decomposition of organic matter with the formation of final residues (ash), which were 1.8, 0.3 and 0.2%, respectively. Through the DTA curves, it can be verified that these second and third mass losses started with an endothermic reaction followed by two exothermic reactions. All the TG–DTA results are shown in Table 1. The action of hydrochloric acid on the cassava starch granules shifted the final temperature of decomposition to higher values.

When starch is heated in the presence of enough water, its crystalline organization decomposes to form amorphous regions. This molecular disordering is called gelatinization and it is frequently observed as an endothermic phenomenon using differential scanning calorimetry (DSC) [5,6].

The DSC curves of untreated and modified cassava starches are shown in Fig. 2.

The characteristics of the transitions, including "onset" temperature (T_o), "endset" or "conclusion" temperature (T_c), peak temperature (T_p) and gelatinization enthalpy (ΔH_{gel}) were calculated. The energy required for the molecular order disrupture, differed with the particular treatment, being lower for untreated corn starch ($\Delta H = 8.37 \pm 0.81$ J g^{-1}), followed by acid modified starch at 30 °C ($\Delta H = 14.23 \pm 1.05$ J g^{-1}) and at 50 °C ($\Delta H = 12.87 \pm 2.36$ J g^{-1}). These results as well as the "onset" temperature (T_o), the "peak" temperature (T_p) and the "conclusion" temperature (T_c) of each sample are shown in Table 2.

The pasting properties of the untreated and treated samples were determined by rapid viscoamylographic analysis, and the RVA curves are shown in Fig. 3. The main results are summarized in Table 3.

The pasting temperature (RVA) for untreated cassava starch was 67.7 ± 0.44 °C, which increased initially to 69 ± 0.95 °C and decreased gradually with higher temperature.

The higher viscosity peak was observed for the untreated cassava starch which decreased with the sample treated with HCl at