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THERMOGRAVIMETRIC ALTERATIONS OF CASSAVA STARCH GRANULES INDUCED BY HYDROGEN PEROXIDE, UV RAYS AND MICROWAVE

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Abstract
Starches are applied in several fields of industry. Amylose and amylopectin (natural polymers) constitute the starch in vegetable cells. In some processes native starches cannot support high stress conditions (high temperatures/acidity). Then, modification methods are developed aiming the improving of starch technological utilization. Oxidative modification with H_2O_2 has been the subject of many researches. UV rays as well microwave irradiation can be used. The aim was to confirm possible thermogravimetric alterations in native cassava starch (A) granules due to a double starch modification: 1st step) H_2O_2 standard solutions 0.1 mol L^{-1} (B), 0.2 mol L^{-1} (C) and 0.3 mol L^{-1} (D) and UV rays exposure for 1h; 2nd step) microwave irradiation for 5 min. The results of thermogravimetric curves (TG-DTA) show that the behaviors of the starch proprieties were modified. Highlighting, the modified samples C and D showed a decrease on the thermal stability step. This alteration turned them suitable to many field of industry like the paper one.

Keywords: Environment-friendly reagent, active oxygen, untreated starch.

1. INTRODUCTION

Higher plants are naturally composed of starch granules as the main source of carbohydrates reserve (HORNUNG et al., 2015a). These native granules are constituted alternately by amorphous (amylose with α-D-1-4-glicopiranose units) and semicrystalline (amylopectin with α-D-1-4-glicopiranose units branched with α-1-6 linkages) shells structures (HORNUNG et al., 2015a, 2015b; ZHANG et al., 2012). Starch is commonly applied in many industry sectors (LEWICKA; SIEMION; KURCOK, 2015). Therefore, the technological characteristics are add in the starch structure with chemical or physical modifications (HORNUNG et al., 2015a, 2015b). The oxidative modification of starch with hydrogen peroxide is a widely used process (HORNUNG et al., 2015b; LEWICKA; SIEMION; KURCOK, 2015). This modification improve the behavior of starch by introducing new functional groups (carbonyls or carboxyl) (HORNUNG et al., 2015b; LEWICKA; SIEMION; KURCOK, 2015). The exposition of the starches granules on ultraviolet rays or on microwave irradiation can alter their properties (FAN et al., 2016; HORNUNG et al., 2015b). The microwave radiation can function as a catalyzer of the oxidation process (LEWICKA; SIEMION;

KURCOK, 2015). The thermal analysis is an analytical technique to investigate the thermal behavior and the morphological alterations of modified and non-modified starches.

2. OBJECTIVE

The aim of the study was to perform the double modifications of the cassava starch granules (oxidation / microwave irradiation) and evaluate the alterations caused using thermal analytical techniques (TG-DTA).

3. MATERIALS AND METHODS

The native cassava starch was acquired in Curitiba, PR, Brazil. The starch was divided into four parts of 40 g (dry basis). The native sample (A), and treated with: 1st step) H_2O_2 standard solutions 0.1 mol.L^{-1} (B), 0.2 mol.L^{-1} (C) and 0.3 mol.L^{-1} (D) and exposure at UV radiation (k = 256 nm; germicide lamp; 9 W; Osram Puritec)for 1 h; 2nd step) domestic microwave oven (MG41R Eletrolux) irradiated at 950 W for 5 minutes. After the samples were filtered, washed and dried (oven; forced air; 24 h at 35 ºC). The thermogravimetric TG-DTA curves were obtained using a thermal analysis system (TA Instruments, TGA-Q500 model); applying a temperature range of 30 ºC to 600 ºC in open alumina crucibles (approximately 8.0 mg of the sample); under a nitrogen flow (50 mL.min^{-1}); heating rate of 10 ºC min^{-1}. All mass loss percentages were determined using TA-60 WS data analysis software (HORNUNG et al., 2015a, 2015b).

4. RESULTS AND DISCUSSION

The thermogravimetric (TG-DTA) curves, Figure 1, show three main events of mass loss of the starches. The endothermic peak in the DTA curves (first event) is attributed to the evaporation of the water and volatile compounds, followed by stability step. Once dehydrated, the second and third main regions in the TG curves are related to the degradation of the organic matter (amylose and amylopectin) and the formation of final residues (ash).

The TG curves show slight similarities between profiles A and B and between C and D samples. The differences showed in the samples C and D could be attributed to the higher concentration of the reagent applied in the oxidizing reaction. DTA curves show differences between the modified starches with the A sample. The sample B demonstrated the intense endothermic event of organic matter degradation, similar to literature results (HORNUNG et al., 2015a, 2015b).

The modified samples showed different results for all parameters studied related to the native sample (A), Table 1. It is also possible to denote that sample C and D, treated with 0.2 and 0.3mol.L^{-1} of H_2O_2 , show the higher onset temperatures for the stability step when compared with the other samples. A similar result was obtained on a previous work of the same study group (HORNUNG et al., 2015b), although, it presented a wider raging of the stability step (200 ºC to 293 ºC) for a sample treated only with the simultaneous modification by UV rays + H_2O_2 (same concentration). The microwave irradiation in the cassava starches altered differently the thermal behavior, mass and temperature variations (Δm; ΔT) and also peak temperature (T_p), of the samples. During an oxidation process the hydroxyl groups of the starches molecules are turned to carbonyl groups and carboxyl groups (HORNUNG et al., 2015b; LEWICKA; SIEMION; KURCOK, 2015). The microwave irradiation, with the catalytic effect, leads the starch molecules to a thermal instability (faster degradation process) (LEWICKA; SIEMION; KURCOK, 2015), as observed on the obtained results for stability steps of the modified samples. These highly oxidized starches are widely applied in the paper industry improving its strength and printability (ZHANG et al., 2012).

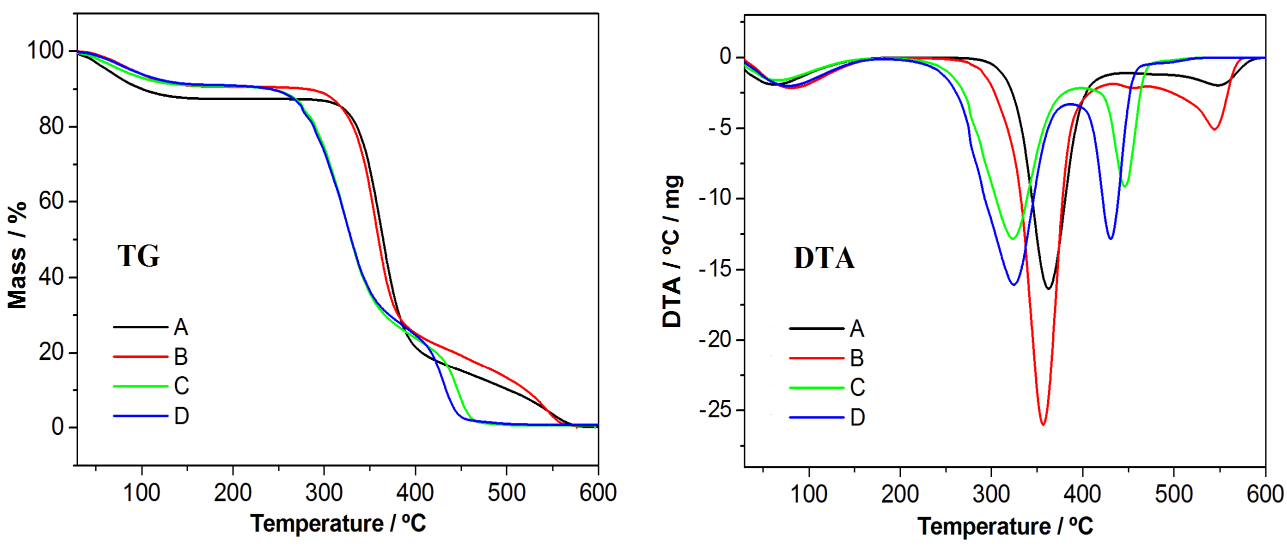

Figure 1. TG-DTA curves: Native cassava starch sample (A) and treated with: 1st step) H_2O_2 standard solutions 0.1 mol.L^{-1} (B), 0.2 mol.L^{-1} (C) and 0.3 mol.L^{-1} (D) and exposure at UV rays for 1 h; 2nd step) microwave irradiated for 5 min.

Table 1. TG/DTA results: (A) – Native cassava starch sample; (B, C and D) native cassava starch treated with H_2O_2 standard solutions 0.1, 0.2 and 0.3 mol.L^{-1} simultaneous exposure at UV rays for 1 –h and subsequently microwave irradiated for 5 min.

Samples	TG Results		DTA Results	
	Step	Δm / %	ΔT / °C	T_p / °C
A	1st	11.96	30 – 129	63.36
	stability	-	129 – 305	-
	2nd	73.99	305 – 518	362.61
	3rd	12.85	518 - 616	547.87
B	1st	9.218	30 - 132	78.23
	stability	-	132 - 295	-
	2nd	74.81	295 - 498	355.09
	3rd	15.36	498 - 568	541.40
C	1st	8.98	30 - 146	74.73
	stability	-	146 - 261	-
	2nd	65.75	261 - 428	333.00
	3rd	24.45	428 - 543	455.06
D	1st	8.65	30 - 154	80.32
	Stability	-	154 - 262	-
	2nd	63.31	262 - 411	329.53
	3rd	27.18	411 - 600	435.17

Δm – mass loss (%), ΔT temperature range, T_p peak temperature

5. CONCLUSION

The treatment applied altered the thermogravimetric behavior of the native cassava starch and could make it suitable for the paper industry.

6. ACKNOWLEGMENT

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