X CONGRESSO BRASILEIRO E IV CONGRESSO PAN AMERICANO DE ANÁLISE TÉRMICA E CALORIMETRIA

17 – 20 de abril de 2016 – São Paulo – SP - Brasil

EVALUATION OF DOUBLE TREATED STARCHES USING THERMAL TOOLS

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Abstract

Starch is the main polysaccharide found in cereals, composed by amylose and amylopectin. Corn is the principal source of starches worldwide. Starches treatment, through physical, chemical and/or biological methods, can improve the applications range. Acid modification in alcoholic solution promotes minimally degradation in the granule. Ball mill is one physical method poorly explored. The aim was to treat the starches using HCl 0.5 mol L^{-1} for 1 hour in 100 ml of aqueous, ethanol or methanol solutions with subsequent ball milling processes. One sample was selected as native sample. The four others, one native sample and three acid modified samples, were treated by physical process with the oscillating ball mill. The DTG-60H equipment was used for the TG and DTA analysis. The TG curves showed three mass losses related to dehydration, decomposition and oxidation. The native sample without physical modification showed major resistance to total degradation. This occurs because the physical modification cleaves hydrogen bonds, leaving a weakened granule. The TG-DTA results showed that the mass loss in the 2nd event was minor in the hydrolyzed samples compared with native samples. The acid modification can provide starch higher resistance to degradation up to 340 °C. These results showed that chemical and physical treatment changed the thermal behaviors of the starches.

Keywords: Acid treated starch, thermal analysis, TG-DTA, ball mill, HCl/alcoholic.

1. INTRODUCTION

Starch is the most abundant reserve carbohydrate found in vegetable and provides industrial application in several sectors such as paper, textiles, building materials, pharmaceuticals and chemicals. Starch is composed of amylose and amylopectin (HORNUNG, P. S. et al., 2015). Corn is the most important source of starch used. However, native corn starch has limitations because of functional and physico-chemical properties. The chemical, physical and biological treatment of the starch can improve the applications range (SANDHU, K. S.; SINGH, N., 2007, ZHANG, W. et al., 2015). The acid starch treatment with the use of alcoholic solution promotes the degradation of the granule molecule, but recovers 90% of the molecule. An option to obtain technological starch products is combining chemical and physical treatment. Ball mill is a mechanical grinding seldom used in starch treatment. This process provides a mechanochemical effect through the combination of friction, collision and the shear of the samples (LIN, J. H. et al., 2011, HUANG, Z. Q. et al., 2008). Thermal analysis has been applied in various sectors of research. The Thermogravimetry (TG) is applied to observe the behavior of starch granules and the Differential Thermal Analysis (DTA) detects the heat effects and physical and chemical variations (IONASHIRO, M.; CAIRES, F. J.; GOMES, D. J. C., 2014).

2. OBJECTIVES

The aim was to treat starches using HCl 0.5 mol L^{-1} in aqueous and alcoholic solutions and ball milling processes. The evaluation of the treatment was through TG-DTA.

3. MATERIAL AND METHODS

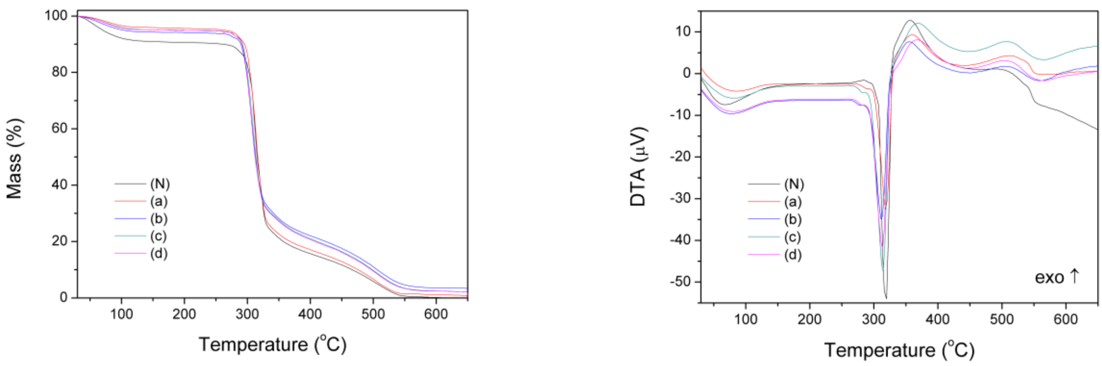
Corn starch was acquired in Colombo-PR. The starch was separated in five samples of 20g (dry basis). Three samples were treated with HCl for 1 hour 0.5 mol L^{-1} in 100 ml of aqueous solution (b), ethanolic (c) or methanolic (d) each one. The treated starches were filtered and washed until the complete elimination of acid (verified with silver nitrate 0.05 mol L^{-1}). The starches were dried for 24 hours in oven at 40 °C and stored in desiccator. One sample was selected as native sample (N). The four others, native sample (a) and acid modified samples (b, c and d), were treated by physical process with the oscillating ball mill model MM 400 (Retsch, Germany). The starches samples were ground separately using 2.2824 ± 0.3187 g. In the process steel spheres were used for dry milling an oscillation frequency of 20 Hz for 30 minutes. The DTG-60H (Shimadzu, Japan) was used for TG and DTA analysis. The samples were heated from 30 ºC to 650 ºC using open alumina crucibles with 3.1935 ± 0.2732 mg of the sample under a nitrogen flow of 100 $mL.min^{-1}$ at a heating rate of 10 ºC min^{-1}. To obtain the results TA-60 WS software was used.

4. RESULTS AND DISCUSSION

The Thermogravimetry Analysis (TG), Figure 1-A, shows similar results for all samples. The first event refers to dehydration and simultaneous DTA curves, Figure 1-B, exhibited an endothermic peak, followed by a period of stability. The second event refers to decomposition, forming carbonaceous organic material and the DTA curves showed the formation of more prominent endothermic peaks. The third event represents the mass loss attributed to oxidation, with two exothermic peaks, leaving some ash: (N) 0.03%, (a) 0.85%, (b) 3.36%, (c) 2.17% e (d) 2.18%. Besides that, the loss mass in the 2nd event were minor in the hydrolyzed samples compared with native samples. The acid modification can provide to starch more resistance to degradation up to 340 °C. Previous study suggested that the starch was converted to a heat-stable structure, leading to the formation of novel crystallites (SHIN, S. I. et al, 2009). On the other hand, the physical treatment in the starches cleaved the hydrogen bonds resulting in an increase of the amorphous part and consequently granule weakening (CAVALLINI, C. M.; FRANCO, C. M. L., 2010). This result was observed comparing the mass lost of the samples (N) with (a), Table 1. From these results it is concluded that chemical and physical treatments changed the thermal behaviors of the starches.

Table 1 - TG and DTA curves for samples of corn starches: native (N), native physically treated (b), physically treated by HCl 0.5 mol L^{-1} in water (b), in ethanol (c) and in methanol (d).

Sample	TG Results		DTA Results	
	Step	Δm(%)	ΔT(°C)	Tp(°C)
(N)	1st	8.09	45 - 105	63.57 (endo)
	Stability	-	105 - 272	-
	2nd	68.01	272 - 337	319.77 (endo)
	3rd	23.06	337 - 446	356.69 (exo)
			446 - 544	490.55 (exo)
(a)	1st	3.69	61 - 108	86.47 (endo)
	Stability	-	108 - 272	-
	2nd	70.99	272 - 335	318.15 (endo)
	3rd	23.84	335 - 442	360.43 (exo)
			442 - 555	513.30 (exo)
(b)	1st	4.90	47 - 101	77.18 (endo)
	Stability	-	101 - 268	-
	2nd	62.55	268 - 328	311.18 (endo)
	3rd	28	328 - 450	354.75 (exo)
			450 - 552	505.94 (exo)
(c)	1st	4.10	56 - 101	82.10 (endo)
	Stability	-	101 - 268	-
	2nd	64.94	268 - 334	314.35 (endo)
	3rd	27.85	334 - 449	368.72 (exo)
			449 - 558	506.75 (exo)
(d)	1st	4.21	61 - 101	82.19 (endo)
	Stability	-	101 - 260	-
	2nd	64.11	260 - 330	313.40 (endo)
	3rd	28.70	330 - 454	367.57 (exo)
			454 - 559	500.76 (exo)



A **B**

Figure 1 – TG (A) and DTA (B) curves for samples of corn starches: native (N), native physically treated (b), physically treated by HCl 0.5 mol L^{-1} in water (b), in ethanol (c) and in methanol (d).

5. CONCLUSION

In the TG curves, three mass losses were observed (dehydration, decomposition and oxidation of organic matter). The hydrolyzed samples had the minor mass loss in the 2nd event when compared with native samples. The acid modification can provide to starch a higher strength at elevated temperatures. The physically treated samples had cleaved the hydrogen bonds resulting in an increase of the amorphous part and consequently granule weakening. Therefore this study concluded that chemical and physical treatment promoted changes in the thermal behavior of starches.

6. ACKNOWLEDGEMENTS

The authors thank CAPES, CNPq, UNESP-Bauru, Embrapa Forests and UEPG.

7. REFERENCES

CAVALLINI, C. M.; FRANCO, C. M. L. Effect of acid-ethanol treatment followed by ball milling on structural and physicochemical characteristics of cassava starch. **Starch/Stärke**, v. 62, p. 236-245, 2010.

HORNUNG, P. S.; OLIVEIRA C. S. de; LAZZAROTTO, M.; LAZZAROTTO, S. R. S.; SCHNITZLER, E. Investigation of the photo oxidation of cassava starch granules: Thermal, rheological and structural behavior. **Journal of Thermal Analysis and Calorimetry**, 20 May 2015. First on line. doi: http://dx.doi.org/10.1007/s10973-015-4706-x.

HUANG, Z. Q.; XIE, X. L.; CHEN, Y.; LU, J. P.; TONG, Z. F. Ball-milling treatment effect on physicochemical properties and features for cassava and maize starches. **Comptes Rendus Chimie**, v. 11, p. 73-79, 2008.

IONASHIRO, M.; CAIRES, F. J.; GOMES, D. J. C. **Giolito**: Fundamentos da termogravimetria e análise térmica diferencial/ calorimetria exploratória diferencial. 2. ed. São Paulo: Giz Editorial, 2014. 191 p.

LIN, J. H.; SINGH, H.; WEN, C. Y.; CHANG, Y. H. Partial-degradation and heat-moisture dual modification on the enzymatic resistance and boiling-stable resistant starch content of corn starches. **Journal of Cereal Science**, v. 54, p. 83-89, 2011.

SANDHU, K. S.; SINGH, N. Some properties of corn starches II: Physicochemical gelatinization, retrogradation, pasting and gel textural properties. **Food Chemistry**, v. 101, p. 1499-1507, 2007.

SHIN, S. I.; LEE, C. J; KIM, M. J.; CHOI, S. J.; CHOI, H. J.; KIM, Y.; MOON, T. W. Structural characteristics of low-glycemic response rice starch produced by citric acid treatment.

Carbohydrate Polymers, v. 78, p. 588-595, 2009.

ZHANG, W.; DING, W.; NDEURUMI, K. H.; WANG, Z.; FENG, Y. Effect of wet ball milling on physicochemical properties and crosslinking reaction performance of corn starch. **Starch/Stärke**, v. 67, p. 958-963, 2015.