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EFFECT OF ACID ALCOHOLIC SOLUTION IN WAXY MAIZE STARCH TREATMENT

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Resumo

O amido é o polissacarídeo mais abundante presente em plantas, composto por amilose e amilopectina. O amido de milho ceroso apresenta somente amilopectina. A modificação do amido é recomendada para melhorar suas aplicações. A hidrólise ácida é utilizada para alterar as propriedades físico-químicas sem modificar o grânulo e o meio alcoólico ajuda na recuperação da molécula após o tratamento. O objetivo do trabalho foi o tratamento químico com HCl 0,5 mol L^{-1} durante 1 hora em 100 ml de água, etanol ou metanol. Os equipamentos SETSYS Evolução TGA-DTA / DSC e Rápido Visco-Analisador (RVA-4) foram usados para avaliar as alterações dos amidos. As curvas TG mostraram três eventos (desidratação, estabilidade e decomposição), com resultados similares para todas as amostras. Este resultado pode estar relacionado a resistência da amilopectina para a hidrólise ácida. Na análise reológica (RVA) o tratamento das amostras mostrou valores mais baixos de perfis de viscosidade. A solução ácida forneceu mudanças nas propriedades de pasta do amido e a solução etanólica (solvente mais apolar) foi maior que as demais soluções. Conclui-se portanto que o tratamento dos amidos forneceu produtos com características térmicas similares e com diferentes respostas mecânicas.

Palavras-chave: Amido tratado com ácido, análises térmicas, TG/DTG, amido de milho ceroso.

Abstract

Starch is the most abundant polysaccharide found in plants, composed by amylose and amylopectin. The waxy maize starch has only amylopectin. Modification of starch is recommended to improve their applications. Acid hydrolysis is used to alter the physicochemical properties without changing the bead and the alcoholic medium helps in the recovery of the molecule after treatment. The aim was the chemical treatment with HCl 0.5 mol L^{-1} for 1 hour in 100 ml of water, ethanol or methanol. The equipment SETSYS Evolution TGA-DTA / DSC and Rapid Visco-Analyzer (RVA-4) was used to evaluate the starches modifications. The TG curves showed three events (dehydration, stability and decomposition), with similar results for all samples. This result may be related to resistance of amylopectin to the acid hydrolysis. In the rheological analysis (RVA) the treated samples showed lower values of the viscosity profiles. The acid solution supplied changes in the starch paste properties and ethanolic solution (solvent more polar) was higher than the other solutions. Concludes therefore that the starches treatment provided products with similar thermal characteristics and with different mechanical responses.

Keywords: Acid treated starch, thermal analysis, TG/DTG, waxy maize starch.

1. INTRODUCTION

Starch is a principal carbohydrate in cereals, tubers and roots. It is composed of amylose (around 20 - 25 %) and amylopectin (around 75 - 80 %). This natural polymer is extracted for many industrial applications such as food, paper, textiles, chemicals and pharmaceuticals (JIMÉNEZ et al., 2012, HORNUNG, P. S. et al., 2015). Maize starches are used in the industry because have low cost and

good natural characteristics. The waxy maize is a product of a genetic improvement made and cultivated in the East and Southeast Asia. Nevertheless, with the intent to improve the technological quality of waxy maize is important to clarify the changes that occur in starch properties during the development of the kernel (KETTHAISONGA, D. et al., 2013). The native starch generally has a low structural resistance and is functionally restricted to certain types of industrial processing. Already the modified starch has the purpose of overcome these limitations, occurring by chemically, physically and/or enzymatically. Among chemical modifications, acid hydrolysis has been widely used because it alters the physicochemical properties of the starch without causing changes in the granule structure. The use of an alcoholic solution besides presenting high recovery of the molecule after acid treatment spends a minor amount of this reagent in the process (HORNUNG, P. S. et al., 2015, LIN, J. H.; LEE, S. Y.; CHANG, Y. H., 2003). As part of the techniques used for starch analysis, the Thermogravimetry (TG) can provide information about the thermal stability of the sample composition, thermal decomposition and composition of the waste (IONASHIRO, M.; CAIRES, F. J.; GOMES, D. J. C., 2014). Already the rheological analysis can monitor the viscosity of the starch paste, and detecting differences in characteristics (HIGLEY, J. S. et al., 2003).

2. OBJECTIVES

The aim was the chemical treatment with HCl 0.5 mol L^{-1} in aqueous or alcoholic solutions. The samples were evaluated using thermal analytical techniques (SETSYS Evolution TGA-DTA / DSC) and Rapid Visco-Analyzer (RVA-4).

3. MATERIAL AND METHODS

Maize starch was bought in Colombo, PR. For acid treatment the starch was divided into four parts each 15g (dry basis). One sample was selected as native sample (a). Three samples were treated with HCl 0.5 mol L^{-1} for 1 hour in 100 ml of water (b), ethanol (c) or methanol (d). These samples were filtered and washed with water until total acid elimination (use of silver nitrate 0.05 mol L^{-1}). The starches were dried for 24 hours in oven at 40 °C and placed in a desiccator. The Setsys Evolution TGA-DTA / DSC (Setaram, France) was used for TG and DTG analysis. The samples were heated from 30 ºC to 650 ºC using open alumina crucibles with 10.2250 ± 0.1258 mg of the sample under argonium flow of 50 mL min^{-1} at a heating rate of 10 ºC min^{-1}. To analyze the rheology of starch a viscometer (Newport Sci., Model RVA-4, Australia) was used. A suspension of about 3 g of starch with 25 grams of distilled water was prepared. This suspension remained in the machine for 23 minutes in total in different cycles of temperature and controlled time.

4. RESULTS AND DISCUSSION

The Thermogravimetry curves (TG/DTG), Figure 1, show the first event (dehydration) followed by a period of stability. The second event refers to the decomposition of organic matter, leaving some carbonaceous residues: (a) 23.47%, (b) 24.69%, (c) 18.48% e (d) 21.59%. The TG/DTG results were similar for all samples, Table 1. This result suggested that the amylopectin had resistance to acid hydrolysis because the dense packing of starch chains does not readily for the H_3O^+ into the regions (intramolecular cleavange) (MIAO, M. et al., 2011). In the rheological analyses the samples showed differences, Table 1. The treatment with ethanolic solution (more apolar solvent) showed differences compared with the aqueous and methanol solutions (more polar solvents) in the RVA curves, Figure 2. Similar behavior of pasting properties was found for cassava and waxy maize starches modified with HCl in aqueous solution. The H_3O^+ ions from HCl in an aqueous solution broke glucosidic bonds (intermolecular cleavange) of the starch changing the reologic properties of the granule (BENINCA, C. et al., 2013, DE OLIVEIRA, C. S. et al., 2014).

Table 1 – TG and RVA: native maize starch (a), modified by HCl 0.5 mol L^{-1} water (b), ethanol (c) and methanol (d).

Sample	TG Results		DTG Results		Pasting Temp	Viscosity Peak	Peak Time	Setback	Break	Final Viscosity
	Step	Δm(%)	ΔT/ºC	Tp/ºC	(ºC)	(cP)	(s)	(cP)	(cP)	(cP)
(a)	1st	5.19	68 - 110	86.69	71,5	2812	5,93	173	1642	1343
	Stability	-	110 - 283	-						
	2nd	62.48	283 - 339	310.68						
(b)	1st	4.80	74 - 110	88.15	71,05	1545	5,93	110	1039	616
	Stability	-	110 - 284	-						
	2nd	61.46	284 - 338	312.15						
(c)	1st	6.75	70 - 112	86.97	71,9	467	5,73	46	337	176
	Stability	-	112 - 282	-						
	2nd	65.70	282 - 339	312.43						
(d)	1st	5.67	72 - 113	87.68	70,7	1472	5,87	56	963	565
	Stability	-	113 - 282	-						
	2nd	63.54	282 - 338	310.79						

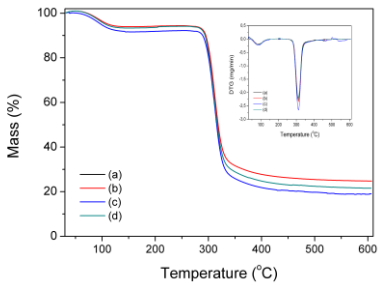

Figure 1 - TG and DTG curves: native maize starch (a), modified by HCl 0.5 mol L^{-1} water (b), ethanol (c) and methanol (d).

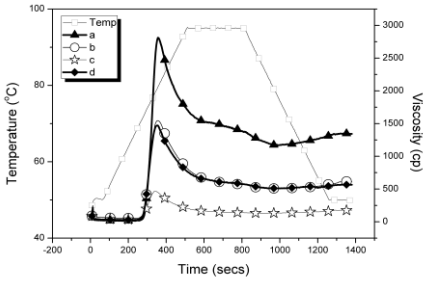

Figure 2 – RVA curves: native maize starch (a), modified by HCl 0.5 mol L^{-1} water (b), ethanol (c) and methanol (d).

5. CONCLUSION

The TG curves show two events of mass losses (dehydration, stability and decomposition), similar results for all samples. This result had relation with waxy starch composition (only amylopectin) and the possible resistance to acid hydrolysis. However, by rheological analysis differences between samples were found. These results show that the starches modifications provide products with similar thermal characteristics and with different mechanical responses.

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