EFFECT OF TREATMENT WITH HCl/ALCOHOLIC IN THE MODIFICATION OF CORN STARCH

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Abstract

Corn is the cereal most produced in the world. Corn starches were modified by HCl 0.1 mol L^{-1} in alcoholic and aqueous solutions. Three mass losses can be observed in the degradation process using TG-DTG curve. The native and treated starches samples don't show differences in the stability region. With DSC curves were observed lower values of the ΔH of gelatinization of the modified starch by HCl in the alcoholic solutions. The modifications using alcoholic solutions demonstrated a good alternative to obtain modifies starches.

Keywords: Acid modified starch, thermal analysis, TG-DTG.

Introduction

Starch is the most abundant storage polysaccharides in plants. It is principally used as a source of carbohydrates in the human diet and as a food ingredient. The starch molecule is composed of polymers amylose (20-25%) and amylopectin (70-75%), this relationship varies according to the starch source [1,2].

Corn starch has great interest to the food industry due to characteristics such thickening and gelling agents, providing volume and water retention. However, native starch has low thermal and shear resistance, thermal decomposition and higher tendency to retrogradation. The way to avoid these negative effects is modifying starch. The possible modifications may be chemical, physical or enzymatic. These macromolecules are extracted for use in the food, paper, chemical and pharmaceutical industries [3-6].

The starch modification using acid-alcoholic treatment allows hydrolysis/degradation more efficient. This modification provides a high recovery and a control of granule of the degradation molecule together with minor changes in their structure. This recovery is about 90% after acid-alcoholic modification. [7].

Thermal analysis is applied in the characterization of various raw materials. The thermogravimetry analysis (TG-DTG) can be helpful to show the behavior of starch granules when heating leads to depolymerization. The Differential Scanning Calorimetry (DSC) can provide data about the gelatinization process that occurs when the starch is heated in the presence of water [8,9].

Objectives

The objective was to evaluate the effects of the modification of corn starch by HCl 0.1 mol L^{-1} in alcoholic and aqueous solutions. The characterization of the starches was using TG-DTG and DSC.

Material and Methods

Corn starch was bought in Colombo, PR. Following the literature methodology [10] with modifications. The starch was divided into four parts of 20 g (dry basis). One of these was maintained as received and was designated the (a) untreated sample. The other three samples were treated for 60 min with

HCl 0.1 mol L^{-1} in aqueous solution (b), ethanolic solution (c) and methanolic solution. The modified starches were washed and filtered until the complete elimination of the reagent. The presence of HCl in the filtrate was performed dripping drops of silver nitrated 0.05 mol L^{-1}. The starches were dried in an oven with air circulation at 40 °C for 24 hours. The samples were stored in a desiccator until constant mass.

The TG-DTG were obtained using the TGA-50 (Shimadzu, Japan). Samples were heated in alumina crucibles with heating from 20 ºC to 650 ºC, with an air flow of 150 mL min^{-1}. The initial mass of the samples were about 7-12 mg. The heating rate was 10 ºC min^{-1}. All mass loss percentages were identified by the analysis software TA 60WS (Shimadzu, Japan) [11].

The DSC curves were obtained from the DSC Q200 (TA Instr., USA). The conditions used were: air flow of 50 mL min^{-1}, heated from 25 to 100 °C at rate 10 °C min^{-1}. The samples weighed about 2.5 mg. The proportion of water/starch was 1:4 (w/w - water/weight). The aluminum pans were sealed and the results evaluated using the Universal Analysis 2000 software (TA Instr., USA). The instrument was previously calibrated with 99.99 % purity Indium, melting point of Tp. = 156.6 ºC, $\Delta H = 28.56$ J.g^{-1} [12].

The analysis of variance (ANOVA) and Tukey's test were used to compare sample means at 95% confidence level ($p<0.05$) using SASM-Agri 8.2 software.

Results and Discussion

The expected modification in the reaction of the starch with HCl is hydrolysis/degradation. In the thermogravimetry (TGA / DTG), Figure 1, that the first mass loss is the dehydration, followed by a stability. The second and third losses are due to the decomposition and degradation of organic matter, leaving ashes only: (a) 0.83%, (b) 1.09%, (c) 0.55% and (d) 0.18%.

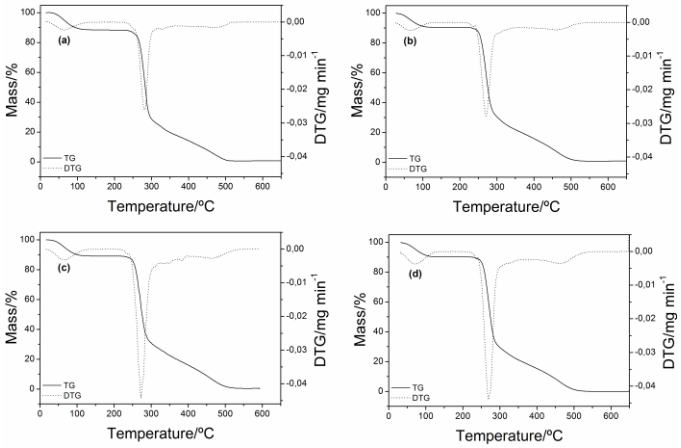

Figure 1 - TG-DTG curves for starches samples native (a) and modified by HCl 0.1 mol L^{-1} in water (b), HCl 0.1 mol L^{-1} in ethanol (c) and HCl 0.1 mol L^{-1} in methanol (d).

In the DTG curves the samples (c) and (d) showed a high peak at the second loss of the mass. This may mean that the hydrolysis was most effective in these samples. The temperature of the third losses of the mass at the treated samples were highest than native sample, showing the thermal stability of the modified starches samples.

The DSC curves, Figure 2, which shows gelatinization of the samples (endothermic peaks). It was observed a slight shift of the curve to the left to the modified samples because these samples the

gelatinization phenomenon began and ended at lower temperatures when compared to native sample (a). The variation of To (ºC) was 66.30 (a) to 65.31 (d) and ΔH_{gel} ($J.g^{-1}$) was 11.53 (a) to 9.39 (d). The results of parameters To, Tp, Tc and ΔH_{gel} were significantly lower for all treated samples. The modification of starches with HCl in water, ethanol and methanol reduce the energy spent for the gelatinization process.

Table 1 - Values obtained by TG-DTG curves for starches samples native (a) and modified by HCl 0.1 mol L^{-1} in water (b), HCl 0.1 mol L^{-1} in ethanol (c) and HCl 0.1 mol L^{-1} in methanol (d).

Sample	TG Results		DTG Results	
	Step	*Δm*/%	*ΔT*/°C	*Tp*/°C
(a)	1st	11.49	30-135	64.17
	stability	-	135-206	-
	2nd	71.26	206-374	281.10
	3rd	16.42	374-524	467.58
(b)	1st	9.51	30-131	65.33
	stability	-	131-208	-
	2nd	69.11	208-356	270.73
	3rd	20.30	356-552	462.95
(c)	1st	10.82	30-136	65.38
	stability	-	136-206	-
	2nd	72.55	206-396	272.30
	3rd	16.09	396-547	462.59
(d)	1st	9.79	30-134	71.62
	stability	-	134 - 209	-
	2nd	69.88	209-358	268.88
	3rd	20.16	358-549	460.85

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

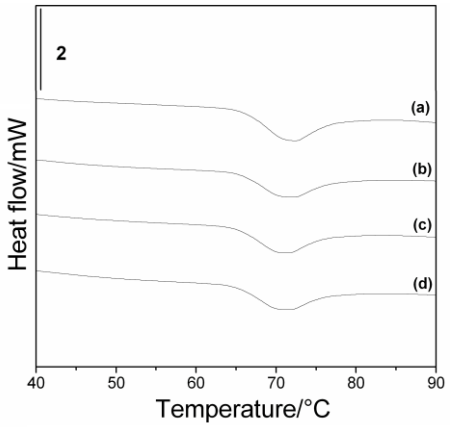

Figure 2 - Curves obtained for the DSC of starches samples native (a) and modified by HCl 0.1 mol L^{-1} in water (b), HCl 0.1 mol L^{-1} in ethanol (c) and HCl 0.1 mol L^{-1} in methanol (d).

Conclusion

The starches modifications were effective. This was showed by increase at speed the second mass losses in the TG-DTG. The temperature of the third mass losses at the treated samples were highest than native sample. Through of DSC were observed that the temperatures (To, Tp e Tc) and the enthalpy decreased in the modified starches samples.

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