TG-DTA AND DSC INVESTIGATIONS OF "PINHÃO" STARCH MODIFIED BY CALCIUM HYPOCHLORITE AND UV LIGHT

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Abstract

Starches, when in its native forms, usually do not have the characteristics required for industrial processing. "pinhão", a seed from the *Araucaria angustifolia* tree, has starch as main presenting as a great alternative source of starch. Samples of native "pinhão" starch were treated with standard calcium hypochlorite solutions (0.1, 0.2 and 0.5 mol L^{-1}) and exposed for one hour under UV light. The modification process applied altered the thermal behavior of the "pinhão" starch as the TGA-DTA and DSC results presented.

Keywords: *$Ca(ClO)_2$, Araucaria angustifolia, "pinhão" starch, oxidation, UV light*

Introduction

Araucaria angustifolia, a pine tree that is found in southern Brazil is at risk of extinction due to excessive extraction for commercial purposes. Its seeds, "pinhão", has starch as main constituent nearly 72 % on dry basis presenting as a great alternative source of starch. For this reason, the development of sustainable use of "pinhão" can further assist on the conservations of the species [1].

Starch is a semi-crystalline polymer principally composed of two macromolecules, amylose and amylopectin. Mainly as a linear polymer, amylose has α-1,4 linked glucose, while amylopectin is a highly branched polysaccharide consisting of α-1.4 linked glucose with α-1,6 linkages at the branch points [2].

There are several modifications techniques applied to native starches performing functional properties of thickening, gelling, adhesion and/or film formation [3]. During the oxidation process, the hydroxyl groups of starch molecules are oxidized to carbonyl groups [4, 5, 6]. The combination of modification methods can accelerate the process, and the UV radiation can induce changes in properties of starches [4, 5, 6].

Objectives

The objective was to investigate the thermogravimetric profile of the "pinhão" starch modified by a combined method of calcium hypochlorite solutions and ultraviolet light exposure.

Materials and Methods

The native "pinhão" starch (200 g) was bought in Colombo, PR, Brazil. The starch was divided into four parts of 50 g (dry basis). One was maintained as received (N). The others were treated following the literature methodology [2, 4]. The starches were treated for one hour with exposure in ultraviolet light (λ = 256 nm) simultaneously with standard $Ca(ClO)_2$ solutions, 0.1 mol L^{-1} (a), 0.2 mol L^{-1} (b) and 0.5 mol L^{-1} (c). The samples were filtered, washed, dried and kept on a dissector until the moment of the analysis.

The thermogravimetry and differential thermal analysis (TG-DTA) curves were obtained using a thermal analysis system (Shimadzu, DTG-60H model); the samples were heated from 30 ºC to 600 ºC using open alumina crucibles with approximately 5.0 mg of the sample under a nitrogen flow of 150 $mL.min^{-1}$ at a

heating rate of 10 ºC min^{-1}. The instrument was preliminarily calibrated with standard weight and with standard calcium oxalate monohydrate. All mass loss percentages were determined using TA-60 WS data analysis software by determining the derivative termogravimetric analysis (DTG) [2, 4].

The DSC curves were obtained using a thermal analysis system (TA-Instruments, DSC-Q200 model, USA). The DSC curves were recorded under an air flow of 50 mL.min^{-1}, heating rate of 10 ºC min^{-1} and the samples weighed about 2.5 mg. The 4:1 (water:starch w/w) mixture was prepared and maintained for 60 minutes in order to equilibrate the moisture content. The aluminum crucibles were sealed and then the curves were performed. The instrument was previously calibrated with 99.99 % purity Indium, melting point of T_p. = 156.6 ºC, ΔH = 28.56 J.g^{-1} [2, 4].

Results and Discussion

The TG-DTA curve of the sample (N), Figure 1, showing a well marked exothermic event (similar profiles of treated samples) at approximately 307 ºC to 315 ºC (2^{nd} event Table 1). The first event that corresponds to endothermic peak (evaporation of the water and volatile compounds) followed by stability. Once dehydrated, the second and third main regions were due to the degradation of the organic matter and the formation of ash. Similar behaviors were found in earlier works [7, 8]. All the obtained values are shown on Table 1.

The determination of moisture can be successfully analyze by TG technique been observed in a few minutes on a temperature range of 30 to 150 ºC [9]. Costa et al [7] verified the same characteristics of native starches of seeds of *Araucaria angustifolia* from four provenances. It can also be verify in Table 1, that the stability values didn't differ significantly from the sample (N) to the modified ones. This result demonstrates that the modification by $Ca(ClO)_2$ +UV changed the thermal properties of the "pinhão" starch.

Table 1. TG and DTA results of: (N) native "pinhão" starch; (a; b; c) native "pinhão" starch treated with $Ca(ClO)_2$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Samples	TG Results		DTA Results	
	Step	Δm/%	ΔT/ºC	Tp/°C
(N)	1st	13.02	30 - 133	59.26 (ENDO)
	stability	-	133 - 209	-
	2nd	71.99	209 - 424	315.60 (EXO)
	3rd	13.25	424 - 576	510.64 (EXO)
(a)	1st	13.29	30 - 150	59.03 (ENDO)
	stability	-	150 - 213	-
	2nd	71.48	213 - 397	310.07 (EXO)
	3rd	13.91	397 - 544	485.13 (EXO)
(b)	1st	11.57	30 - 152	66.15 (ENDO)
	stability	-	152 - 219	-
	2nd	73.33	219 - 403	307.25 (EXO)
	3rd	14.32	403 - 582	488.85 (EXO)
(c)	1st	13.07	30 - 147	57.68 (ENDO)
	stability	-	147 - 208	-
	2nd	74.33	208 - 395	310.32 (EXO)
	3rd	11.29	395 - 567	477.77 (EXO)

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

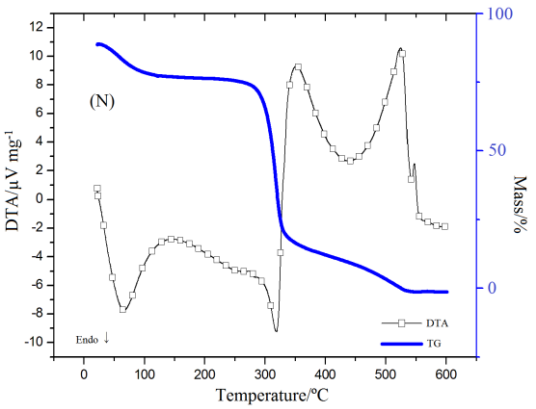

Figure 1. TG-DTA curves of the native "pinhão" starch (N).

Regarding the thermograms (Figure 2), it can be seen that they are very different between the (N) and the modified ones, (a) and (b), it can be said that the modification process applied altered the thermal behavior of the "pinhão" starch. Observing the presented results, when compared with the (N) native sample, the onset temperatures (T_o), Table 2, showed a slight decrease for samples (a) and (b) and an increase for sample (c). However, the peak temperatures (*Tp*) presented an increase for (b) and (c) that significant differ from the (N) sample. The calculated gelatinization enthalpy (ΔH_{gel}) for the modified samples showed a high decrease in comparing with the result observed for the (N) sample, enhancing sample (a) that presented the lower value. These results characterize that the modification of the thermal behavior occurred. Similar and even lowest values for enthalpy were found in the literature [10]. The reduction in ΔH_{gel} can be attributed to degradation of the starch chains caused by modification. Consequently, less energy was needed to gelatinize starch [11].

Table 2. DSC gelatinization, of (N) native "pinhão" starch; (a; b; c) native "pinhão" starch treated with $Ca(ClO)_2$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Samples	DSC gelatinization			
	***To*/ºC**	***Tp*/ºC**	***Tc*/ºC**	**ΔH_{gel}/J.g$^{\pm 1}$**
(N)	59.08±0.04^{b}	66.02±0.05^{a} (ENDO)	75.54±0.03^{a}	14.64±0.02^{c}
(a)	58.25±0.55^{a}	66.00±0.30^{a} (ENDO)	78.54±0.29^{b}	6.48±0.55^{a}
(b)	58.21±0.64^{a}	67.19±0.34^{b} (ENDO)	79.15±0.45^{b}	7.28±0.05^{b}
(c)	60.59±0.25^{c}	67.52±0.43^{b} (ENDO)	81.68±0.23^{c}	7.54±0.39^{b}

(*) *To* "onset" initial temperature, *Tp* peak temperature, *Tc* "endset" final temperature, ΔH_{gel} gelatinization enthalpy.
(**) different letters in the same column represents significative difference according to Duncan test ($p<0.05$).

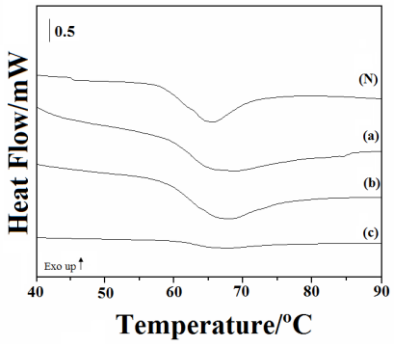

Fig. 2 DSC gelatinization curves: (N) native "pinhão" starch; (a; b; c) native "pinhão" starch treated with $Ca(ClO)_2$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Conclusions

Considering the obtained results, "pinhão" starch presented distinct thermal profile after the modification process with simultaneous action of calcium hypochlorite and ultraviolet light. The peak temperatures (DSC) were shifted to higher values and the gelatinization enthalpy decreased.

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