SIMULTANEOUS TG-DTA AND DSC TECHNIQUES ON PINHÃO STARCH DOUBLE MODIFIED

[1]Polyanna Silveira Hornung, [1]Simone Rosa da Silveira Lazzarotto, [1]Cristina Soltowski de Oliveira, [2]Marcelo Lazzarotto, [1]Egon Schnitzler (polyanna14silveira@gmail.com)
[1]Universidade Estadual de Ponta Grossa. Av. Carlos Cavalcanti, 4748 - CEP 84.030-900 - Ponta Grossa - PR – Brasil.
[2]EMBRAPA Florestas - Estrada da Ribeira, KM 111 - P.O. Box 319 - CEP 83.411-000 - Colombo, PR- Brasil.

Abstract

The "pinhão" is the seed of *Araucaria angustifolia* (known as Paraná pine). This specie is in danger due to reckless exploration. Thus, the development of new applications could motivate its preservation. Samples of native "pinhão" starch were oxidized with standard NaClO solutions (0.1, 0.2 and 0.5 mol L^{-1}) and exposed for one hour under UV light (UVC radiation with $\lambda = 256$ nm). The TG curves showed similar behavior. The oxidative modification caused a decrease in the gelatinization enthalpy (DSC).

Keywords: *TG/DTA, DSC, Starch, Oxidation, UV light*

Introduction

Parana tree *(Araucaria angustifolia)* belongs to conifer group. The seeds ("pinhão") are use on food preparations [1]. Araucaria is endangered due to irresponsible extraction. Developing researches for coherent use of Araucaria derived products could motivate the conservation of the species [2]. The mainly composition of the "pinhão", in wet basis, includes: starch (36 %), proteins (3 %), lipids (1 %) [3, 4].

Starch granules are made up of two macromolecules, amylose (linear) and amylopectin (branched). Amylose presenting a α 1,4-linked glucose, while amylopectin consisting of α 1,4 -linked glucose with α 1,6- linkages at the branch points [5].

The modifications seek to improve the native starch and a well-known technique is the oxidative modification [6]. The starches can be modified by oxidant agents such as sodium hypochlorite, hydrogen peroxide, periodic acid and potassium permanganate among many others [5, 6]. The technique applying ultraviolet irradiation of starch could leads to a depolymerisation. A relevant study [7] found that the treatment of starch with UV light induced changes such as increased water binding capacity and solubility.

The thermogravimetry analysis (TGA) can show the behavior of starch granules when heating leads to depolymerization. The differential scanning calorimetry (DSC) is used to investigate the phase transitions of starch/water systems (gelatinization process) and the estimation of transition enthalpies [8]. The starch gelatinization properties have an important role on developing food processing and new products [9].

Objectives

The aim was to study the thermal behavior of the modified "pinhão" starch by the sodium hypochlorite solutions (NaOCl) with simultaneously exposure to ultraviolet light by TG-DTA and DSC.

Materials and Methods

The starch native "pinhão" starch (200 g), was divided into parts of 50 g (dry basis). One was maintained as received (N). The others were treated following the literature methodology [5, 6] with modifications. The "pinhão" starches were treated for one hour with exposure in ultraviolet light (λ = 256 nm) simultaneously with standard sodium hypochlorite (NaOCl) 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}. All mass loss percentages were determined using TA-60 WS data analysis software [5, 6]. The DSC curves were obtained using a thermal analysis system (TA-Instruments, DSC-Q200 model, USA), 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 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} [5, 6].

Results and Discussion

The TG-DTA profile curves, Fig. 1, showed an endothermic peak in the DTA curves in the first event. This is attributed to the evaporation of the water and volatile compounds, followed by stability of the anhydrous compounds. The second and third regions in the TG curves were due to the degradation (second endothermic peak in DTA profiles) of the organic matter (amylose) and the pyrolysis of the organic matter associated with the two last exothermic peaks observed in the DTA curves. Samples (a, b, c) show a slight endothermic peak for the second event and a higher exothermic peak for the third event (DTA curves profiles), different from to the (N) sample. By these results it can be said that the modification applied generated compounds more stable on thermal basis, forming functional groups with strong internal and external molecular bonds. Similar behavior was found in earlier works [1, 4]. The TG-DTA results are shown in Tab. 1.

Table 1: TG and DTG results of: untreated starch (N); treated starch with UV-light and NaClO standard solutions 0.1 mol L^{-1} (a); 0.2 mol L^{-1} (c) and 0.5 mol L^{-1} (c).

Samples	TG Results		DTG 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	14.88	30 - 159	53.28 (ENDO)
	stability	-	159 - 246	-
	2nd	72.76	246 - 403	308.16 (EXO)
	3rd	11.13	403 - 587	512.54 (EXO)
(b)	1st	13.08	30 - 126	58.93 (ENDO)
	stability	-	126 - 245	-
	2nd	73.04	245 - 391	309.51 (EXO)
	3rd	12.10	391 - 551	524.75 (EXO)
(c)	1st	13.57	30 - 142	60.84 (ENDO)
	stability	-	142 - 243	-
	2nd	68.79	243 - 393	308.24 (EXO)
	3rd	15.85	393 - 550	527.91 (EXO)

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

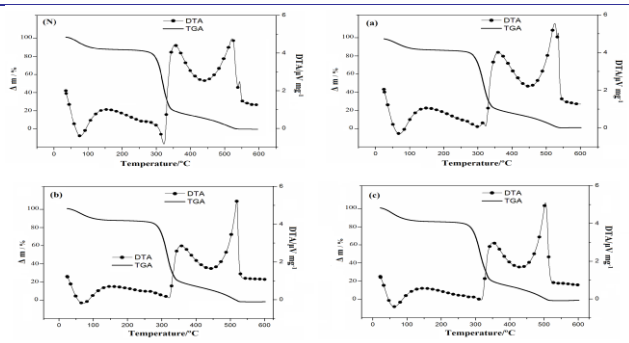

Figure 1 TG/DTG curves: untreated starch (N); treated starch with UV-light and NaClO standard solutions 0.1 mol L^{-1} (a); 0.2 mol L^{-1} (c) and 0.5 mol L^{-1} (c).

The DSC curves profiles, Fig. 2, show the variation of *To* (ºC) was 59.08 (N) to 54.30 (c), Tab. 2, with these results conclude that initial temperature of gelatinization were inversely proportional to the increase of the NaClO concentration in the starches modification. The same is observed in peak temperature *Tp* (endothermic event) that range was 66.02 (N) to 63.55 (c). The (*Tc*) results, didn't present significant differences for the modified samples (a) and (c) comparing to the (N) sample and the range was 75.54 (N) to 72.60 (b). The oxidation process applied promoted a high reduction in gelatinization enthalpy (ΔH_{gel}) where the value from 14.64 J g^{-1} for the (N) sample dropped to 4.40 J g^{-1} for sample (b), treated with 0.2 mol L^{-1} (NaOCl). 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 [10].

Table 2: DSC gelatinization results of: untreated starch (N); treated starch with UV-light and NaClO standard solutions 0.1 mol L^{-1} (a); 0.2 mol L^{-1} (c) and 0.5 mol L^{-1} (c).

Samples	DSC gelatinisation			
	***To*/ºC**	***Tp*/ºC**	***Tc*/ºC**	**ΔH_{gel}/J g^{-1}**
(N)	59.08±0.04^{c}	66.02±0.05^{c} (ENDO)	75.54±0.03^{b}	14.64±0.02^{d}
(a)	58.42±0.03^{c}	65.57±0.03^{c} (ENDO)	75.47±0.06^{b}	9.67±0.03^{c}
(b)	55.73±0.06^{b}	64.55±0.08^{b} (ENDO)	72.60±0.13^{a}	4.40±0.14^{a}
(c)	54.30±0.10^{a}	63.55±0.09^{a} (ENDO)	74.75±0.42^{b}	5.25±0.03^{b}

(*) *To* "onset" initial temperature, *Tp* peak temperature, *Tc* "endset" final temperature, ΔH_{gel} gelatinization enthalpy. (**) Different letters of the same column differ statistically according with Duncan test ($p<0.05$).

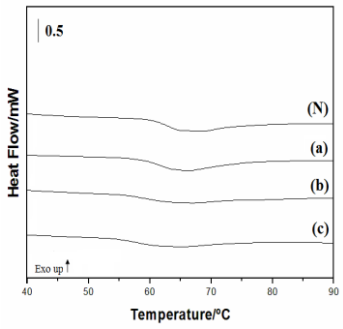

Figure 2 DSC gelatinization curves: untreated starch (N); treated starch with UV-light and NaClO standard solutions 0.1 mol L^{-1} (a); 0.2 mol L^{-1} (c) and 0.5 mol L^{-1} (c).

Conclusions

The modifications applied by the treatment with sodium hypochlorite (NaOCl) solutions for one hour of simultaneously exposure in ultraviolet light (λ = 256 nm) originated starches thermally more stable.

Acknowledgements

EMBRAPA-Brazil, CAPES-Brazil and CNPq-Brazil.

References

[1] Costa FJOG, Leivas CL, Waszczynsky N, Godoi RCB, Helm CV, Colman TAD, Schnitzler E. Characterization of native starches of seeds of *Araucaria angustifolia* from four germplasm collection. Thermochim. Acta. 2013; 565:172-77.

[2] Pinto NL, Vanier B, Klein ER, Zavareze MC, Elias LC, Helbig E, Dias ARG. Physicochemical, crystallinity, pasting and termal properties of heat–moisture-treated pinhão starch. Starch/Stärke. 2012; 64:855–63.

[3] Bello-Pérez LA, García-Suárez FJ, Méndez-Montealvo G, Do Nascimento JRO, Lajolo FM, Cordenunsi BR. Isolation and Characterization of Starch from Seeds of *Araucaria brasiliensis*: A Novel Starch for Application in Food Industry. Starch/Stärke. 2006; 58:283–91.

[4] Bicudo SCW, Demiate IM, Bannach G, Lacerda LG, Carvalho-Filho MAS, Ionashiro M, Schnitzler E. Thermoanalytical study and characterization of native starches of Paraná pine seeds (*Araucaria angustifolia*, Bert O. Ktze) and European chestnut seeds (*Castanea sativa* Mill). Eclet. Quim. 2009:34:7-12.

[5] Hornung PS, Granza AG, Oliveira CS, Lazzaroto M, Schnitzler E. Study of the effects of ultraviolet light and sodium hypochlorite solutions on properties of cassava starch granules. Food Biophysics. 2015;doi:10.1007/s11483-015-9402-7.

[6] Hornung PS, Oliveira CS, Lazzaroto M, Lazzarotto SRS, Schnitzler E. Investigation of the proto-oxidation of cassava starch granules. J Therm Anal Calorim. 2015;doi:10.1007/s10973-015-4706-x

[7] El-Sheikh MA, Ramadan MA, El-Shafie A. Photo-oxidation of rice starch. Part I: Using hydrogen peroxide. Carbohydr. Polym. 2009:80:266-269.

[8] Bicudo SCW, Demiate IM, Bannach G, Lacerda LG, Carvalho-Filho MAS, Ionashiro M, Schnitzler E. Thermoanalytical study and characterization of native starches of Paraná pine seeds (*Araucaria angustifolia*, Bert O. Ktze) and European chestnut seeds (*Castanea sativa* Mill), Eclet. Quim. 2009:34:7-12.

[9] Sangseethong K, Termvejsayanon N, Sriroth K. Characterization of physicochemical properties of hypochlorite- and peroxide-oxidized cassava starches. Carbohydr Polym. 2010:82:446-53.

[10] Klein B, Pinto VZ, Vanier NL, Zavareze ER, Colussi R, Evangelho JA, Gutkoski LC, Dias ARG. Effect of single and dual heat-moisture treatments on properties of rice, cassava, and pinhão starches. Carbohydr Polym. 2013:98:1578-84.