THERMAL TOOL IN THE EVALUATION OF THE "PINHÃO" (SEED OF *Araucaria angustifolia*) STARCH AIMED AGROINDUSTRIAL PROCESS

[1]Marcelo Lazzarotto, [2]Lucas Stiegler Ribeiro, [2]Layse do Prado Cordoba, [1]Rossana Catiê Bueno de Godoy, [2]Egon Schnitzler *marcelo.lazzarotto@embrapa.br*
[1]EMBRAPA Florestas - Estrada da Ribeira, KM 111 - P.O. Box 319 - CEP 83.411-000 - Colombo, PR- Brasil.
[2]Universidade Estadual de Ponta Grossa. Av. Carlos Cavalcanti, 4748 - CEP 84.030-900 - Ponta Grossa - PR – Brasil.

Abstract
"Pinhão" is an important source of food for inhabitants in the subtropical region of South America. Gelatinization temperatures for "pinhão" are smaller than for corn and cassava starches, bringing advantages in industrial processes. The "pinhão" starches of the 4 different provenances were subjected to dilutions of 1:4, 1:5 e 1:6, in water. The starches were evaluated using DSC to determine gelatinization characteristics of them. The results showed that the source and dilutions have influence in the gelation process of the starch.

Keywords: Differential Scanning Calorimetry, gelatinization process, pinhão starch.

Introduction
The "pinhão" is the seed of *Araucaria angustifolia*, typical tree of the South America. It has 84% of carbohydrate in dry matter. The chemical composition of the "pinhão" is: 7.9% protein, 5.1% fiber, 1.3% fat and 1.1% ash [1]. Despite the great commercial and cultural significance, the *Araucaria angustifolia* is endangered. This is due to uncontrolled exploitation of timber, cleared for territory expansion and limitations on self propagating the species [2]. In this context, targeting studies, conservation and sustainable use of genetic resources, germplasm banks were created, one being at EMBRAPA Forests in Colombo – PR [3].

Starch is the main energy reserve in plants. Its application, besides the food industry, is widespread in the pulp and paper industries, textile and others. This versatility is due its properties to form viscous gels and also to act as a stabilizer. Starch is composed of two chains, amylose and amylopectin. Amylose is linear and has α 1-4 glycosidic linkages; amylopectin has α 1-4 and α 1-6, with ramifications. The percentage of each of these chains causes the properties of starches from different botanical sources vary widely [3,4].

The Differential Scanning Calorimetry (DSC) is a thermal analysis applied in the characterization of raw materials. An example is the evaluation of the gelling process that occurs when the starch and water are heated. Can be determined the temperatures onset (T_o), peak (T_p) and end (T_c) and enthalpy involved in this process (ΔH_{gel}). Thermal properties of the starches are evaluated and compared with industrial conditions [5].

Objectives
This study aimed to extract and characterize samples of "pinhão" starch using DSC technique and study the influence of starch:water ratio in the gelling process.

Material and Methods
In this study, four different genetic materials trees were selected from the germplasm bank of Embrapa Forests, Colombo, PR, Brazil. The samples were identified and numbered from 1 to 4.

The extraction "pinhão" starch was carried out according to Pinto et al. [1], with some modifications: the husk has been removed, as well as the second film (thinner layer) that is adhered to the seeds. The isolated seeds were ground and equal volume of distilled water was added to this mass. After the samples were shaken for 5 minutes, were sieved (200 mesh) and the dispersion was centrifuged (5000 rpm, 4 °C, 10 min). The resulting starch was dried in an oven with air circulation at 35 °C and kept in desiccator with anhydrous calcium chloride until constant weight.

The DSC curves were obtained using a equipment DSC thermal analysis system-Q 200 (TA-Instruments, USA). The samples were hydrated in a test tube for half hour, with ratio starch:water varying at 1:4 (A) 1:5 (B) and 1:6 (C). The volume of 20µL of the suspension was added to the closed aluminum pan and curves were obtained. The conditions for obtaining the curve were: heating rate 10 °C min^{-1} from 20 °C to 100 °C with synthetic air flow of 50 mL min^{-1} [6].

All the results were analysed for variance (ANOVA) with the Tukey test to compare sample means at 95% confidence level ($p<0.05$) using SASM-Agri 8.2 software.

Results and Discussion

The gelling process occurs when the starch granules undergo heating in the presence of water, from an ordered to a disordered phase, forming the gel [7,8]. Other studies are found in the literature, analyzing the influence of starch:water ratio, and the influence of the amount of water in the gelling process [9,10]. It is observed that the differences in genetic material between the extracted starch lead to different results in the results of enthalpy of gelatinization (ΔH_{gel}). These results are shown in Table 1 where the highest values ΔH_{gel} of samples 1 and 2 were observed when the amount of water was more abundant (1C and 2C). The results of the ΔH_{gel} for samples 3 and 4 show the highest values in dilutions of 1:5 (3B and 4B).

Table 1. Values obtained from DSC for the four starch samples in its different dilutions. The proportions of starch:water ranging from 1:4 (A) 1:5 (B) and 1:6 (C)

Sample		DSC			
		T_o/°C	T_p/°C	T_c/°C	ΔH_{gel}/J g^{-1}
1	A	61.21±0.03^a	67.23±0.01^a	68.88±0.01^a	7.62±0.03^c
	B	60.56±0.02^b	65.96±0.01^c	68.01±0.01^b	8.22±0.06^b
	C	60.30±0.02^c	66.14±0.01^b	67.67±0.01^c	11.32±0.12^a
2	A	57.20±0.01^c	61.34±0.10^a	67.30±0.04^a	5.82±0.03^a
	B	57.36±0.04^b	61.38±0.01^a	64.20±2.46^{ab}	4.46±0.12^b
	C	57.47±0.01^a	61.41±0.01^a	63.00±0.04^b	5.88±0.10^a
3	A	56.40±0.01^a	61.42±0.02^b	62.92±0.01^c	7.27±0.10^c
	B	55.84±0.03^c	62.17±0.29^a	69.56±0.12^a	12.59±0.16^a
	C	56.13±0.01^b	61.37±0.01^b	67.19±0.02^b	9.57±0.04^b
4	A	52.85±0.01^b	58.15±0.02^b	62.10±3.11^a	7.90±0.04^b
	B	52.73±0.01^c	57.81±0.01^c	59.63±0.01^a	9.08±0.04^a
	C	53.63±0.02^a	59.03±0.02^a	60.47±0.01^a	7.90±0.31^b

* T_o "onset" initial temperature, T_p peak temperature, T_c "endset" final temperature, ΔH_{gel} gelatinisation enthalpy.

Different letters of the same sample differ statistically according with Tukey test ($p<0.05$) Altay and Gunasekaran [11] observed similar results for conventional and waxy maize starches. The results show increase in ΔH_{gel} value with the greatest amount of water in the preparation of the dispersions. Resio and Suarez [10] analyzed the influence of the water content in the amaranth starch gelatinization. They concluded that increasing the water content is directly proportional to the enthalpy of gelatinisation, until it reaches the maximum value, for reasons starch:water equal to or greater than 1:3. The gelatinization enthalpy is associated with the loss of molecular organization (double helix breaking), which justifies its linear variation with the water content. This means that the more water available, the greater the disorder generated in the starch structure, reaching stability in ΔH_{gel} value for water quantities above 70% [12].

The differences of the samples of "pinhão" were T_p values ranging from 57.81 ± 0.01 °C (Sample 4) and 67.23 ± 0.01 °C (Sample 1). This demonstrates how the botanical origin from which is extracted the starch has a strong influence on the properties. Costa et al. [3] observed similar behavior for "pinhão" samples from region of Ipiúna de Caldas and Irati. The literature also found 62.44 ± 0.02 °C values for T_p to "pinhão" starch from the region of Ponta Grossa – PR [13].

The ratio starch:water caused significant changes in the analyzed parameters, changing the ΔH_{gel}, influencing energy consumption in the process, the initial temperature (T_o), changing the initial gelatinization temperature, the conclusion temperature (T_c), which may prolong the process gelatinization. In Figure 1 show the variations of the DSC curves for the "pinhão" starch samples and different concentrations of water.

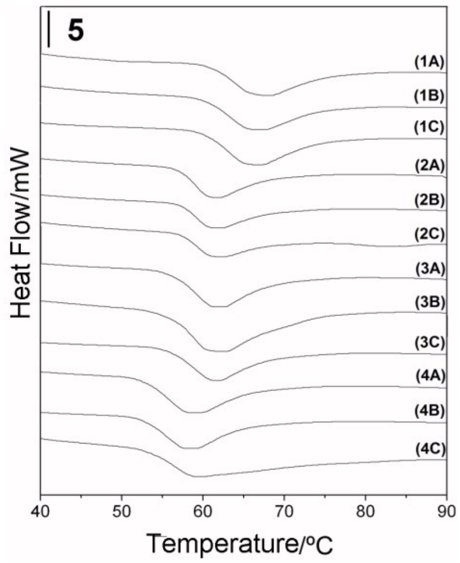

Figure 1. DSC curves obtained. The numbers represent which said sample is starch and the letters indicate the dilution made for analysis. As for the ratio starch:water 1:4 (A), 1:5 (B) and 1:6 (C).

Conclusion

The DSC curves allowed evaluating the temperatures involved in the gelling process, with significant variations between 4 different samples of "pinhão" starch. For all samples were found low temperatures onset for the "pinhão" starch, with the smallest value for the sample 4, indicating that the starch of this genetic material requires a less heating to gel and increase viscosity medium. From the industrial applications this feature is very interesting because it requires less energy to gel some product.

Acknowledgements

The authors thank for Araucária Foundation – PR, CAPES, CNPq and Embrapa Forestry.

References

[1] Pinto VZ, Vanier NL, Klein B, Zavareze ER, Elias MC, Gutkoski LC, Helbig E, Dias ARG. Physicochemical, crystallinity, pasting and thermal properties of heat-moisture-treated pinhão starch. Starch/Stärke 2012:64:855–863.

[2] Spada JC, Noreña CPZ, Marczak LDF, Tessaro IC. Study on the stability of β-carotene microencapsulated with pinhão (*Araucaria angustifolia* seeds) starch. Carbohydrate Polymers 2012:89:1166–1173.

[3] Costa FJOG, Leivas CL, Waszczynskyj N, Godoi RCB, Helm CV, Colman TAD, Schnitzler E. Characterisation of native starches of seeds of *Araucaria angustifolia* from four germplasm collections. Thermochimica Acta 2013:565:172–177.

[4] Bello-Pérez LA, García-Suárez FJ, Méndez-Montealvo G, 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 2006:58:283-291.

[5] Stephen H, Kelly M, Day L. Determination of the thermo-mechanical properties in starch and starch/gluten systems at low moisture content–A comparison of DSC and TMA. Carbohydrate polymers 2014:108:1-9.

[6] Oliveira CS, Andrade MMP, Colman TAD, Costa FJOG, Schnitzler E. Thermal, structural and rheological behaviour of native and modified waxy corn starch with hydrochloric acid at different temperatures. Journal of Thermal Analysis and Calorimetry 2014:115:13-18.

[7] Goñi O, Escribano MI, Merodio C. Gelatinization and retrogradation of native starch from cherimoya fruit during ripening, using differential scanning calorimetry. LWT - Food Science and Technology 2008:41:303–310.

[8] Bogracheva TY, Wang YL, Wang TL, Hedley CL. Structural Studies of Starches with Different Water Contents. Biopolymers 2002:64:268-281.

[9] Spigno G, Faveri DM. Gelatinization kinetics of rice starch studied by non-isothermal calorimetric technique: influence of extraction method, water concentration and heating rate. Journal of Food Engineering 2004:62:337–344.

[10] Resio AC, Suarez C. Gelatinization kinetics of amaranth starch. International journal of food science & technology 2001:36:441-448.

[11] Altay F, Gunasekaran S. Influence of Drying Temperature, Water Content, and Heating Rate on Gelatinization of Corn Starches. J. Agric. Food Chem. 2006:54:4235−4245.

[12] Lelièvre J, Liu H. A review of thermal analysis studies of starch gelatinization. Thermochimica Acta 1994:246:309-315.

[13] Ribeiro LS, Cordoba LP, Colman TAD, Oliveira CS, Andrade MMP, Schnitzler E. Influence of some sugars on the thermal, rheological and morphological properties of "pinhão" starch. Journal of Thermal Analysis and Calorimetry 2014:117:935-942.