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EFFECT OF THE $KMnO_4$ TREATMENT ON THE "PINHÃO" STARCH

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Resumo

O pinhão, sementes de *Araucaria angustifolia*, tem o amido como componente principal. Os amidos oxidados melhoram as características físico-química, de pasta e térmicas dos produtos em processos industriais. O amido de pinhão nativo foi tratado com soluções padronizadas de permanganato de potássio ($KMnO_4$) e amostras foram analisadas por técnicas termoanalíticas (TG-DTA) em atmosfera inerte. As amostras foram oxidadas da seguinte forma: quatro porções de 20 g (base seca) foram separadas e três foram suspensas em solução de $KMnO_4$ (0,001; 0,002; 0,005 mol L^{-1}) em agitação constante durante 30 minutos, a quarta amostra foi mantida como recebida. As suspensões de amido foram filtradas, lavadas, secas e analisadas. As modificações oxidativas provocaram mudanças estruturais das moléculas de amido, registradas pelos diferentes resultados calculados a partir das curvas TGA e DTA. A amostra (3) teve as mudanças mais significativas na degradação com o 3ª evento exotérmico com temperaturas acima de 330 °C.

Palavras-chave: modificação oxidativa, análises térmicas, atmosfera inerte, nitrogênio.

Abstract

The "pinhão", seeds of the Araucaria angustifolia, has the starch as main constituent. The oxidized starches improving physicochemical, paste and thermal characteristics of products in industrial processes. The native "pinhão" starch was treated with standardized solutions of potassium permanganate ($KMnO_4$) and the samples were analyzed by thermoanalytical techniques (TG-DTA) in inert atmosphere. The samples were oxidized as follows: four portions of 20 g (dry basis) were separated and three were suspended in $KMnO_4$ solution (0.001; 0.002; 0.005 mol L^{-1}) at constant stirring for 30 minutes, the fourth sample was kept as it was received. The starch suspensions were filtered, washed, dried and analyzed. The oxidative modifications promoted the structural changes of the starches molecules registered by the different results calculated from the TGA and DTA curves. The sample (3) had the most significant changes in the degradation with the 3rd exothermic event with temperatures above 330 °C.

Keywords: oxidative modification, thermal analysis, inert atmosphere, nitrogen.

1. INTRODUCTION

Araucaria angustifolia is found in southern Brazil and the excessive extraction for commercial purposes put this tree in risk of extinction. The sustainable use of "pinhão", seeds of the Araucaria angustifolia, can help on the conservations of the species. The starch is the main constituent of the "pinhão" (nearly 72 % on dry basis) (DAUDT et al., 2014). The use of oxidized starches in industrial processes improving physicochemical, paste and thermal characteristics of products (HORNUNG et al., 2015; KLEIN et al., 2014). For example, the oxidized starches can be applied in the paper industry promoting more bleaching and printing ink adherence. The more used oxidants of the starches are sodium hypochlorite, hydrogen peroxide and potassium permanganate (HORNUNG et al., 2015; KLEIN et al., 2014). In the oxidation reaction some hydroxyl groups (C2, C3 and C6), Figure 1, starches are first oxidized the carbonyl groups and consequently the carboxyl groups (SILVA et al., 2008). Nervertheless, occurs glycosidics bonds cleavage and partially depolymerization of starch (SILVA et al., 2008). Generally oxidized starches have better solubility, low viscosity and setback when compared the native starches (LEWICKA, SIEMION, KURCOK,2015). Thermogravimetric Analysis and Differential Thermal Analysis (TGA-DTA) are important techniques used to evaluate the thermal behavior of starches granules (HORNUNG et al., 2015).

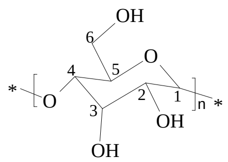

Figure 1: Glycosidic unity of starch structure with carbon identification (C1 - C6).

2. OBJECTIVE

The aim was the chemical treatment of “pinhão” starches with potassium permanganate solutions ($KMnO_4$). The evaluation of the modifications was through the TG-DTA techniques.

3. MATERIALS AND METHODS

The sample of “pinhão” starch (500 g) was bougth in Colombo, PR, Brazil. The starch was divided into four parts of 20 g (dry basis). The modifications were according to the literature procedure (HORNUNG et al., 2015) with adaptations. One was maintained as received (N). The others were treated with standardized solutions of $KMnO_4$: 0.001 mol L^{-1} (1), 0.002 mol L^{-1} (2) and 0.005 mol L^{-1} (3), under constant agitation for 30 minutes. The starches were filtered, washed, dried for 24 hours in oven at 40 °C and stored in desiccator. The DTG-60H (Shimadzu, Japan) was used for DTA and TG analysis. The samples were heated from 30 ºC to 650 ºC using open alumina crucibles with approximately 2.380 mg of the sample under a nitrogen flow of 100 mL.min^{-1} at a heating rate of 10 ºC min^{-1} (HORNUNG et al., 2015). To obtain the results was used TA-60 WS software.

4. RESULTS AND DISCUSSION

The structure or organization the starch macromolecules are changed by treatments. The changes can be identified through analytical techniques and the thermal analysis is a good tool to evaluate. The inert atmosphere helps to show molecular reorganization effect isolating the oxidative effect of O_2. The “pinhão” starches untreated and treated with $KMnO_4$, when subjected to heating in an N_2 atmosphere, showed the first mass loss event due to dehydration of the samples, Figure 2a, followed by stability. The second event corresponds to decomposition of organic matter and formation of carbonaceous residues. As the analytic atmosphere is inert, the oxidation reaction was blocked and the two events were endothermic for samples in DTA, Figure 2b.

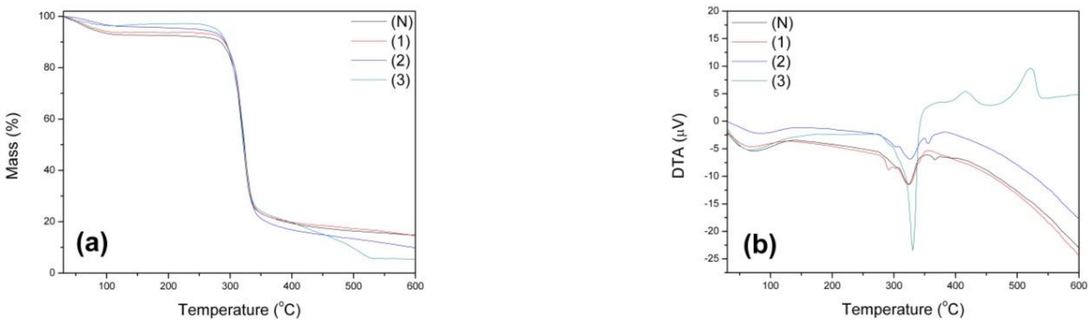

Figure 2: Curves TGA (a) and DTA (b) of native “pinhão” starch (N) and treated “pinhão” starches by 30 minutes with $KMnO_4$ 0.001 mol L^{-1} (1), 0.002 mol L^{-1} (2) and 0.005 mol L^{-1} (3). The curves were obtained in nitrogen flow of 100 ml min^{-1} at heating rate of 10 ° C min^{-1}.

Table 1: TG-DTA events of native “pinhão” starch (N) and treated “pinhão” starches by 30 minutes with $KMnO_4$ 0.001 mol L^{-1} (1), 0.002 mol L^{-1} (2) and 0.005 mol L^{-1} (3). The curves were obtained in nitrogen flow of 100 ml min^{-1} at heating rate of 10 ° C min^{-1}.

Sample	**TGA**		**DTA**	
	Step	**Δm(%)**	**ΔT(°C)**	**Tp(°C)**
(N)	1ª	6.43	31-97	72 (endo)
	stability	-	97-270	-
	2ª	74.72	270-412	323 (endo)
	Carbonaceous residues	18.85		
(1)	1ª	5.67	32-97	70 (endo)
	stability	-	97-276	-
	2ª	74.38	276-397	323 (endo)
	Carbonaceous residues	19.95		
(2)	1ª	3.21	30-97	84 (endo)
	stability	-	97-271	-
	2ª	79.62	271-393	326 (endo)
	Carbonaceous residues	17.17		
(3)	1ª	3.55	38-98	67 (endo)
	stability	-	98-253	-
	2ª	69.51	253-340	331 (endo)
	3ª	21.23	340-531	416 (exo), 521 (exo)
	Ash	5.72		

The sample (3), when exposed to temperatures higher than 340 °C, Table 1, showed exothermic decomposition events. This sample was treated with 0.005 mol L^{-1} of $KMnO_4$, the oxidant reagent. This starch can react with $KMnO_4$ with production of COO^- groups (SILVA et al., 2008; KLEIN et al., 2014). The energy involved in this event can be attributed consecutive reactions related to the higher rate of O_2 present in the sample. The results of carbonaceous residues, Table 1, they are described in literature for samples (N), (1) and (2) (COSTA et al., 2011). The sample (3), with 5.72% of ash was differentiated from the other due to loss of mass related to exothermic events at temperatures above 340 °C.

5. CONCLUSION

The sample treated with 0.005 mol L^{-1} of $KMnO_4$ showed exothermic decomposition events when exposed to temperatures higher than 340 °C in the TG-DTA curves in inert atmosphere. The chemical treatment of "pinhão" starches with potassium permanganate solutions ($KMnO_4$) changed the thermal behavior of samples.

6. ACKNOWLEDGEMENTS

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