Induced effects of oxidation with potassium permanganate in the modification of corn starch

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Abstract

The corn is one of the most cultivated and consumed cereals in the world. This agricultural product is mainly used for food and feed and in some countries for the production of ethanol. In this work were studied samples of unmodified and modified corn starch. The potassium permanganate ($KMnO_4$) was used in the concentrations 0.1, 0.2 and 0.5 $mol.L^{-1}$ for one hour to oxidize the samples a2, a4 and a6, respectively. One sample (N) was maintained as received for comparisons of the analysis results. The samples were analyzed by the thermoanalytical techniques: thermogravimetry and differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC); and by the rheological analysis: Rapid Viscoamylographic Analysis (RVA). TGA showed a decrease in the values of the stability of modified samples compared with the native sample. The DSC showed increase on the gelatinization enthalpy. The oxidation promoted by potassium permanganate caused reduction in pasting temperature, trough (hot paste viscosity), viscosity peak, setback, breakdown and final viscosity compared with sample (N). The obtained results showed that the modification method applied altered the thermal behavior and rheological properties of corn starch.

Keywords
Modified Starch; Potassium permanganate, Corn, TG/DTA, DSC

Introduction

The corn is one of the most cultivated and consumed cereals in the world. It's an important role as human staple food, mainly in less developed countries. Maize is a plant indigenous to Central America. [1]. Corn flours typically present a high starch and a wide range of food and non-food applications [2]. A great deal of research and technical work has been carried out with a view to expanding the industrial utilization of starch and starch-based products [3].
The use of starch in the food industry is to impart functional properties and to modify food texture and consistency. Efforts have been made to find native starches with the necessary properties (syneresis, transparency, freeze/thaw stability). In this way, the knowledge about the characteristics of different starches is important to select the most suitable for a specific application. The modifications seek to improve the native starch so it becomes more efficient. The technique more studied is the oxidative modification [4].
Starch granules are made up of glucose polymers, amylase and amylopectin, and they are found inside vegetable cells. The glucose polymers that make up the starch come in two molecular forms, linear (amylase) and branched (amylopectin). Amylose is a polymer of α 1,4-linked glucose, whereas amylopectin is a polysaccharide consisting of α 1,4 - linked glucose with α 1,6 - linkages at the branch points [5].
In general, maize starches contain approximately 25% amylase [6]. However, there are commercially available maize starches with very high amylose levels (75%) [7]. Then there are waxy maize starches which have practically no amylase [8].
The thermogravimetry analysis (TGA) can be helpful to show the behavior of starch granules when heating leads to depolymerization. The differential scanning calorimetry (DSC) is particularly appropriate to investigate the phase transitions of starch/water systems, because it allows the study of the starch gelatinization over a wide range of starch/water ratio, and the estimation of transition enthalpies [4]. O RVA promotes heating and the swelling of the starch granules causing an increase time and temperature pasting. The granules begin to break down and solubilisation of the polymers provides a reduction in viscosity (break). Through reorganization of some amylose and amylopectin polymers, increasing opacity and viscosity of the paste in a process called setback that occurs due to the strong tendency to form hydrogen bonds between adjacent molecules.
The aim of this work was study the modification of corn starch by potassium permanganate (KMnO4) in concentrations 0.1, 0.2 and 0.5 mol.L-1 at exposure time 60 minutes under constant stirring. In this way were investigate the changes using the following thermoanalytical techniques: thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) and pasting properties by using a rapid viscoamylographic analysis (RVA).

Materials and Methods

Origin and modifications of the starch

The native maize starch (80 g) was bought in the commercial area of Colombo, PR, Brazil. The starch was divided into four parts of 20 g (dry basis). One of these was maintained as received and was designated the (N) untreated sample. The other three samples were treated for 60 min with standard potassium permanganate ($KMnO_4$), following the literature methodology [9, 6] with modifications, at a concentrations of 0.1 $mol.L^{-1}$, 0.2 $mol.L^{-1}$ 0.5 $mol.L^{-1}$, called a2, a4 and a6 respectively. The modified samples were then washed and filtered until the complete elimination of the reagent. The samples were dried in an oven with forced air circulation for 24 hours at 35 ºC and then analysis was performed.

Thermogravimetric study (TG/DTA)

The 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 [7, 10].

Differential scanning calorimetry (DSC)

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 $J.g^{-1}$ [7, 10].

Rapid viscoamylographic analysis (RVA)

The pasting properties of the samples were obtained by using a viscometer (Newport Sci., RVA-4 model, Australia). A suspension of 3.0 g of starch in 25.0 g of distilled water underwent a controlled heating and cooling cycle under constant shear where it was held at 50 ºC for two min, heated from 50 to 95 ºC at 6 ºC min^{-1}, held at 95 ºC for 5 min, cooled to 50 ºC at 6 ºC min^{-1} and held at 50 ºC for 2 min [10,11].

Statistical analysis

All the results were studied and analysed its variance (ANOVA) with the Tukey test to compare sample means at 95% confidence level ($p<0.05$) was performed using STATISTICA 7.0 software (StatSoft, Inc., Tulsa, OK, USA).

Results and Discussion

Simultaneous thermogravimetry and differential thermal analysis (TG–DTA)

The thermogravimetric curves (TG/DTA), Figure 1, were performed and it was possible to verify that the profile of each curve were similar showing three main events of mass loss. The first event, well marked with an endothermic peak in the DTA curve, is attributed to the evaporation of the water and volatile compounds, followed by stability. Once dehydrated, the second and third main regions in the TG curves were due to the degradation of the organic matter (amylose) and the formation of final residues (ash). Similar behaviors were found in earlier works [8,12]. The calculated results (TG/DTA) are shown in Table 1.

On Table 1, the first steps correspond to the evaporation, which can be related to the moisture content of the samples. Thermal analysis permit the determination of moisture content in samples on a temperature range of 30 to 150 ºC [13]. The thermogravimetric analysis presents advantages in relation of the official method by requiring a much less amount of sample and it is faster could show the results in less than a half hour [14]. It can also be observed in Table 1, that the stability values decreased significantly from the sample (N) to the modified ones, in a range of 215 - 249 ºC, demonstrating that the modification by $KMnO_4$ caused alterations on the thermal properties of the corn starch.

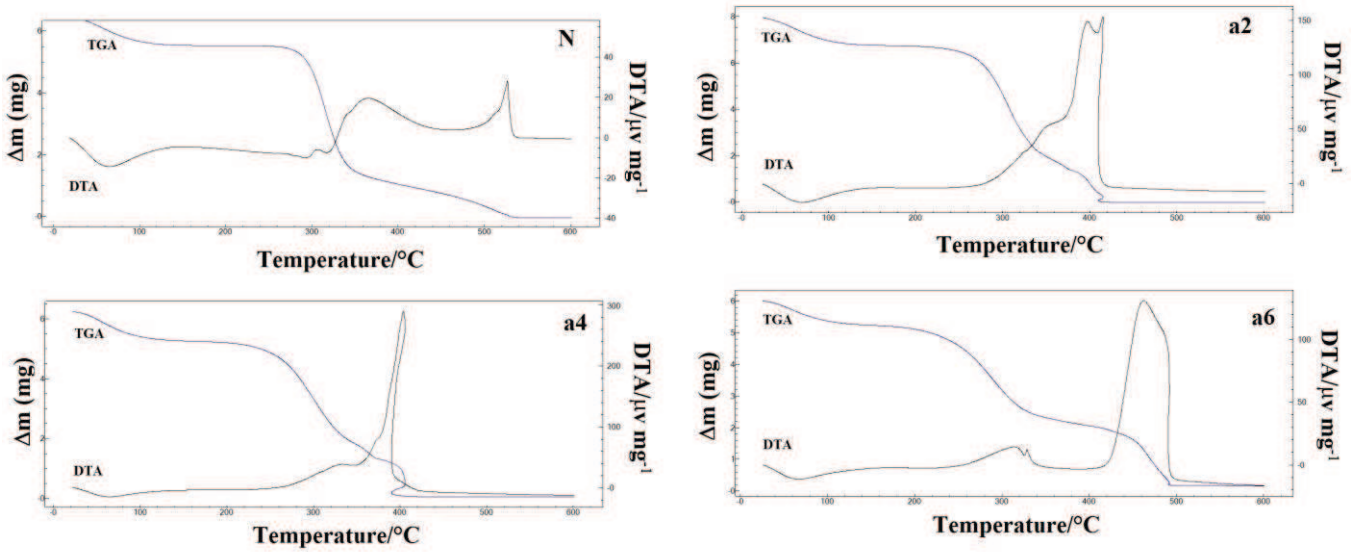

Figure 1 - TG/DTA curves: (N) native corn starch; (a2, a4 and a6) modified starches with $KMnO_4$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Table 1 TG and DTA results of: (N) native corn starch; (a2, a4 and a6) modified starches with $KMnO_4$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Samples	TG Results		DTA Results	
	Step	Δm/%	ΔT/°C	Tp/°C
(N)	1st	13.28	33 - 158	58.74
	stability	-	158 - 249	-
	2nd	71.89	249 - 431	316.27
	3rd	14.07	431 - 592	512.23
(a2)	1st	14.50	30 - 159	62.22
	stability	-	159- 224	-
	2nd	61.42	224 - 360	308.56
	3rd	22.32	360 - 592	397.73
(a4)	1st	14.99	27 - 136	27.09
	stability	-	136 - 215	-
	2nd	52.80	215 - 346	215.24
	3rd	28.94	346 - 594	479.19
(a6)	1st	12.14	35 - 146	67.48
	stability	-	146 - 237	-
	2nd	52.07	237 - 406	313.88
	3rd	32.28	406 - 599	462.27

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

Differential scanning calorimetry (DSC)

DSC was used to determine de gelatinization properties of native and oxidized corn starch samples. The results are showed in Figure 2 and Table 2.

As can be seen in Table 2, the oxidized samples a2 and a4 had a higher onset temperature (To) than sample (N), however samples (a2, a4, a6) differed significantly from sample (N) with respect to the peak temperature (Tp). Final temperature (Tc) decreased significantly for the samples (a2, a4, a6) that were modified with $KMnO_4$ compared with the sample (N). Oxidation promoted an increase in gelatinization enthalpy (ΔH_{gel}).

The single transition in the Figure 2 corresponded to the dissociation of the amylase and amylopectin molecules within the starch granules and leaching out of amylase to tue continuous phase [15]. The results in Table 2 of native and oxidized starches are similar of the obtained by Liu et al [16].

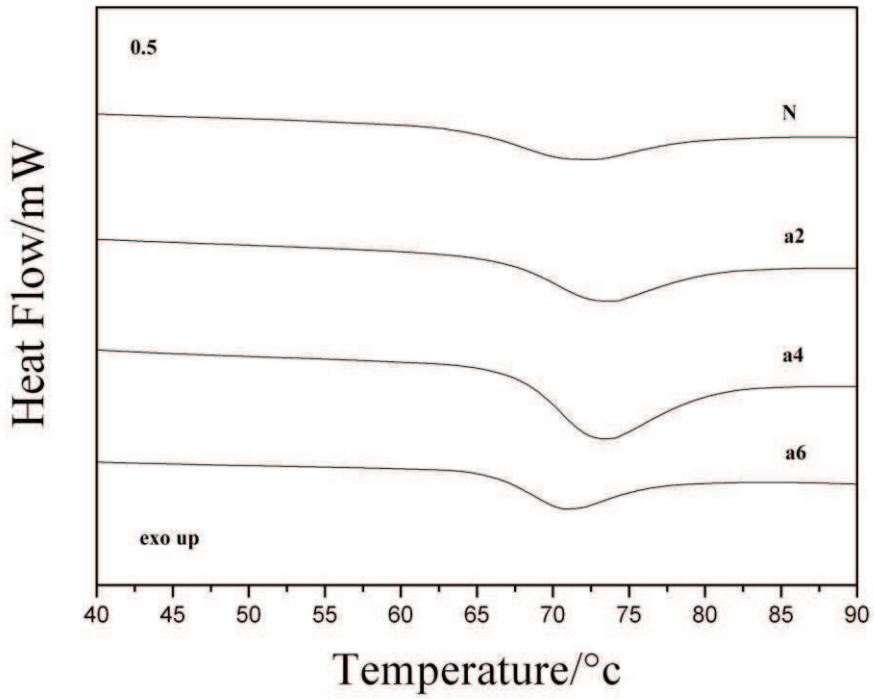

Figure 2 DSC gelatinization curves: (N) native corn starch; (a2, a4 and a6) modified starches with $KMnO_4$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Table 2 DSC gelatinization curves: (N) native corn starch; (a2, a4 and a6) modified starches with $KMnO_4$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Samples	DSC gelatinization			
	***To*/°C**	***Tp*/°C**	***Tc*/°C**	**ΔH_{gel}/J.g$^{\pm 1}$**
(N)	66.07±0.03^{c}	70.83±0.01^{d}	83.25±1.96^{a}	7.37±0.33^{c}
(a2)	67.67±0.02^{a}	73.04±0.01^{b}	79.71±1.11^{b}	13.11±0.17^{a}
(a4)	66.40±0.18^{b}	73.05±0.01^{a}	79.76±1.46^{b}	10.41±1.61^{b}
(a6)	63.82±0.02^{d}	71.05±0.01^{c}	79.31±1.00^{b}	9.46±0.80^{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 ($p<0.05$).

Rapid viscoamylographic analysis (RVA)

The RVA results are shown in Figure 3 and Table 3. Oxidation caused a reduction in trough (hot paste viscosity) and viscosity peak, samples (a2) and (a4) had a greater reduction (a6) that the sample compared with sample (N). The reduction in these viscosities can be attributed to degradation of the starch chains caused by oxidation, with consequent reduction of the molecular weight [17].

The final viscosity of sample (a2), was much lower that the sample (N). Which refers to pasting temperature, oxidation provided a reduction, for the sample (a6) was even more significantly different when compared with the sample (N). Breakdown is an average resistance to degradation of the starch granule [18]. The oxidized samples (a2), (a4) e (a6) had a reduction in breakdown indicating the higher tendency of starch to resist shear force. The setback greatly reduced in the samples oxidized with potassium permanganate in comparison with native starch sample.

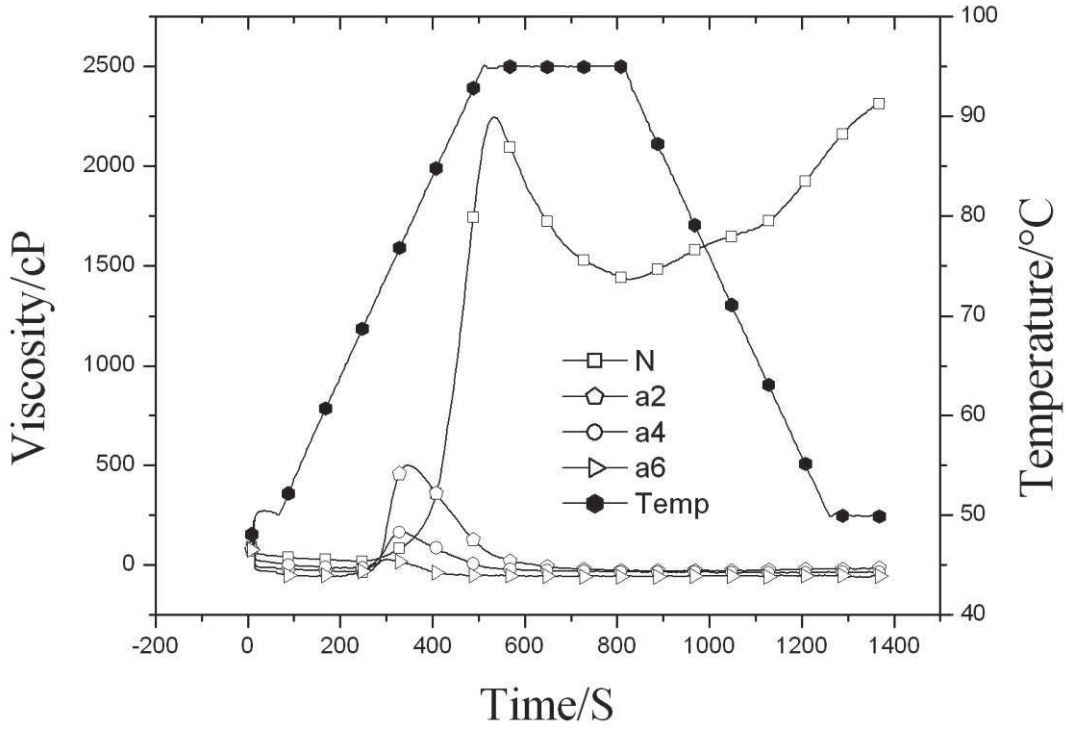

Figure 3 RVA curves: (N) native corn starch; (a2, a4 and a6) modified starches with $KMnO_4$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Table 3 RVA results of: (N) native corn starch; (a2, a4 and a6) modified starches with $KMnO_4$ standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively.

Samples	Pasting temperature/°C	Trough/cP	Viscosity peak/cP	Setback/cP	Break/cP	Final viscosity/cP
(N)	82.50±0.01[a]	1433±1.53[a]	2248±1.00[a]	899±1.00[a]	814±1.00[a]	2323±1.00[a]
(a2)	71.85±0.01[c]	-8.00±0.01[c]	501.0±1.00[b]	15.00±1.00[b]	533±1.00[b]	-17.00±0.01[b]
(a4)	73.65±0.01[a]	-40.0±1.00[d]	165.0±1.00[c]	5.00±1.00[a]	205±1.64[c]	-35.00±1.00[c]
(a6)	ERROR	90.0±1.00[b]	30.00±1.00[d]	6.00±1.00[d]	90.0±1.00[d]	-54.00±1.00[d]

(*) cP "centipoises", sec "seconds", (**)(**) different letters in the same column represents significative difference according to Duncan test ($p<0.05$).

Conclusions

The TG-DTA analysis showed that the thermal properties of the corn starch was altered. The TG-DTA analysis showed that the thermal properties of maize starch were changed. DSC curves showed no such similarities in their profiles compared with the native starch sample (N) mainly sample (a4) and the calculated results showed a significant increase in enthalpy of gelatinization. The RVA results showed that the oxidation caused a reduction in pasting temperature, trough (hot paste viscosity), viscosity peak, setback, breakdown and final viscosity compared with sample (N). By the results obtained with the thermal analysis performed, it could be said that the modification by $KMnO_4$ at a concentrations of 0.1 mol.L^{-1}, 0.2 mol.L^{-1} 0.5 mol.L^{-1} for 60 minutes were promote much degradation of corn starch. A softer methodology will be tested in the future works.

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