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The Effect of Reaction Temperature on Hypochlorite Oxidation of Cassava Starch

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Abstract

Cassava starch was oxidized by sodium hypochlorite (3% active chlorine) at different reaction temperature (30 – 50°C) for different lengths of reaction time (30 – 300 min) and the physicochemical properties of the oxidized cassava starches were determined. Hypochlorite oxidized starch had higher carbonyl and carboxyl groups but lower viscosity than native starch. Reaction temperature and time in the range used in this study did not seem to have significant influence on the formation of both functional groups; however, they showed substantial effect on starch viscosity. Starch viscosity decreased with increasing reaction time; the rate of viscosity reduction was greater when the oxidation was conducted at higher temperature. Onset of gelatinization temperature (T_o) of oxidized starch modified at 30°C was lower than that of the native starch. Reaction temperature showed significant influence on the T_o of oxidized starch. Starch modified at higher temperature had higher T_o than that modified at lower temperature. Retrogradation enthalpies (ΔH_r) of all oxidized starches were not significantly different from that of native starch suggesting that oxidation did not have much influence on amylopectin retrogradation. All samples of oxidized starch had an improved whiteness when compared to native starch; however, starch modified at higher reaction temperature tended to have lower whiteness, especially for the samples with longer reaction time.

Introduction

Oxidized starch is widely used in both food and nonfood industries where film formation and adhesion properties are desired. The major application of oxidized starch is in paper industry where it is used as a surface sizing agent and a coating binder. In food industry, it is used as a coating and sealing agent in confectionery, as an emulsifier, as a dough conditioner for bread, as a gum arabic replacer and as a binding agent in batter application (Kuakpetoon and Wang, 2001). Several oxidizing agents such as hydrogen peroxide, chromic acid, permanganate and periodate have been used for oxidizing starch; however, hypochlorite is the most common chemical used for the production of oxidized starch in an industrial scale. During the course of reaction, several reactions occur which lead to the introduction of carbonyl and carboxyl groups and the degradation of starch molecules. Hence, oxidized starch exhibits low viscosity due to depolymerization and improved stability of starch dispersion from the presence of functional groups.

Reaction conditions such as amount of oxidant, pH, temperature and time are known to be main factors in controlling the course of all reactions occurred during starch oxidation (Forssell et al., 1995; Parovuori et al., 1995; Wang and Wang, 2003). The combination of all changes in starch molecules *i.e.* the number of carbonyl and carboxyl groups and the extent of starch degradation dictates the properties of the resulting modified starch. Although

several studies have reported on the effects of reaction conditions on the structural changes of starch molecules, relatively few studies reveals such effects on the physicochemical properties of the modified starch. The aim of the present work was to study the influence of reaction temperature on the physicochemical properties of oxidized cassava starch.

Materials and Methods

Preparation of oxidized starch

Cassava starch slurry containing 40% dry solid was prepared and the pH was adjusted to 9 with sodium hydroxide solution. The slurry was maintained at a constant temperature (30, 40 or 50°C), and sodium hypochlorite (3% active chlorine based on starch) was added dropwise over a period of 15 min with stirring. During the addition of the reagent and the course of reaction, the pH of the slurry was maintained with sodium hydroxide and/or hydrochloric acid solution. Then the mixture was stirred under the defined conditions and the sample was then collected at the reaction time of 30, 60, 120 and 300 min. The reaction in the collected samples was terminated by addition of sodium bisulphite and the pH was adjusted to 6.5-7.0. The sample was then filtered and thoroughly washed and oven dried at 50°C.

Determination of carbonyl content

The carbonyl content was determined as described by Kuakpetoon and Wang (2001). Starch sample (4 g) was slurried in 100 mL of distilled water. The slurry was gelatinized in a boiling water bath for 20 min, cooled to 40°C, adjusted to pH 3.2 with 0.1 M HCl, and 15 mL of hydroxylamine reagent was added. The flask was stoppered and agitated in a water bath at 40°C. After 4 hours, the sample was rapidly titrated to pH 3.2 with 0.1 M HCl. A blank determination with only hydroxylamine reagent was performed in the same manner. The hydroxylamine reagent was prepared by dissolving 25 g hydroxylamine hydrochloride in 100 mL of 0.5 M NaOH. The final volume was then adjusted to 500 mL with distilled water.

Determination of carboxyl content

The carboxyl content of hypochlorite-modified cassava starch was determined following FAO method (2001). Starch sample (5 g) was stirred in 25 mL of 0.1 M HCl for 30 min. The slurry was then filtered and washed with distilled water until free of chloride ions. The filtered cake was transferred to 300 mL water and the starch slurry was heated in a boiling water bath with continuous stirring until gelatinized and continue stirring at that temperature for another 15 min. The hot sample was titrated with 0.1 M NaOH using phenolphthalein as an indicator. A blank determination was run on the original sample in the same manner but stirred in 25 mL distilled water instead of 0.1 M HCl.

Viscosity measurement

The measurement of viscosity of oxidized starch was performed on a rotational Physica MCR 300 rheometer (Physica Messtechnik GmbH, Ostfildern, Germany) using a concentric cylinder. Samples for all measurements were prepared by heating 15% starch suspension in a water bath at 95°C for 15 min with continuous stirring. The samples were then immediately transferred to the rheometer. The viscosity of oxidized starch was measured over a shear rate range of 0.1 – 500 s^{-1} at 80°C. The viscosity value at 22 s^{-1} was used for comparison between different samples.

Gelatinization and retrogradation properties by DSC

The gelatinization and retrogradation of native and modified starches were measured using a Perkin-Elmer Differential Scanning Calorimeter (DSC7, Norwalk, CT). Starch was weighted into a stainless steel DSC pan and deionized water was added to give 70% moisture content. The pan was sealed, equilibrated at room temperature overnight, and scanned from 0 to 120°C at a rate of 10°C/min. After scanning, the gelatinized sample was stored at 4°C for 7 days, after which the sample was left at room temperature for 1 hour and rescanned under the same conditions with the first scanning. An empty pan was used as the reference and the DSC was calibrated with indium. The onset (T_o), peak (T_p) and conclusion (T_c) temperatures and the enthalpy of gelatinization (ΔH_g) and retrogradation (ΔH_r) were determined.

Measurement of Whiteness

Starch whiteness was determined by using Kett Digital Whiteness Meter model C-100 (Kett Electric Laboratory, Japan).

Results and Discussion

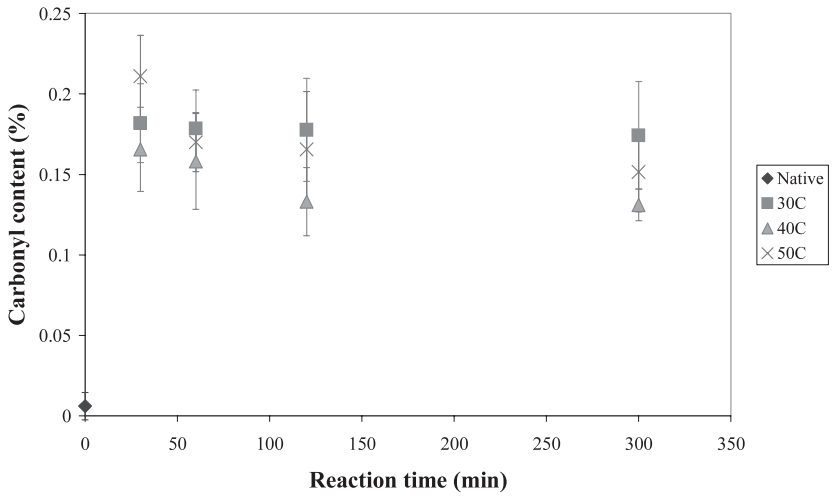
The carbonyl and carboxyl contents of hypochlorite-oxidized cassava starch produced under various reaction temperatures and times are shown in Figure 1. Reaction temperature did not seem to have significant influence on the amount of both functional groups formed during oxidation. However, there is a trend of decreasing in carbonyl content when the reaction time was increased especially at the higher reaction temperature (40 and 50°C). Since carbonyl is quite a reactive group, the reduction in carbonyl content with reaction time is possibly due to its involvement in other side reactions which would be flavored under the higher reaction temperature conditions.

Viscosity of oxidized starch was measured in a 15% starch paste and at 80°C. Under these conditions, the paste from native cassava starch was too viscous to measure, hence; its viscosity was not determined. The viscosity of oxidized starch generally decreased with increasing reaction time (Figure 2). The decrease in viscosity was caused by oxidative cleavage of the glycosidic linkage, resulting in a decrease in starch molecular weight. The rate of viscosity reduction was faster when oxidation was conducted at the higher temperature. However, given long enough reaction time (*i.e.* 300 min), the viscosity of starch modified at lower temperature (30 and 40°C) could come down to the value closer to that of the one modified at 50°C.

Gelatinization and retrogradation properties of starch samples as measured by DSC are presented in Table 1. The onset of gelatinization temperature (T_o) of starch oxidized at 30°C was lower than that of native starch which could be attributed to the introduction of carboxyl group into starch granules. When comparing among oxidized starch samples, the results indicated that the T_o of oxidized starch increased with increasing reaction temperature. Since starch oxidized at different temperature contained similar amount of carboxyl group, the content of this functional group could not be used to explain the difference in T_o. It is possibly that oxidation conducted at higher reaction temperature could flavor the hydrolysis of amorphous lamella in the starch granule, which functions to destabilize the crystalline regions during gelatinization process. Once amorphous lamella was degraded, the gelatinization transition thus shifted to a higher temperature. All oxidized samples showed similar enthalpies of gelatinization (ΔH_g) which was lower than that of native starch implying that the crystalline lamellae was also degraded during hypochlorite oxidation. The enthalpies of retrogradation (ΔH_r) of all oxidized starches were not significantly different from that of

native starch suggesting that oxidation did not have much influence on amylopectin retrogradation.

a)



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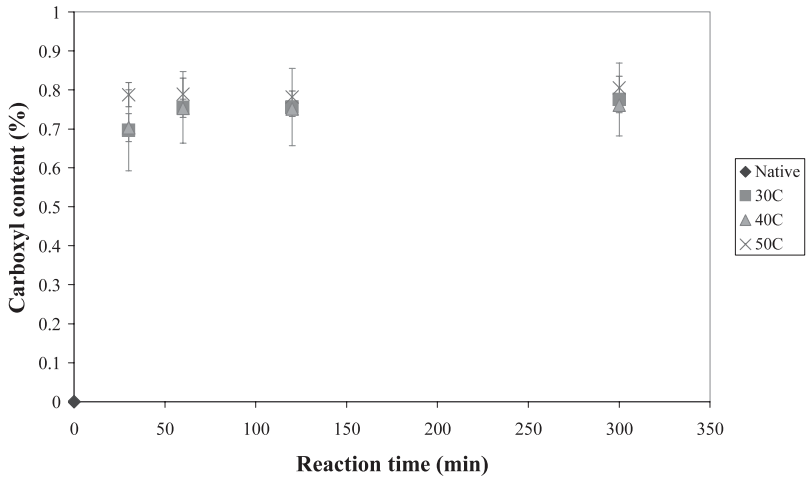

Figure 1 Carbonyl (a) and carboxyl (b) content of native and oxidized cassava starches prepared under different reaction temperatures and times.

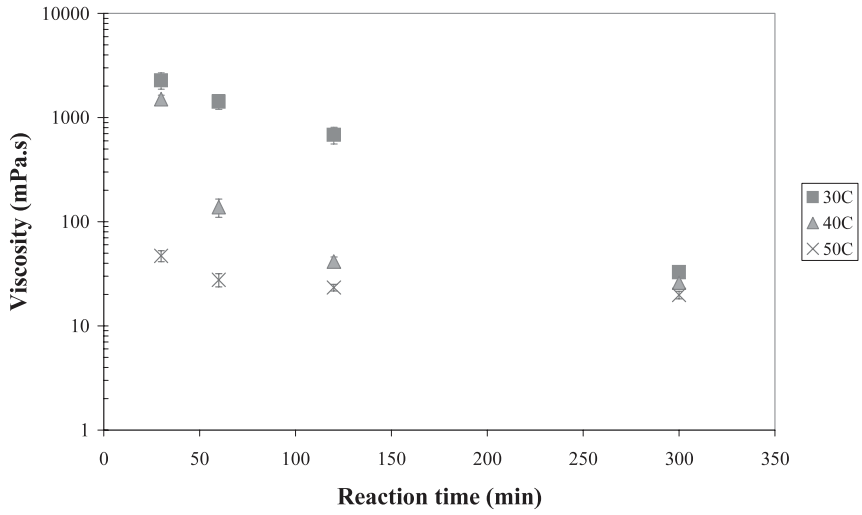

Figure 2 Viscosity of oxidized cassava starches prepared under different reaction temperatures and times.

Table 1 Gelatinization and retrogradation properties of native and oxidized cassava starches prepared with 300 min of reaction time and under various reaction temperature.

Reaction temperature (°C)	Gelatinization properties		Retrogradation properties	
	T_o (°C)	ΔH_g (J/g)	T_o (°C)	ΔH_r (J/g)
Native	64.26± 0.02	17.40 ± 0.13	42.80 ± 0.25	6.13 ± 0.21
30	59.63± 0.18	14.92 ± 0.02	41.46 ± 0.10	6.18 ± 0.15
40	63.00± 0.04	14.80 ± 0.13	41.52 ± 0.07	6.56 ± 0.10
50	64.77 ± 0.04	14.89 ±0.03	40.86 ± 0.10	6.37 ±0.04

All oxidized starch samples were whiter than the native starch. Starch oxidized with the shortest reaction time (30 min) under various reaction temperatures showed the same degree of whiteness; however, the influence of reaction temperature became apparent when the oxidation was conducted with the longer time (Figure 3). The whiteness of oxidized starches prepared at the reaction temperature of 40 and 50°C decreased with increasing reaction time. The extent of reduction in whiteness was stronger when the reaction was conducted at the higher temperature. It has been reported that the decrease in whiteness or increase in yellowness of oxidized starch is related to the carbonyl content (Rutenberg and Solarek, 1984). It is possibly that carbonyl group may serve as a precursor for the formation of color compound in oxidized starch. This is in accordance with the result on carbonyl content presented in Figure1a. The conditions with longer reaction time under higher temperature may favor some side reactions that could change carbonyl group into color compounds; thus carbonyl content also decreased with increasing reaction time.

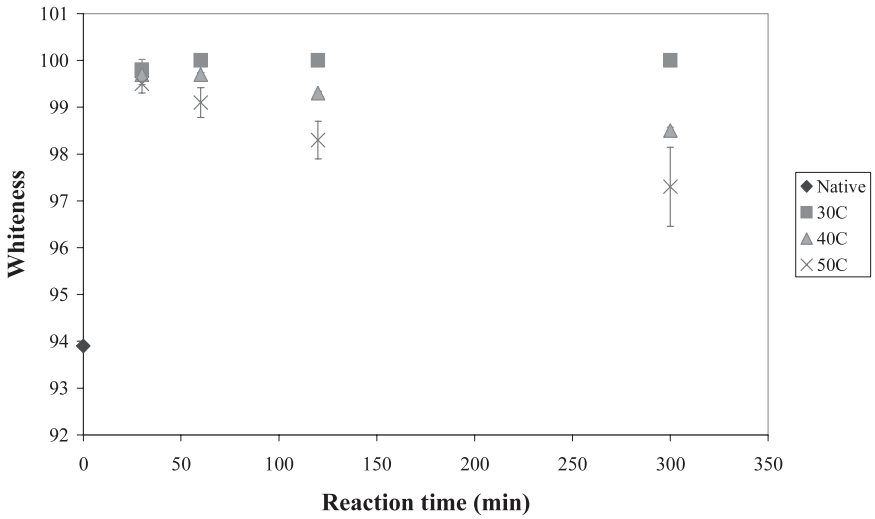

Figure 3 Whiteness of native and oxidized cassava starches prepared under different reaction temperatures and times.

Reference

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