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EFFECT OF HYPOCHLORITE LEVELS ON THE MODIFICATION OF CASSAVA STARCH

S u m m a r y

The effect of oxidant levels on the structure and physico-chemical properties of modified cassava starch was investigated. Cassava starch was treated with various amounts of sodium hypochlorite (1,000-20,000 ppm of active chlorine on dry starch basis) at 30°C and pH 10.5. The substantial amount of carboxyl groups was formed only when more than 5,000 ppm of hypochlorite was used and it increased with increasing hypochlorite levels. With these high levels of hypochlorite, the resulting modified starches exhibited the pasting properties of a typical oxidized starch with low peak viscosity, little breakdown and low setback. With the lower levels of hypochlorite (1,000 and 2,500 ppm), the modified starches showed high peak viscosity, reduced breakdown and high setback. Results from high-performance size-exclusion chromatography reveals that both amylose and amylopectin were degraded and the extent of degradation increase with the increasing levels of the oxidant. Starch modified with hypochlorite concentration lower than 2,500 ppm showed a pronounced reduction in the paste clarity indicating that the starch granule becomes more resistant to disintegration after the modification.

Introduction

Hypochlorite is the most commonly used chemical for the production of oxidized starch. The desired properties from such modification are low viscosity and improved stability of starch paste. Oxidation alters properties of native starch through the introduction of carbonyl and carboxyl groups, which minimizes retrogradation, and depolymerization, which causes drastic decrease in hot paste viscosity [1, 2]. Oxidized starch is widely used in the paper industry as surface sizing and coating binder where

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low paste viscosity at relatively high starch concentration and viscosity stability of starch paste during storage are most desired.

In addition to pH, temperature, time, starch concentration and starch origin, hypochlorite concentration seems to be an important factor affecting the properties of modified starch. For the production of oxidized starch of commerce, hypochlorite is normally used at relatively high level. The Code of Federal Regulation (CFR) of the U.S. Food and Drug Administration [3], classifies the process of treating starch with sodium hypochlorite not to exceed 8,200 ppm as bleaching whereas the process when using higher level of the chemical but not more than 55,000 ppm is classified as oxidation. The bleaching process aims to improve whiteness and remove impurities from starch but oxidation intends to alter the rheological properties of starch as previously mentioned. Most studies on hypochlorite modification of starch are pertinent to the oxidation process [4-7]. Very few studies have reported on the effect of low levels of hypochlorite [8-9]. The systematic study covering the range of extremely low and high levels of hypochlorite has not been reported.

The present work aims to study the effect of hypochlorite concentration (1,000-20,000 ppm of active chlorine, dry starch basis) on the physico-chemical properties of cassava starch.

Materials and methods

Materials

Cassava starch was from Chor Chaiwatana Tapioca Co., Ltd. (Thailand). Sodium hypochlorite was from Carlo Erba Reagenti (Italy). The amount of active chlorine was determined according to Iodometric procedure as described in the Standard Methods [10] prior to used. All other chemicals used were of reagent grade.

Preparation of hypochlorite-modified starch

Cassava starch was modified by sodium hypochlorite as described by Kettlitz and Coppin [9]. A 40% starch slurry was prepared by adding 750 g of distilled water to 500 g starch (dry basis) and pH was adjusted to 10.5 with 3% NaOH solution. The temperature of the slurry was brought to 30°C and NaOCl was added slowly to the stirred slurry to reach different final concentrations (1,000, 2,500, 5,000, 10,000, 20,000 ppm). After 3 hours, the pH of slurry was adjusted to 6.5 with sodium bisulfite, filtered, washed three times with distilled water and oven dried at 45°C.

Determination of carboxyl content

The carboxyl content of hypochlorite-modified cassava starch was determined by the ISO method [11]. Starch sample (5 g) was stirred in 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.

Determination of carbonyl content

The carbonyl content was determined as described by Kuakpetoon and Wang [7]. 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 stopped and placed in a water bath at 40°C. After 4 hour, the excess hydroxylamine was determined by rapid titration to pH 3.2 with 0.1 M HCl.

Pasting properties of starch

The pasting properties of starch were determined with a Rapid Visco Analyser (RVA-4, Newport Scientific, Australia) using standard program Number 1. The starch sample was 3.00 g (on 14% moisture basis). The starch suspension was held at 50°C for 1 min and subsequently heated to 95°C at 12.2°C/min. Holding time at 95°C was 2.5 min. The sample was then cooled to 50°C at 12.2°C/min, and kept at that temperature for 2.1 min. A rotation speed of the paddle was at 160 rpm.

Molecular weight distribution

The molecular weight distributions of starch samples were determined by High Performance Size Exclusion Chromatography (HPSEC) using one Ultrahydrogel linear and two Ultrahydrogel 120 columns connected in series (Waters Corporation, MS) according to the method of Govindasamy et al. [12].

Light transmittance of starch paste

The light transmittance of a starch paste was determined by the procedure of Lim and Seib [13]. Starch suspension (1%) was heated in a boiling water bath for 30 min with occasional shaking. After the suspension was cooled to room temperature for 60 min, the percent transmittance was determined at 650 nm.

Results and discussion

The carboxyl and carbonyl contents of NaOCl-modified cassava starch are presented in Table 1. Carboxyl content increased as the hypochlorite concentration increased whereas the amount of carbonyl groups formed did not show any dependence on the concentration of the oxidant.

Table 1

Carboxyl and carbonyl group contents of NaOCl-modified starch

NaOCl level (ppm)	Carboxyl content (%)	Carbonyl content (%)
1,000	0.005	0.08
2,500	0.005	0.13
5,000	0.03	0.08
10,000	0.14	0.10
20,000	0.33	0.06

The pasting profiles of native and modified cassava starches using various NaOCl levels are shown in Figure 1. Native cassava starch is characterized by high peak viscosity with drastic breakdown during a heating cycle followed by low setback during cooling. After modification with hypochlorite in the levels of higher than 5,000 ppm, the modified starch exhibited pasting properties of a typical oxidized starch, which has low peak viscosity, little breakdown and low setback.

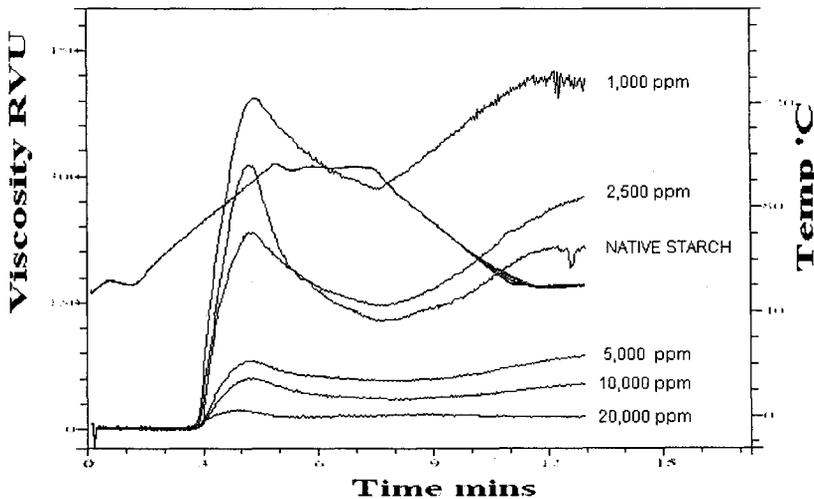


Fig. 1. Pasting profiles of native and NaOCl-modified cassava starches determined by a Rapid Visco Analyser. The levels of active chlorine employed in the reaction are labeled on individual curves.

The reduction in peak viscosity was due to partial degradation of starch molecules, which caused a decrease in the molecular weight. As a result, starch granules of these modified samples fragmented before reaching maximum swelling. These modified starches also showed relatively low setback signifying that they had less tendency for retrogradation. Wurzburg [2] suggested that carboxyl groups introduced into the starch molecules during oxidation were bulkier than hydroxyl groups; they are more effective in preventing the reassociation of amylose molecules thus minimizing retrogradation phenomena. The formation of carboxyl content observed in this work also supports this explanation.

Starch modified with lower levels of hypochlorite showed different pattern of pasting curves. With 1,000 ppm of oxidant, modified sample exhibited higher peak viscosity, lower breakdown and higher setback when compared to native starch. Kettlitz and Coppin [9] also observed similar phenomena when employing this low level of hypochlorite to waxy starch. The increase in peak viscosity suggests that after modification starch granules were easier to swell and they swelled to a greater extent than the native starch. This could be due to the introduction of a small amount of negatively charged carboxyl groups to the starch, which weakens the association forces between starch molecules. However, the significant decrease in breakdown and the high final viscosity suggests that the increase in swelling of starch granules occurred without loss of granule structure. Even though the mechanism for such phenomena is not clear, the results demonstrate that modification with low level of sodium hypochlorite somehow strengthens the structure of cassava starch granule. The pasting properties of starch obtained from this modification are similar to that of lightly crosslinked starch.

The HPSEC chromatograms of native and modified cassava starches are showed in Figure 2. Fraction eluted at 13 min was mainly high molecular weight amylopectin; the lower molecular weight fraction of amylose was eluted at about 22 min. The molecules with intermediate size were eluted at 17 min. The extent of depolymerization of starch during modification depended on the concentration of NaOCl. At 1,000 ppm of active chlorine, no change in the molecular weight distribution can be detected on the chromatogram. The shift to the longer retention time of amylose fraction and the appearance of a new peak at 16 min in the sample treated with 2,500 ppm of hypochlorite indicated that both amylose and amylopectin began to degrade at this condition. With the higher levels of the oxidant, both fractions were degraded to a greater extent and the amylose fraction disappeared.

The paste clarity of native and NaOCl-modified cassava starch is shown in Table 2. NaOCl – modification had a dramatic effect on the paste clarity of the resulting starch pastes. Native cassava starch produced a translucent paste with 62% light transmittance. The results demonstrate that modification with high levels of oxidant (5,000–20,000 ppm) increased light transmittance. The negatively charged carboxyl

groups that formed in these samples caused the repulsion between adjacent starch molecules and reduced interchain association leading to a high clarity paste. On the other hand, starch modified with low level of hypochlorite showed a pronounced decrease in the paste clarity when compared to native starch. It has been reported that crosslinking caused the reduction in the paste clarity [13] possibly due to the presence of undisrupted swollen granules. The decrease in the light transmittance of the resulting modified starch in this study could be due to the remaining of such undisrupted swollen granules.

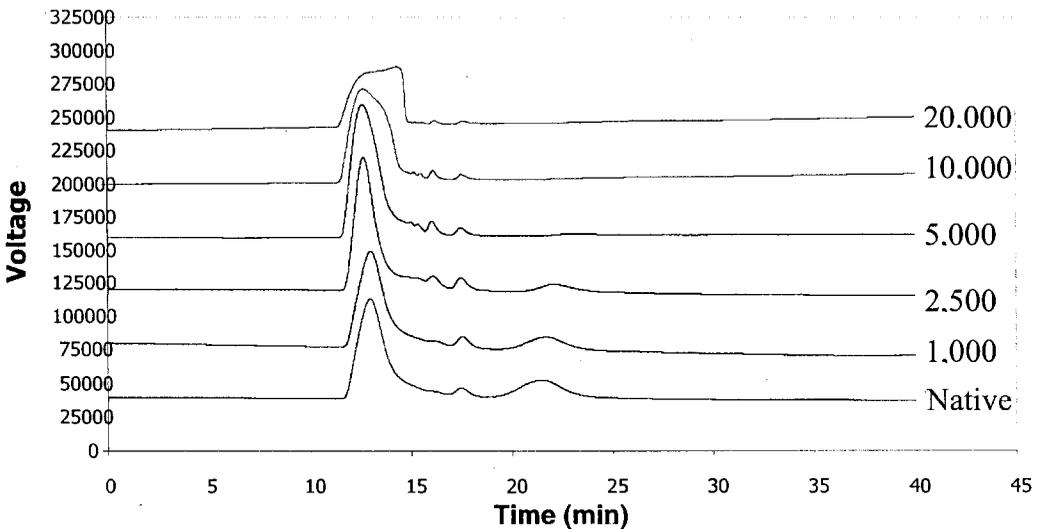


Fig. 2. Molecular weight distribution of native and NaOCl-modified cassava starch determined by high-performance size-exclusion chromatography.

Table 2

Light transmittance of pastes from native and NaOCl-modified cassava starches.

Sample/NaOCl level (ppm)	Transmittance (%)
Native starch	62.3 ± 0.87
1,000	18.4 ± 1.39
2,500	24.5 ± 0.61
5,000	80.1 ± 1.39
10,000	95.0 ± 0.70
20,000	98.9 ± 0.12

References

- [1] Whistler R.L., BeMiller J.N., Paschall E.F.: *Starch: Chemistry and Technology*, Academic Press Inc., 1984, 315-323.
- [2] Wurzburg O.B.: *Modified Starches: Properties and Uses*, CRC Press, Florida, 1986, 23-28.
- [3] Code of Federal Regulation (CFR): Food starch-Modified, U.S. GPO, Washington, D.C., 1995, 21/1/172/172.892.
- [4] Forssell P., Hamunen A., Autio K., Suortti T., Poutanen K.: *Starch/Starke*, 1995, **47**, 371-377.
- [5] Autio K., Suortti T., Hamunen A., Poutanen K.: *Carbohydr. Polym.*, 1996, **29**, 155-161.
- [6] Kantouch F., Tawfik S.: *Starch/Starke*, 1998, **50**, 114-119.
- [7] Kuakpetoon D., Wang Y.J.: *Starch/Starke*, 2001, **53**, 211-218.
- [8] Fuller A.D.: U.S.Pat. 2317752, 1943.
- [9] Kettlitz B.W., Coppin, J.V.J.M.: U.S.Pat. 6235894, 2001.
- [10] Standard Methods for the Examination of Water and Wastewater: 13th ed., APHA, AWWA, WPCT, New York, 1971, 316-318.
- [11] International Standard: ISO11214-1996(E).
- [12] Govindasamy S., Oates C.G., Wang H.A.: *Carbohydr. Polym.*, 1992, **18**, 89-100.
- [13] Lim S., Seib P.A.: *Cereal Chem.*, 1993, **70**, 137-144.

WPLYW POZIOMU PODCHLORYNU NA MODYFIKACJĘ SKROBI TAPIOKOWEJ

Streszczenie

Zbadano wpływ poziomu podchlorynu jako utleniacza na strukturę i właściwości fizykochemiczne modyfikowanej skrobi tapiokowej. Skrobię tę utleniono w 30°C przy pH 10.5 podchlorynu sodu zawierającego 1000 do 20 000 ppm aktywnego chloru w suchej masie. Znaczące ilości grup karboksylowych powstawały dopiero wtedy, gdy ilość aktywnego chloru wynosiła powyżej 5 000 ppm i wzrastały one w miarę wzrostu stężenia utleniacza. Tak utleniona skrobia wykazywała właściwości kleikujące typowe dla utlenionych skrobi o niskiej lepkości maksymalnej. Gdy stężenie utleniacza wahało się między 1000 i 2500 ppm aktywnego chloru, utlenione skrobie miały wysoką lepkość maksymalną. Badania za pomocą wysokosprawnej chromatografii żelowej pokazały, że zarówno amyloza jak i amylopektyna uległy degradacji i stopień degradacji wzrastał ze stężeniem użytego utleniacza. Skrobia utleniana podchlorynem o stężeniu poniżej 2 500 ppm wykazywała daleko idące zmniejszenie przejrzystości kleików, wskazujące na odporność gałeczek na zniszczenie przez kleikowanie. ☒