DOI 10.1002/star.200400299 *Starch/Stärke* **57** (2005) 166–172

Rungtiwa Wongsagon[a]
Sujin Shobsngob[b]
Saiyavit Varavinit[a]

[a] Department of Biotechnology, Faculty of Science, Mahidol University, Bangkok, Thailand
[b] Department of Chemistry, Faculty of Science, Mahidol University, Bangkok, Thailand

Preparation and Physicochemical Properties of Dialdehyde Tapioca Starch

Tapioca starch was oxidized by periodic acid (sodium metaperiodate plus hydrochloric acid) to form dialdehyde tapioca starch (DAS). The influence of periodate concentration ($NaIO_4$, 0.05 N, 0.1 N, 0.2 N and 0.3 N) on the physicochemical properties of DAS such as aldehyde and carboxyl contents, relative crystallinity, thermal properties, pasting properties, swelling power, solubility and molecular weight distribution was investigated. The results indicated that aldehyde and carboxyl contents of DAS increased linearly with the increasing of periodate concentration. X-ray diffraction patterns of DAS remained unchanged after periodate oxidation whereas the relative crystallinity decreased as periodate concentration increased. Furthermore, the gelatinization temperatures (T_o and T_p) of DAS were also increased, whereas the gelatinization enthalpy decreased. As determined in the Rapid Visco Analyser, the periodate oxidation increased the pasting temperature and peak viscosity as well as breakdown of the tapioca starch. The swelling power of DAS was higher than that of unmodified tapioca starch at 60°C and 70°C, but was lower at 80°C and 90°C. However, the solubility was higher than that of native tapioca starch at all incubation temperatures. Both amylose and amylopectin fractions were degraded during the oxidation reaction as measured by HPSEC. The thermal stability of DAS at boiling temperature was also investigated and depolymerization of the DAS could not be detected at any heating time as demonstrated for the thermal stability of the DAS.

Keywords: Tapioca starch; Dialdehyde starch; Periodic acid; Periodate oxidation

1 Introduction

Dialdehyde starch is obtained by oxidation of starch with periodic acid at controlled temperature and pH. Periodic acid is a highly selective oxidizing agent, which cleaves the C-2 – C-3 linkage of anhydroglucose units with the formation of dialdehyde groups [1–6]. The highly reactive dialdehyde groups in starch can be used as crosslinking agents. Therefore, most of the applications of dialdehyde starch are based on a crosslinking reaction, e.g. with cellulose in paper, cotton in textiles, with proteins, pharmaceuticals and leather [4–8]. The presence of aldehyde groups is attributed to form internal crosslinks through hemiacetalization [5, 9]. The acid production and molecular degradation of dialdehyde starch under alkaline condition and high temperature have been reported [9].

Most periodate oxidation in the literature was conducted using high concentration of periodate. However, little work has been done to study the changes in properties using low periodate concentration. Moreover, the production and properties of dialdehyde tapioca starch have not been studied up to now.

In this study, tapioca starch was to be oxidized by various concentrations of periodate in order to investigate the physicochemical properties changes after periodate oxidation, such as formation of aldehyde and carboxyl groups, relative crystallinity, thermal properties, pasting properties, swelling power, solubility and molecular weight distribution.

2 Materials and Methods

2.1 Materials

Tapioca starch was supplied by General Starch Co., Ltd. (Nakornrachasima, Thailand). Sodium metaperiodate was purchased from Asia Pacific Specialty Chemical Co., Ltd. (Seven Hills, NSW, Australia). Other reagents were of analytical grade, and were purchased from Merck Co., Ltd. (Darmstadt, Germany).

Correspondence: *Saiyavit Varavinit*, Department of Biotechnology, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand. Phone: +66-2-2015315, Fax: +66–2-3547160, e-mail: scsva@mucc.mahidol.ac.th.

2.2 Proximate analysis and amylose content of tapioca starch

Proximate analysis of native tapioca starch was performed according to the standard methods described in the AOAC, 1990 (Official Methods of Analysis, Association of Official Analytical Chemists), i.e. moisture and ash contents [10]. Protein content was estimated from the nitrogen content obtained by the Kjeldahl method (model VAPODEST 50 Carousel 250 mL autosample, and model Kjeldatherm-Digestion units, with 20 digestion tubes 6100, 250 mL, both by Gerhardt, Königswinter, Germany) multiplied by 6.25 [11]. Fat content of the sample was determined by the method described elsewhere [12]. Carbohydrate content was calculated by subtracting the percentage of aforementioned compounds from 100. Amylose content of native tapioca starch (based on weight that is free of moisture, protein, fat and ash) was determined by the iodine affinity method [13].

2.3 Preparation of dialdehyde tapioca starch (DAS)

Dialdehyde tapioca starch (DAS) was prepared by following the modified method for bagasse dialdehyde cellulose described by *Varavinit* et al. [14]. Tapioca starch (200 g, dry basis) was suspended in 500 mL solutions of various concentration of sodium metaperiodate (0.05 N, 0.1 N, 0.2 N and 0.3 N). The pH of the starch suspension was adjusted to 3.0 by adding 2% (w/v) HCl. The reaction was performed in a water bath at 32°C while stirring at 400 rpm for 1 h. At the end of the oxidation, the starch suspension was washed three times (3×1.6 L) with distilled water. Next, the washed starch was immersed in 500 mL 0.5% (w/v) aqueous sodium metabisulfite solution for 1 h in order to destroy the residual oxidant (sodium metaperiodate). Consequently, the suspension was washed three times again with distilled water (3×1.6 L). Then, the water was removed by centrifugation (Sorvall RC 3B Plus, Du Pont, Delaware, USA). The starch cake was dried overnight in a hot air oven at 45°C. Afterwards, the dried starch was milled and sieved through a 100 mesh sifter to obtain DAS powder. Also, the residual of periodate in DAS was tested according to the method described elsewhere [15].

2.4 Determination of aldehyde content

The aldehyde group content was determined using the modified method described by *Smith* [16]. Two grams of a starch sample were suspended in 50 mL distilled water in a 250 mL flask. The suspension was gelatinized in a boiling water bath for 20 min. Then it was cooled to 40°C and adjusted to pH 3.2 with 0.1 N HCl. Finally, 30 mL of hydroxylamine reagent were added. The flask was stoppered and placed in a 40°C water bath for 4 h while stirring slowly. The excess hydroxylamine was determined by rapidly titrating the reaction mixture to the end point at pH 3.2 with standardized 0.1 N HCl. A blank determination with only hydroxylamine reagent was performed in the same manner. The hydroxylamine reagent was prepared by first dissolving 25 g hydroxylamine hydrochloride in 100 mL of 0.5 N NaOH before the final volume was adjusted to 500 mL with distilled water. Aldehyde content was calculated as follows:

$$\text{Percentage of aldehyde content} = \frac{0.028 \times N \times (V_B - V_S) \times 100}{W}$$

Where N is the normality of HCl, V_B is the volume of HCl used for titrating the blank in milliliter, V_S is the volume of HCl used for titrating the sample in milliliter, and W is the weight of starch sample (dry basis) in gram.

2.5 Determination of carboxyl content

The carboxyl content was determined using the modified method described by *Chattopadhyay* et al. [17]. Two grams (dry basis) of a starch sample were mixed with 25 mL of 0.1 N HCl, and the slurry was stirred occasionally for 30 min with a magnetic stirrer. The slurry was then vacuum filtered through Whatman #40 filter paper and washed with 500 mL distilled water until the filtrate was free of chloride (by testing with silver nitrate). After that, the starch cake was carefully transferred to a 500 mL beaker, and the volume was adjusted to 300 mL with distilled water. The starch slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure complete gelatinization. Next, the hot starch dispersion was titrated with standardized 0.01 N NaOH using phenolphthalein as indicator. A blank test was performed with unmodified starch. Carboxyl content was calculated as follows:

$$\text{Percentage of carboxyl content} = \frac{0.045 \times N \times (V_S - V_B) \times 100}{W}$$

Where N is the normality of NaOH, V_S is the volume of NaOH used for titrating the sample in milliliter, V_B is the volume of NaOH used for titrating the blank in milliliter, and W is the weight of starch sample (dry basis) in gram.

2.6 X-ray powder diffraction measurement

The X-ray diffraction patterns of native starch and DAS were recorded with a Bruker X-ray powder diffractometer (D-8 type, Bruker, Rheinfelden, Germany) with copper

anode X-ray tube (Cu-K_α radiation) at 30 kV and 30 mA. The scanning region of the diffraction angle (2θ) was from 5° to 30° at a step size of 0.4° with a count time of 1.0 s and the rotary speed of the sample holder was 30 min^{-1}. The starch samples were equilibrated in a 100% RH chamber for 24 h at room temperature prior to measurement.

The relative crystallinity of starch samples was quantitatively estimated by the method described by *Komiya* and *Nara* [18]. The ratio of upper crystalline area to total diffraction area was calculated as the relative crystallinity.

2.7 Determination of thermal properties

Thermal properties of unmodified starch and DAS were assessed by a Differential Scanning Calorimeter (DSC, Pyris, Perkin Elmer, Belerica, MA, USA). Both native starch and DAS (base on weight free from moisture) were adjusted to a starch to water ratio of 1:2. Each starch suspension was then transferred to an aluminum pan (30 μL) and hermetically sealed. After equilibration at room temperature for 1 h, the sample was heated from 20°C to 120°C at the rate of 10°C/min. 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 melting enthalpy (ΔH in J/g of dried starch) were recorded.

2.8 Determination of pasting properties

A Rapid Visco Analyser (Series 4V, Newport Scientific Pty. Ltd, Warriewood, Australia) was employed to investigate the pasting properties of native starch and DAS. In this assay, 2.5 g (dry basis) of starch sample and 25 mL of distilled water (10%, w/v) were mixed in an aluminum can with a paddle. The heating and cooling cycles were programmed in the following manner: The starch suspension was held at 50°C for 1 min, heated from 50°C to 95°C at a rate of 12°C/min and held at 95°C for 2.5 min, then it was cooled down to 50°C at a rate of 12°C/min and held at 50°C for 2 min.

2.9 Determination of swelling power and solubility

The swelling power and solubility were measured according to the modified procedure described by *Holm* et al [19]. A 3.3% starch suspension (1 g starch in 30 mL water) was suspended in a centrifuge tube with cap and then vortexed. The starch suspension was incubated in a water bath at various temperatures from 60°C to 90°C with a temperature increment of 10°C and the sample was kept at that temperature for 30 min. The sample was then cooled to room temperature for 30 min and centrifuged at $1000 \times g$ for 15 min at 25°C. The swelling power was determined by measuring the sediment paste weight and solubility by the solid content of the supernatant.

2.10 Determination of molecular weight distribution

The average molecular weight (weight average) as well as the degree of polymerization (DP) of native and dialdehyde tapioca starches were determined by using high-performance size-exclusion chromatography (HPSEC) using the method developed by *Govindasamy* et al. [20]. A Water Associates (Milford, MA, USA) series liquid chromatography system with a refractive index (RI) detector and a guard column with three Ultrahydrogel columns was used. The columns, maintained at 40°C, were connected in the following order: guard column with Ultrahydrogel linear followed by two Ultrahydrogel 120 columns. Deionized water was used as mobile phase. The columns were calibrated with polysaccharide standards with molecular weights of 788,000, 404,000, 212,000, 112,000, 47,300, 22,800, 11,800, 5,900, 738 and 180 (Polymer Laboratory Inc, Amherst, MA, USA), respectively.

HPSEC starch samples were prepared by following the method of *Jane* and *Chen* [21]. Dried starch (0.05 g, base on weight free of moisture and protein) was mixed with 0.5 mL of distilled water, and dimethyl sulfoxide (4.5 mL) was added. The suspension was mechanically stirred while heating in a boiling water bath for 1 h and then stirred for 24 h at 25°C to prepare a 1% starch solution. Absolute ethanol (20 mL) was then added to the solution to precipitate the starch, followed by centrifugation to separate the precipitated starch. Precipitated starch was redissolved in boiling water (10 mL) and stirred for 30 min and the final solution was passed through a 8.0 μm Millipore Filter (Sartorius, Göttingen, Germany) in order to remove the protein and other impurities prior to HPSEC analysis. Standard polysaccharides were used for preparing the calibration graph used for determination of the degree of polymerization.

2.11 Determination of thermal stability

The procedure was similar to the method of *Jane* and *Chen* [21], but the heating time in boiling water was varied (5, 15, 30 and 60 min) prior to HPSEC measurement.

3 Results and Discussion

3.1 Residual periodate

Residual periodate could be detected in DAS before washing with sodium metabisulfite. After the washing, DAS was free from periodate. Residual periodate would interfere and change the physicochemical properties of the DAS.

3.2 Proximate analysis and amylose content of tapioca starch

The native tapioca starch employed in this investigation contained 0.04% protein, 0.03% fat, 0.16% ash, 12.8% moisture and 86.97% carbohydrate (amylose content 28.5%), it is thus of high purity. Because of its high purity tapioca starch is suitable for use as a starting material for chemical modification including periodate oxidation to minimize the effect of side reaction between chemical reagent and impurities.

3.3 Aldehyde and carboxyl groups contents

The relationships between periodate concentration and contents of aldehyde and carboxyl groups of DAS are shown in Fig. 1. Both aldehyde and carboxyl contents of DAS increased as periodate concentration increased. The increase was much stronger for the aldehyde content than for the carboxyl content because periodate is a selective oxidizing agent, which promotes the production of dialdehyde groups. Some aldehyde groups can be further oxidized to carboxyl groups due to the Cannizzaro reaction [9]. In this reaction, two aldehydes can be converted into a carboxylic acid and an alcohol. Alternatively, carboxylic acid production has been explained by a sequence of reactions, initiated by β-elimination and followed by hemiacetal hydrolysis and a benzil-benzilic acid type of rearrangement [9]. The numbers of aldehyde and carboxyl groups on DAS indicated the extent of oxidation [22].

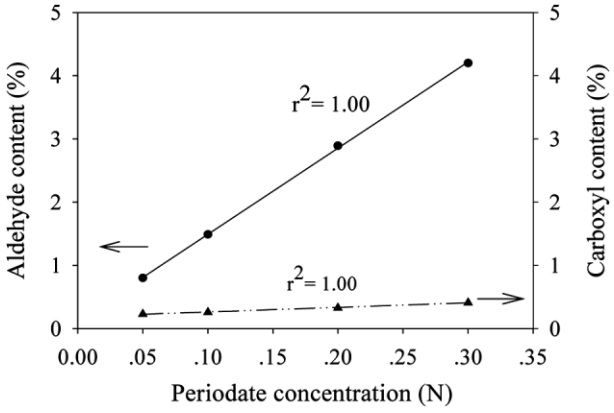

Fig. 1. Relationship among percentages of aldehyde and carboxyl contents of DAS prepared by oxidation of tapioca starch with various periodate concentrations.

3.4 X- ray diffraction

X-ray diffraction patterns of DAS resembled the pattern of unmodified tapioca starch (figures not shown). It indicated that periodate oxidation did not result in any significant change in type A diffraction peak pattern of tapioca starch.

The ratio of crystalline region to total area was taken as quantitative measurement of percent relative crystallinity. These values were plotted against the periodate concentration as shown in Fig. 2. The relative crystallinity decreased as periodate concentration increased. It can be assumed that the periodate oxidation of tapioca starch caused a loss of crystallinity and long range ordering. This implies that periodate oxidation occurred at both amylopectin and amylose fractions of the crystalline and amorphous regions of starch granules. The hydrophilicity of aldehyde and carboxyl groups in DAS caused the decrease in crystallinity [6].

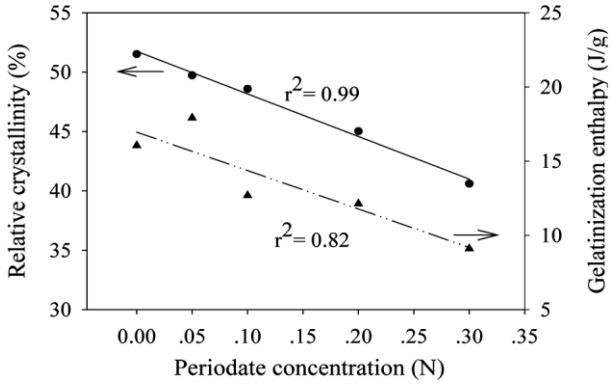

Fig. 2. Relationship among percentage of relative crystallinity and gelatinization enthalpy of DAS prepared by oxidation of tapioca starch with various periodate concentrations.

3.5 Thermal properties

The DSC thermograms of DAS prepared from various periodate concentrations are displayed in Fig. 3. The DSC endothermic patterns of DAS were sharper than that of the native starch. It was found that gelatinization temperature (T_o and T_p) increased with the increasing of periodate concentration. It was probably due to the formation of hemiacetal crosslinking within DAS molecules, increasing the stability of the molecules.

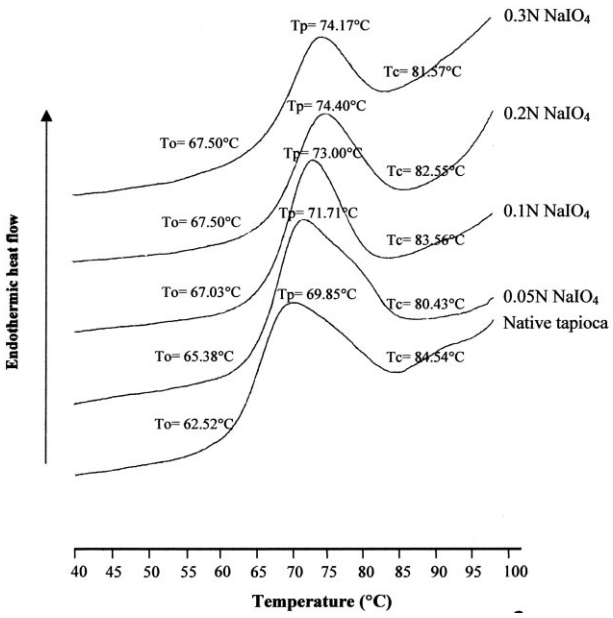

Fig. 3. DSC thermograms of DAS prepared by oxidation of tapioca starch with various periodate concentrations.

The gelatinization enthalpy (ΔH) of DAS decreased as the periodate concentration increased as shown in Fig. 2. Generally, the gelatinization enthalpy (ΔH) of DAS was positively related to the degree of crystallinity. When a loss of ordering or crystallinity resulted, the energy required to melt the starch granules was also decreased [6].

3.6 Pasting properties

The pasting profiles of DAS prepared with various periodate concentrations differed from the native one as shown in Fig. 4. The pasting temperatures, pasting time and the peak viscosity of DAS increased as periodate concentration increased. These properties were similar to that of slightly crosslinked starch [23]. *Veelaert* et al. [5, 9] suggested that the C-2 and C-3 aldehyde groups are prone to form several inter- and intramolecular hemiacetal and acetal crosslinks. These linkages contributed to the reinforcement of starch granules and stabilized the swelling of the granules [5, 24]. In addition to the presence of carboxyl groups, DAS granules showed a higher swelling than native tapioca starch because of their higher hydration capacity [24, 25]. However, unlike the chemically crosslinked starch, which usually exhibits a lower breakdown, DAS had higher breakdown than the native one. It may be proposed that the hemiacetalization linkages in DAS are weak and easily broken [4]. The final viscosities of DAS were lower than that of the native one due to the degradation of starch molecules during periodate oxidation.

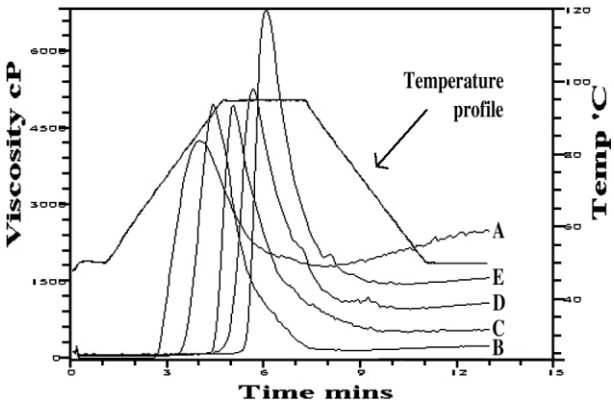

Fig. 4. Pasting profiles of DAS prepared by oxidation of tapioca starch with various periodate concentrations. A: native tapioca starch, B: 0.05 N $NaIO_4$, C: 0.1 N $NaIO_4$, D: 0.2 N $NaIO_4$ and E: 0.3 N $NaIO_4$.

3.7 Swelling power and solubility

Swelling power and solubility of DAS are shown in Fig. 5. The swelling power of DAS was higher than that of the native one at 60°C and 70°C but was lower at 80°C and

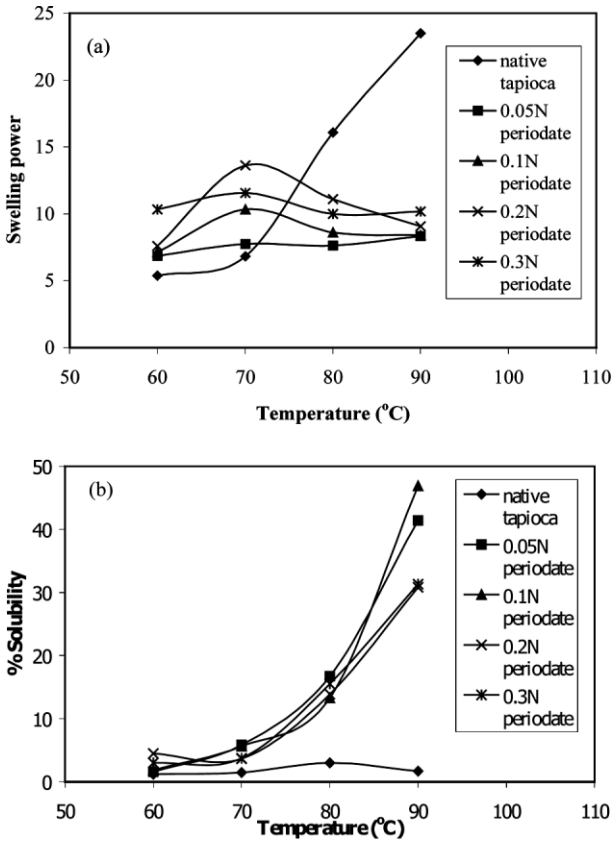

Fig. 5. (a) Swelling power and (b) % solubility as a function of temperature of DAS prepared by oxidation of tapioca starch with various periodate concentrations.

90°C. Although 60°C was below the average onset gelatinization temperature of all starches as measured by DSC (63°C−67°C), some starch granules were capable of swelling. These results indicated that DAS had a higher hydration capacity than the native starch at 60°C and 70°C due to the hydration capacity of the aldehyde and carboxyl groups. When the incubation temperature was increased to 80°C and 90°C, the ability of holding the absorbed water was lost due to the unstable hemiacetal crosslinks accompanied with the degradation of DAS during oxidation [9].

Solubility represents the amount of solubilized starch molecules at a certain temperature. The solubility of DAS was higher than that of native tapioca starch at all incubation temperatures (60, 70, 80 and 90°C). In general, the solubility increased as the incubation temperature increased. The solubility was related to the swelling power. At 60°C and 70°C, most of the swollen DAS granules still maintained their water holding capacity so that a small amount of starch molecules were leached out from them. In contrast, DAS cannot maintain the swollen granules at 80°C and 90°C incubation temperatures and a large amount of solubilized starch molecules were capable of leaching out of the granules.

3.8 Molecular weight distribution

The HPSEC chromatogram of native tapioca starch can be divided into two major fractions: fraction I and II (Fig. 6). Fraction I, which eluted first (first peak), consisted of high molecular-weight carbohydrates, mainly amylopectin. Fraction II which eluted later (second peak), consisted of low molecular-weight carbohydrates, mainly amylose. Native tapioca starch showed the first peak at DP 9.4×10^4 and second peak at DP 2.2×10^4 (calculated from calibration curve). After periodate oxidation, the eluted fractions of DAS shifted to longer retention time, indicating the decreasing of degree of polymerization. The elution patterns showed the progressive appearance of peaks at the lower degree of polymerization and the disappearance of peaks at higher degree of polymerization with increasing periodate concentration. It implied that both amylopectin and amylose fractions were degraded during the periodate oxidation.

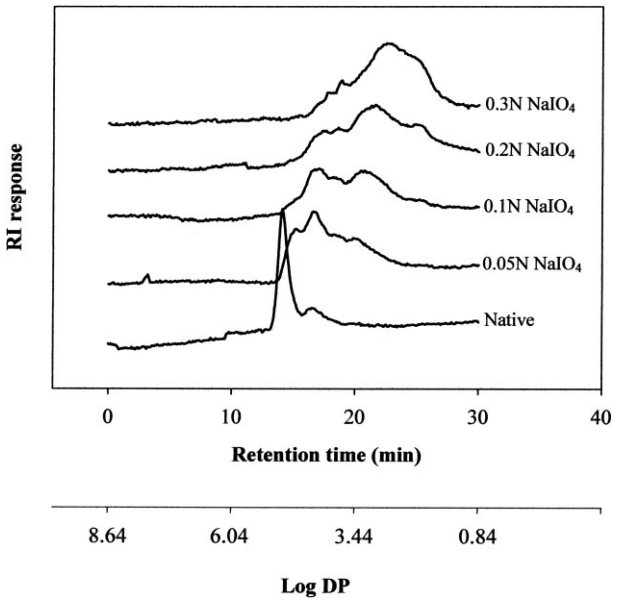

Fig. 6. HPSEC patterns of DAS prepared by oxidation of tapioca starch with various periodate concentrations.

3.9 Thermal stability

Periodate oxidized starch sample prepared with 0.3 N periodate was heated at 100°C at various length of heating times (5, 15, 30 and 60 min) prior to HPSEC analysis, depicted in Fig. 7. Surprisingly, it was found that all chromatograms showed similar patterns, which consisted of two major peaks; a large peak with lower degree of polymerization (approx. 6.2×10^2) and a small peak with higher degree of polymerization (approx. 5.6×10^3) appearing as a shoulder of the large peak. This demonstrated the absence of depolymerization at any heating time and accounted for the thermal stability of DAS. It has been reported previously [9] that the molecular weight decreased with the increasing heating time and concluded that the DAS was thermally unstable. However, such finding was proven to be inaccurate. In reality, degradation was caused by the oxidation of DAS by residual periodate during the heating periods.

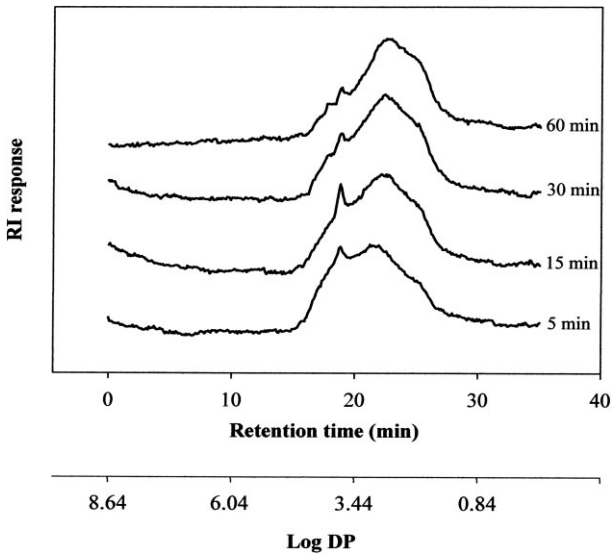

Fig. 7. HPSEC patterns of DAS prepared by oxidation of tapioca starch with 0.3 N periodate after heating at various length of times prior to HPSEC analysis.

4 Conclusion

It was found that the physicochemical properties of tapioca starch changed during periodate oxidation. The presence of aldehyde and carboxyl groups, causing hemiacetal linkages, contributed to the increasing of gelatinization temperature of DAS. Moreover, the periodate oxidation caused a loss of crystallinity. The hemiacetal and acetal crosslinks as well as aldehyde and carboxyl groups in DAS affected the pasting properties such as high pasting temperature and peak viscosity. The degradation of DAS molecules during oxidation resulted in a decrease in final viscosity. This also suggested that the swollen DAS granules were not able to tolerate high incubation temperature, which resulting in higher solubility. In fact, the degradation of both amylose and amylopectin fractions occurred during the periodate oxidation and the oxidized product was not depolymerized during the heating as demonstrated for the thermal stability of the DAS.

Acknowledgements

The authors would like to thank the ministry of education for Ph. D. scholarship.

References

[1] V. F. Pfeifer, V. E. Sohns, H. F. Conway, E. B. Lancaster, S. Dabic, E. L. Griffin, Jr.: Two-stage process for dialdehyde starch using electrolytic regeneration of periodic acid. *Ind. Eng. Chem.* **1960**, *52*, 201–206.

[2] C. L. Mehltretter: Some landmarks in the chemical technology of carbohydrate oxidation. *Stärke* **1963**, *15*, 313–319.

[3] T. A. McGuire, C. L. Mehltretter: Chemical process for making dialdehyde starch. *Stärke* **1971**, *23*, 42–44.

[4] O. B. Wurzburg: Converted Starches, in *Modified starches: Properties and Uses* (Ed. O.B. Wurzburg) CRC Press, Boca Raton, FL, **1986**, 28–29.

[5] S. Veelaert, D. de Wit, K. F. Gotlieb, R. Verhe: The gelation of dialdehyde starch. *Carbohydr. Polym.* **1997**, *32*, 131–139.

[6] S. Veelaert, M. Polling, D. de Wit: Structural and physicochemical changes of potato starch along periodate oxidation. *Starch/Stärke* **1994**, *46*, 263–268.

[7] J. W. Rhim, A. Gennadios, C. L. Weller, C. Cezeirat, M. A. Hanna: Soy protein isolate-dialdehyde starch films. *Ind. Crops Prod.* **1998**, *8*, 195–203.

[8] A. Gennadios, A. Handa, G. W. Froning, C. L. Weller, M. A. Hanna: Physical properties of egg white-dialdehyde starch films. *J. Agric. Food Chem.* **1998**, *46*, 1297–1302.

[9] S. Veelaert, D. de Wit, K. F. Gotlieb, R. Verhe: Chemical and physical transitions of periodate oxidized potato starch in water. *Carbohydr. Polym.* **1997**, *33*, 153–162.

[10] AOAC, Official Method of Analysis, *Ash and Moisture Content*, 15th ed., Association of Official Analytical Chemistry, Arlington, USA, **1990**, 777.

[11] AOAC, Official Method of Analysis, *Protein*, 15th ed., Association of Official Analytical Chemistry, Arlington, USA, **1990**, 781.

[12] AOAC, Official Method of Analysis, *Fat*, 15th ed., Association of Official Analytical Chemistry, Arlington, USA, **1990**, 780.

[13] C. A. Knutson: A simplified colorimetric procedure for determination of amylose in maize starches. *Cereal Chem.* **1986**, *63(2)*, 89–92.

[14] S. Varavinit, N. Chaokasem, S. Shobsngob: Covalent immobilization of a glucoamylase to bagasse dialdehyde cellulose. *World J. Microbiol. Biotechnol.* **2001**, *17*, 1–5.

[15] U.S. Pharmacopeia **1990**, 22, 1986.

[16] R. J. Smith, R. L. Whistler, E. F. Paschall: Production and use of hypochlorite oxidized starches, *Starch Chemistry and Technology*, Academic Press, New York, **1967**, 620–625.

[17] S. Chattopadhyay, R. S. Singhal, P. R. Kulkarni: Optimization of conditions of synthesis of oxidized starch from corn and amaranth for use in film-forming applications. *Carbohydr. Polym.* **1997**, *34*, 203–212.

[18] T. Komiya, S. Nara: Changes in crystallinity and gelatinization phenomena of potato starch by acid treatment. *Starch/Stärke* **1986**, *38*, 9–13.

[19] J. Holm, L. Björck, N. G. Asp, L. B. Sjöberg, I. Lundquist: Starch availability in vitro and in vivo after flaking steam cooking and popping of wheat. *J. Cereal Sci.* **1985**, *3*, 193–206.

[20] S. Govindasamy, C. G. Oates, H. W. Wong: Characterization of changes of sago starch components during hydrolysis by thermostable alpha-amylase. *Carbohydr. Polym.* **1992**, *18*, 89–100.

[21] J. L. Jane, J. F. Chen: Effect of amylose molecular size and amylopectin branched chain length on paste properties of starch. *Cereal Chem.* **1992**, *69*, 60–65.

[22] D. Kuakpetoon, Y.-J. Wang: Characterization of different starches oxidized by hypochlorite. *Starch/Stärke* **2001**, *53*, 211–218.

[23] O. B. Wurzburg: Cross-Linked Starches, in *Modified starches: Properties and Uses* (Ed. O. B. Wurzburg) CRC Press, Boca Raton, FL, **1986**, 41–53.

[24] Y.-J. Wang, L. Wang: Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. *Carbohydr. Polym.* **2003**, *52*, 207–217.

[25] F. F. Farley, R. M. Hixon: Oxidation of raw starch granules by electrolysis in alkaline sodium chloride solution. *Ind. Eng. Chem.* **1942**, *34*, 677–681.

(Received: March 27, 2004)
(Revised: November 16, 2004)
(Accepted: November 17, 2004)

