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A Study of some Physicochemical Properties of Dialdehyde Tapioca Starch (DAS)

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1. Introduction

Dialdehyde starch (DAS) is a product obtained by oxidation of starch with periodate under controlled temperature and pH. Periodate or periodic acid is highly specific, oxidizing only the hydroxyls at carbon atom C-2 and C-3 in anhydroglucose unit to aldehydric groups and severing the C-2 and C-3 linkage resulting in the formation of two aldehydes per anhydroglucose unit [1-6]. Because of its reactive aldehyde groups, dialdehyde starch is used as the crosslinking agent. Therefore, most of the applications of dialdehyde starch are based on a crosslinking reaction with, e.g. cellulose in paper, cotton in textile or protein in pharmaceuticals of leather [4-8]. The present of aldehyde groups is attributed to form internal crosslinks by 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 and little work has been done to study the properties changes by 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 oxidized by different concentrations of periodate to investigate the physico-chemical properties changes after periodate oxidation such as aldehyde and carboxyl contents, relative erystallinity, thermal properties, pasting properties, swelling power and % solubility.

2. Materials and Methods

2.1. Materials

Tapioca starch was the product of General Starch Co., Ltd. (Thailand). Sodium metaperiodate was purchased from Asia Pacific Specialty Chemical Co., Ltd. (Australia). Other reagents were analytical grades, purchased from Merck Co., Ltd.

2.2 Preparation of dialdehyde tapioca starch (DAS)

Dialdehyde tapioca starch was prepared by following the modified method for bagasse dialdehyde cellulose preparation of *Varavinit* et al. [10]. The 200g (dry basis) of tapioca starch was suspended in 500 ml of various concentration of sodium metaperiodate solution (0.05N, 0.1N, 0.2N and 0.3N). The pH of starch suspension was then adjusted to 3.0 by using 2% (v/v) HCl. The reaction was performed in water bath at 32 °C and 400 rpm for 1 h. After the end of the periodate oxidation, the starch suspension was washed with distilled water for 3 cycles (1.6L/ cycle). The washed starch was immersed in 500 ml of 0.5% (w/v) of sodium metabisulfite solution for 1h in order to destroy the residual oxidizing substance (sodium metaperiodate). Consequently, the suspension was washed again with distilled water for 3 cycles (1.6L/ cycle). The washed water was removed by centrifugation (Sorvall RC 3B Plus, Du Pont Company, Delaware, USA). The starch cake was dried in oven at 45 °C, overnight. The dried starch was milled and sieved through 100-mesh sifter to obtain dialdehyde tapioca starch powder.

2.3 Determination of aldehyde content

The aldehyde group content was determined by following the modified titrimetric method of *Smith* [11]. Aldehyde content was calculated as follows:
Percentage of aldehyde content = [(Blank – Sample) ml × Acid normality × 0.028 × 100]/Sample weight (dry basis) in g

2.4 Determination of carboxyl content

The carboxyl content was determined by following the modified method of *Chattopadhyay, Singhal* and *Kulkarni* [12]. Carboxyl content was calculated as follows:
Milliequivalents of acidity/100g starch = [(Sample – Blank) ml × Normality of NaOH × 100]/ Sample weight (dry basis) in g
Percentage of carboxyl content = [Milliequivalents of acidity/100g starch] × 0.045

2.5 X-ray power diffraction measurement

The X- ray diffraction patterns of native and DAS were recorded with a copper anode X-ray tube (Cu-K_α radiation) using Bruker X-ray powder diffractometer (D-8 type, Bruker, Germany). The starch powers were packed tightly in sample holder. Each sample was exposed to the X-ray beam at 30kV and 30nA. The scanning region of the diffraction angle (2θ) was from 5° to 30°A at 0.4° step size with a count time of 1.0 s and rotary speed of sample holder is 30 min^{-1}. The starch samples were equilibrated in a 100% RH chamber for 24 h at room temperature before measurement.

The relative crystallinity of starch samples was quantitatively estimated by the method of *Komiya* and *Nara* [15]. The ratio of upper crystalline area to total diffraction area was calculated as the relative crystallinity.

2.6 Thermal properties

The thermal properties of unmodified and DAS were assessed by Differential Scanning Calorimeter (DSC Pyris, Perkin Elmer,Belerica, MA, USA). Both native and DAS (base on weight free from moisture) was adjusted 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 to 120 ^oC at 10^oC/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 (Tc) temperatures, and melting enthalpy (ΔH in J/g of dried starch) were recorded.

2.7 Pasting properties

A Rapid Visco-Analyzer (Series 4V,Newport Scientific Pty. Ltd, Warriewood, Australia) was employed to investigate the pasting properties of native 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 aluminum can with 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, held at 95 °C for 2.5 min, cooled down to 50 °C at a rate of 12 °C/min and held at 50 °C for 2 min.

2.8 Swelling power and % Solubility

The swelling power (SP) and %solubility were measured according to the modified procedure of *Holm, Björck, Asp, Sjoberg* and *Lundquist* [17] by suspending a 3.3% starch suspension (1 g starch in 30 ml water) into a centrifuge tube with cap and then stirring with vortex. The starch suspension was incubated in water bath from 60 to 90 °C at 10°C intervals and the sample was kept at that temperature for 30 min. The heated sample was cooled to room temperature for 30 min and then centrifuged at 1000 × g for 15 min at 25 °C. Swelling power was determined by measuring the sediment paste weight and % solubility by the solid content of the supernatant.

Results and Discussion

3.1 Aldehyde and carboxyl groups contents

The relationship between periodate concentration and aldehyde and carboxyl groups contents of DAS are shown in Fig.1. Both aldehyde and carboxyl contents of DAS increased as periodate concentration increased. The increase was much greater for the aldehyde content than for the carboxyl content because of the selective oxidation conducted by periodate which promoted the production of dialdehyde groups per anhydroglucose unit. 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 [18].

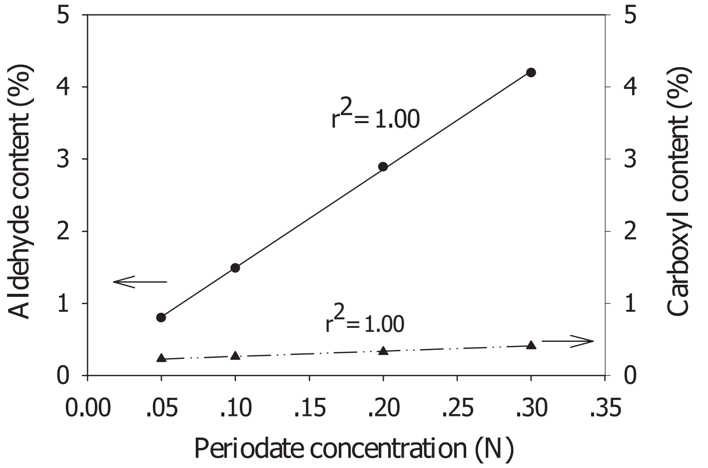

Fig. 1. Percentages of aldehyde and carboxyl contents of DAS oxidized by various periodate concentrations

3.2 X- ray diffraction

X- ray diffraction patterns of DAS resembled the pattern of unmodified tapioca starch (figures not shown). It was dictated 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 could be assumed that the periodate oxidation of tapioca starch caused a loss of crystallinity and long range ordering. It is implied that periodate oxidation occurred at both amylopectin and amylose fraction of the crystalline and amorphous region of starch granules. The present of hydrophilicity of functional groups as aldehyde and carboxyl contents on DAS caused the decrease of crystallinity [6].

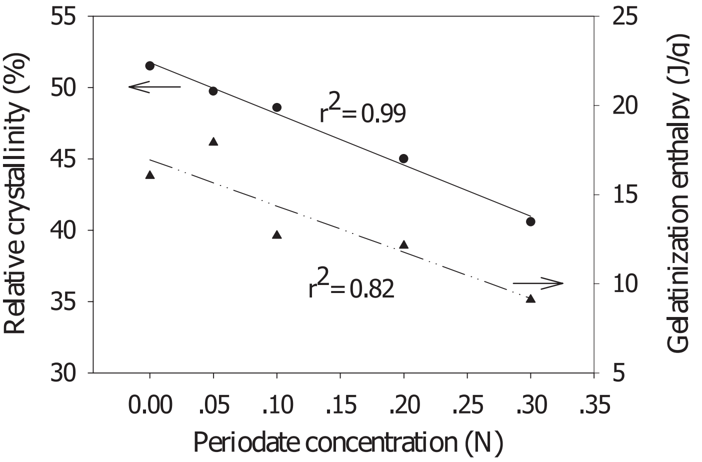

Fig. 2. Relative crystallinity and gelatinization enthalpy of DAS as a function of periodate concentration.

3.3 Thermal properties

The endotherm patterns of DAS exhibited sharper than that of the native one (figures not shown).The onset (To), peak (Tp) and conclusion (Tc) temperatures, and gelatinization enthalpy (ΔH) are summarized in Table 1. It was found that gelatinization temperature (To and Tp) increased with increasing periodate concentration. It was probable due to the high polarity of functional groups (aldehyde and carboxyl groups), Van der Waal and H-bonding within DAS molecules can be promoted causing the integrity molecules.

Periodate concentration (N)	DSC characteristics			
	To(°C)	Tp(°C)	Tc (°C)	ΔH (J/g)
0	62.522	69.851	84.541	16.058
0.05	65.375	71.711	80.434	17.919
0.1	67.027	73.006	83.556	12.690
0.2	67.499	74.401	82.552	12.134
0.3	67.497	74.171	81.568	9.111

To, Tp and Tc ; onset temperature, peak temperature and concluse temperature
Tc-To ; temperature range
ΔH ; gelatinization enthalpy

Tab. 1. DSC characteristics of DAS oxidized by various periodate concentrations.

The gelatinization enthalpy (ΔH) of DAS decreased as the periodate concentration increased as shown in Tab.1 and Fig. 2. Gelatinization enthalpy indicates the amount of energy required to gelatinize the starch [19]. Generally, the gelatinization enthalpy (ΔH) of DAS was positively related to their degree of crystallinity. When the loss of ordering or crystallinity was performed, the energy that used to melt starch granule was also decreased [6].

3.4 Pasting properties

The pasting profiles of DAS with various periodate concentrations differed from the native one (figures not shown). All of the pasting properties of native and DAS were plotted against the extent of oxidation in term of aldehyde contents in Fig. 3. and carboxyl contents in Fig. 4. The pasting temperatures, pasting time as well as the peak viscosity of DAS increased as the extent of aldehyde and carboxyl contents increased when compared with the native tapioca starch. These properties were similar to the characteristic of slightly crosslinked starch [20]. *Veelaert* et al. [5,9] suggested that the C-2 and C-3 aldehydes are prone to form several inter- and intramolecular hemiacetal and acetal cross-links. These linkages contributed the reinforcement of starch granules and stabilized the swelling of the granules [5,21]. In addition to the present of carboxyl groups, DAS granules shown the higher swelling than native tapioca starch because of their higher hydration capacity [21,22]. However, unlike the conventional chemically crosslinked starch, which usually exhibits a lower breakdown, DAS had higher breakdown than the native one. It may be proposed that the chain scission was occurred at high temperature. Veelaert et al. [9] proposed that extensive chemical degradation of DAS occurred at neutral conditions and upon heating at 90 °C. Moreover, the hemiacetalization linkages in DAS are weak and easily broken [4]. Consequently, the final viscosity of DAS was lower than that of native one due to the starch depolymerization.

3.5 Swelling power and % Solubility

Swelling power and %solubility of DAS are shown in Fig. 5. The swelling powers of DAS were higher than that of native one at 60 and 70 °C but lower at 80 and 90 °C. Although 60°C was below the average onset gelatinization temperature of all starches as measured by DSC (63-67°C), some starch granules were capable of swelling. From this results indicated that DAS had the hydration capacity more than the native one at 60 and 70 °C due to the hydration capacity of functional groups (aldehyde and carboxyl groups). When the incubation temperature was increased to 80 and 90 °C, the ability of holding the absorbed water is lost due to the occurrence of depolymerization [9].

Solubility represents the amount of solubilized starch molecules at a certain temperature. Percent 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 increases as the incubation temperature increased. The solubility results were related to the swelling power. At 60 and 70°C, the most of swollen DAS granules still maintained the water holding capacity so that the small amount of starch molecules were leached out from them. In contrast, due to the degradation of DAS molecules at 80 and 90 °C incubation temperatures, the large amount of solubilized starch molecules were capable of leaching out of granules.

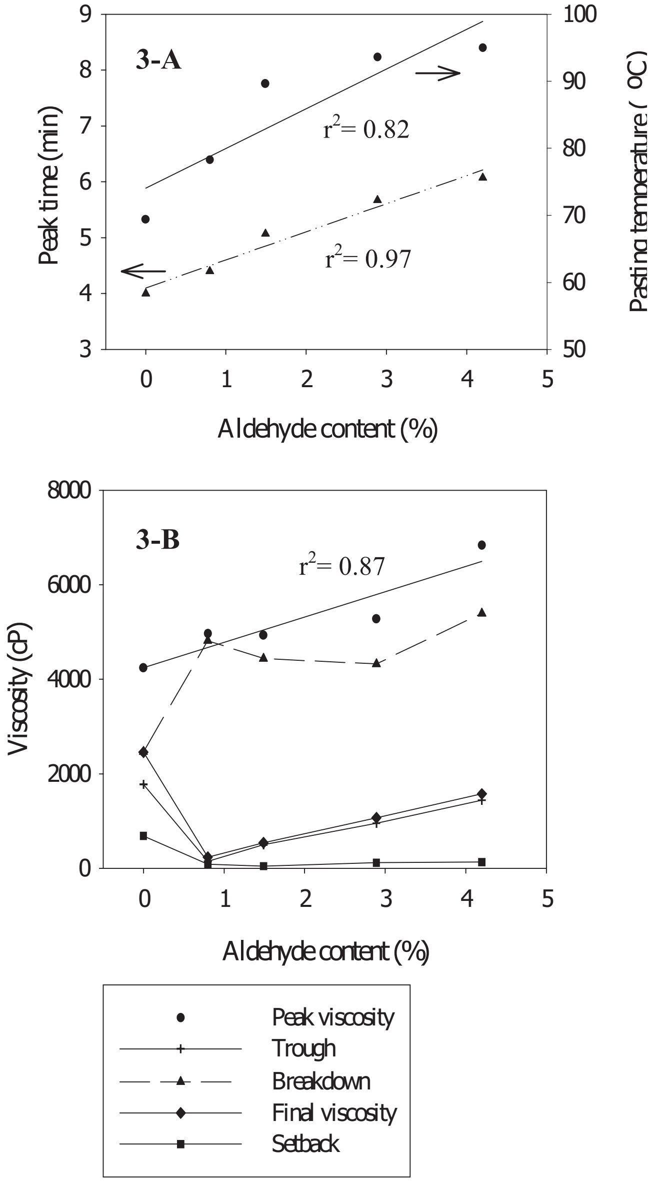

Fig. 3. Relationship among aldehyde content and pasting properties: peak time and pasting temperature (A), peak viscosity, though, breakdown, final viscosity and setback (B).

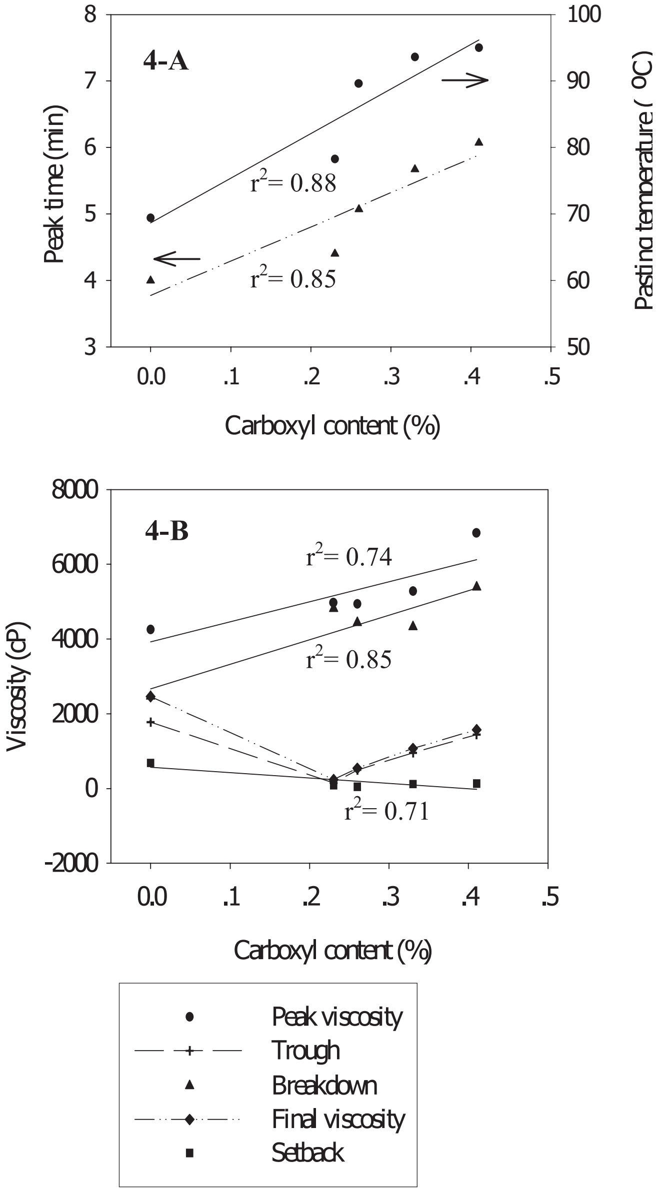

Fig. 4. Relationship among carboxyl content and pasting properties: peak time and pasting temperature (A), peak viscosity, though, breakdown, final viscosity and setback (B).

4. Conclusion

The physicochemical properties changes of native tapioca starch were occurred during periodate oxidation. The present of aldehyde and carboxyl contents affected to the increasing of gelatinization temperature of DAS. Periodate oxidation caused the loss of crystallinity. The hemiacetal and acetal formation cross-links as well as aldehyde and carboxyl groups in DAS affected the pasting property as high pasting temperature and peak viscosity. The swollen DAS granules were not tolerant to high incubation temperature therefore theirs solubility at this temperature was shown as high level.

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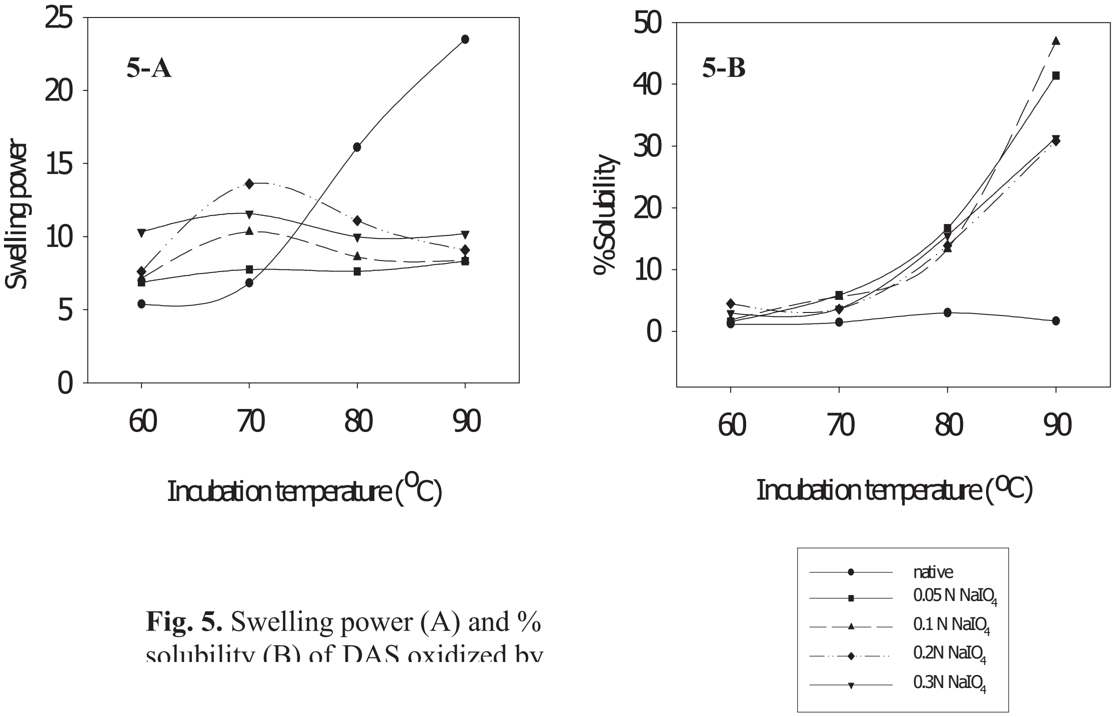

Fig. 5. Swelling power (A) and % solubility (B) of DAS oxidized by

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