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Effect of sodium hydroxide concentration on properties of carboxymethyl rice starch

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Abstract: Effect of sodium hydroxide (NaOH) concentrations on properties of carboxymethyl rice starch (CMS_r) was investigated. Fourier transform-infrared (FTIR) spectrum confirmed that carboxymethylation took place on the starch molecules. The DS value of CMS_r increased with increasing NaOH concentrations (10-40% w/v). However, when the level of NaOH concentration reached 50%, the DS of the CMS decreased. The viscosity of CMS_r decreased with increasing NaOH concentrations. The morphology of native rice starch and CMS_r was further investigated through scanning electron microscope (SEM). The mirco-structure revealed that the morphology of CMS_r granules were more damage with increasing NaOH concentration which related with DS.

Keywords: Biopolymer, carboxymethyl rice starch, degree of substitution, morphology, NaOH, sodium hydroxide

Introduction

Rice is the most widely consumed basic foodstuff in the world and the main crop grown in most parts of Asia including China, India, Japan, Vietnam and Thailand. In Thailand, as the main export good, rice is relatively cheap with little fluctuation in its price. Modified rice starch is one of the alternatives to add value to rice. Rice starch is well known in food and non-food industrial applications. It is used in the manufacturing of corrugated board adhesives, paper, textiles, pharmaceuticals, cosmetics (Dong-fang *et al*., 2005). Starch is regarded as an attractive starting material for such products because it is a natural polymer which can be mass-produced form sustainable agricultural products (Takahashi *et al.*, 2002). However, the applications of native rice starch have still been limited because it is slightly opaque and insoluble in cold water (Phan *et al.*, 2005).

Starch modification is one of the methods that can improve the physical and chemical properties of rice starch. Carboxymethyl starch (CMS) derivatives with etherified starches have attracted a lot of attention recent years (Lawal *et al.*, 2008b). CMS is obtained by a reaction between native starch and chloroacetic acid in an alkaline condition. The first step is an alkalization procedure where sodium hydroxide (NaOH) reacts with the hydroxyl groups of the starch molecule and is transformed into an alkoxide form (St-O-) (Lawal *et al.*, 2008b):

$$St\text{–}OH + NaOH \longleftrightarrow St\text{–}ONa + H_2O \quad (1)$$

In the second step etherification occurs:

$$St\text{–}ONa + Cl\text{-}CH_2\text{-}CO\text{-}ONa \rightarrow St\text{–}O\text{-}CH_2\text{–}COONa + NaCl \quad (2)$$

Additionally, a side reaction also occurs which competes with the carboxymethylation process, that being the reaction between sodium hydroxide (NaOH) and sodium monochloro acetate (SMCA) to form sodium glycolate:

$$NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl \quad (3)$$

In the literature, many starches have been used for synthesis of CMS such as cassava starch (Sangseethong *et al.*, 2005), corn starch (Kamel and Jahangir, 2007), sago starch (Fadzlina *et al*., 2005), mungbean starch (Kittipongpatana *et al.*, 2008; Kittipongpatana *et al.*, 2006), arrowroot starch (Kooijman *et al.*, 2003), water yam starch (Lawal *et al.*, 2008a) and rice starch (Kittipongpatana *et al*., 2006a). Much research has also been done to investigate the effect of reaction parameters on the caboxymethylation of starch such

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as molar ratio or concentration of NaOH (Fadzlina *et al.*, 2005; Jie *et al*., 2004; Kamel and Jahangir, 2007; Lawal *et al*., 2008b; Sangseethong *et al.*, 2005), amount of etherifying agent (Sangseethong *et al*., 2005; Jie *et al.*, 2004; Fadzlina *et al*., 2005; Lawal *et al.*, 2008b), types of solvents (Kooijman *et al.*, 2003; Heinze *et al.*, 2004; Jie *et al*., 2004; Kittipongpatana *et al*., 2006; Kamel and Jahangir, 2007; Lawal *et al.*, 2008b) and amylose content (Kittipongpatana *et al*., 2006a). The major properties of CMS include a low gelatinized temperature, swelling ability and cold water solubility (Fadzlina *et al*., 2005). These properties of CMS can be characterized by the degree of substitution (DS), the average number of hydroxyl groups substituted by carboxymethyl groups (Zhou *et al*., 2007).

The properties of CMS are of benefit in many applications more so than native starch. CMS is widely used in many fields of food science, for example, it can be used as a stabilizing agent for ice-cream, vegetable product, soft drinks and as a preservative for fresh meat, vegetable and fruit. CMS has also been applied in non-food industries, for example, being used as a sizing and printing agent in the textile industry (Ragheb *et al.*, 1997; Dong-fang *et al.,* 2005), a film-former for tablet coating and a gel base coating in the pharmaceutical industry (Kittipongpatana *et al*., 2008).

However, only a few investigations into the preparation of carboxymethyl rice starch have been published (Kittipongpatana *et al*., 2006a; Takahashi *et al.,* 2002). Besides the effect of sodium hydroxide (NaOH) concentrations on the synthesis process of carboxymethyl rice starch (CMSr), few additional properties have been studied in any great detail (Bhattacharyya *et al*., 1995; Yanli *et al*., 2009). Therefore, this research was aimed at determining the effect of NaOH concentration on the degree of substitution (DS), color, viscosity, crystallinity and morphology of CMSr powder.

Materials and Methods

Materials

Native rice starch was donated by Thaiflour Industry Co.,Ltd (Nakornprathom, Thailand). Sodium hydroxide, glacial acetic acid, isopropanol, hydrochloric acid, sodium chloride (Merck), chloro acetic acid (Fluka) are all of analytical grade. Absolute methanol is commercial grade from Northern Chemical. Co., Ltd. (Chiang Mai, Thailand).

Instrumentation

Infrared spectroscopy (IR) was performed using a Tensor 27 (Bruker, England). A scanning electron microscope (SEM), JSM-5910LV (JEOL, USA) was used to investigate physical surface properties. CMSr L*, where a* and b* color values were analyzed using a Color Quest XE 3317 (Hunterlab, USA). Viscosity was determined with a Rapid Visco Analyzer (Model : RVA-4, Newport Scientific Pvt., Ltd., Australia). The X-ray diffraction data were collected at room temperature using a Brucker D8 Advance diffractormeter, Germany.

Synthesis of carboxymethyl starch (CMSr)

The synthesis of carboxymethyl rice starch followed the method of Kittipongpatana *et al.* (2006a) with some modifications. First, thirty grams of monochloroacetic acid was dissolved in 400 mL of isopropyl alcohol. Then 100 g of native rice starch was dispersed in the solution with continuous stirring. One hundred mililiters of aqueous NaOH solution with various amounts of NaOH (10, 20, 30, 40, 50 and 60% w/v of water) were added into the mixture and heated up to 50ºC for 20 minutes. At the end, the slurry was neutralized with glacial acetic acid and purified by filtration and washing with 95 % methanol four times. The resulting modified carboxymethyl starch (CMSr) was dried in an oven at 50ºC for 17 hours before being passed through a no. 80 mesh sieve.

Fourier transform-infrared (FTIR) spectroscopy

The FTIR absorbtion spectra of rice starch and carboxymethyl starch were run using the KBr disc technique with a Nicole 510 FT-IR in the range of 4000–500 cm^{-1}.

Degree of substitution (DS)

The degree of substitution (DS) was defined as the average number of substitution per anhydroglucose unit (AGU) and varied between 0 and 3. The DS of the carboxymethyl starch was measured by the USP XXIII method described for crosscarmellose sodium which included two steps-titration and residue on ignition. The DS of CMSr was then calculated using Equation (4) (Kittipongpatana *et al*., 2006):

$$DS = A + S \quad (4)$$

where A is the degree of substitution of carboxymethyl acid, S is the degree of substitution of sodium carboxymethyl, and A and S can be calculated using the data from the titration and ignition steps:

$$A = 1150M / (7120 - 412M - 80C) \quad (5)$$

$$S = (162 + 58A)C / (7120 - 80C) \quad (6)$$

where M is the net milliequivalent of base required for the neutralization of 1 g CMS_r as determined in titration testing and C is the percentage of residue on ignition of CMS_r as determined by residue ignition testing.

Titration

About one gram of CMS_r, was added to a 500 ml Erlenmyer flask with 300 ml of sodium chloride (NaCl) solution (10% w/v). After that NaOH 0.1 N concentration 25 ml was added into the mixture. The erlenmyer flask was closed with aluminium-foil and shook for 5 minutes. Then, five drops of m-cresol purple was added and the mixture turned violet. Fifteen mililiters of 0.1 N hydrochloric (HCl) solution was then added to the mixture. If the mixture was still violet, 0.1 N HCl solution 0.1 ml portions were added until the solution became yellow. In the next step, the mixture was back titrated with 0.1 N sodium hydroxide until the mixture turned to violet at the endpoint. The net milliequivalent of base required for the neutralization of 1 g CMS_r (M) was calculated using Equation (7):

$$M\ (mEq) = m\ mole \times Valence \qquad (7)$$

Where m is 10^{-3} ; the mole is the mass in grams per molecular weight of NaOH and the Valence of NaOH is 1 (Kittipongpatana *et al*., 2006).

Residue on ignition

The crucible was dried in the oven at 100°C for 1 h. and kept in the desiccator until attaining a constant weight. About one gram of CMS_r was then added into the crucible. The crucible containing CMSr was ignited at 400°C around 1-1.5 h until the residue turned black and was placed into the desiccator. About one mililiter of sulfuric acid (H_2SO_4) was added to the black residue and heated until there were no white fumes. The crucible containing residue was then ignited at 800±25°C to obtain the white residue and again placed in the desiccator following AOAC method 900.02 (AOAC official method 900.02, 2005). Finally, the white residue was weighed. The percentage of residue on ignition (C) was calculated using Equation (8):

$$C = (\text{weight of residue} / \text{weight of CMSr}) \times 100 \qquad (8)$$

Scanning electron microscopy (SEM)

The morphology of native rice starch and carboxymethyl rice starch was investigated using a scanning electron microscope (SEM) at an acceleration voltage of 15 kV with 1000x.

Color measurement

The color characteristics were assessed using a Color Quest Spectrocolorimeter to determine L* value (lightness or brightness), a* value (redness or greenness) and b* value (yellowness or blueness) of native rice starch and CMCr samples. The colorimeter was warmed up for 30 min and calibrated with a white standard tile: L* = 94.37, a* = -0.83, and b* = 0.02. Measurements were taken for three samples and then an average of Hunter L*, a*, and b* value were obtained. Utilizing these Hunter color values, total color difference (TCD or ΔE) and whiteness index (WI) was calculated as given by Equation. (9) and (10)

$$\Delta E = Total\ color\ difference = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (9)$$

$$WI = 100 - \sqrt{(100 - L^*)^2 + (a^*)^2 + (b^*)^2} \qquad (10)$$

where ΔL*, Δa* and Δb* were obtained as differences in L*, a* and b* values of the sample with the white standard.

Viscosity

The viscosities of the samples were determined using a Rapid Visco Analyzer. Three grams of starch or CMSr samples were added into 25 ml of distilled water in a RVA sample cup (12% moisture basis), which was controlled by a computer software, the thermo cycle for windows (TCW) (American Association of Cereal Chemists, AACC (Anon., 1998)). Peak viscosity (PV) and final viscosity were determined from the RVA plots. Each sample was run in triplicate to determine the mean value.

X-ray diffraction

The X-ray diffraction data were collected at room temperature using a Brucker D8 providing CuKα radiation (λ =1.54 Å) and operating at 40 kV and 20mA. A scan step mode was used with a step size of 0.04° per second. Each sample was scanned for a 2 θ range from 3-40 degrees.

Statistical analysis

A completely randomized experimental design was used to study the effect of NaOH on the properties of CMS_r powder. Analysis of variance (ANOVA) was used to determine the effect of NaOH. If differences in

mean existed, multiple comparisons were performed using Duncan's Multiple Range Test (DMRT) range test ($P<0.05$).

Results and Discussion

Percent yield of carboxymethyl rice starch (CMSr)

The percent yield of carboxymethyl rice starch powder synthesized with various NaOH concentrations is shown in Figure 1. Percent yield of carboxymethyl rice starch increased with increasing NaOH concentrations because when native starch reacts with chloroacetic acid in an alkaline condition, the hydroxyl groups of the starch molecule were transformed into an alkoxide form (St-O-) which then reacted with chloro acetic acid resulting in the St –O -CH_2 –COO- form (Lawal *et al*., 2008b). Therefore, the increase in percent yield is attributable to the presence of carboxymethyl group with their higher mass (Selke *et al*., 2004).

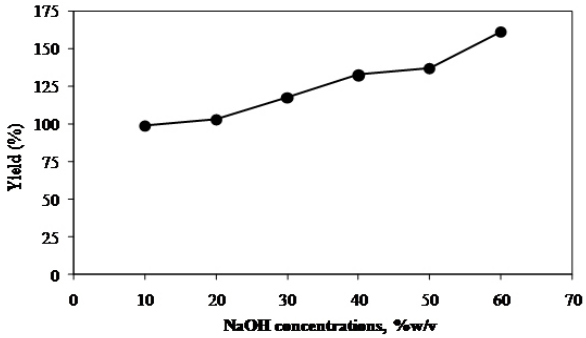

Figure 1. Percent yield of carboxymethyl rice starch synthesized with various NaOH concentrations (10, 20, 30, 40, 50 and 60 %w/v)

Fourier transform-infrared (FTIR) spectroscopy

Fourier transform-infrared spectroscopy was used to confirm the effectiveness of the synthesis (Zhou *et al*., 2007). The FTIR spectra of native rice starch and CMS_r is presented in Figure 2. The native rice starch and CMS_r had the same functional groups: hydroxyl group (-OH stretching) at 3400 cm^{-1}, methyl group (-CH_2 stretching vibrations) at 2931 cm^{-1}, carbonyl group (C=O stretching) at 1600 cm^{-1}, -CH^2 scissoring at 1420 cm^{-1} and -OH bending vibration at 1320 cm^{-1} (Rachtanapun, 2010). In CMS_r samples, when NaOH concentrations were increased, the bands of the carbonyl group (C=O), methyl group (-CH_2) and ether group (-O-) concurrently increased, but the band of the hydroxyl group (-OH) decreased. This result confirms that carboxymethylation took place on the starch molecules and similar observations were reported for carboxymethylated mungbean starch (Kittipongpatana *et al*., 2006) and yam starch (Lawal *et al*., 2008a).

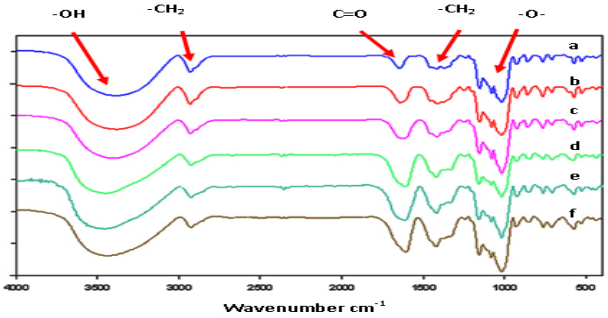

Figure 2. Infrared spectrum of a) native rice starch, CMS_r synthesized with various NaOH concentrations at b) 10%, c) 20%, d) 30%, e) 40% and f) 50%

Degree of substitution (DS)

The effect of NaOH concentration on the degree of substitution (DS) of CMS_r was investigated. The relationship between the use of various NaOH concentrations and DS values of CMS_r is shown in Figure 3. The values of the obtained carboxymethyl rice starch were from 0.08 – 0.38. Many researches have been studied on modification of starch via single step carboxymethylation. The similar results for the DS values such as carboxymethyl rice starch (0.24–0.40) (Kittipongpatana *et al*., 2006a), cross-linked carboxymethyl rice strach (0.30-0.38) (Suriyatem and Kittipongpatana, 2010), carboxymethyl chinese

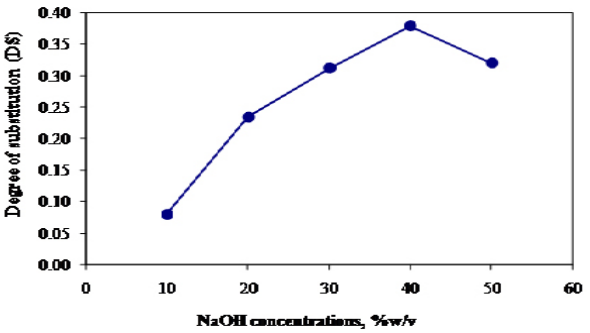

Figure 3. Effect of various NaOH concentrations on DS of CMSr

yam starch (0.05-0.45) (Yanli *et al*., 2009) and carboxymethyl corn starch (0.3–0.5) (Zhou *et al*., 2007) were reported. Lawal *et al*. (2008a) reported that multiple carboxymethylation by repeating in the optimal condition of single-step carboxymethylation for 9 times provided the very high DS carboxymethyl water yam starch (2.24). Zhou *et al*. (2007) found that DS value of CMS increased with increasing NaOH use level when the mole ratio of chloroacetic acid to starch was constant. However, incremental NaOH use level had no effect on DS value of CMS again when the mole addition of NaOH was two times as much as that of chloroacetic acid.

In this study, an increasing NaOH concentration resulted in an increasing DS which reached an optimum value at 40% NaOH concentration. This indicates

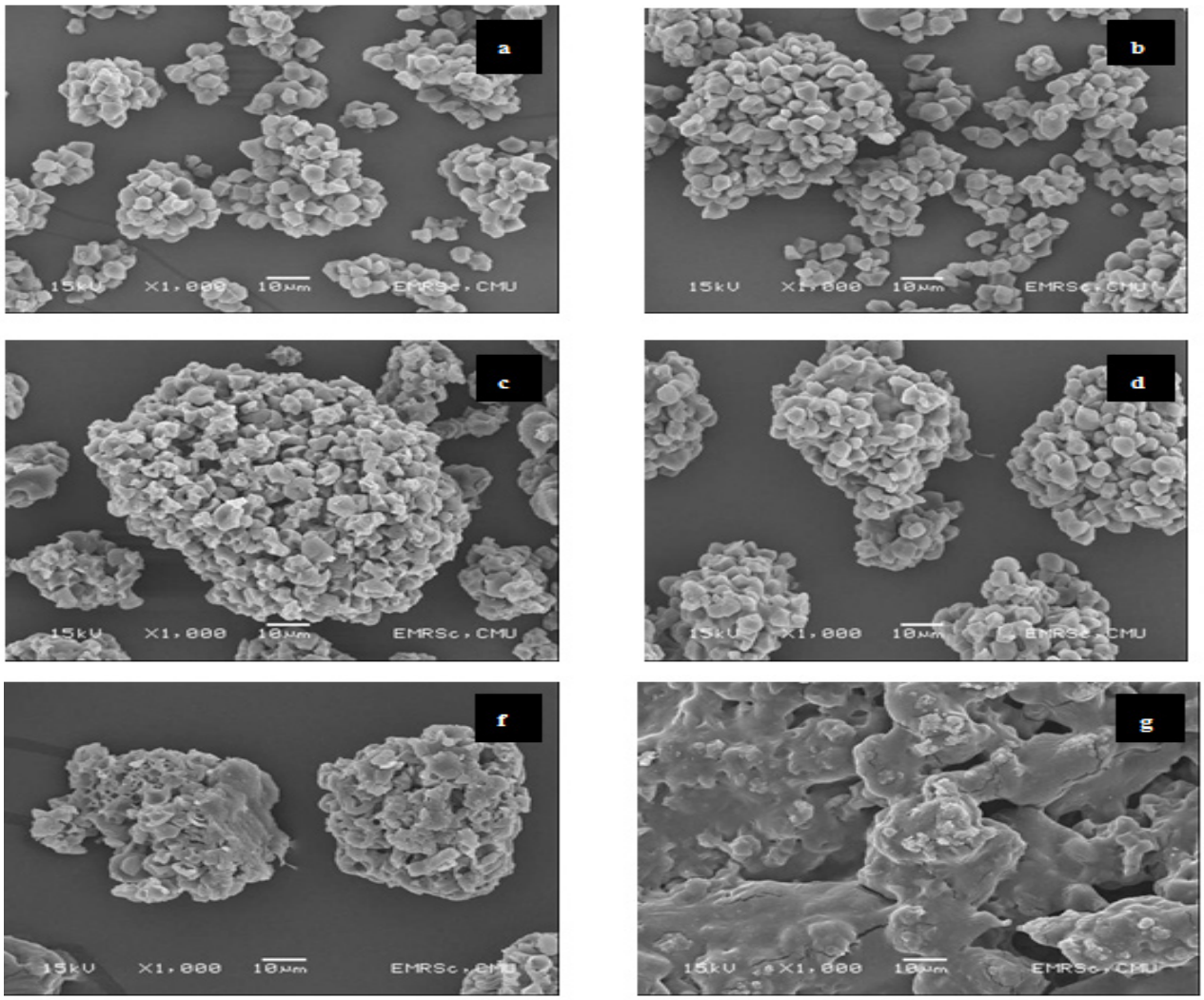

Figure 4. Scanning electron micrographs of a) native rice starch and CMS_r synthesized with NaOH concentrations at b) 10%, c) 20%, d) 30%, e) 40%, f) 50% and g) 60%: 1000x

that NaOH functions as a catalyst to activate starch molecules (Sangseethong *et al*., 2005). It facilitates the swelling of starch with an increased surface area for the etherification process to form starch alkoxide (Lawal *et al*., 2008b). However, when the NaOH concentration was 50%, the degree of substitution (DS) of CMSr decreased due to degradation of starch chains by the alkaline hydrolysis (Ragheb *et al*., 1997). Increases in the NaOH concentration also enhanced the formation of sodium glycolate (Tijsen *et al*., 2001). Similar results were also reported in previous investigations on maize starch (Khalil *et al*., 1990) corn and corn and amaranth starch (Bhattacharyya *et al*., 1995), cassava starch (Sangseethong *et al*., 2005), potato starch (Tijsen *et al*., 2001) and pigeon pea starch (Lawal *et al*., 2008b) as well as Chinese yam starch (Yanli *et al*., 2009).

Morphology of native rice starch and cmsr

A scanning electron microscope was used to investigate the granule morphology of both native rice starch and carboxymethyl rice starch. The results are shown in Figures 4a-g. The native rice starch granules appear smooth, polyhedral in shape and contain many individual granules (Figure 4a). This result is similar to Poochinya *et al.* (Poochinya *et al*., 2008). Their morphology and size (between 3 and 8 µm) are in agreement with the literature data (Tester and Morrison, 1990; Dang and Copeland, 2003; Qi *et al*., 2003; Singh Sodhi and Singh, 2003; Wang and Wang, 2004; Cardoso *et al*., 2007).

The CMS_r granules reacted with 10 and 20% NaOH concentrations appear smooth with very minimal damage (Figures 4b, c) whereas the CMS_r granules reacted with 30 and 40% NaOH concentrations had a more indented, rough and collapsed surface (Figures 4d, e). While the CMS_r granule synthesized with 50% concentration took on a more agglomeration like structure (Figure 4f), isolated granules of CMS_r synthesized with 60% NaOH concentration were not observed since the sample exhibited a gel-like aspect (Figure 4g). Thus, it could be concluded

Table 3. Effect of NaOH concentrations on viscosity of native rice starch and CMS powder

Type	Peak viscosity	Trough viscosity	Breakdown	Final viscosity	Setback
Native rice starch	230.42±2.44^{ab}	212.92±3.19^{a}	17.50±2.28^{a}	258.36±5.17^{a}	27.95±3.49^{a}
CMS_r 10%NaOH	215.72±1.52^{ab}	196.92±2.17^{b}	18.81±2.44^{a}	231.16±2.08^{b}	15.44±1.20^{a}
CMS_r 20%NaOH	296.66±23.97^{c}	80.05±5.39^{c}	216.61±19.10^{b}	191.19±3.78^{c}	-105.47±20.60^{b}
CMS_r 30%NaOH	204.00±21.43^{a}	81.36±4.63^{c}	122.64±16.87^{c}	182.55±5.51^{c}	-21.44±16.60^{c}
CMS_r 40%NaOH	182.33±44.00^{b}	52.14±1.20^{d}	130.19±42.81^{c}	125.67±5.09^{d}	-56.67±38.92^{d}
CMS_r 50%NaOH	118.59±1.89^{d}	42.92±2.34^{e}	75.67±2.91^{d}	89.28±4.20^{e}	-29.31±3.94^{cd}
CMS_r 60%NaOH	32.17±7.79^{e}	23.19±3.42^{f}	8.97±4.58^{a}	49.22±8.66^{f}	17.05±4.22^{a}

Number followed by the same letter within a column are not statistical significantly different at P<0.05 using Duncan's Multiple Range Test (DMRT).

that increasing NaOH concentrations damaged the surface area of rice starch granules. Alkaline solution probably reduces the rigidity and the stability of the molecular organization of the starch granule causing the loss of granule structure (Donald *et al*., 2001). Cardoso *et al.* (2007) reported that rice starch treated with NaOH concentrations higher than 0.24% (w/v) resulted in a progressive loss of granular morphology, likely due to an alkaline gelatinization phenomenon (Cardoso *et al.*, 2006). This result is also similar to the results found in carboxymethyl cassava starch (Sangseethong *et al*., 2005). The alkalization was the main parameter for changing of granule to be weaker with a swelling of starch (Marchant and Blanshard, 1978; Donovan, 1979; Cardoso *et al*., 2006; Cardoso *et al*., 2007; Singh *et al*., 2007) and subsequent loss of crystallinity (Cardoso *et al*., 2007) which allowed the etherifying agents to have more access to the starch molecules for the carboxymethylation processes (Lawal *et al.*, 2008a; b). Therefore, this result accords well with the DS value.

Color of CMSr powder

The result of the measurements performed on CMS_r powder synthesized with various NaOH concentrations (10, 20, 30, 40, and 50% w/v) was expressed in accordance with the CIELAB system. Rectangular coordinates (L*, a*, and b*), total color difference (TCD or ΔE) and white index were used. Native rice starch was white powder and its color became to yellowish white after synthesis by carboxymethylation. With increased NaOH concentrations, brightness (L*), a*, total color difference (TCD or ΔE) and white index (WI) slightly decreased while the yellowness (b*) value of CMS_r increased (Table 1). Veiga-Santos *et al*. (2005) reported cassava starch based film yellowness increased with alkaline pH. The yellowness increase probably is due to the characteristic color of the NaOH solution.

Viscosity of native rice starch and CMSr

The effect of NaOH concentration on viscosity of CMSr was investigated. The RVA viscograms of native rice starch and modified rice starches which prepared from various NaOH concentrations are presented in Figure 5. The relationship between the use of various NaOH concentrations and viscosity of CMSr is shown in Table 3. When NaOH concentration increased (20-60%), the peak viscosity and the breakdown of CMSr gradually decreased. Both the peak viscosity and the breakdown of all CMS_r were lower than that of native rice starch while the CMS_r which reacted with 20% NaOH concentrations was slightly higher than other samples. The trough viscosity and final viscosity of CMS_r were also decreased with increasing of NaOH concentration.

Table 1. Profile of Rapid Visco Analyzer for native rice starch [standard method AAACC (no. 61-02) and RACI (no. 60-05))]

Time (sec)	Speed (rpm)	Temp (°C)
0 – 10	960	50
10 – 60	160	50
60 – 438	160	95
438 – 666	160	50

The setback of CMS_r showed the trend in contrary with the other values. This provides further evidence that the CMS_r granules were less rigid and more elastic, thus partly contributing to the reduced viscosity (Fadzlina *et al*., 2005). Karim *et al*. (2008) suggested that higher peak viscosity exhibited by native starch due to higher granule rigidity and integrity contributed by the presence of amylose, but in alkaline treatment starches, the amorphous region containing primarily amylose had been largely disrupted which consequently weakened the granule structure. Therefore, during pasting, the granule could not attain their maximum swelling capacity,

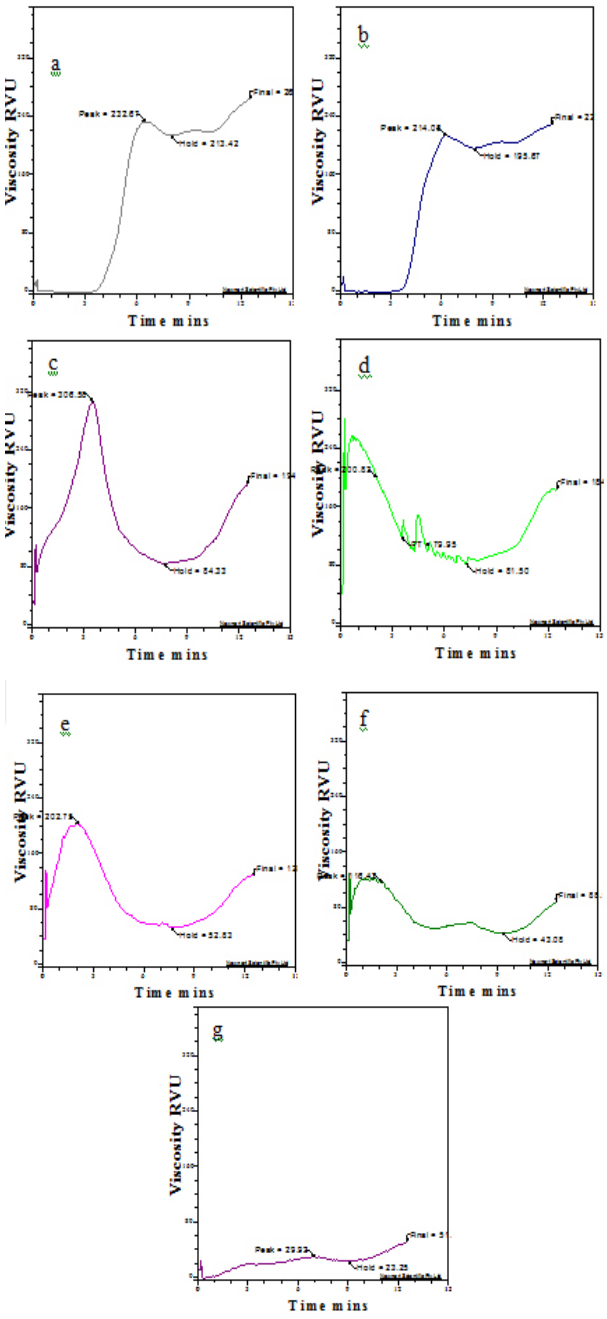

Figure 5. RVA viscograms of a) native rice starch and CMSr powder synthesized with various NaOH concentrations; a) 0%, b) 10%, c) 20%, d) 30%, e) 40%, f) 50% and g) 60 % w/v

resulting in subsequent reduction of the peak viscosity. They also reported that breakdown of all alkali treatment starches was substantially lower than that of native starch because of the weaken structure of the granules on alkaline treatment, thus facilitating disruption of the granule structure (Karim *et al*., 2008). These results agree with morphology of our native rice starch and CMS_r (Figure 4), and similar to previous reports for viscosity of crosslink-phosphorylated rice starch (Deetae *et al*., 2008). They pointed out that the peak viscosity and breakdown of the crosslink-phosphorylated rice starch decreased when the reaction time increased from 7.5 min to 120 min.

X-ray diffraction patterns of native rice starch and CMSr with various NaOH concentrations

The diffraction patterns of native rice starch indicated strong peaks at 15.3°, 17.2°, 18.3° and 23.5° 2θ (Figure 6). These results agree with Cardoso *et al*. (2007) and Karim *et al.* (2008). The peak of rice starch exhibits a typical C-type crystallinity pattern (Karim *et al*., 2008; Yanli *et al*., 2009) (Figure 6). The X-ray diffraction pattern peaks of native rice starch decreased as NaOH concentrations increased. This means that the crystallinity of the samples dramatically decreased with an increase in NaOH concentration during the modification of carboxymethylation. These results suggest that the loss of crystallinity is due to the rupture of starch granules (Figure 4.). These results agree well with previous publications on carboxymethy Chinese yam starch (Yanli *et al*., 2009). Cardoso *et al*. (2007) studied the influence of alkali concentrations on gelatinization of rice starch. They found that diffraction intensities and crystallinity of rice starch decreased as well as the loss of granules morphology which was observed with an increase in NaOH concentrations, but they found that the diffraction patterns of the rice starch could still be recognized. On the other hand, in our study, the diffraction pattern of CMS_r disappeared as NaOH concentrations increased above 40% (Figure 6). This behavior should be investigated further.

Conclusions

The effect of NaOH concentration (10-60% w/v) on yield, degree of substitution (DS), morphology, viscosity, thermal properties and color of native rice starch and carboxymethyl rice starch (CMSr) powder was investigated. Increasing NaOH concentrations in the range (10-40%) resulted in increasing DS, however, when the NaOH concentration reached 50%, the DS of CMSr decreased. The morphology of native rice starch appeared smooth, polyhedral in shape and contained many individual granules. The CMSr granules which reacted with 10 and 20% NaOH concentrations appeared smooth with very minimal damage, whereas CMSr granules which reacted with 30 and 40% NaOH concentrations had a more indented, rough and collapsed surface. While the CMSr granule synthesized with 50% and 60% NaOH concentrations took on a more agglomeration like structure. The chroma (yellowness, b*) values and the viscosity of CMSr increased but brightness (L*), a*, total color difference (TCD or ΔE) and

white index (WI) slightly decreased as NaOH concentration increased. In addition, as NaOH concentrations increased, the crystillinity of the CMSr decreased.

These rice starch properties characterize the benefits found using modified rice for industrial applications. For water soluble films, the optimal degree of substitution (DS) was found with rice modified using 40% NaOH which also had a slightly increased yellow tint and decreased viscosity. For other industrial applications like pharmaceutical drug development the DS level has to be properly balanced with the degree of cross-linkage. Depending on the particular industrial application, the results presented here allow the NaOH concentrations to be optimized for the required use. Modified rice starch is also used in a wide variety of food industries which could find the results presented here to be useful. Understanding methods to modify rice starch such as varying the NaOH levels examined in this paper provide insight into new and potentially beneficial uses for rice starch.

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References

Anon. 1998. General pasting methods for wheat or rice flour using the rapid visco analyser Method 76-21 MN: American Association of Cereal Chemistry (AACC).

AOAC official method 900.02. 2005. Sugar and sugar products. In: Horwitz, W. (ed.), p. 3. AOAC Official Method of Analysis. Wisconsin: Official Methods of Analysis of Aoac International.

Bhattacharyya, D., Singhal, R.S. and Kulkarni, P.R. 1995. A comparative account of conditions for synthesis of sodium carboxymethyl starch from corn and amaranth starch. Carbohydrate Polymers 27: 247-253.

Cardoso, M.B., Putaux, J.-L., Samios, D. and da Silveira, N.P. 2007. Influence of alkali concentration on the deproteinization and/or gelatinization of rice starch. Carbohydrate Polymers 70: 160-165.

Cardoso, M.B., Samios, D. and Silveira, N.P. 2006. Study Rice Starch during Alkaline Extraction. Starch - Stärke 58: 345-352.

Dang, J.M.C. and Copeland, L. 2003. Imaging Rice Grains Using Atomic Force Microscopy. Journal of Cereal Science 37: 165-170.

Deetae, P., Shobsngob, S., Varanyanond, W., Chinachoti, P., Naivikul, O. and Varavinit, S. 2008. Preparation, pasting properties and freeze–thaw stability of dual modified crosslink-phosphorylated rice starch. Carbohydrate Polymers 73: 351–358.

Donald, A.M., Kato, K.L., Perry, P.A. and Waigh, T.A. 2001. Scattering Studies of the Internal Structure of Starch Granules. Starch - Stärke 53: 504-512.

Dong-fang, Z., Ben-zhi, J., Shu-fen, Z. and Jin-zong, Y. 2005. Progress in the synthesis and application of green chemicals, carboxymethyl starch sodium. Proceeding of the 3rd International Conference on Functional Molecules, p. 25-30. Dalian, China:Dalian University of Technology

Donovan, J.W. 1979. Phase transitions of the starch–water system. Biopolymers 18: 263-275.

Fadzlina, Z.A.N., Karim, A.A. and Teng, T.T. 2005. Physicochemical Properties of Carboxy-methylated Sago (Metroxylon sagu) Starch. Journal of Food Science 70: C560-C567.

Heinze, T., Liebert, T., Heinze, U. and Schwikal, K. 2004. Starch derivatives of high degree of functionalization 9: carboxymethyl starches. Cellulose 11: 239-245.

Jie, Y., Wen-ren, C., Manurung, R.M., Ganzeveld, K.J. and Heeres, H.J. 2004. Exploratory Studies on the Carboxymethylation of Cassava Starch in Water-miscible Organic Media. Starch - Stärke 56: 100-107.

Kamel, S. and Jahangir, K. 2007. Optimization of Carboxymethylation of Starch in Organic Solvents. International Journal of Polymeric Materials 56: 511 - 519.

Karim, A.A., Nadiha, M.Z., Chen, F.K., Phuah, Y.P., Chui, Y.M. and Fazilah, A. 2008. Pasting and retrogradation properties of alkali-treated sago (Metroxylon sagu) starch. Food Hydrocolloids 22: 1044-1053.

Khalil, M.I., Hashem, A. and Hebeish, A. 1990. Carboxymethylation of Maize Starch. Starch - Stärke 42: 60-63.

Kittipongpatana, O., Burapadaja, S. and Kittipongpatana, N. 2008. Development of phamaceutical gel base containing sodium carboxymethyl mungbean starch. Chiang Mai University Journal of Natural Sciences 7(1): 23-32.

Kittipongpatana, O.S., Chaitep, W., Charumanee, S. and Kittipongpatana, N. 2006a. Effects of amylose content on the physicochemical properties of sodium carboxilmethyl rice starches. Chiang Mai University Journal of Natural Sciences 5(2): 199-207.

Kittipongpatana, O.S., Sirithunyalug, J. and Laenger, R. 2006b. Preparation and physicochemical properties of sodium carboxymethyl mungbean starches. Carbohydrate Polymers 63: 105-112.

Kooijman, L.M., Ganzeveld, K.J., Manurung, R.M. and Heeres, H.J. 2003. Experimental Studies on the Carboxymethylation of Arrowroot Starch in

Isopropanol-Water Media. Starch - Stärke 55: 495-503.

Lawal, O.S., Lechner, M.D. and Kulicke, W.M. 2008a. Single and multi-step carboxymethylation of water yam (Dioscorea alata) starch: Synthesis and characterization. International Journal of Biological Macromolecules 42: 429-435.

Lawal, O.S., Lechner, M.D. and Kulicke, W.M. 2008b. The synthesis conditions, characterizations and thermal degradation studies of an etherified starch from an unconventional source. Polymer Degradation and Stability 93: 1520-1528.

Marchant, J.L. and Blanshard, J.M.V. 1978. Studies of the Dynamics of the Gelatinization of Starch Granules Employing a Small Angle Light Scattering System. Starch - Stärke 30: 257-264.

Phan, T.D., Debeaufort, F., Luu, D. and Voilley, A. 2005. Functional properties of edible agar-based and starch-based films for food quality preservation. Journal of Agricultural and Food Chemistry 53: 973-981.

Poochinya, P., Naivikul, O., Poapun, Y. and Umrung, P. 2008. Morphological changes of rice starch during grain development. Journal of Microscopy Society of Thailand 22: 76-79.

Qi, X., Tester, R.F., Snape, C.E. and Ansell, R. 2003. Molecular Basis of the Gelatinisation and Swelling Characteristics of Waxy Rice Starches Grown in the Same Location During the Same Season. Journal of Cereal Science 37: 363-376.

Rachtanapun, P. 2010. Carboxymethyl Cellulose from Papaya Peel/Corn Starch Film Blends. Kasetsart Journal (Natural Science) 43: 259-266.

Ragheb, A.A., El-Sayiad, H.S. and Hebeish, A. 1997. Preparation and Characterization of Carboxymethyl Starch (CMS) Products and Their Utilization in Textile Printing. Starch - Stärke 49: 238-245.

Sangseethong, K., Ketsilp, S. and Sriroth, K. 2005. The Role of Reaction Parameters on the Preparation and Properties of Carboxymethyl Cassava Starch. Starch - Stärke 57: 84-93.

Selke, S.E.M., Culter, J.D. and Hernandez, R.J. 2004. Plastics Packaging. Hanser Publishers, Cincinnati.

Singh, J., Kaur, L. and McCarthy, O.J. 2007. Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications--A review. Food Hydrocolloids 21: 1-22.

Singh Sodhi, N. and Singh, N. 2003. Morphological, thermal and rheological properties of starches separated from rice cultivars grown in India. Food Chemistry 80: 99-108.

Suriyatem, K. and Kittipongpatana, N. 2010. Preparation and physicochemical properties of cross-linked carboxymethyl rice starches. Proceeding of 1st Polymer Conference of Thailand, p. 151-158. Bangkok, Thailand: Chulabhorn research institute

Takahashi, K., Ogata, A., Yang, W.H. and Hattori, M. 2002. Increased hydrophobicity of carboxymethyl starch film by conjugation with zein. Biosci Biotechnology Biochemistry 66: 1276-1280.

Tester, R.F. and Morrison, W.R. 1990. Swelling and Gelatinization of Cereal Starches II. Waxy Rice Starches. Cereal Chemistry 67: 558-563.

Tijsen, C.J., Voncken, R.M. and Beenackers, A.A.C.M. 2001. Design of a continuous process for the production of highly substituted granular carboxymethyl starch. Chemical Engineering Science 56: 411-418.

Veiga-Santos, P., Suzuki, C.K., Cereda, M.P. and Scamparini, A.R.P. 2005. Microstructure and color of starch-gum films: Effect of gum deacetylation and additives. Part 2. Food Hydrocolloids 19: 1064-1073.

Wang, L. and Wang, Y.-J. 2004. Application of High-Intensity Ultrasound and Surfactants in Rice Starch Isolation. Cereal Chemistry 81: 140-144.

Yanli, W., Wenyuan, G., and Xia, L. 2009. Carboxymethyl Chinese yam starch: synthesis, characterization, and influence of reaction parameters. Carbohydrate Research. 344: 1764-1769.

Zhou, X., Yang, J. and Qu, G. 2007. Study on synthesis and properties of modified starch binder for foundry. Journal of Materials Processing Technology 183: 407-411.