



## Comparative study of pasting and thermal transition characteristics of osmotic pressure and heat–moisture treated corn starch

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### Abstract

Osmotic-pressure-treatment (OPT) was introduced in order to produce the physically modified products similar to conventional heat–moisture treatment (HMT) starches. OPT is a new method for physical modification of starch in the presence of excess amounts of salt or sugar. Corn starch is selected for the comparative study of OPT and HMT. For the OPT method, corn starch is suspended in a saturated solution of sodium sulfate and heated in an autoclave at 120 °C, which corresponds to a calculated osmotic pressure of 34,552 kPa (assuming sodium sulfate dissociates completely) for 15, 30, and 60 min, respectively. For the HMT method, starch with 20% of moisture content is packed in Duran bottle, then the same heat treatment method in an autoclave is followed. Scanning electron microscopy (SEM) show a deformed structure in OPT starch granules, while HMT starch has slight change from the native starch. In the OPT, the onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ ) gelatinization temperatures of starch increase significantly with increasing treatment time, whereas only  $T_p$  and  $T_c$  of HMT starches increase. Also the biphasic broadening of  $T_p$  for the HMT is found. The broadening of the peaks (high  $T_c$ – $T_o$ ) can be explained by an inhomogeneous heat transfer during the HMT of starch. Narrow DSC peaks can be indication of a better homogeneity for the OPT samples. Both methods provided similar decreased pattern of gelatinization enthalpy. RVA visco-grams of OPT starch exhibited decrease of peak, breakdown and final viscosities, similar to those for HMT starch. Pasting temperature of OPT starch increased with treatment time, whereas that of HMT starches remained unchanged. These properties indicate that OPT starch is suitable for large scale production.

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### 1. Introduction

Annealing and heat–moisture treatment (HMT) are common physical modifications of starch that do not rupture granules. Annealing generally involves heating granular starch in the presence of high quantity of water between glass transition and onset temperature, whereas HMT is carried out at limited moisture content and at elevated temperature (Eliasson & Gudmundsson, 1996).

In HMT, pressure is often required to assure sufficient heating, although uniform heat distribution and penetra-

tion into the starch is not easy to accomplish. HMT starch displays an increased paste stability and gelatinization temperature regardless of origin (Abraham, 1993; Collado & Corke, 1999; Donovan, Lorenz, & Kulp, 1983; Hoover & Vasanathan, 1994; Kulp & Lorenz, 1981; Lorenz & Kulp, 1982, 1983; Stute, 1992). Donovan et al. (1983) reported that HMT makes starch melting endotherm biphasic as indicated in a differential scanning calorimetry thermogram, and claimed that there is new crystal formation or crystallite rearrangement in the treated starch granules. Lim, Chang, and Chung (2001) proposed that the increased melting range caused by the generation of high temperature endotherm during HMT is due to annealing of starch crystalline regions. This transformation in the crystalline region

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results in the new high temperature endotherm. Biphasic endotherm indicate that the annealing is likely to take place heterogeneously in the crystalline regions. A number of authors have claimed that HMT induces changes not only in crystalline regions but also in amorphous regions of the starch granules (Hoover & Manuel, 1996; Hoover, Swamidas, & Vasanthan, 1993; Hoover & Vasanthan, 1994). These investigators also found that amylose content and starch chain length are two significant factors determining the physical properties of the final products.

Pukkahuta, Shobsngob, and Varavinit (2007) introduced a new method of physical modification of starch in the presence of excess amount of sodium sulfate solution, called “Osmotic-pressure-treatment” (OPT), in order to produce physically modified products similar to those from conventional HMT of starch. The excess amount of sodium sulfate not only increases the osmotic pressure of the solution mixture but inhibits the gelatinization of starch granules during the high temperature treatment.

Osmotic pressure is the pressure that must be applied to prevent the spontaneous movement by osmosis of a solvent across a semipermeable membrane from a more dilute solution to a more concentrated one. Normally osmotic pressure can be measured by an osmometer. The osmotic pressure at a given temperature depends upon the molar concentration. The mathematical relationship is as follows:

$$\pi = MRT$$

where  $\pi$ , osmotic pressure in kPa;  $M$ , molarity;  $R$ , gas constant ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  or  $8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$ );  $T$ , temperature in Kelvin.

In this study, the effects of OPT and HMT on pasting and thermal transition characteristics of corn starch were compared.

## 2. Materials and methods

### 2.1. Materials

Corn starch was purchased from Choheng Rice Vermicelli Factory Co., Ltd., Nakornpathom, Thailand, and sodium sulfate from Carlo Erba Reagenti SpA (Rodano, MI, Italy). All other reagents were of analytical grade, purchased from Merck Co., Ltd. (Darmstadt, Germany).

### 2.2. Methods

#### 2.2.1. Preparation of OPT corn starch

In a 500-ml Duran glass bottle (Schott, Mainz, Germany), 100 g (dry basis) of starch was suspended in 200 ml of saturated solution of sodium sulfate (100 g  $\text{Na}_2\text{SO}_4$  per 200 ml of distilled water) and heated in an autoclave (TOMY ES-315, TOMY Digital Biology Co., Ltd., Tokyo, Japan) at  $120^\circ\text{C}$ , corresponding to a calculated osmotic pressure of 34552 kPa (assuming complete dissociation of sodium sulfate) for 15, 30, and 60 min. The glass bottle was then allowed to cool to room temper-

ature before the starch was removed and washed with distilled water ( $500 \text{ ml} \times 8$ ) by sedimenting at 4552g (J-6M/E centrifuge, Beckman Coulter Inc., CA, USA). The presence of residue sodium sulfate in the starch was tested by precipitating with barium chloride solution. Starch was dried overnight at  $40^\circ\text{C}$  in a hot air oven (Memmert GmbH, Schwabach, Germany).

#### 2.2.2. Preparation of HMT corn starch

The moisture content of starch was adjusted to 20% by spraying the calculated amount of distilled water onto the starch in a mixing bowl and then mixing thoroughly for 15 min. The exact moisture content was measured using a moisture analyzer (MA-30, Sartorius AG, Goettingen, Germany). The moist starch was then placed in a Duran glass bottle fitted with a screw cap and left to equilibrate for 1 h before being placed in an autoclave at  $120^\circ\text{C}$  for 15, 30, and 60 min. After cooling to room temperature, HMT starch was removed from the Duran bottle and dried overnight at  $40^\circ\text{C}$  in a hot air oven.

#### 2.2.3. Proximate analysis and amylose content

Proximate analysis of native corn starch was performed using standard methods described in AOAC (1990a, 1990b, 1990c). Protein content was estimated from nitrogen content obtained by Kjeldahl method (model VAPODEST 50 Carousel 250 mL autosampler and model Kjeldatherm-Digestion unit equipped with 250 mL digestion tubes, Gerhardt, Königswinter, Germany), multiplied by 6.25 (AOAC, 1990a, 1990b, 1990c). Fat content of the sample was determined by standard method (AOAC, 1990a, 1990b, 1990c). Carbohydrate content was calculated by subtracting the percentage of aforementioned compounds from 100. Amylose content of native corn starch (based on weight that is free of moisture, protein, fat, and ash) was determined by iodine affinity method (Knutson, 1986).

#### 2.2.4. Morphology observation

2.2.4.1. *Light microscopy.* Native, OPT, and HMT corn starch were suspended in distilled water and viewed under normal and polarized light microscope (Olympus BX 51, Olympus, Tokyo, Japan) equipped with a camera set (Olympus DP 12, Olympus, Tokyo, Japan).

2.2.4.2. *Scanning electron microscopy (SEM).* Starch sample was mounted on SEM stub with double-sided adhesive tape and coated with gold. Scanning electron micrographs were taken using a JOEL JSM-5410LV microscope (JOEL, Tokyo, Japan). The accelerating voltage and the magnification are indicated on the micrograph.

#### 2.2.5. Determination of thermal property

Thermal property of native and OPT corn starch was assessed in a differential scanning calorimeter (DSC) (Pyris, Perkin Elmer, Belerica, MA, USA). Both native and modified starch (based on weight free of moisture) were dispersed in distilled water to obtain a starch:water ratio

of 1:2. Corn starch in the presence of saturated solution of sodium sulfate was also assessed by DSC, by dispersing in sodium sulfate solution (distilled water:sodium sulfate = 2:1) to obtain starch/sodium sulfate solution ratio of 1:2. Starch suspension was then transferred to an aluminum pan (30  $\mu$ L) and hermetically sealed. After equilibration at room temperature for 1 h., sample was heated from 20 to 150  $^{\circ}$ C at a rate of 10  $^{\circ}$ C/min. The empty pan was used as reference and the DSC was calibrated with indium. Onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ ) gelatinization temperatures, and gelatinization enthalpy ( $\Delta H$ ) (J/g of dry starch) were recorded.

#### 2.2.6. Determination of pasting property

A Rapid Visco Analyzer (Series 4V, Newport Scientific Pty. Ltd, Warriewood, Australia) was employed to investigate the pasting property of native and modified starch. Starch sample (2.5 g dry basis) and 25 mL of distilled water were mixed with a paddle in an aluminum can. Heating and cooling cycles were programmed as follows: holding at

50  $^{\circ}$ C for 1 min, heating from 50 to 95  $^{\circ}$ C at a rate of 12  $^{\circ}$ C/min, holding at 95  $^{\circ}$ C for 2.5 min, and finally cooling to 50  $^{\circ}$ C at a rate of 12  $^{\circ}$ C/min and holding at 50  $^{\circ}$ C for 2 min.

#### 2.2.7. Determination of swelling power and percent solubility

Swelling power (SP) and percent solubility (%SOL) were determined by a modified method of Schoch (1964). Starch samples (0.5 g dry basis (db) suspended in 15 mL of distilled water) were placed in 30 mL centrifuge tubes fitted with screw caps and heated in a water bath shaker (150 rpm) at 60–95  $^{\circ}$ C for 30 min. After heating, the centrifuge tubes were cooled to room temperature and centrifuged at 1638g (18/80R Sanyo Harrier Centrifuge, Osaka, Japan) for 15 min. The supernatants were dried to constant weight in a hot air oven at 100  $^{\circ}$ C. Precipitated paste and dried supernatant were weighed. All measurements were done in triplicate. Swelling power and percent solubility were calculated as follows:

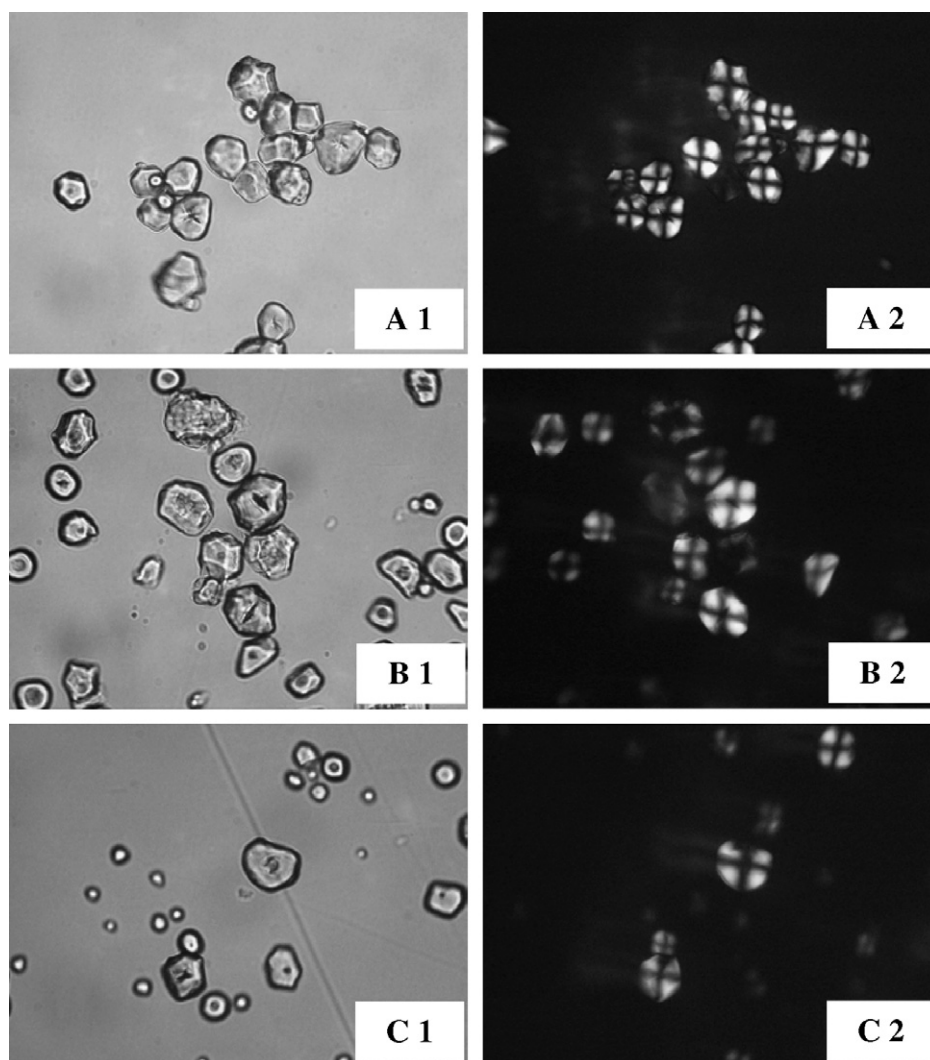


Fig. 1. Light and polarized light micrograph of native corn starch (A1 and A2), OPT corn starch treated at 120  $^{\circ}$ C, 60 min (B1 and B2), and HMT corn starch treated at 120  $^{\circ}$ C, 60 min (C1 and C2).

$$\%SOL = \frac{A}{S} \times 100$$

$$SP = \frac{B \times 100}{S(100 - \%SOL)}$$

where %SOL, percent solubility; SP, swelling power; *A*, weight of dried soluble starch; *B*, weight of sediment paste; *S*, weight of dried sample.

#### 2.2.8. Wide-angle X-ray powder diffraction measurement

Wide-angle X-ray diffraction patterns of native and modified starch were recorded with a Bruker X-ray powder diffractometer (D-8 type, Bruker, Rheinfelden, Germany) with copper anode X-ray tube (Cu-K<sub>α</sub> radiation) at 30 kV and 30 mA. A scanning region of the diffraction angle (2θ) was adjusted from 5° to 30° at a step size of 0.4° with a count time of 1.0 s and rotary speed of sample holder of 30 min<sup>-1</sup>. The starch samples were equilibrated in

a 100% RH desiccator for 24 h at room temperature prior to measurement.

#### 2.2.9. Statistical analysis

Analytical determinations of individual samples were conducted in triplicate and mean values and standard deviations reported. Data were analyzed using variance (ANOVA) test procedure. Statistically significant difference was identified by Tukey's HSD test (*p* < .05) using SPSS 12.0 program for Windows (SPSS Inc., IL, USA).

### 3. Results and discussion

#### 3.1. Proximate analysis and corn starch amylose content

Native corn starch used contained 0.25% protein, 0.07% fat, 0.06% ash, 13.16% moisture, and 86.46% carbohydrate, with amylose content 33.73%.

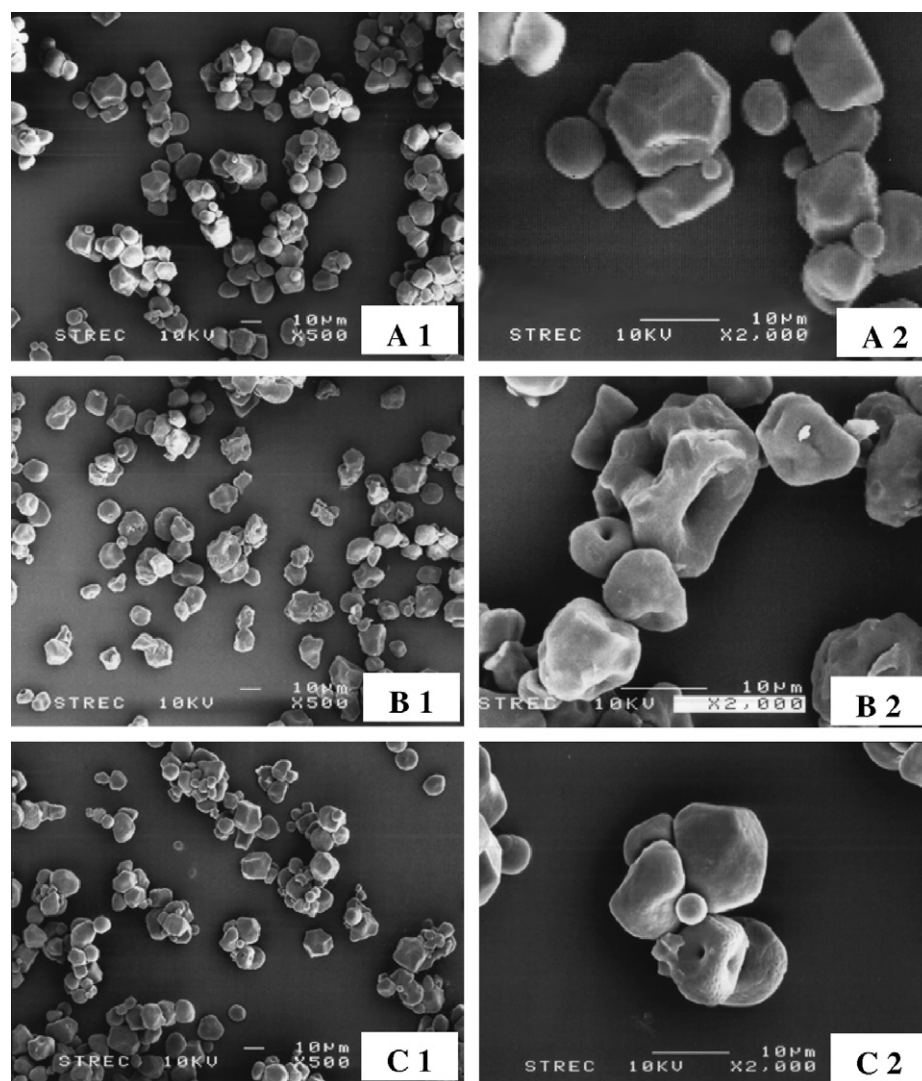


Fig. 2. Scanning electron micrograph of native corn starch (A1 and A2), OPT corn starch treated at 120 °C, 60 min (B1 and B2), and HMT corn starch treated at 120 °C, 60 min (C1 and C2).



### 3.2. Granule morphology

#### 3.2.1. Light microscopy

Light and polarized light micrographs of native, OPT, and HMT corn starch are shown in Fig. 1. There was no significant change between native and modified starch when observing under light microscope. Polarized light micrographs of both HMT and OPT starch show birefringence confirming the presence of non-gelatinized granules.

#### 3.2.2. Scanning electron microscopy

Scanning electron micrographs of native, OPT, and HMT corn starch are shown in Fig. 2. Native corn starch granules were in the form of a polyhedron without any pores (A1 and A2), but the deformation of surface was observed in OPT corn starch (B1 and B2), similar to previous studies on HMT potato starch (Pukkahuta et al., 2007). On the other hand, HMT corn starch showed only a few number of starch granules that have deformed structure (C1 and C2).

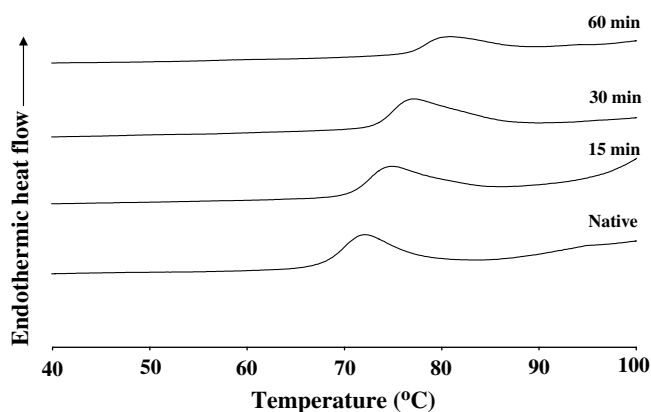


Fig. 3. Differential scanning calorimetry thermogram of native and OPT corn starch after various treatment times.

### 3.3. Thermal property

DSC thermogram of corn starch in the presence of saturated sodium sulfate solution showed  $T_o$ ,  $T_p$ , and  $T_c$  of 121, 129, and 134 °C, respectively, indicating that OPT corn starch can be prepared without gelatinization at a maximum temperature of 120 °C.

Ahmad and Williams (1999), using DSC, showed that  $T_p$  of sago starch increased with increasing concentration of sodium sulfate. Jane (1993) proposed that the higher  $T_o$  of corn starch in sodium sulfate solution can be attributed to the diminished fraction of free water and the higher viscosity of the solution. Increased viscosity retards diffusion of salt into the starch granules and further decreases the diluent concentration within the granules. Also, repulsion between the electronegative OH groups of starch and the strongly negatively charged  $SO_4^{-2}$  ions increases the resistance of starch to gelatinization.

The melting peak appeared as a single narrow curve at every treatment time (Fig. 3, Table 1). When corn starch was treated at 120 °C for 60 min, the melting range was 10.93 °C, only 0.43 °C greater than that of untreated starch.  $T_o$ ,  $T_p$ , and  $T_c$  gelatinization temperatures increased linearly with treatment time (Fig. 5a–c). These results indicate that the reformation of crystalline regions results in newly developed high temperature endotherm. Narrow endotherm curve with small increase of melting range indicate the possibility of having homogeneously annealing process in the crystalline regions of OPT starch. The OPT process of starch provided the same results of the thermal properties as that of the annealing process. However, the higher temperature used in the OPT process can accelerate the annealing process.

For HMT, corn starch was treated at 120 °C with 20% moisture content for 15, 30, and 60 min. The melting curve appeared to be biphasic in every treatment time (Fig. 4). These phenomena have been described by Donovan et al. (1983) as being due to new crystal formation or crystallite rearrangement in the treated starch granules. Lim et al.

Table 1

Differential scanning calorimetry characteristics of OPT and HMT of corn starches treated at 120 °C after various treatment times

Treatment	Treatment temperature (°C)	Treatment time (min)	Transition temperatures				
			$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$T_c - T_o$ (°C)	$\Delta H$ (J/g)
Native	–	–	67.84 ± 0.02 <sup>b</sup>	72.05 ± 0.04 <sup>a</sup>	78.34 ± 0.04 <sup>a</sup>	10.50 ± 0.03 <sup>a</sup>	12.30 ± 0.03 <sup>c</sup>
OPT	120	15	70.80 ± 0.05 <sup>c</sup>	74.72 ± 0.03 <sup>c</sup>	82.37 ± 0.03 <sup>b</sup>	11.57 ± 0.03 <sup>c</sup>	11.73 ± 0.04 <sup>c</sup>
		30	73.23 ± 0.03 <sup>f</sup>	77.03 ± 0.03 <sup>f</sup>	85.39 ± 0.03 <sup>c</sup>	12.16 ± 0.04 <sup>d</sup>	11.78 ± 0.02 <sup>c</sup>
		60	76.77 ± 0.01 <sup>g</sup>	80.39 ± 0.04 <sup>i</sup>	87.70 ± 0.03 <sup>g</sup>	10.93 ± 0.04 <sup>b</sup>	6.71 ± 0.03 <sup>a</sup>
HMT	120	15	67.98 ± 0.03 <sup>c</sup>	72.38 ± 0.04 <sup>b</sup> , 77.87 ± 0.03 <sup>g</sup>	83.76 ± 0.03 <sup>c</sup>	15.78 ± 0.05 <sup>c</sup>	12.00 ± 0.04 <sup>d</sup>
		30	67.73 ± 0.04 <sup>a</sup>	72.71 ± 0.03 <sup>c</sup> , 80.21 ± 0.03 <sup>h</sup>	85.14 ± 0.03 <sup>d</sup>	17.41 ± 0.06 <sup>f</sup>	12.00 ± 0.03 <sup>d</sup>
		60	68.15 ± 0.04 <sup>d</sup>	72.90 ± 0.04 <sup>d</sup> , 82.22 ± 0.03 <sup>j</sup>	86.73 ± 0.03 <sup>f</sup>	18.58 ± 0.02 <sup>g</sup>	8.87 ± 0.03 <sup>b</sup>

All data represent the mean of three determinations.

Mean ± standard deviation.

Means with the same letter in each column are not significantly different ( $p < .05$ ).

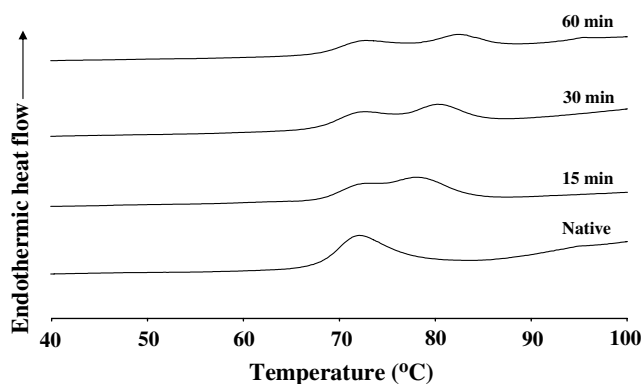


Fig. 4. Differential scanning calorimetry thermogram of native and HMT corn starch after various treatment times.

(2001) indicated that biphasic endotherm might reflect annealing taking place heterogeneously in the location of crystalline regions.  $T_o$  remained unchanged whereas  $T_p$  and  $T_c$  gelatinization temperatures increased linearly with the treatment time (Table 1, Fig. 5b and c). The transition temperature range ( $T_c - T_o$ ) increased linearly with treatment time (Figs. 4 and 5d). When corn starch with 20% moisture was treated at 120 °C for 60 min, the melting range of the treated starch was 18.58 °C, 8.08 °C greater

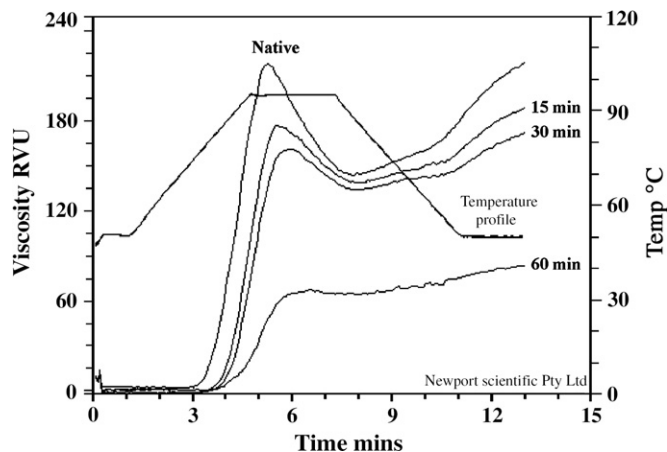


Fig. 6. Pasting profile of native and OPT corn starches after various treatment times.

than that of the untreated starch. The increased melting range by HMT has already been reported (Pukkahuta et al., 2007). Furthermore, Hoover et al. (1993) and Hoover and Manuel (1996) claimed that HMT allows amylose molecules located in the bulk amorphous regions to interact with the branched segments of amylopectin in the crystalline regions. These interactions consequently reduce the

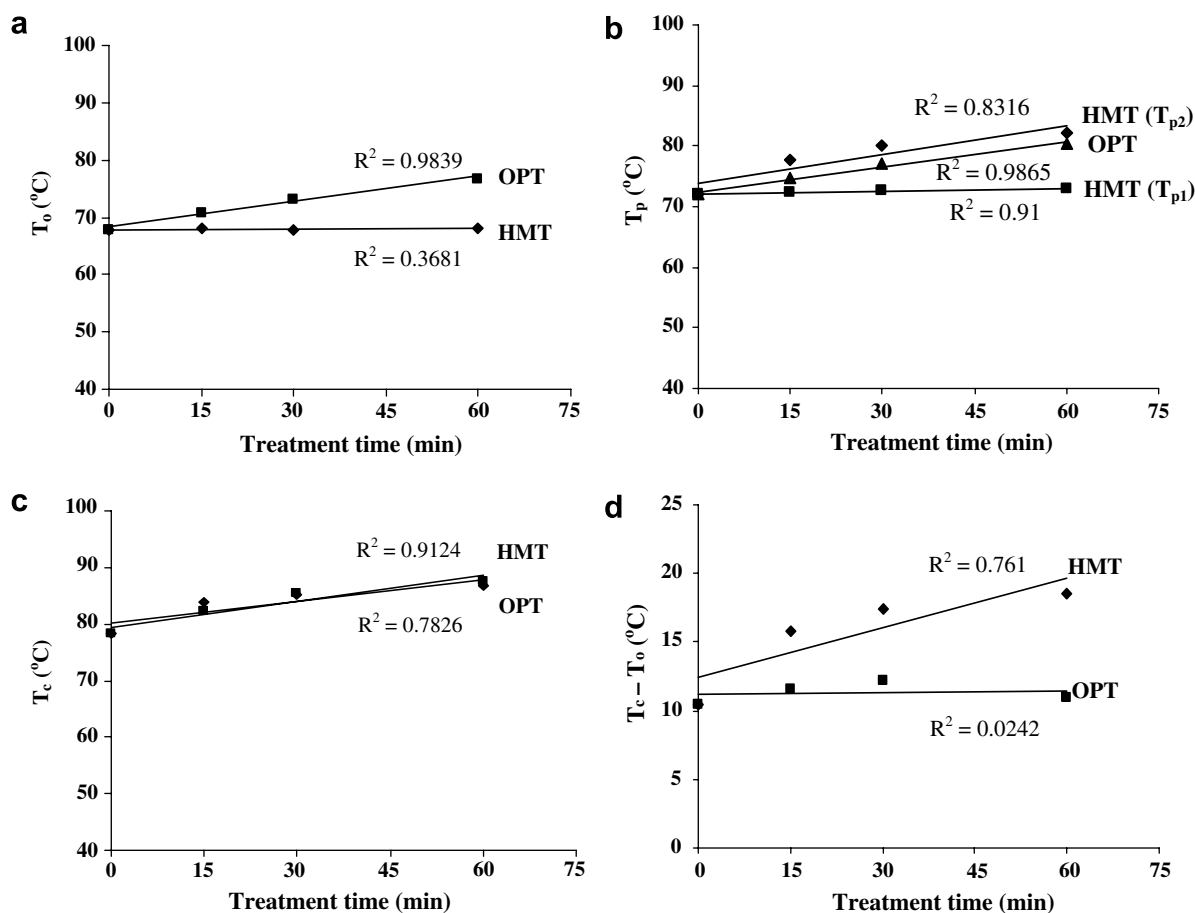


Fig. 5. Relationship between treatment time and  $T_o$  (a),  $T_p$  (b),  $T_c$  (c), and  $T_c - T_o$  (d) of HMT and OPT corn starch.

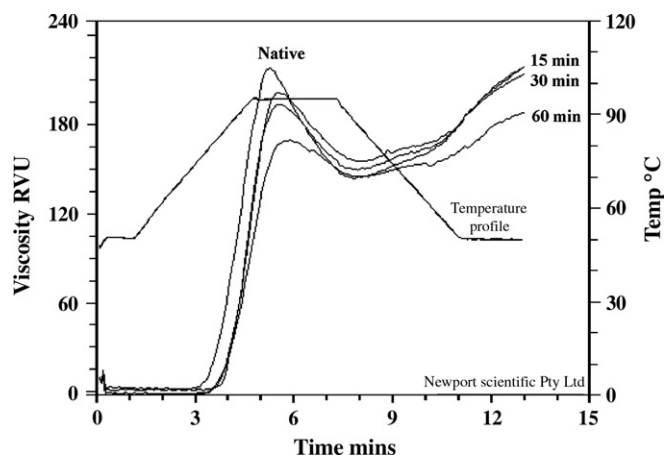


Fig. 7. Pasting profiles of native and HMT corn starch after various treatment times.

mobility of the amylopectin chains and thus increase the transition temperature for melting. The transition, perhaps by rearrangement of the shorter amylopectin chains, is facilitated by thermal energy and water provided in the treatment. Lim et al. (2001) proposed that the increased melting range caused by the generation of high temperature endotherm was due to annealing of starch crystalline regions during HMT. This transformation in the crystalline region results in the new high temperature endotherm. Vermeulen, Goderis, and Delcour (2006) also reported that both annealing and HMT of potato starch increase DSC

gelatinization temperatures, the former narrowing the gelatinization temperature range while the latter broadening it. However, both methods provide similar decreased pattern of gelatinization enthalpy, indicating a partial loss of crystallinity of the treated starch.

### 3.4. Pasting property

RVA pasting curves of native, OPT, and HMT modified starch are presented in Figs. 6 and 7. The major RVA parameters, such as PKV (peak viscosity), BDV (breakdown viscosity), FNV (final viscosity), and PT (pasting temperature), are listed in Table 2. RVA viscomograms for both OPT (Fig. 6) and HMT (Fig. 7) starch exhibited a decrease of PKV, BDV, and FNV in comparison with native corn starch and an increase with treatment time (Fig. 8a–c). Lower PKV, reduced BDV, and higher FNV have been reported for heat–moisture treated potato starch (Stute, 1992). Decrease of PKV, BDV, and FNV can be attributed to the formation of amylose–lipid complex during HMT and OPT processes (Hoover et al., 1993). These pasting properties can be accounted for the reduction in granular swelling and improvement in paste stability upon prolonged heating. However, only PT of OPT starch increased with increase of treatment time, whereas PT of the HMT starch remained unchanged (Fig. 8d). These pasting properties confirm the similarity of pasting characteristics for both HMT and OPT starch except for PT, which is

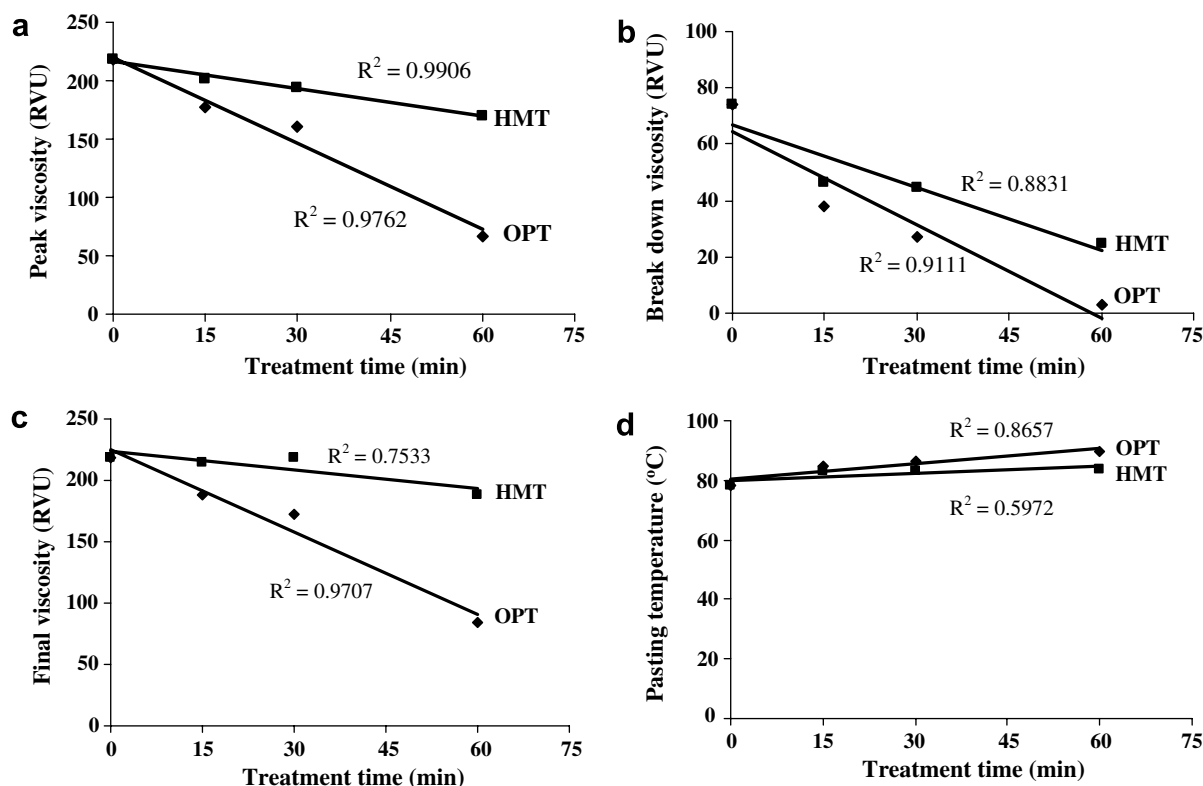


Fig. 8. Relationship between treatment time of HMT and OPT corn starch and peak viscosity (a), breakdown viscosity (b), final viscosity (c), and pasting temperature (d).

Table 2  
Pasting properties of OPT and HMT of corn starches treated at 120 °C after various treatment times

Treatment	Treatment temperature (°C)	Treatment time (min)	Peak (RVU)	Holding strength (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
Native	–	–	217.83 ± 0.76 <sup>g</sup>	143.92 ± 1.27 <sup>d</sup>	73.92 ± 0.99 <sup>c</sup>	218.92 ± 1.01 <sup>c</sup>	75.00 ± 1.08 <sup>g</sup>	78.35 ± 0.30 <sup>a</sup>
OPT	120	15	176.67 ± 1.11 <sup>d</sup>	138.83 ± 1.75 <sup>c</sup>	37.83 ± 1.33 <sup>c</sup>	188.50 ± 0.72 <sup>c</sup>	49.67 ± 1.15 <sup>d</sup>	84.70 ± 0.61 <sup>c</sup>
		30	160.92 ± 1.73 <sup>b</sup>	133.83 ± 1.04 <sup>b</sup>	27.08 ± 0.99 <sup>b</sup>	172.08 ± 1.51 <sup>b</sup>	38.25 ± 0.66 <sup>b</sup>	86.40 ± 0.53 <sup>d</sup>
		60	67.25 ± 1.09 <sup>a</sup>	64.25 ± 0.95 <sup>a</sup>	3.00 ± 0.30 <sup>a</sup>	83.67 ± 0.70 <sup>a</sup>	29.42 ± 1.07 <sup>a</sup>	89.60 ± 0.53 <sup>c</sup>
HMT	120	15	201.75 ± 1.08 <sup>f</sup>	155.33 ± 1.01 <sup>f</sup>	46.42 ± 0.73 <sup>d</sup>	214.42 ± 0.81 <sup>d</sup>	59.08 ± 1.03 <sup>e</sup>	83.05 ± 0.83 <sup>b</sup>
		30	193.92 ± 1.16 <sup>e</sup>	149.25 ± 1.09 <sup>e</sup>	44.67 ± 0.76 <sup>d</sup>	219.00 ± 1.32 <sup>e</sup>	69.75 ± 1.01 <sup>f</sup>	83.10 ± 0.36 <sup>bc</sup>
		60	169.42 ± 1.02 <sup>c</sup>	144.58 ± 1.24 <sup>d</sup>	24.83 ± 0.97 <sup>b</sup>	188.33 ± 0.65 <sup>c</sup>	43.75 ± 0.66 <sup>c</sup>	83.80 ± 0.72 <sup>bc</sup>

All data represent the mean of three determinations.

Mean ± standard deviation.

Means with the same letter in each column are not significantly different ( $p < .05$ ).

in agreement with the increase of onset temperature ( $T_o$ ) of OPT starch with treatment time seen in the DSC measurements.

### 3.5. Swelling power (SP) and % solubility (%SOL)

SP and %SOL of OPT and HMT corn starch at 120 °C for 15, 30, and 60 min are shown in Figs. 9 and 10, respectively. All samples from OPT process exhibited a good lin-

ear relationship ( $R^2 > .9$ ) between the increase in SP and %SOL with the increase of heating temperature from 60 to 95 °C. However, OPT corn starch exhibited a decrease of SP value with treatment time in the tested temperature range, whereas an increase of %SOL value with treatment time was observed. These results demonstrated that OPT corn starch inhibits starch swelling and allows amylose to leach out from the starch granules, suggesting that %SOL of OPT corn starches is influenced by the gelatinization

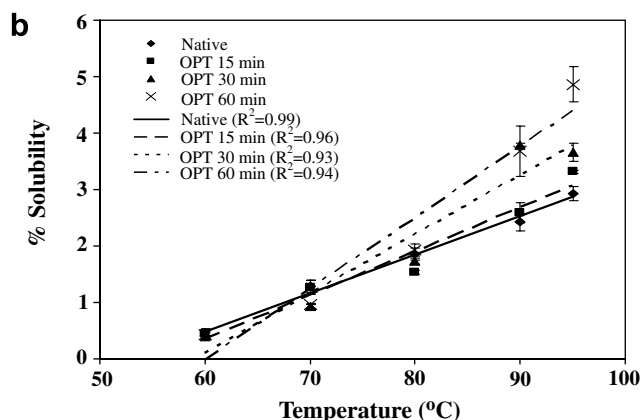
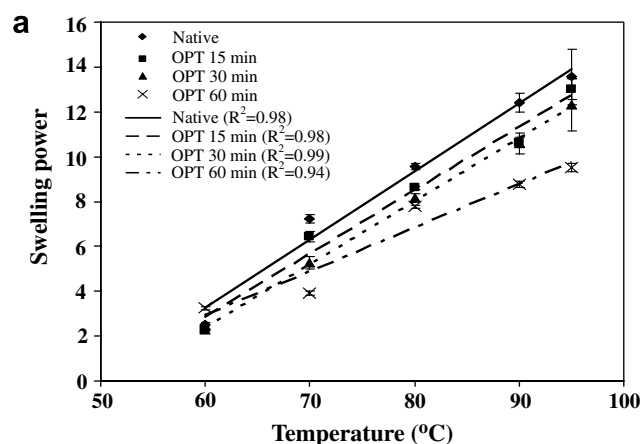


Fig. 9. Swelling power (a) and % solubility (b) as a function of temperatures of OPT corn starch at various treatment times. Error bars represent standard deviations.

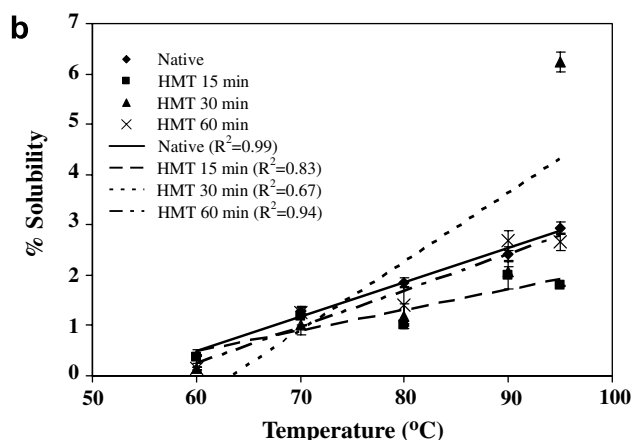
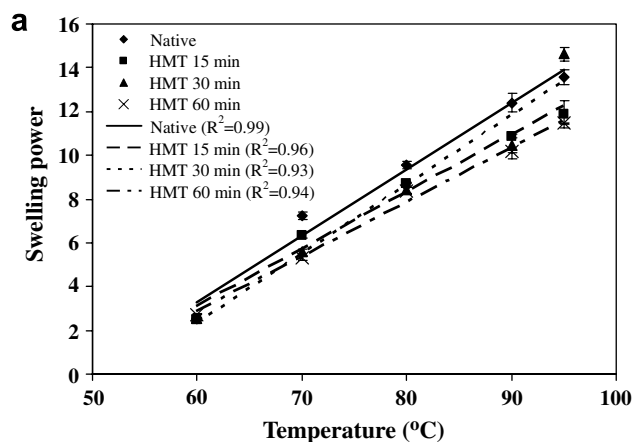


Fig. 10. Swelling power (a) and % solubility (b) as a function of temperature of HMT corn starch at various treatment times. Error bars represent standard deviations.



enthalpy of starch. The decrease of gelatinization enthalpy ( $\Delta H$ ) after OPT process at various treatment times correlated well with that of the increase of %SOL ( $R^2 = .92$ ) at 95 °C (data not shown). The reduction of  $\Delta H$  after OPT process results in an increase in the amorphous region within the starch granules. This could be attributed to the fact that amorphous regions are more susceptible to be dissolved in hot distilled water than those of the crystalline regions and thus high amorphous region has high solubility. The results of SP of HMT starch gave similar patterns as those of OPT starch. However, the pattern of %SOL of HMT starch was different from that of OPT starch. Some graphs were not linear and were not in ordered positions as those of the OPT process. These properties indicate the heterogeneous treatment by HMT process. Furthermore, there was no relationship between  $\Delta H$  and %SOL at 95 °C.

### 3.6. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction pattern of the native, OPT, and HMT corn starch is given in Figs. 11 and 12. Treated corn starch retained the typical A-type diffraction pattern with strong peaks at  $2\theta$  of about 15° and 23° and a doublet at 17° and 18° of the original starch. Thus, OPT and HMT starch in this study do not have basically changed molecular arrangements in residual granules. Vermeulen et al. (2006), studying wide-angle X-ray diffraction and small-angle X-ray scattering (SAXS) of hydrothermal treated potato starch, found that annealed samples compared to native showed a more intense 9 nm scattering maximum, suggesting a more efficient packing of crystallites in dense lamellae. HMT, on the other hand, results in the development of a diffuse SAXS background, which becomes more prominent for samples treated at higher temperatures, and eventually replaces the 9 nm scattering maximum. The stacked lamellae, present in native and annealed starches, are thus clearly disrupted by the HMT process.

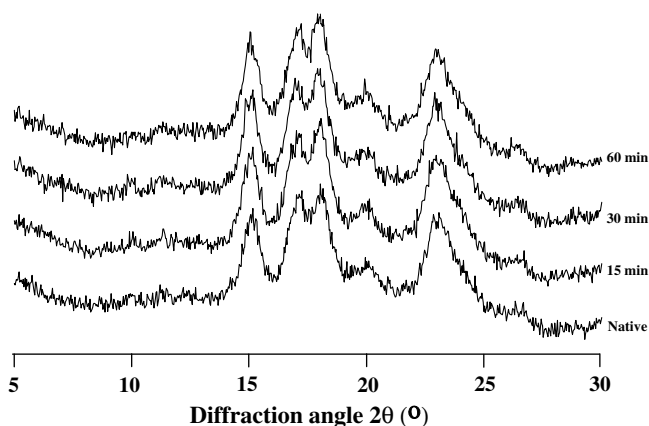


Fig. 11. X-ray diffraction pattern of native corn starch and OPT corn starch treated at 120 °C after various treatment times.

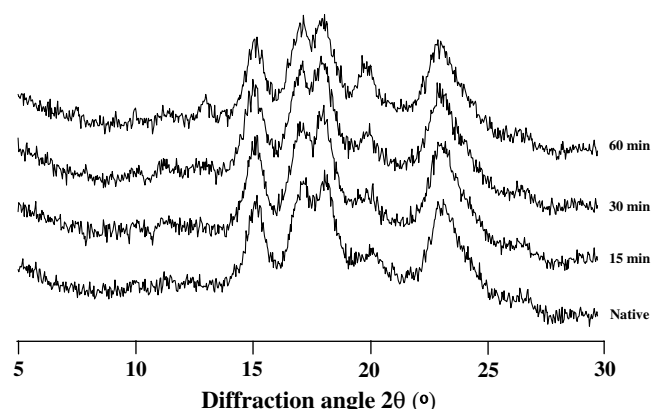


Fig. 12. X-ray diffraction patterns of native corn starch and HMT corn starch treated at 120 °C after various treatment times.

## 4. Conclusion

Corn starch was used for the comparative study of HMT and OPT methods. In OPT, gelatinization temperature ( $T_0$ ) together with  $T_p$  and  $T_c$  of starch increased significantly with increase in treatment time, whereas only  $T_p$  and  $T_c$  of HMT starch increased with treatment time. The biphasic broadening of the peaks (high  $T_c - T_0$ ) can be explained by an inhomogeneous heat transfer during HMT of starch. Narrow peak of DSC curve can be used as an indication of improved homogeneity of OPT samples. However, both methods provided similar decreased pattern of gelatinization enthalpy, indicating a partial loss of crystallinity of the starch granules during treatment. The RVA viscosograms for OPT exhibited a decrease of PKV, BDV, and FNV with treatment time, which is in agreement with the patterns of RVA viscosograms for HMT starch. It is also observed that only PT of OPT starch increased with treatment time, whereas the PT of HMT starch remained unchanged. As a result, these pasting properties confirm the similarity of the pasting characteristics of both HMT and OPT starch except for PT. OPT of starch provided a uniform heat distribution in the starch suspension, thus allowing OPT modified starch to be produced in large scale.

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