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Effect of urea and sodium chloride on the pasting properties and gelatinisation kinetics of corn starch

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RESEARCH ARTICLE

Abstract

The effect of urea and sodium chloride (NaCl) on the pasting properties and gelatinisation kinetic of corn starch was determined using rapid visco-analyser. Starch slurry (3 g in 25 g H_2O) was heated at 3, 5, 7, 10, 15, and 20 °C/min. Peak viscosity, setback, and pasting temperature were recorded at all heating rates as well as the swelling power. The pasting temperature was used for activation energy (Ea) calculation according to the Kissinger plot and Ozawa model. The peak viscosity significantly ($P \leq 0.05$) increased in presence of urea and NaCl at all heating rates compared to the control, while the setback dropped in NaCl and increased in urea. This indicates better amylose-amylose interaction prevention by NaCl. The pasting temperature exhibited higher values in NaCl and lower in urea. This signifies action of urea on the hydrogen bonding between starch molecules in the amorphous region of the granule (dominated by amylose). The protective action of NaCl is obvious on the high pasting temperature of corn starch. Kissinger and Ozawa kinetics equations exhibited similar Ea values for corn starch under the experimental conditions used in this work. Urea exhibited higher Ea compared to NaCl indicating ineffectiveness of urea to break hydrogen bonding at the conditions of the experiment.

Keywords: starch, corn, kinetics, RVA, urea

1. Introduction

Starch is a polymeric carbohydrate of anhydro glucose units linked through α-D-(1→4) glucosidic bond. It is commonly accepted that starch is a heterogeneous material consisting of varying proportions of amylose and amylopectin (Buléon *et al.*, 1998; Whistler and BeMiller, 1997; Wurzburg, 1986; Zobel and Stephen, 1995). Amylose is a linear polymer α-D-(1→4) whereas amylopectin is a branched polymer with α-D-(1→4) glucosidic bond with periodic branches at the O-6 position of the glucose unit (Buléon *et al.*, 1998; Wurzburg, 1986). Recent studies revealed that starch granules can be described as a three entities, namely semi-crystalline stacks containing alternating crystalline and amorphous lamellae, which are set in a matrix of amorphous material (Jenkins and Donald, 1996). When starch granules are heated in an aqueous medium, a transition from an ordered to a disordered state occurs. This process is known as gelatinisation. It can be defined as the process which turns the insoluble starch granules into a suspension of its individual constituent molecules (Oosten, 1982). Gelatinisation according to Donovan (1979) involves: (1) hydration of the starch which is accompanied by granule swelling; (2) disruption of granule structure as measured by loss of granule birefringence when viewed under polarised light; (3) heat absorption; and (4) loss of crystallinity as measured by X-ray diffraction. When starch is heated under low moisture content, it changes to resistant starch which is considered dietary fibre (Kahraman and Köksel, 2013; Van der Kaaij *et al.*, 2009).

Spigno and De Faveri (2004) reported that there were two steps in gelatinisation of wheat starch. It might include the swelling and disruption followed by dissolution of starch granules at different temperatures. Kokini *et al.* (1992) established a model for starch gelatinisation with an assumption of a two steps process. It has been generally postulated that two steps are involved in the phase transition of starch. However, the experimental evidence is limited and the distinction between swelling and disruption/dissolution steps remains unclear. Kinetics of the phase transition of starch provides important information for selecting process conditions. Several investigators have reported that the phase transition of starch followed a pseudo-first order in the presence of high moisture content.

Many studies have been reported on the gelatinisation kinetics of starch-water systems in excess water (>70%, w/w) by differential scanning calorimetry (DSC) (Freitas *et al.*, 2004; Ojeda *et al.*, 2000; Pielichowski *et al.*, 1998; Pravisani *et al.*, 1985; Wirakartakusumah, 1981). Regarding starch gelatinisation, activation energy (Ea) can be defined as the least amount of energy needed to unfold the amorphous region of the granule (typically amylose) and the crystalline region (mostly amylopectin). The Ea of starch is greatly affected by the starch-water ratio, where the least needed Ea for starch gelatinisation was reported at 45% water content (Mendes da Silva *et al.*, 1996). Higher temperature does not mean higher Ea, but if the reaction starts at higher temperature it reaches the required peak of the Ea faster. Although, the Ea of starch gelatinisation is affected by temperature change but it can be influenced by other factors. For instance, the increase in granule volume due to hydration of the amorphous region can cause breaking of the secondary bonds that hold the crystalline region together, causing drop on the Ea. This process can occur at a minimum of 45% moisture content which means that Ea of starch gelatinisation is moisture dependent besides temperature change and amylose content (Kim and Wang, 1999). The need for two steps to describe starch gelatinisation process was first quantified and introduced by Suzuki and Kubota (1976) for rice starch and was confirmed by other researchers (Bakshi and Singh, 1980; Juliano and Pérez, 1986; Ojeda, 2000; Pravisani *et al.*, 1985; Yeh and Li, 1996). Therefore, researchers confirmed that starch gelatinisation kinetics is a two steps process by introducing the break temperature (BT) concept (Ozawa, 1970; Ojeda, 2000). The BT is the temperature that separates the unfolding of the outer layer of the starch granule (amylose) from the melting of the inner crystalline portion (amylopectin). The point that separates the two temperatures is known as the BT. Consequently, the first step describes the increase in the molecular mobility of the amorphous part of the starch granule (rich in amylose) whereas the second step represents the melting of the crystalline region (rich in amylopectin) (Ojeda, 2000; Ozawa, 1970).

The influence of salts on starch swelling and gelatinisation depends on their type and concentration. Some salts were reported to depress or elevate gelatinisation temperature.

Gelatinisation inhibitors such as salts cause increase in gelatinisation temperature and are listed at the top of Hofmeister lyotropic electrolytes list, such as sodium sulphate, sodium and potassium citrate (Villwock and BeMiller, 2005). For instance, magnesium sulphate at high concentration delays gelatinisation to 115 °C rather than 70-80 °C. Conversely, salts listed lower on the list causes lower gelatinisation temperature, even as low as room temperature, such as lithium chloride and sodium iodide (Sandstedt *et al.*, 1960). Whereas, salts in the middle of the electrolytes list maintain mixed effect, i.e. at low concentration increase gelatinisation temperature otherwise promote gelatinisation (decrease gelatinisation temperature). Up to 0.1 M monovalent salts are known to protect starch against gelatinisation, but at higher molarity chlorides and nitrates behaved differently as noted on starch viscosity, as well. Consistency coefficient (R^2) decreased at higher chlorides content and increased at higher nitrates. The effect of these salts on starch granules swelling was also observed. The underline mechanism of salts effect on gelatinisation is not yet understood. In addition, most studies were done using DSC which overlooks the flowing (rheological) properties of starch during the course of gelatinisation. Specifically, the temperature at which starch undergoes most structural and viscosity changes which is denoted by the pasting temperature. Zhu *et al.* (2009) reported pronounced swelling inhibitory effect of sodium chloride (NaCl) at 1% and noticeable swelling starts at 5% NaCl concentration.

The objectives of this work were to determine the effect of urea and NaCl on the rates of phase transition (gelatinisation) of native corn starch by determining the pasting properties. The pasting temperature will be determined by rapid visco-analyser (RVA) and used for calculating phase transition kinetics (Ea).

2. Materials and methods

Rapid visco-analyser measurements

Corn starch was donated by Tate & Lyle North America, A.E. Staley MFG Co. (Decatur, IL, USA). Pasting parameters of corn starch, including pasting temperature, were determined using a rapid visco-analyser (Newport Scientific, Sydney, Australia). Starch (3 g at 14% moisture basis) and distilled water weighed into aluminium RVA canisters to a total weight of 28 grams. The obtained slurry was held at 50 °C for 30 seconds, heated to 95 °C at 3, 5, 7, 10, 15, and 20 °C/min, and held at 95 °C for 4 minutes. It was then cooled to 50 °C at the same rates. The RVA rotating paddle was set at 960 rpm for first 10 seconds which was then reduced to 160 rpm and kept through the remainder of the experiment. Measurements were done in triplicate and Thermocline® for Windows software (Hägersten, Sweden) was used for data processing.

Swelling power

Swelling power of corn starch in distilled water, 0.5, and 1.0 M NaCl or urea solutions was determined according to the method of Subramanian *et al.* (1994) with slight modification. Starch (0.5 grams dry basis) was placed in a centrifuge tubes and 40 ml of distilled water, NaCl, or urea solutions were added. The tubes were heated at 70 °C in a shaking water bath (JULABO GmbH, Seelbach, Germany) for 30 minutes. Samples were cooled by immersing in an ice bath (JULABO GmbH) for 5 minutes and centrifuged (3,000×*g*) for 25 minutes (Thermo Fisher Scientific Inc., Waltham, MA, USA). The swelling power was calculated as the ratio of sediment weight to dry starch (g/g).

Statistical analysis

All measurements were done in triplicate. One way analysis of variance technique was used to determine the effect salt molarity (0.5 and 1.0) at different heating rates (3, 5, 7, 10, 15, and 20 °C/min) on corn starch. Duncan's multiple range test at $P \leq 0.05$ was used to compare means using PASW® Statistics 18 software (Quarry Bay, Hong Kong).

Theoretical

The fundamental assumption in reaction kinetics studies using different methods such as DSC is that heat flow, measured in (W/g), is comparative to the DSC baseline and proportional to the reaction rate (Wunderlich, 1990). Accordingly, a hypothesis was made and considered the RVA pasting temperature as the average alteration on the physical properties (pasting properties) of starch. Bear in mind that, the pasting temperature given by RVA is an average temperature between the initial viscosity increase, caused by granule hydration with subsequent swelling, and the peak viscosity (PV) of the system just before granules rupture (break down). The maximum physical change of starch granule, which leads to viscosity increase, indicates leaching out of amylose and disentanglement of the amylopectin within the swollen granule (Keetels and Van Vliet, 1994). Therefore, the increase in starch volume fraction which leads to increase in viscosity is due to higher interaction between starch components (amylose and amylopectin) and entrapment of water. Starch hydration denotes interaction with water, which is irreversible alteration of starch granules and reduction in intra-molecular interaction and subsequent increase in inter-molecular interaction with water (Murphy, 2000). The change in pasting temperature as a function of heating rate permits the calculation of kinetics parameters such as Ea. A number of researchers reported starch gelatinisation kinetics using DSC, but no reports with respect to using starch pasting temperature.

In most existing kinetics methods, the nth reaction order is according to Kissinger (1957) and others based on the following relationship (Alamri *et al.*, 2015).

$$\frac{d\alpha}{dt} = k\,(1-\alpha)^n \qquad (1)$$

Where t = time; α = degree of reaction; n = reaction order; and k = pre-exponential factor.

By taking the derivative of the Arrhenius equation and Equation 1, Kissinger (1957) assumed that dα/dt (the reaction rate) reaches a maximum at the peak temperature (T_p) where the DSC curve reaches its peak, which is represented by the peak temperature at the complete starch gelatinisation. In addition, Kissinger assumed that $n(1-\alpha)^{(n-1)}$ is a number close to one, and dT/dt = β (heating rate) is constant. Therefore:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \qquad (2)$$

Where β = heating rate; A = pre-exponential factor; R = universal gas constant; Ea = activation energy; and Tp = peak temperature .

The Kissinger equation showed that for a particular DSC profile at a heating rate (β) one can observe the maximum reaction rate at the peak temperature, T_p. That can be true for a set of DSC curves with different heating rates. The plot of $\ln(\beta/T_p^2)$ against $1/T_p$ can be an approach to obtain Kissinger's plot (Equation 2). The Ea can be calculated from the slope of Kissinger's plot, whereas the intercept can provide the pre-exponential factor (A).

Another researcher (Ozawa, 1970) made a presumption that at the peak of any DSC profile, the degree of reactions is constant and independent of its heating rate and proceeded to derive the following equation:

$$\ln(\beta) = \text{constant} - 1.052\, E_a/R/T_p \qquad (3)$$

Where β = heating rate; E_a = activation energy; R = gas constant; and T_p = peak temperature.

In accordance with Equation 3, various DSC experiments with different heating rates can be performed and the temperature at the peak of the profile can be determined. The Ozawa Ea can be calculated from the slope of plotting ln(β) against $1/T_p$. The method (Ozawa theory) is used by the ASTM E698 approved method for thermal stability of materials. Usually, three or more experiments with different heating rates are required for proper use of this method. In this work the Ea will be calculated using corn starch pasting temperature at different heating rates (3, 5, 7, 10, 15 and 20 °C/min) and the linear regression for slope determination will be done using Sigma Plot (Systat Software, San Jose, CA, USA).

3. Results and discussion

Corn starch swelling test showed clear granules swelling when heated in distilled water, but limited swelling was observed for samples in presence of NaCl. This data agrees with Zhu *et al.* (2009) who reported slow granules swelling for up 1.0% NaCl after which swelling starts to improve around 5%. In contrast, swelling was so intense in urea where some granules increased in size by 160 and 73.7% in 0.5 M and 1.0 M urea, respectively (Figure 1). Some granules were completely ruptured at 1.0 M (Figure 2).

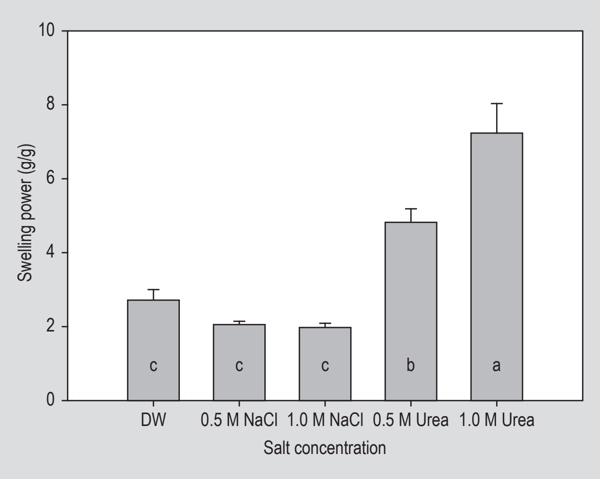

Figure 1. Swelling power (g/g) of corn starch in distilled water (DW), sodium chloride (NaCl), and urea. Bars with the same letter are not significantly different.

As indicated in Figure 1, starch exhibited same degree of swelling within the used concentration NaCl, but higher urea concentration significantly increased swelling. NaCl suppressed swelling by 28.2% compared to the control.

The RVA PV of corn starch significantly increased ($P \leq 0.05$) due to the action of NaCl and urea at all heating rates compared to starch cooked in distilled water, except for the 3 °C/minute heating rate, where 1.0 M urea had no significant effect on PV (Table 1). In general, granule swelling inhibition is expected to have negative effect on PV. Since higher molarity of urea maintained increase in PV, one can infer that urea promoted swelling by spacing starch molecules within the granule by breaking the hydrogen bonding thus allowing water molecules to penetrate into the granule and bring about swelling followed by complete gelatinisation. Assumptions had been made to determine whether cations or anions of monovalent salts penetrate first into starch granules at specific temperature (Abd Ghani *et al.*, 1999; Brumovsky *et al.*, 2006; Chinachoti *et al.*, 1991; Lii *et al.*, 2002; Maaruf *et al.*, 2001; Oosten, 1982). Potassium chloride and NaCl were found to impose similar protective effect at 65 °C, but not at higher temperatures. Generally, the final viscosity of starch significantly increase at higher heating rates due to NaCl and urea, while different salt molarity showed mixed effect on the final viscosity. With respect to the final viscosity, higher urea molarity further reduced the final viscosity by depressing hydrogen bonding between the starch gel molecules, while higher NaCl molarity had mixed effect (Oakenfull, 1987).

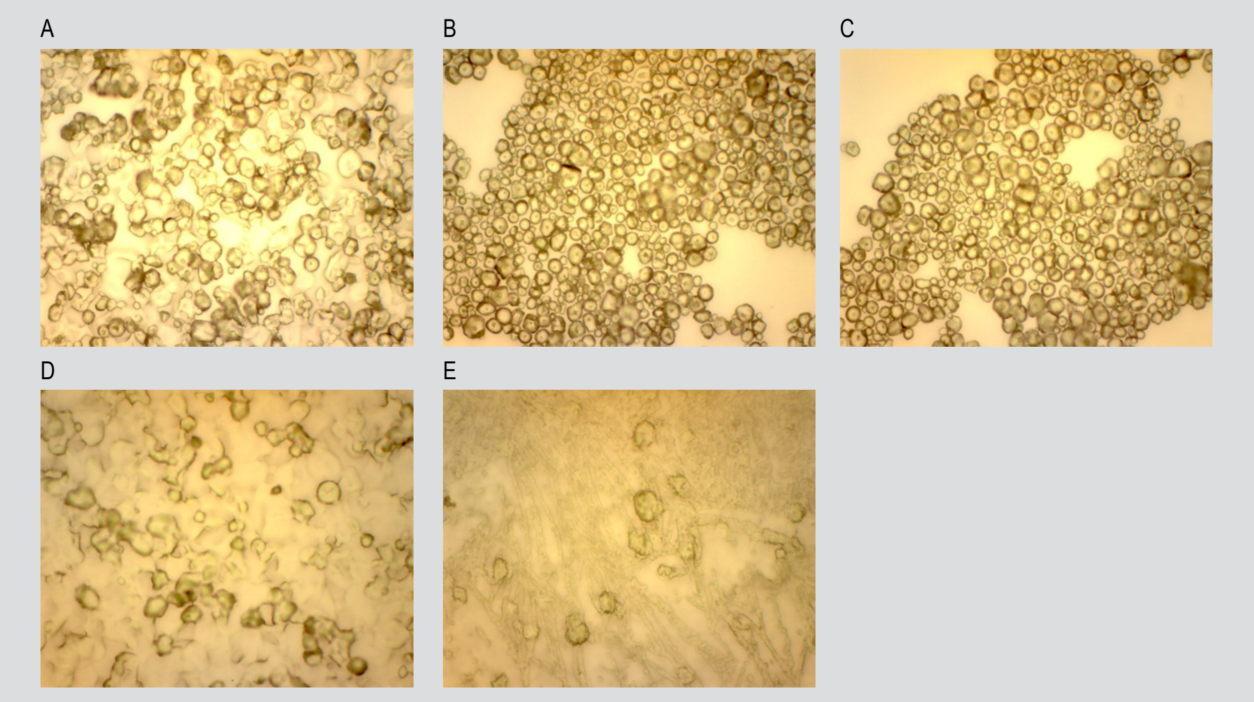

Figure 2. Light microscopic images of corn starch gels (40×magnification) in sodium chloride (NaCl) and urea. Swollen corn starch granules in (A) distilled water; (B) 0.5 M NaCl; (C) 1 M NaCl; (D) 0.5 M Urea; and (E) 1.0 M urea.

Table 1. Rapid visco-analyser pasting properties of corn starch in sodium chloride (NaCl) and urea at different heating rates.

Heating rate (°C) per minute	Molarity	Pasting properties[1]			
		Peak viscosity (cP)	Final viscosity (cP)	Setback (cP)	Pasting temperature (°C)
NaCl					
3	DW[2]	2,421±21c	2,818±213b	1,801±237b	72.03±15.10c
	0.5 M	2,512±51b	3,359±164a	2,508±25a	81.25±0.34b
	1.0 M	2,643±19a	1,551±144c	393±33c	82.53±0.14a
5	DW	2,327±25c	2,397±37b	1,060±44a	74.98±11.40c
	0.5 M	2,533±30b	2,641±111a	736±79b	81.47±0.32b
	1.0 M	2,691±49a	2,553±105b	405±52c	83.22±0.03a
7	DW	2,397±31b	2,520±18a	1,109±9a	75.47±9.20c
	0.5 M	2,439±74b	2,312±69b	288±6b	82.71±0.32b
	1.0 M	2,684±14a	2,499±25a	240±3c	84.03±0.28a
10	DW	2,262±9c	2,375±34c	1,063±28a	76.93±7.20c
	0.5 M	2,438±40b	2,249±43b	845±5b	83.43±0.37b
	1.0 M	2,702±26a	2,484±54a	379±34c	85.07±0.63a
15	DW	2,238±37c	2,371±19a	1,042±70a	78.58±5.60b
	0.5 M	2,446±58b	2,215±34b	461±51b	84.97±0.50a
	1.0 M	2,623±54a	2,403±67a	320±32c	85.42±0.29a
20	DW	2,245±23c	2,292±56b	860±99a	79.07±6.90 b
	0.5 M	2,362±34b	2,128±41c	359±35b	84.78±0.10a
	1.0 M	2,635±56a	2,454±56a	298±29b	85.78±0.63a
Urea					
3	DW	2,421±21a	2,818±214a	1,800±237a	72.03±15.10a
	0.5 M	1,447±68b	2,468±49b	1,270±13b	71.95±0.31b
	1.0 M	2,382±101a	2,197±54c	1,123±18b	68.15±0.08c
5	DW	2,327±25c	2,397±37b	1,060±44c	74.98±11.40a
	0.5 M	2,640±22b	2,515±40a	1,357±19a	72.40±0.36b
	1.0 M	2,974±68a	2,432±07b	1,287±21b	68.83±0.19c
7	DW	2,397±31c	2,520±18b	1,109±09c	75.47±9.20a
	0.5 M	2,669±34b	2,597±24a	1,394±10a	72.85±0.30b
	1.0 M	3,046±129a	2,461±34c	1,313±10b	69.75±0.43c
10	DW	2,262±9c	2,375±34c	1,063±28c	78.58±5.60a
	0.5 M	2,564±35b	2,616±11a	1,419±10a	74.50±0.74b
	1.0 M	2,933±43a	2,496±68b	1,365±17b	71.35±0.74c
15	DW	2,238±37c	2,371±19b	1,042±70b	78.58±5.60a
	0.5 M	2,445±85b	2,585±65a	1,431±04a	75.77±0.50b
	1.0 M	2,827±53a	2,567±06a	1,400±20a	73.57±0.48c
20	DW	2,245±23c	2,292±56b	860±1b	79.07±6.90a
	0.5 M	2,479±56b	2,666±39a	1,396±11a	75.60±0.72b
	1.0 M	2,829±21a	2,639±01a	1,435±14a	72.95±0.53c

[1] Means carrying different letters in columns under a specific heating rate are significantly different.

[2] DW = distilled water.

The setback, which is caused by amylose retrogradation during the cooling cycle from 95 at 50 °C which promotes hot gel formation, was significantly reduced by NaCl at higher molarity at all heating rates except for the 3 °C/min. This could be attributed to the slow cooling effect that allows amylose granules to align, thus forming a network that creates firmer gel texture. Higher NaCl concentration reduced the setback, which can be attributed to its ability to reduce amylose association, therefore, weaker final gel (Table 1). Conversely, urea increased the setback at 0.5 M from 3 to 10 °C/minute heating rates but the setback was lower at 1.0 M urea (Table 1). A mixed effect of urea on setback was noted for the 3 to 10 °C/min, while 15 and 20 °C exhibited higher setback under both molarities. Although, urea is known to break hydrogen bonding and was expected to reduce amylose retrogradation, but it appears that was not accomplished because retrogradation measurements were done at 50 °C. This could be attributed to higher molecular mobility of urea molecules at that temperature which prevented its ability to break hydrogen bonding between amylose granules.

Starch pasting temperature, as determined by RVA, is the temperature where the starch exhibits the highest rate of viscosity changes resulting from water absorption followed by swelling. Higher NaCl molarity significantly increased the pasting temperature compared to the control (no salt), whereas higher urea concentration caused the opposite effect of that of the NaCl (Table 1). The pasting temperature of corn starch in presence of NaCl as a function of heating rate was significantly higher than the control, i.e. higher pasting temperature at higher heating rate (Figure 3). In addition, the effect of salt on the pasting temperature was different, where starch pasting temperature in 1.0 M NaCl > 0.5 M > distilled water, but the pasting temperature in distilled water > 0.5 M urea > 1.0 M. The effect of heating rate within NaCl molarity was shown to stay plateau after 7 °C/minute (Table 1 and Figure 3). The effect of heating rate on the pasting temperature of corn starch was plotted in Figure 3. One can calculate the slopes of lines in Figure 3 using linear regression and compare the slopes as indicators of magnitude of the effect of salt concentration on the pasting temperature as a function of heating rate. Since 0.5 M of both salts exhibited the highest slope, one can say that it has more influence on pasting temperature (Figure 3). NaCl has elevated the pasting temperature more than urea which is consistent with the protective action of NaCl as reported in the literature (Zhu *et al.*, 2009) and with the ability of urea to break hydrogen bonding thus initiating gelatinisation at lower temperature due to weaker association between starch granule molecules. Jihong *et al.* (2012) reported that when pre-heating corn starch at a sub-gelatinisation temperature, i.e. 61 °C which is 5 °C below the onset of starch gelatinisation, for 30 min, the presence of urea greatly facilitated corn starch hydrolysis by breaking the intra-hydrogen bonding. Urea seems to be more effective in breaking hydrogen bonding by reducing starch elastic modulus at temperatures below 30 °C (Tamaki *et al.*, 2011) and that could explain the ineffectiveness of urea on reducing amylose retrogradation at 50 °C as stated above.

Traditionally, starch gelatinisation kinetics was investigated using DSC which is based on the assumption that the heat flow, measured in W/g, is comparative to the baseline and proportional to the reaction rate (Wunderlich, 1990). Therefore, an assumption can be made by considering the pasting temperature obtained during RVA run is the maximum change on the physico-chemical properties of the starch. Take into account that, starch pasting temperature given by the RVA is considered the temperature at the maximum change in viscosity between the initial and the maximum increase in viscosity. Starch gelatinisation kinetics is considered a two steps process. This classification was first introduced by Suzuki and Kubota (1976) who required two activation energies to describe starch gelatinisation (rice starch) which was later confirmed by a number of authors (Juliano and Pérez, 1986; Ojeda *et al.*, 2000; Ozawa, 1970; Pravisani *et al.*, 1985). The first step represents increase in the molecular mobility of the amorphous region of the starch granule (rich in amylose) followed by melting of the crystalline region (rich in amylopectin) signifying the second step.

Ea was calculated using different heating rates of starch slurry, which allows the determination of the difference between the two steps of starch gelatinisation. The Ea is the

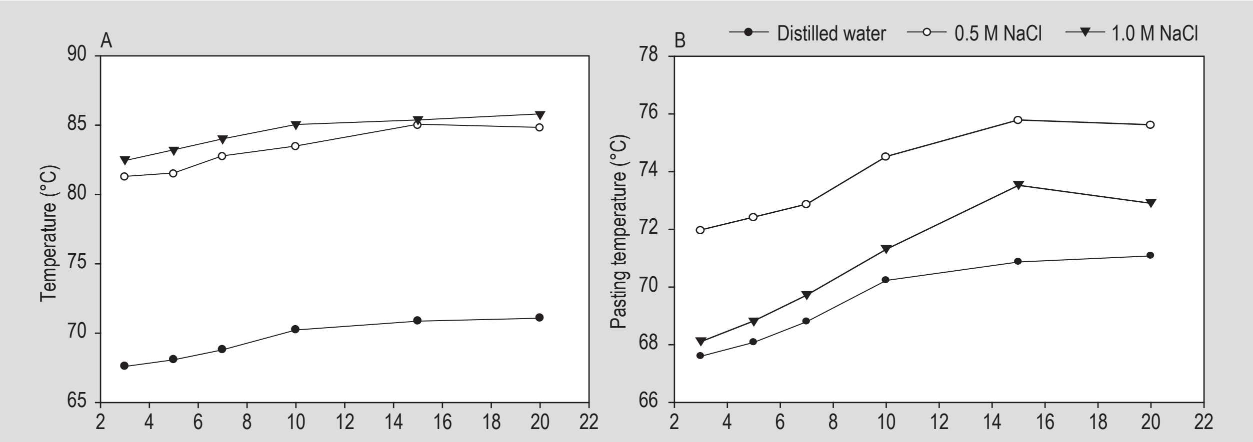

Figure 3. Effect of distilled water, sodium chloride (NaCl) and urea on the pasting temperature of corn starch. (A) The effect of NaCl on the pasting temperature of corn starch; (B) the effect of urea on the pasting temperature of corn starch.

slope of the end result line of the Arrhenius relationship, while the pre-exponential factor is represented by the intercept. Kissinger and Ozawa models were applied to the pasting temperature of corn starch in NaCl or urea. Kinetics parameters resulting from different heating rates are listed in Table 2. The plots of ln (β/T_p^2) against $1/T_p$ and $\ln(\beta)$ as a function of $1/T_p^2$ are the parameters used for Ea calculation according to Kissinger plot and Ozawa model, respectively. Two representative graphs of these relationships were illustrated in Figure 4, where the two lines used for slope calculation and the BT are presented. The BT listed in Table 3 was statistically determined (ANOVA) and defined as the temperature that separates the unfolding of the amorphous from the melting of the crystalline regions of the starch granule. The high coefficient of determination (R^2) of the Ea at the specified BT indicates the suitability of Kissinger plot for fitting the data (Table 3). In Table 3, the values were recorded as > and < the BT because the slope of the two lines will be taken separately for Ea calculation. The BT values in urea was < distilled water < NaCl, which shows similarity between the effect of salt on starch gelatinisation kinetics and pasting properties. This can be attributed to the ability of urea to break hydrogen bonding, especially of the amorphous region of the starch granule which is rich in amylose. Conversely, NaCl played a protective role and delayed water absorption (limited swelling) imposing higher pasting temperature. This occurrence is supported by both of the kinetic models. As mentioned above, higher heating

Table 2. Corn starch gelatinisation kinetics-parameters in distilled water, 0.5 M and 1.0 M sodium chloride (NaCl), or 0.5 M and 1.0 M urea at different heating rates.

Heating rate (β)	Peak temp. (°C)	Peak temp. (T_p) (K)	$1/T_p$ ($\times10^{-3}$)[a]	T_p^2	β/T_p^2 ($\times10^{-5}$)	$-\ln(\beta/T_p^2)$($\times10^{-5}$)[b]
Distilled water						
3	72.03±0.79	345.23	2.90	119,183.8	2.52	10.5898
5	74.98±0.53	348.18	2.87	121,229.3	4.12	10.0961
7	75.47±0.08	348.67	2.87	121,570.8	5.76	9.76234
10	76.93±0.03	350.13	2.86	122,591.0	8.16	9.41402
15	78.58±0.98	351.78	2.84	123,749.2	12.10	9.01796
20	79.07±0.83	352.27	2.83	124,094.2	16.11	8.73306
0.5 M NaCl						
3	81.25±0.35	354.45	2.821	125,634.8	2.39	10.6425
5	81.47±0.35	354.67	2.820	125,788.4	3.97	10.1329
7	82.72±0.32	355.92	2.810	126,676.7	5.53	9.80348
10	83.43±0.38	356.63	2.804	127,187.3	7.86	9.45083
15	84.97±0.50	358.17	2.792	128,283.4	11.71	9.05395
20	84.78±0.10	357.98	2.793	128,152.1	15.62	8.76524
1.0 M NaCl						
3	82.53±0.14	355.73	2.811	126,546.2	2.37	10.6498
5	83.22±0.03	356.42	2.806	127,032.8	3.94	10.1428
7	84.03±0.28	357.23	2.799	127,615.7	5.49	9.81087
10	85.07±0.63	358.27	2.791	128,355	7.79	9.45997
15	85.42±0.29	358.62	2.788	128,605.9	11.71	9.05646
20	85.78±0.64	358.98	2.786	128,869	15.52	8.77082
0.5 M urea						
3	71.95±0.31	345.15	2.897	119,128.5	2.52	10.5893
5	72.40±0.36	345.60	2.894	119,439.4	4.19	10.0811
7	72.85±0.30	346.05	2.890	119,750.6	5.85	9.74726
10	74.50±0.74	347.70	2.876	120,895.3	8.27	9.40009
15	75.77±0.50	348.97	2.866	121,777.7	12.30	9.00191
20	75.60±0.72	348.80	2.867	121,661.4	16.41	8.71327
1.0 M urea						
3	68.15±0.09	341.35	2.931	116,519.8	2.57	10.5672
5	68.83±0.19	342.03	2.924	116,986.8	4.27	10.0604
7	69.75±0.43	342.95	2.916	117,614.7	5.95	9.72926
10	71.35±0.74	344.55	2.902	118,714.7	8.42	9.38189
15	73.57±0.49	346.77	2.884	120,247.1	12.52	8.98925
20	72.95±0.53	346.15	2.889	119,819.8	16.71	8.69801

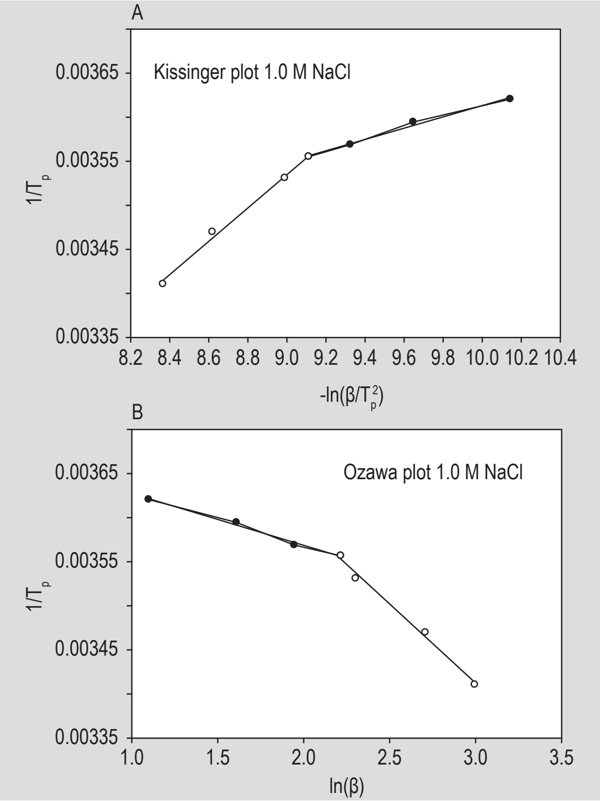

Figure 4. Relationship between heating rate and pasting temperatures (in K) according to (A) Kissinger (1957) and (B) Ozawa (1970) based on Equation 2 and 3. Each point is the average of at least three replicates.

Table 3. Comparison of activation energy according to Kissinger (1957) and Ozawa (1970) plots.

Corn starch	Break temperature (°C)	Activation energy (kJ/mol)	R^2
Kissinger plot			
Distilled water	>76	227.8	0.98
	<76	217.3	0.99
0.5 M urea	>73.3	267.6	0.91
	<73.3	687.7	0.98
1.0 M urea	>70.4	205.5	0.97
	<70.4	481.8	0.95
0.5 M NaCl	>83.0	43.3	0.98
	<83.0	138.1	0.99
1.0 M NaCl	>84.4	44.1	0.99
	<84.4	129.3	0.99
Ozawa plot			
Distilled water	>77.6	48.4	0.99
	<77.6	127.9	0.97
0.5 M urea	>73.3	287.6	0.87
	<73.3	652.4	0.99
1.0 M urea	>70.4	214.6	0.95
	<70.4	446.9	0.96
0.5 M NaCl	>83.0	46.7	0.99
	<83.0	135.9	0.99
1.0 M NaCl	>84.4	46.4	0.99
	<84.4	141.6	0.99

rates allow for higher pasting temperature as illustrated in Figure 3, but the Ea was significantly different in urea compared to NaCl. The obvious trend showed lower Ea at higher heating rates and vice versa for both salts, but it was more pronounced in urea (Table 3). Higher urea concentration dropped the Ea by 23% for the line above BT and by 30% below BT, for Kissinger plot, and by 25% above BT and 31% below BT, for Ozawa models. In contrast, NaCl exhibited minimal change in Ea due to higher molarity. Since corn starch gelatinisation Ea in urea was higher than NaCl which is the opposite of what expected because urea disrupts hydrogen bonding and is expected to reduce Ea. This phenomenon can be explained by considering urea less effective at higher temperatures, as shown by other researchers, that urea reduced elastic modulus of amylose gel at 30 °C and lower. On contrast, higher Ea at higher NaCl signifies protective action as shown in Table 3 which is in agreement with reports in the literature. The ineffectiveness of urea at higher temperatures is also notice on the high setback data recorded above.

4. Conclusions

NaCl increased PV and reduced the setback of corn starch. The pasting temperature has increased at higher NaCl molarity which was consistent with low swelling power of starch granules. PV has increased in urea but the pasting temperature was reduced and setback was increased indicating incapacity of urea to prevent amylose retrogradation. The heating rate effect on starch pasting properties was noticeable at higher salt molarity. The BT of corn starch was lower in urea, whereas the Ea in urea was higher compared to NaCl and the control. The protective action of NaCl on starch was obvious of the high Ea recorded by Kissinger plot and Ozawa model.

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