



Effect of sodium chloride concentration on the pasting and thermal properties of rice starch in the presence of non-ionic and ionic hydrocolloids

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Abstract

The effect of sodium chloride (NaCl) concentration on the pasting and thermal properties of rice starch (RS) in the presence of non-ionic (guar gum; GG) and ionic (xanthan gum; XG) hydrocolloids was studied. NaCl at various concentrations were added to RS and RS/hydrocolloid mixtures. The rapid visco-analysis (RVA) showed that the addition of NaCl significantly ($p \leq 0.05$) increased peak viscosity and pasting temperature of RS and RS/hydrocolloid mixtures, whereas the setback values were decreased as compared to the control without added NaCl. The pasting characteristics of RS/XG were predominantly affected in the presence of NaCl, while RS/GG showed the same trend with RS. On the contrary, the thermal properties determined by differential scanning calorimetry (DSC) revealed that addition of NaCl significantly ($p \leq 0.05$) increased the gelatinization onset (T_o), peak (T_p), and conclusion (T_c) temperatures, and gelatinization enthalpy (ΔH) of RS, while these thermal properties were less affected in the presence of either XG or GG. These results can be used as a guideline for developing food products containing salts in which the starch/hydrocolloid mixture plays a role as a main ingredient (starch-based products) or as a thickening/gelling agent

Keywords: rice starch, hydrocolloid, salt, pasting, thermal properties

Introduction

Starch/hydrocolloid mixtures have been widely used in the food industry. However, the problem that food manufacturers faced with is that the native starches generally have poor properties for the preparation of food products, such as retrogradation of gel producing syneresis, production of weak bodied, cohesive, rubbery pastes, and undesirable gel (BeMiller, 2007) etc. These shortcomings can be overcome by blending native starches with polysaccharide hydrocolloids (gums). The mixtures of starch and hydrocolloids have been used to modify and control rheological and textural properties, improve moisture retention, control water mobility, and maintain overall product quality during processing and storage of food products. In general, however, starch-hydrocolloid combinations usually co-exist with other ingredients in many food formulations. One example of such ingredients is salt. Salts have been reported to have effects on the properties of starch, such as pasting properties (Oosten, 1983; Jyothi et al., 2005; Viturawong et al., 2008; Samutsri and Suphantharika, 2012), thermal properties (Oosten, 1982; Jane, 1993; Ahmad and William, 1999), swelling power (Mandala and Bayas, 2004; Song et al., 2006), and retrogradation (Chang and Liu, 1991).

Starch/hydrocolloid mixture was studied by many researchers, but the effect of salt on this blending was only some reported in the literature, such as wheat starch/xanthan gum (Mandala and Bayas, 2004), rice starch/xanthan gum (Viturawong et al., 2008), rice

starch/guar gum (Samutsri and Suphantharika, 2012). In a particularly, study the effect of NaCl concentration on this blending have not been carried out yet. The objective of this research was to investigate the effect of NaCl concentration on the pasting and thermal properties of rice starch in the presence of non-ionic and ionic hydrocolloids.

Materials and methods

Materials

Commercial rice starch (RS) was kindly supplied by Cho Heng Rice Vermicelli Factory Co., Ltd., Nakhon Pathom, Thailand. RS had 22.66% amylose contents. Xanthan gum (XG) was purchased from CP Kelco Co., San Diego, CA, USA. Guar gum (GG) was purchased from Sigma Aldrich, Inc., St. Louis, MO, USA. Sodium chloride (NaCl) was of reagent grade and purchased from Merck KGaA, Darmstadt, Germany.

Determination of pasting properties

Pasting properties of 8% (w/w) RS and RS/hydrocolloid blends (19:1, w/w ratio) as well as 0.4% hydrocolloid suspended in distilled water and 0.1 M, 0.5 M, 1.0 M, 1.5 M, and 2.0 M NaCl solutions were determined by a rapid visco-analyzer (Model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia). RS slurry was prepared by dispersing weighted amounts of RS (dry basis) in distilled water or salt solution. In the case of RS/gum blends, RS was added into the gum solution and stirred for 1 h until a smooth solution was obtained. The weighed of 28 g were then poured into aluminum canisters and stirred manually using plastic paddles for 20-30s before insertion into the RVA instrument. The heating and cooling cycles were programmed following the general pasting method (STD 2). The viscosity was expressed in rapid visco units (RVU).

Determination of thermal properties

Thermal properties, namely gelatinization temperature and enthalpy, of RS and RS/gum mixtures in the presence and absence of NaCl were measured by a differential scanning calorimetry (DSC 1, Mettler-Toledo GmbH, Schwerzenbach, Swetzerland). The total solids content of samples was 16% (w/w, db), while keeping the RS/gum ration constant at 7.6/0.4 (w/w). The samples were prepared by the procedure describe above. After hydration for 1 h at room temperature, 10-15mg of the well-stirred sample suspension were exactly weight into 40 μ L aluminum crucibles, which were immediately sealed to prevent moisture lose. Scans were performed from 25 to 100°C at a controlled constant rate of 10°C/min. A sealed empty crucible was used a reference and the DSC was calibrated using indium. The gelatinization enthalpy (ΔH) and transition temperatures, namely the onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c), were determined, based on the DSC heating curves. The ΔH was evaluated, based on the area of the main endothermic peak, and expressed in terms of J/g of dry starch using the equipment software.

Results and discussion

Pasting properties

The pasting properties of RS and RS/hydrocolloid mixtures (RS/XG and RS/GG) in the presence and absence of NaCl determined by RVA are expressed in Figure 1. The statistical analyses of all the pasting parameters of RS alone and RS/hydrocolloid blends in the presence and absence of salt were displayed and summarized in Table 1.

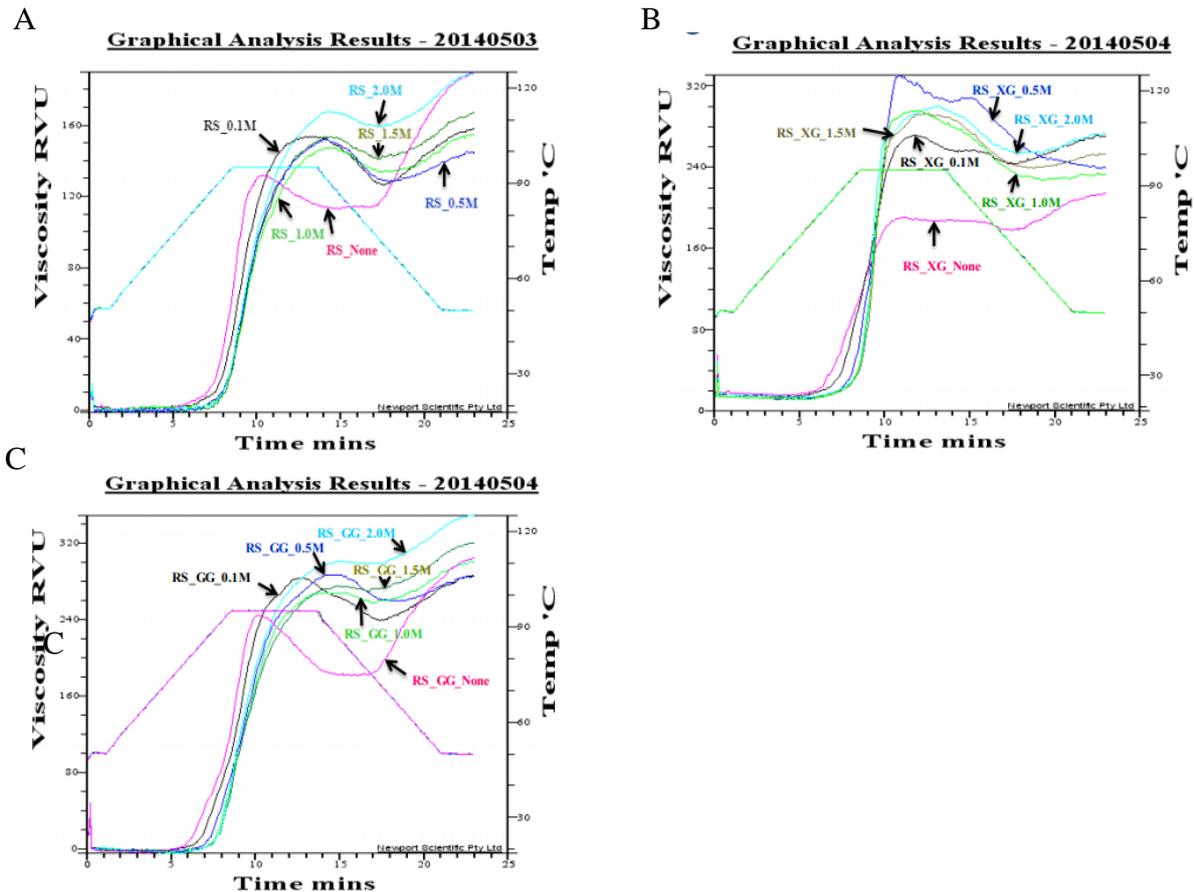


Figure 1 Typical RVA pasting profiles of 8% (w/w) (A) rice starch (RS), (B) rice starch/xanthan gum (RS/XG) and (C) rice starch/guar gum (RS/GG) (19:1, w/w ratio) dispersed in aqueous solution without and with NaCl at different concentration, i.e. 0.1 M, 0.5 M, 1.0 M, 1.5 M and 2.0 M.

Considering the effect of salt on RS, addition of NaCl to RS suspension significantly ($p \leq 0.05$) increased peak viscosity (PV) of the RS as compared to that of the control without added salt. As concentration of NaCl increased from 0.1 to 1.5 M, the PV seemed to be unchanged, while when the NaCl concentration was raised up to 2.0 M, the PV was significantly increased. The increasing of PV could be attributed to starch/salt interactions, which reduced the mobility of starch granules, leading to higher viscosity, as pointed out by Bircan and Barringer (1998). Oosten (1983) reported that starch, being a weak acidic ion-exchanger, adsorbs the more cations such as sodium from the solution in exchange with the smaller hydrogen ion, consequently starch matrix is stretched to some extent, resulting in an increase of granule volume. This also seems to be responsible for the increase in PV of a starch suspension by addition of salt. Jyothi et al. (2005) reported that a higher PV of a starch suspension during pasting in the presence of salts generally indicates a higher swelling power of starch granules due to the weakening of the granules structure by those salts. Viturawong et al. (2008) reported that addition of 0.1 M NaCl increased breakdown viscosity (BV) of RS alone, which is consistent with our results, that BV was increased from 14.2 RVU (RS without salt) to 26.3 RVU for the RS with 0.1 M NaCl. Generally, NaCl has been reported to inhibit the swelling power of starch, leading to the decreasing of BV. Jyothi et al. (2005) reported a reduction of the BV with increasing salt concentration. So, the reduction of BV

may be due to the inhibition of swelling power of rice starch by NaCl. The effect of salt on final viscosity (FV) was very complicated in this system.

Table 1 Pasting properties of 8% (w/w) rice starch and rice starch in the presence of xanthan gum (RS/XT) or guar gum (RS/GG) (19:1, w/w ratio) dispersed in aqueous solutions without and with NaCl at different concentrations, i. e. 0.1 M, 0.5 M, 1.0 M, 1.5 M and 2.0 M.

Sample	NaCl (M)	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
RS	None	131.3 ± 0.6 ^d	15.3 ± 1.5 ^c	190.8 ± 2.0 ^a	74.9 ± 1.9 ^a	88.1 ± 0.2 ^d
	0.1	152.6 ± 1.1 ^b	28.8 ± 2.3 ^a	157.4 ± 1.0 ^c	33.6 ± 2.7 ^b	90.3 ± 0.6 ^c
	0.5	150.7 ± 2.1 ^b	23.6 ± 0.3 ^b	143.4 ± 1.7 ^d	16.3 ± 0.9 ^e	92.4 ± 0.5 ^b
	1.0	147.2 ± 1.8 ^c	13.8 ± 0.9 ^c	155.3 ± 0.9 ^c	21.9 ± 1.1 ^e	93.3 ± 0.4 ^a
	1.5	150.0 ± 2.2 ^b	11.0 ± 1.6 ^d	166.2 ± 0.5 ^b	25.1 ± 0.8 ^d	92.9 ± 0.3 ^{a,b}
	2.0	168.7 ± 2.4 ^a	8.6 ± 0.4 ^d	190.4 ± 2.4 ^a	30.5 ± 0.2 ^c	92.4 ± 0.3 ^b
RS/XG	None	191.7 ± 2.0 ^e	14.2 ± 1.8 ^f	215.1 ± 2.0 ^e	37.7 ± 1.7 ^a	83.1 ± 0.4 ^e
	0.1	270.3 ± 1.4 ^d	26.3 ± 1.5 ^e	271.0 ± 1.5 ^a	27.0 ± 2.3 ^b	86.7 ± 0.1 ^d
	0.5	328.1 ± 2.9 ^a	83.5 ± 3.8 ^a	240.8 ± 2.6 ^c	0.0 ± 0.0 ^f	89.9 ± 0.0 ^c
	1.0	298.1 ± 1.7 ^b	69.5 ± 1.1 ^b	235.6 ± 2.1 ^d	7.0 ± 0.5 ^e	91.6 ± 0.3 ^b
	1.5	292.9 ± 1.1 ^c	54.0 ± 0.7 ^c	252.6 ± 0.1 ^b	13.7 ± 1.7 ^d	92.4 ± 0.8 ^a
	2.0	301.4 ± 2.2 ^b	46.7 ± 0.7 ^d	274.1 ± 2.0 ^a	19.3 ± 0.4 ^c	92.6 ± 0.0 ^a
RS/GG	None	246.2 ± 1.6 ^f	60.1 ± 0.8 ^a	305.5 ± 1.1 ^c	122.7 ± 1.5 ^a	80.3 ± 0.0 ^e
	0.1	281.8 ± 1.6 ^c	41.6 ± 2.5 ^b	286.1 ± 3.4 ^e	45.9 ± 2.7 ^c	83.9 ± 0.0 ^d
	0.5	285.3 ± 2.5 ^b	25.3 ± 2.6 ^c	287.3 ± 1.2 ^e	27.2 ± 1.7 ^e	86.6 ± 0.4 ^c
	1.0	267.4 ± 1.1 ^e	10.8 ± 0.1 ^d	295.5 ± 4.4 ^d	39.5 ± 3.4 ^d	88.4 ± 0.2 ^b
	1.5	274.6 ± 0.6 ^d	3.8 ± 0.7 ^e	319.7 ± 0.5 ^b	59.8 ± 1.5 ^b	89.4 ± 0.4 ^a
	2.0	300.2 ± 1.8 ^a	1.6 ± 1.3 ^e	350.5 ± 1.9 ^a	63.6 ± 3.1 ^b	88.8 ± 0.2 ^b

Assays were performed in triplicate. Mean ± standard deviation values in the same column for each sample followed by different letter are significantly different ($p \leq 0.05$).

The pasting temperature was significantly increased by added salt. This may be attributed to the ability of salt to modify the gelatinization temperature of starch, which influences the structure of water. The strong hydrated ions increase the structural order of water with consequent decrease in its ability to gelatinize starch (lower temperature). The same author, Jyothi et al. (2005), found that increasing concentration of NaCl from 0.05 to 5% (~ 0.1 to 0.86 M) increased the pasting temperature from 71.2 to 77.5°C. However, those salt concentrations are lower than that used in the present study.

In the absence of salt, addition of any of these hydrocolloids at the concentration used resulted in significantly increased PV and FV, whereas the pasting temperature was decreased. The effect of hydrocolloid on PV of the RS/hydrocolloid blends was explained by assuming that the system is biphasic, with the hydrocolloid located entirely in the continuous phase. Its concentration would then increase as the volume of the phase accessible to the hydrocolloid was reduced, due to swelling of the starch granules during pasting. This resulted in a pronounced increase in the viscosity of the continuous phase and in turn the overall viscosity of the suspension itself, owing to the thickening properties of hydrocolloids (Alloncle et al., 1989). An increase in the FV values could be suggested that retrogradation of starch would be promoted as a very early stage of storage by addition of hydrocolloids. The promotion of retrogradation was attributed to an increase in the effective concentration of starch, specifically amylose in the continuous phase due to mutual exclusion between solubilized starch and hydrocolloid (Alloncle et al., 1989). Surprisingly, a decrease in the pasting temperature of RS in the presence either XG or GG may be attributed to an increase in the effective concentration of leached starch molecules, primarily amylose, in the continuous phase upon heating (Alloncle et al., 1989) due to phase separation as a result of mutual exclusion between leached starch and hydrocolloid molecules based on thermodynamic incompatibility between the two polysaccharides (Alloncle and Doublier, 1991; Annable et al., 1994). Increases in the effective concentration of leached starch molecules as well as hydrocolloid in the continuous phase improved interactions between swollen starch granules, leading to a detection of pasting at a lower temperature.

Addition of salt to the RS/XG mixture significantly increased PV, BV, FV and pasting temperature, whereas the setback values were decreased as compared to the control without added salt. At lower concentrations of 0.1 to 0.5 M of NaCl, PV increased dramatically. This may be attributed to the cations reduced intermolecular repulsion and promoted network formation of XG. Anyways, when increased the NaCl concentration further up to 2.0 M, the PV was decreased. A decrease in setback value could be attributed to a lower amount of amylose leaching out the starch granule. In case RS/GG mixture, addition of NaCl had a lesser effect on the pasting properties, as expected, due to non-electrolyte characteristic of GG. In general, the effect of salt on the pasting parameters of RS/GG showed a similar trend to that of RS alone systems, indicating a predominant effect of starch-salt interaction. It was concluded that the pasting behaviors of starch/ionic hydrocolloid combination were predominantly influenced by hydrocolloid-salt interaction, while those of the starch/non-ionic hydrocolloid systems were predominantly by starch-salt interaction.

Thermal properties

The thermal properties, i. e. onset (T_o), peak (T_p), and conclusion (T_c) gelatinization temperatures, range of gelatinization temperature (ΔT) and the gelatinization enthalpy (ΔH)

of RS alone and RS/hydrocolloid mixtures (RS/XG and RS/GG) in the presence or absence of NaCl at various concentrations determined by DSC instrument are summarized in Table 2.

For RS, addition of NaCl significantly ($p \leq 0.05$) increased the magnitudes of T_o , T_p , T_c and ΔH values as compared to the control without added salt, whereas the ΔT values were less affected. Effects of salt on the gelatinization properties of rice starch can be attributed to various factors, such as the effects on water structure, the influence on polymer-solvent interaction and the electrostatic interaction between starch and ion. Oosten (1979, 1982, 1983, and 1990) reported that when swelling inhibitor such NaCl is added to a starch suspension, some proton of alcohol groups in the starch granules was converted to sodium alcoholate groups by sodium ions. These compounds were better dissociated, thus causing a rise in the Donnan potential, which more effectively excluded the gelatinizing Cl^- from the granule. However, the absorption of Na^+ was limited since, in our systems, was no agent to bind the released H^+ ; thus, the increase in gelatinization temperature was also limited. Consequently, once gelatinization began (at a high temperature), Cl^- assisted gelatinization by breaking hydrogen bonds between starch chains. Moreover, when the concentration of NaCl was raised beyond a certain level, the influence of the anion becomes more effectively and dominant, which would contribute to a decrease in gelatinization temperature. In our study, we found that addition of NaCl at various concentrations tested significantly increased the gelatinization peak temperature of rice starch as compared to the control without NaCl added.

Table 2 Thermal properties of 16% (w/w) rice starch (RS) and rice starch in the presence of xanthan gum (RS/XT) or guar gum (RS/GG) (19:1, w/w ratio) dispersed in aqueous solutions with and without NaCl at various concentrations 0.1 M, 0.5 M, 1.0 M, 1.5 M and 2.0 M.

Sample	NaCl (M)	T_o ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔT ($T_c - T_o$) ($^{\circ}\text{C}$)	ΔH_1 (J/g)
RS	None	73.5 ± 0.3^e	77.4 ± 0.2^e	81.4 ± 0.3^e	7.9 ± 0.0^b	9.8 ± 0.2^f
	0.1	76.7 ± 0.3^d	80.5 ± 0.5^d	84.3 ± 0.6^d	7.6 ± 0.2^c	10.2 ± 0.1^e
	0.5	80.3 ± 0.2^c	83.9 ± 0.1^c	87.7 ± 0.0^c	7.4 ± 0.1^c	10.9 ± 0.3^d
	1.0	82.2 ± 0.0^b	85.9 ± 0.1^b	89.6 ± 0.0^b	7.4 ± 0.0^c	11.8 ± 0.1^c
	1.5	83.1 ± 0.1^a	86.7 ± 0.1^a	90.7 ± 0.2^a	7.6 ± 0.1^c	12.4 ± 0.2^b
	2.0	82.3 ± 0.1^b	86.5 ± 0.0^a	90.4 ± 0.1^a	8.1 ± 0.1^a	13.4 ± 0.3^a
RS/XG	None	74.2 ± 1.8^e	78.5 ± 0.2^e	82.7 ± 0.2^e	8.4 ± 0.1^a	9.3 ± 0.1^e
	0.1	77.0 ± 0.2^d	81.2 ± 0.3^d	85.2 ± 0.4^d	$8.2 \pm 0.1^{a,b}$	10.4 ± 0.1^d
	0.5	80.7 ± 0.4^c	84.9 ± 0.4^c	88.7 ± 0.4^c	8.0 ± 0.0^b	11.6 ± 0.1^c
	1.0	82.6 ± 0.2^b	86.8 ± 0.3^b	90.6 ± 0.3^b	8.0 ± 0.2^b	12.3 ± 0.2^b
	1.5	83.5 ± 0.3^a	87.6 ± 0.1^a	91.5 ± 0.1^a	8.0 ± 0.3^b	12.6 ± 0.1^a
	2.0	83.2 ± 0.1^a	87.8 ± 0.1^a	91.7 ± 0.2^a	8.5 ± 0.2^a	12.8 ± 0.1^a
RS/GG	None	73.9 ± 0.2^e	77.4 ± 0.2^e	81.7 ± 0.3^f	8.1 ± 0.1^b	9.1 ± 0.1^f
	0.1	76.8 ± 0.1^d	80.9 ± 0.1^d	84.8 ± 0.2^e	$8.0 \pm 0.1^{b,c}$	10.3 ± 0.0^e
	0.5	80.6 ± 0.1^c	84.6 ± 0.1^c	88.5 ± 0.1^d	7.9 ± 0.1^c	11.3 ± 0.1^d
	1.0	82.7 ± 0.3^b	86.9 ± 0.4^b	90.7 ± 0.4^c	$8.0 \pm 0.0^{b,c}$	11.8 ± 0.8^c
	1.5	83.6 ± 0.2^a	87.8 ± 0.2^a	91.7 ± 0.1^b	8.0 ± 0.0^b	12.3 ± 0.2^b
	2.0	83.6 ± 0.0^a	88.0 ± 0.0^a	92.1 ± 0.0^a	8.5 ± 0.0^a	12.7 ± 0.1^a

Assays were performed in triplicate. Mean \pm standard deviation values in the same column for each sample followed by different letter are significantly different ($p \leq 0.05$).

Ahmad and Williams (1999) studied the effect of salts on the gelatinization and rheological properties of sago starch found that increasing the NaCl concentration up to 2.0 M significantly increased T_p temperature of sago starch. Another report by Maaurf et al. (2000) showed that in the presence of 1.0 to 2.0 M NaCl, the T_p of sago starch significantly increased and at the concentration of 2.0 to 5.0 M, the T_p decreased with increasing salt concentration. These results were completely agreed with our results. However, those salt concentrations are much higher than that used in the presence study. There are various explanations about the mechanism of gelatinization of starch by various salts. Salts have been reported to increase or decrease the gelatinization temperature and gelatinization enthalpy of starch, depending on the type of salts and their concentration used (Oosten, 1979, 1982, 1983, and 1990; Chungcharoen and Lund, 1987; Jane, 1993; Ahmad and Williams, 1999; Maaurf et al., 2001; Jyothi et al., 2005). NaCl at lower concentrations has been reported that slightly increased the T_o of corn starch (Jane, 1993), T_p of wheat starch (Chinachoti et al., 1991; Wootton and Bamunurarachchi, 1980), T_p of corn, potato, rice, canna, and lotus tuber starch (Lii and Lee, 1993); T_p of sago starch (Ahmad and Williams, 1999; Maaurf et al., 2001). But when the concentration increased further (over 2.0 M), these gelatinization temperatures decreased. The gelatinization enthalpy (ΔH) of starches has been reported to be significantly decreased in the presence of 0.1 M of either NaCl or CaCl₂ (Viturawong et al., 2008), ~ 0.3 M NaCl (Chungcharoen and Lund, 1987), while other reports on wheat starch (Wootton and Bamunurarachchi, 1980) and corn starch (Chinachoti et al., 1991) found that ΔH was significantly decreased when NaCl concentration was increased up to 1.0 M. In this study, the ΔH of RS showed the opposites results with those reports. We found that the addition of NaCl to RS suspension significantly increased ΔH values with various concentrations. This data was agreed with report for corn starch by Jane (1993). This author found that in the presence of NaCl, ΔH of corn starch significantly increased to a maximum and then decreased as the concentration increased further up to 6.0 M. However, these concentrations are much higher than that used in this study.

Surprisingly, addition of either XG or GG to RS at a concentration used in this study, did not significantly effects the T_o , T_p , T_c and ΔH values as compared to the control without added hydrocolloids. It is clear that, in a combination of starch, hydrocolloid, and salt, the effect of salt on the gelatinization temperature of starch is unchanged. The ΔH , in contrast, was slightly decreased by hydrocolloids addition. This could be attributed to the reduction in water availability and/ or mobility, causing incomplete melting of crystalline region in the starch granules, and the effect of starch/hydrocolloid interaction (Chaisawang and Suphantharika, 2006). The similar trend was reported by Viturawong et al. (2008) for RS/XG/salts mixtures.

Conclusion

It is clarified that in a complex system like starch/ hydrocolloid/ salt combinations, it would be assumed that salt added can interact with both the starch and hydrocolloids. Rapid visco-analysis (RVA) showed that addition of sodium chloride (NaCl) significantly ($p \leq 0.05$) increased the peak viscosity and pasting temperature of both RS and RS/hydrocolloid blends with various concentration as compared to the control without added salt. The pasting characteristics of RS/ionic hydrocolloid (RS/XG) were predominantly affected in the presence of NaCl, whereas the RS/non-ionic hydrocolloid (RS/GG) showed the same trend with RS. It was concluded that the pasting behaviors of starch/ionic hydrocolloid combinations were predominantly influenced by hydrocolloid-salt interaction, while those of the starch/non-ionic hydrocolloid systems were predominantly by starch-salt interaction. On the other hand, the thermal behavior of the starch determined by differential scanning

calorimetry (DSC), seemed to be unaffected by hydrocolloids added, but significantly influenced by the presence of salt within various concentrations. These results can apply in food products and would be used as a guideline for developing starch-based food products containing salts.

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