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Effect of NaCl on the thermal behaviour of wheat starch in excess and limited water

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ABSTRACT

The effect of NaCl on the thermal behaviour of wheat starch was investigated with particular focus on starch at low moisture contents (25–45 wt%). Increasing the level of NaCl reduced the starch peak viscosity (in 90% water) as measured by RVA and shifted all of the thermal peaks (up to 120 °C) to higher temperatures as observed by DSC. Above a moisture content of 45%, the temperature difference of the first thermal transition of starch in the presence of 2% NaCl and in the absence of NaCl was found to be constant. In the absence of NaCl, the peak temperature of gelatinisation (T_p) increased by 12 °C (from 62 to 74 °C) as the water content was reduced from 35% to 25%. In the presence of 2% NaCl, the variation in T_p due to changes in water content was significantly reduced. At NaCl concentrations greater than 2% (w/w total), the T_p of the starch remained constant irrespective of water content. Evidence of this effect was observed in situ using confocal microscopy. In the presence of 2% NaCl, images taken at elevated temperatures show little difference in the extent of starch swelling at 25% compared to 45% water content. However, in the absence of NaCl, significantly more swelling was observed at 45% than at 25% water content. With increasing NaCl concentration, the interaction of starch and NaCl became dominate. Thus the on-set of the thermal transitions of starch granules is primarily controlled by the amount of NaCl present, and secondarily by the water content which becomes dominant when the NaCl concentration is low.

1. Introduction

Starch gelatinisation plays an important role in determining the textural properties of cereal-based foods. This is due to the loss of starch granule crystalline structure and dissolution of starch biopolymers upon heating in the presence of water. Changes in starch granule structure, its hydration and swelling and the re-association of starch biopolymers to form new networks during heating and cooling can contribute significantly to the crumb structure and eating quality of finished cereal products (Biliaderis, 1992; Delcour et al., 2010). Thus, knowledge of the structural re-organisation of starch at the granular level during heating and cooling for given moisture contents at each processing step is important. In order to achieve a high quality end-product, understanding how other ingredients such as salt and sugar affect the thermal transitions of starch at a given moisture is also needed to assist product formulation.

Salt is one of the key ingredients used in the making of cereal based foods such as bread, biscuits and breakfast cereals. However, excess sodium intake is well-known to be one of the risk factors for elevated blood pressure and associated cardiovascular diseases (Alderman & Cohen, 2002; Brown, Tzoulaki, Candeias, & Elliott, 2009; Cook, 2008; Law, 1997). Recent surveys of sodium content in processed foods in the UK and Australia showed that bread and bakery goods, cereals and cereal products are one of largest processed food groups that contribute the most sodium to the average diet (Mhurchu et al., 2011; Webster, Dunford, & Neal, 2010). With calls for reducing salt in processed foods by consumers, public health advocates and government agencies, the food manufacturing sector is facing an increasing challenge to re-formulate their products to significantly lower the salt content, whilst still maintaining the product quality, sensory characteristics and microbiological safety.

Salt (specifically sodium chloride) is used not only for enhancing the flavour perception, but more importantly for its functional role in the transformation of starch during processing of cereal based products. This can be attributed to the profound effect salt has on the microstructure, physical characteristics and sensory properties of the finished products (Miller & Hoseney, 2008; Nunez, Sandoval, Muller, Della Valle, & Lourdin, 2009; Uthayakumaran, Batey, Day & Wrigley, 2011). Sodium chloride can have a significant effect on the gelatinisation temperature of starch which has been found to depend on the moisture content and salt concentration. At starch to water ratios greater than 1:1, salt concentration can impart a variety of effects on starch gelatinisation which seem to be linked to

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water content (Chiotelli, Pilosio & Le Meste, 2002; Evans & Haisman, 1982; Lii & Lee, 1993; Wootton & Bamunuarachchi, 1980). Low concentrations (e.g. below 7%) of NaCl increase the temperature at which starch gelatinisation begins, whereas high concentrations have been shown to have the opposite effect (Chiotelli et al., 2002). The early work by Wootton and Bamunuarachchi (1980) showed that at a starch to water ratio of 1:2, the gelatinisation temperature (T_p) of wheat starch increased in the presence of sodium chloride (up to 9% in the aqueous phase), but remained relatively constant with further increases in salt concentration. One recent study showed that wheat starch granule swelling decreased in the presence of NaCl at low concentrations (<0.5 M which is equivalent to 3% NaCl in 3% starch solution), particularly when the starch solution was heated to 55–65 °C (Zhu, Gayin, Chatel, Dewettinck, and Van der Meeren (2009).

The role of salt in the production of low moisture foods such as extruded snacks or breakfast cereals has only attracted researchers attention fairly recently (Nunez et al., 2009; Sandoval, Nunez, Muller, Della Valle, & Lourdin, 2009). The first step in processing these types of foods generally involves water addition ranging from ~20 to 35% which is much less than for conventional dough making and baking. Salt is added to breakfast cereal formulations because of its technological function in assisting in microstructure formation, flavour and colour generation (Moreau, Lagrange, Bindzus, & Hill, 2009). At low moisture content, salt plays a key role in the formation of the molten state of cereal biopolymers and subsequently the expansion of extruded starch based products. Most of the research on the effect of salt(s) on starch gelatinisation and the processability of cereal based foods has been carried out in medium to high water content, i.e. starch/water ratios greater than 1:1. There have been few reports on the impact of salt on the thermal behaviour of native starches or wheat flour in limited moisture content (e.g. below 45%). Low moisture processing is used for the production of breakfast cereals through either cooking the grain or extruding the flour mix. Salt is one of the key ingredients in these food products. Therefore understanding the thermal behaviour of starch as a function of salt and water content under low moisture conditions is important for the optimum processing of cereal based foods when salt content is reduced in formulations.

The aim of this work is to investigate the effect of NaCl on the thermal behaviour of wheat starch at a wide range of water contents, from ~90% (excess) to as low as 25% (limited). The effect of NaCl concentrations (0–4%) was also investigated in starch-water systems in which water content was limited (25–45%). The development of starch swelling at these low water contents upon heating was followed in situ by confocal laser scanning microscopy (CLSM) with a controlled temperature heating stage. Information obtained from this study should help to extend our understanding into the effect of salt on starch gelatinisation in low moisture environments. A better understanding of starch–salt and starch–water interactions could provide a basis for modifying processing conditions to ensure the quality of starch-based foods with reduced salt in the formulation is not negatively impacted.

2. Materials and methods

2.1. Preparation of samples

Native wheat starch (8.5% moisture, 0.2% protein) was provided by Manildra Group (Nowra, NSW, Australia) and samples of this starch were prepared at various moisture and salt contents. The total weight of each sample was 50 g. Sodium chloride was solubilised in the correct amount of water required to achieve the target moisture content. The salt contents used were 0, 1, 2, 3 and 4% (w/w total). The salt solution was then added to the starch drop by drop and mixed using a hand held mixer (Braun Minipimer® advantage blender, 400 W) to ensure a good dispersion of water into the powder and to avoid clumping. The starch samples were then left in a sealed plastic bag overnight at 4 °C to allow full moisture equilibration.

2.2. Determination of moisture content

The moisture content of the prepared samples was measured by the oven drying method (AACC method 44-40). Each sample (2 g) was weighed into pre-dried metal dishes and dried in an oven at 135 °C for 3–4 h until a constant weight was achieved.

2.3. Rapid visco-analysis (RVA)

The gelatinisation properties of starch in excess water were measured using the Rapid Visco-Analyser (Newport Scientific, Division of Perten Instruments, Sydney, Australia). Moisture conditioned samples (3 g dry weight) containing various amounts of salt were weighed into the RVA canisters and additional water was added to the canisters to make up a total weight of 28.5 g. The canisters were then inserted into the instrument and each sample was run using the following heating and cooling profile: heat to 50 °C and maintain for 1 min, warm to 95 °C at 12 °C/min, maintain at 95 °C for 3.5 min, cool to 50 °C at 12 °C/min and maintain for 2.5 min at 50 °C. This method is known as the Standard 1 profile of the Rapid Visco-Analyser.

2.4. Differential scanning calorimetry (DSC)

DSC studies were carried out using a STAR System DSC I instrument (Mettler-Toledo Ltd., Melbourne, Australia) with STARe version 9.30 software. The instrument was calibrated using water, indium and zinc and the resultant traces were normalised on the basis of sample weight. Samples (30 ± 3 mg) were accurately weighed into sealable aluminium pans (40 μl). Sample pans were placed in the instrument along with an empty reference pan and cooled to −10 °C, then heated at a rate of 10 °C/min to 120 °C. Enthalpies, onset and peak temperatures were calculated using the software. Each sample was analysed in duplicate or triplicate (see reference to errors in figures) and the results were expressed as the averages of duplicate or triplicate runs.

2.5. Confocal laser scanning microscopy (CLSM)

Starch swelling was observed using a Leica TCS SP5 confocal laser scanning microscope (Leica Microsystems, Wetzlar, Germany) fitted with a Leica MA TS Heating stage. Starch samples were conditioned to either 25 or 45% moisture with or without 2% NaCl according to the method specified above except that a fluorescent dye (Safranin, 10%) was added to the water used to condition the starch. After overnight hydration, a couple of drops of each sample were deposited onto a cavity slide. A cover slide was placed on top and the two slides were sealed with glue to prevent water evaporation during heating. The slides were then placed in the heating stage and heated at a rate of 10 °C/min to 60 °C, followed by 2 °C/min to 74 °C. Images of the samples were taken prior to heating at 60 °C and every 2 °C thereafter.

3. Results and discussion

3.1. Salt concentration on thermal behaviour of starch in excess water

The RVA is an effective instrument for determining the functional performance of starch or flour when exposed to heat and

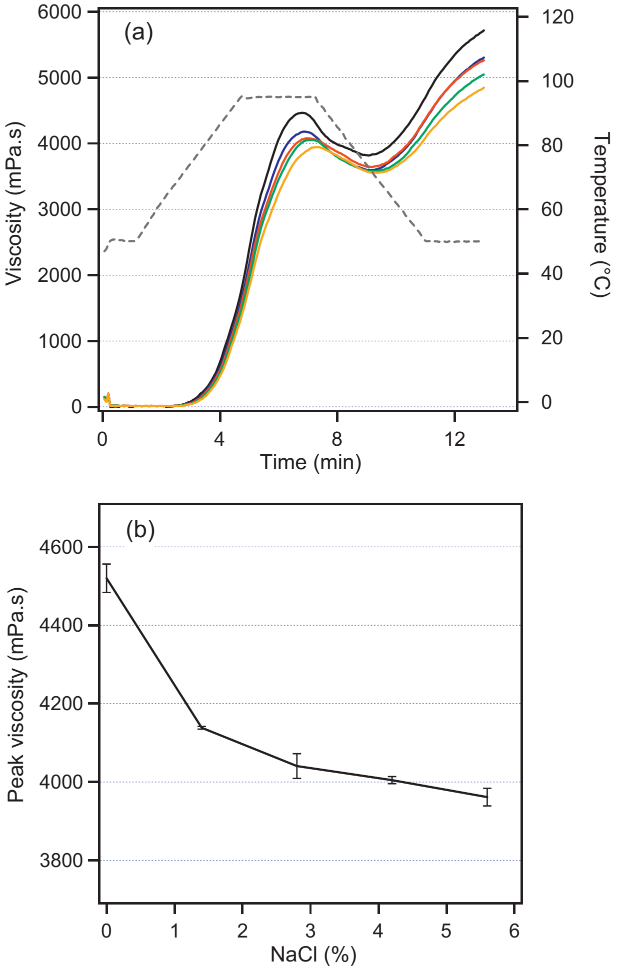

Fig. 1. (a) Typical RVA profiles of wheat starch containing: 0 (black line), 1.4 (blue), 2.8 (red), 4.2 (green) and 5.6% (orange) NaCl (w/w starch base, equivalent to 0–120 mM in water); and (b) peak viscosity as a function of NaCl content. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shear in excess water (Batey, Curtin, & Moore, 1997; Collar, Santos, & Rosell, 2006; Zhu & Corke, 2011). Fig. 1(a) shows the typical pasting curves of starch in the presence of different levels of salt. It shows that as salt concentration increased, the time taken to reach starch peak viscosity increased from 6.8 to 7.4 min. This was accompanied by a reduction in peak viscosity as shown in Fig. 1(b). It was noted that the final viscosity was also lowered with increasing salt concentration. In excess water the levels of salt in the samples (1.4–5.6% of starch weight) were equivalent to 30–120 mM in solution. Even at low salt concentration (e.g. 1.4% starch weight or 30 mM in solution) there was a reduction in starch peak and final viscosities compared to starch in water only. Most studies showing the effect of NaCl on the gelatinisation temperature of starch have been carried out by DSC alone. The RVA results however show that salt also delayed the time to reach peak viscosity and resulted in a reduction in the final viscosity of the starch gel upon cooling.

Starch granule structural transformation upon heating in water is a complex process. When heated in the presence of excess water, starch granules swell resulting in the loss of crystalline structure. This is followed by a conformational change in the molecular structure through an order–disorder phase transition (Cooke & Gidley, 1992). The disruption of molecular order within the granule along with all concomitant and irreversible changes in properties such as water uptake, granular swelling, crystallite melting, birefringence loss, starch solubilisation and viscosity development are defined as the starch gelatinisation process (Biliaderis, 2009). Studies have shown that in the presence of salt at concentrations as low as 10 mM (e.g. 0.06%) the apparent gel strength of heated and cooled starches is reduced (Muhrbeck & Eliasson, 1987). Zhu et al. (2009) showed that at NaCl concentrations below 1 M (~6%), the presence of salt in a 3% starch dispersion reduced the swollen granule volume when the starch dispersion was heated to 55–65 °C. This is in agreement with our RVA results.

The amorphous regions in the starch granule play an essential part in determining the gelatinisation temperature (Donovan, 1979; Evans & Haisman, 1982). The swelling of amorphous regions of the granule initiates a force which then destabilises the crystallites. Direct ion–macromolecule interactions as well as interactions with water molecules are involved in the hydration of the macromolecule (Zhang & Cremer, 2006). The presence of NaCl influences the starch–water interactions. In excess water, it is unlikely that water availability is a limiting factor at low salt concentrations (e.g. less than 6%). It is more likely that the presence of the NaCl acts via electrostatic screening of starch molecules and inhibits initial water ingress into the granules, thus reducing the swelling. Even a small reduction in starch granule swelling could result in a reduction in particle–particle interactions and hence the viscosity of the starch solution would be lowered.

3.2. *The effect of water content on the thermal transition of starch in the presence of 2% NaCl*

In order to investigate how water content impacts the effect of NaCl on the thermal behaviour of wheat starch, DSC was used to determine the temperatures and enthalpies of starch thermal transitions in the presence of 2% NaCl (w/w total) across a wide range of water contents, from 25 to 90% (w/w total). The results are shown in Fig. 2(a) and compared to the thermal transitions of starch at the same water contents in the absence of salt, shown in Fig. 2(b). Three thermal transitions denoted as peak M1, M2 and M3, were observed when starch–water mixtures were heated up to 120 °C. The melting endotherm M1 is often known as the gelatinisation endotherm (*G*) at relatively high water levels, i.e. where the volume fraction of starch is less than ~0.45 (Biliaderis, 2009). This transition is caused primarily by the loss of starch molecular helical order when starch is heated in the presence of water (Cooke & Gidley, 1992). Peak M2 which is associated with the melting of the remaining starch crystallites (Burt & Russell, 1983; Donovan, 1979) started to appear as a shoulder to peak M1 at a water content of 65%. Peak M2 moved towards higher temperatures and became increasingly broad as the water content was reduced. At 40% water content, the M1 and M2 peaks were found to occur at approx. 70 °C and 100 °C in the presence of 2% NaCl and at 62 °C and 92 °C respectively in the absence of salt. Hence, NaCl increased the peak temperature of both these endotherms. The water-dependence of these starch transitions as measured by DSC is well known (Biliaderis, 2009; Donovan, 1979; Svensson & Eliasson, 1995). A reduction in water forces the loss of final crystalline structure towards higher temperatures (Evans & Haisman, 1982; Svensson & Eliasson, 1995). The third peak, M3, which is associated with the melting of the amylose–lipid complex (Biliaderis, Page, & Maurice, 1986; Biliaderis, Page, Slade, & Sirett, 1985) was observed at approximately 99 °C for wheat starch in 90% water in the presence of 2% NaCl and 96 °C in the absence of NaCl. This peak was also found to shift to higher temperatures as water content was reduced in all samples (both in the presence and absence of salt) and was above the maximum temperature of the experiment (120 °C) at moisture contents below 40%.

Overall similar patterns were observed for the starch–water systems in the presence or absence of salt, however there were a number of key differences. Between 35 and 90% water content, the thermal transition peak M1 was observed at approximately 72 °C

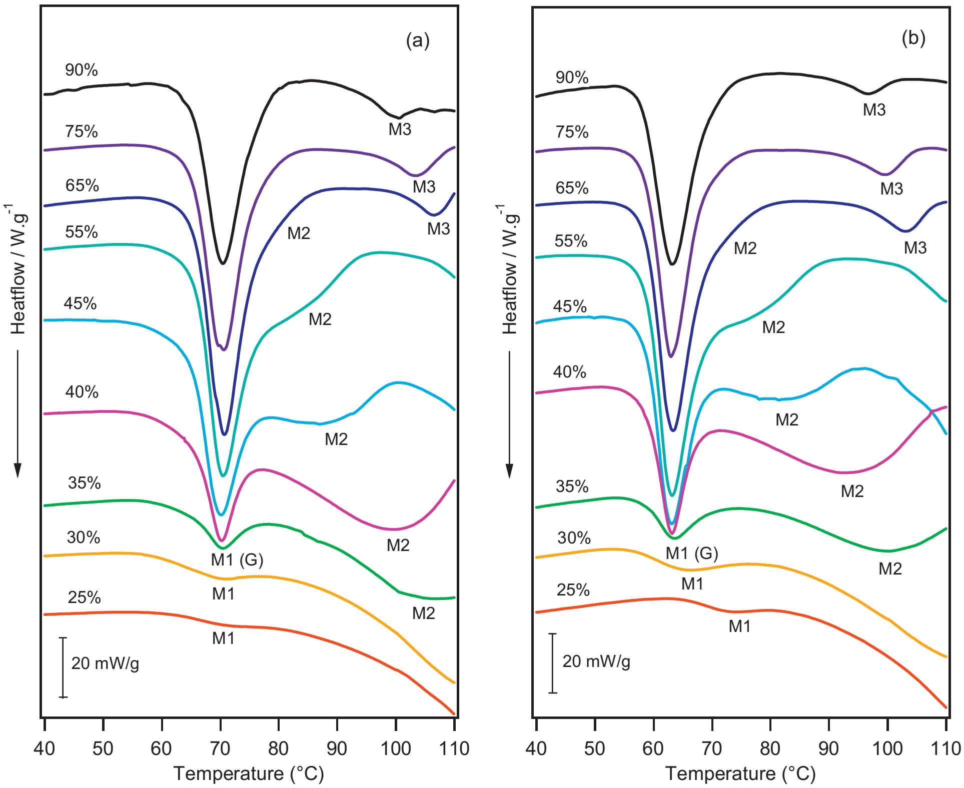

Fig. 2. DSC thermograms of wheat starch in a wide range of water from excess (90%) to limited water content (25%) in the presence (a) and absence (b) of 2% NaCl (w/w total).

in the presence of 2% salt and reduced to 62 °C in the absence of salt, a shift of 10 °C in temperature. Both M2 and M3 transitions for starch–water mixtures in the presence of salt also shifted to higher temperatures by approximately 5 °C and 3 °C respectively, compared to the corresponding peak temperatures of starch with the same water content but in the absence of salt. However, a key finding in this study was the similarity between the thermal behaviour of starch–water mixtures with and without salt at low water contents (e.g. below 35%, Fig. 2). In the presence of 2% NaCl, the temperature of peak M1 remained constant, at approximately 72 °C, independent of the water content in the mixture (Fig. 2(a)). However, in the absence of salt, the thermal transition of peak M1 was raised above the peak temperature at which the transition was observed when water was in excess (Fig. 2(b)). It appears that the extent of increase in peak temperature is correlated to the incremental reduction of water from 35% downwards (Fig. 2(b)). The other main difference between the DSC endotherms was seen in the peak enthalpy values. Table 1 shows that the energy required for the thermal transition of starch in the presence of salt was lower than when salt was absent, particularly at 40% water content and below.

The thermal transition behaviour e.g. endotherms and size of enthalpy of other cereal, tuber and legume starches in excess water (>50%) has been widely examined by DSC (Biliaderis, Maurice, & Vose, 1980; Burt & Russell, 1983; Donovan, 1979; Tester & Morrison, 1990). Our results and thermal transition patterns for wheat starch–water mixtures at water contents above 40% (Fig. 2(b)) were similar to those already reported in the literature. However, the difference in the thermal behaviour of starch in the absence or presence of NaCl at water contents below 35% has not been reported. These results are of great interest as the thermal behaviour of starch at low moisture conditions will have a significant impact on the processing of starch-based foods such as breakfast cereals. Only limited research has been conducted on the thermal transitions of starch in limited water, probably due to the difficulties of measuring the thermal transition endotherms at

Table 1
Onset temperatures, peak temperatures and enthalpies for the thermal transition (peak M1) of starch at various water content in the presence and absence of 2% NaCl (w/w total). The results were calculated based on starch dry weights with standard errors of 1.0% for temperatures and 8.0% for enthalpies based on triplicate measurements.

Moisture content (%w/w total)	Starch in 2% NaCl (w/w total)			Starch in water		
	Onset (°C)	T_p (°C)	Enthalpy (J g^{-1})	Onset (°C)	T_p (°C)	Enthalpy (J g^{-1})
25	64.9	71.0	0.11	67.5	73.9	0.13
27.5	62.1	69.0	0.07	64.6	71.5	0.18
30	64.4	69.0	0.30	57.8	65.9	0.45
35	64.6	69.7	0.87	56.8	62.1	0.96
40	65.1	70.0	3.19	57.9	62.2	3.55
45	64.6	70.0	4.90	57.7	62.6	5.35
55	65.5	70.0	8.31	58.2	62.4	8.07
65	64.9	70.0	10.47	58.5	63.2	9.70
75	64.8	70.2	12.76	58.0	62.5	14.50
90	64.9	70.2	11.60	58.1	63.2	12.90

such low water contents. With the advancement of more sensitive instruments, we were able to clearly detect the thermal transition of this peak at water contents as low as 25% and therefore able to demonstrate differences in the thermal behaviour of wheat starch in the presence and absence of NaCl.

It has been proposed that there are several populations of water molecules presenting different mobilities in wheat starch/water dispersions (Chiotelli et al., 2002; Botlan, Rugraff, Martin, & Colonna, 1998; Tang, Godward, & Hills, 2000). Three distinct proton relaxation times have been determined in wheat starch by NMR (Chiotelli et al., 2002). The shortest T_2 values originate from the non-exchanging CH protons of amylose and amylopectin. This peak can be seen to be sensitive to the starch chain mobility within the granule (Chiotelli et al., 2002). The intermediate T_2 (at ~1–3 ms) is attributed to the hydrogen of water molecules bound to the starch granule e.g. ‘bound’ water (Le Botlan et al., 1998). This less mobile water is independent on the initial water content suggesting that this water fraction is fairly constant for each type of starch granule (Tananuwong & Reid, 2004). The long relaxation time arises from more mobile water protons that exchange with hydroxyl protons in the amylopectin and amylose molecules on the starch surface (Tang et al., 2000). In the presence of NaCl, the relaxation time of the mobile water protons increased with salt concentration (Chiotelli et al., 2002). This also suggests that there are specific ionic interactions between the solute and the starch granule. Evidence of such interaction between Na^+ and starch has been indicated by a line broadening of ^{23}Na spectra by high-resolution NMR (Chinachoti, White, Lo, & Stengle, 1991). In excess water, ionic interactions between the Na^+ cations and the negatively charged hydroxyl groups on the starch effectively reduced the interactions between water and starch, thus reducing starch swelling. Consequently the temperature required for the onset of the gelatinisation process rises. The reduced peak viscosity in the presence of salt in the RVA results is an indication that starch granule swelling was likely to have been reduced even if excess water is present.

3.3. *Loss of starch granular structure upon heating observed by CLSM*

Changes in starch granular structure upon heating were investigated using CLSM with a heating attachment. Fig. 3 shows micrographs of starch granules at three key temperatures in the presence and absence of salt which were hydrated overnight at 45% and 25% water content respectively. The micrographs shown were taken: just before heating (top); after heating to 64 °C (middle) and after heating to 72 °C (bottom). The heating temperature of 64 °C was chosen as this is just above the M1 peak for starch in 45% water (no salt). 72 °C was chosen as the second temperature as this is where M1 occurs for starch at the lowest water content of 25%. When compared with the granules at room temperature in the presence of salt, the granules were seen to have swelled slightly when heated to 64 °C, but were otherwise largely intact (Fig. 3, left two columns). These granules started to show changes in granule morphology when heated to 72 °C. The extent of starch swelling in the presence of 2% salt was found to be fairly independent of water content (at each temperature). In contrast, when starch was heated in the absence of salt, clear differences between the morphology of the granules at the two different water contents was evident (Fig. 3, right two columns). At 64 °C, a greater extent of swelling was observed in 45% water than in 25% water (Fig. 3, middle). At 72 °C, many starch granules were broken and a significant release of starch biopolymers from the ruptured granule could be observed as indicated by the smearing of the image in the sample containing 45% water. However, little change in granule morphology was observed when the water content was reduced to 25% in the absence of salt (Fig. 3, bottom). In the presence of salt, leaching

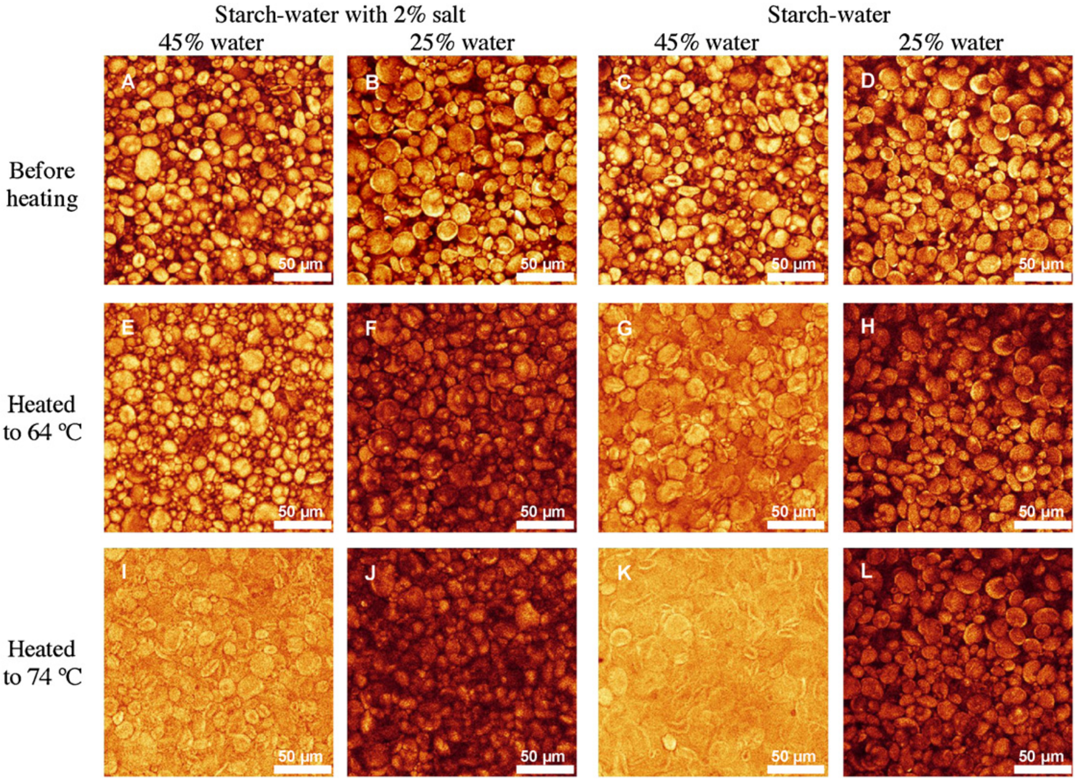

Fig. 3. The morphology of starch granules hydrated at room temperature and granule swelling and dissolution after being heated to 64 °C and 74 °C visualised by confocal microscopy. The starch samples were prepared with or without 2% NaCl at a water content of 45% or 25% respectively.

of starch biopolymers was significantly reduced, indicating that salt has an ability to control the extent of granule swelling. The results are in agreement with the study by Zhu et al. (2009) who demonstrated that NaCl inhibits starch swelling at temperatures between 60 and 80 °C.

The effect of salt on the changes in granule structure at 25% and 45% water content observed by CSLM in situ supports the results obtained by DSC. Starch swelling appears to be associated with the temperature at which the thermal transition of starch began in the DSC profiles. These results suggest that the onset of the thermal transition of starch is associated with its swelling when heated, and the ability of granules to swell is partly determined by the amount of water available to the granules and the temperature. However, the presence of NaCl appears to have a compound effect on the extent of starch granule swelling in addition to the extent governed by the amount of water present. The thermal events associated with the changes in starch structure are actually a number of simultaneous events occurring together or at least in close succession. As water penetrates the granule, the amorphous regions begin to swell. This is closely followed by the water assisted melting of the least stable crystallites from the outer layers and progresses towards the centre of the granule (Cooke & Gidley, 1992; Donovan, 1979; Evans & Haisman, 1982). When water is limited, the initial melting of starch crystallites through the action of water ingress can only go so far. It is then superseded by conventional melting at high temperatures as shown by peak M2 (Evans & Haisman, 1982; Svensson & Eliasson, 1995). This is the basis for the change in peak height ratios between peaks M1 and M2 as water content is decreased. The presence of NaCl restricts starch granule swelling when water is in excess, presumably through the reduction of water ingress by the interactions of Na^+ and starch. This raises the temperature for the initial water assisted melting of the least stable crystallites at the surface of the starch granule. It also means that less water is needed for the limited starch granule swelling, thus the onset of the gelatinisation process (e.g. the initial melting) is influenced principally by the presence of NaCl, rather than by the water content which even at 25% is still in excess.

3.4. NaCl concentration on the thermal behaviour of starch at limited water content (<45%)

Further studies were carried out using DSC to investigate how changes in NaCl concentration (0–4%) influenced the thermal behaviour of wheat starch at water contents below 45%. Starch samples were conditioned overnight and the moisture content of all samples were analysed within ±1% of the target moisture content. Fig. 4 presents the peak temperature of peak M1 as a function of NaCl concentration (1–4%) at 45, 35, 30, 27.5 and 25% water content. Most differences in the thermal peak temperature were found between 0 and 2% NaCl, in which not only the salt content, but also the water content in starch had an impact on the peak temperature. When salt concentration was increased beyond 2%, up to 4% (w/w total), the peak temperature remained relatively constant regardless of the water content. At a water content of 30% and above, the peak temperature increased with increasing NaCl concentration. However, it should be noted that at 30% moisture content, the peak temperature at 0% NaCl was seen to be higher than that of the samples with 35–45% moisture content. Furthermore, when the water content was reduced to 27.5 and 25%, the opposite trend was observed. The M1 peak temperature of the sample with a 25% moisture content in the absence of salt was 74 °C. The addition of 1% NaCl led to a ∼2 °C reduction in this peak temperature. The peak temperature was then reduced further to ∼70 °C when 3% NaCl was used. Similar results were found with the sample prepared at 27.5% moisture content except that the peak temperature at 0% could be seen to be lower than that found in the sample with 25% moisture content. In fact the most dramatic change in peak temperature at 0 and 1% NaCl could be seen between samples prepared at 27.5 and 30% moisture content.

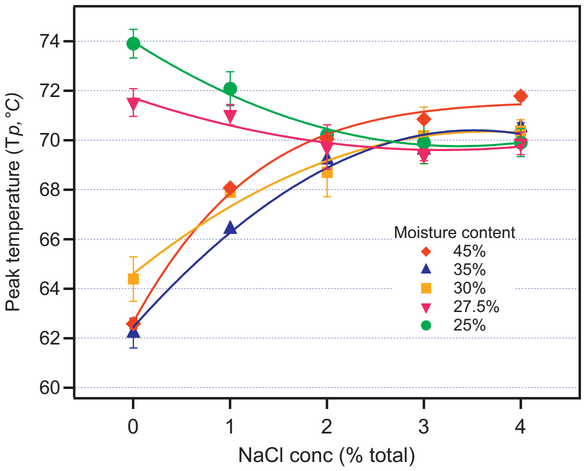

Fig. 4. DSC peak (M1) temperature of starch containing different levels of NaCl at 25, 27.5, 30, 35 and 45% moisture content. Bar represent standard deviation of triplicate measurements for each sample.

The effect of NaCl concentration on the thermal behaviour of starch has been studied by numerous researchers. Many of them have reported that NaCl has a peculiar effect when it comes to varied salt concentrations (Ahmad & Williams, 1999; Chiotelli et al., 2002; Evans & Haisman, 1982; Lii & Lee, 1993; Wootton & Bamunuarachchi, 1980). Wootton and Bamunuarachchi (1980) found that the gelatinisation temperature (T_p) of wheat starch increased in the presence of sodium chloride, up to a certain level (9% with a ratio of starch/water 1:2), but remained relatively constant with further increases in salt concentration. Similarly, Chiotelli et al. (2002) showed a steep increase in the T_p of the wheat starch (at 60%, w/w water) with the addition of NaCl up to 1.5% and thereafter, a much slower increase when salt content was increased up to 10%. The results presented here at water contents above 35% were broadly in agreement with these findings. However, the opposite effect was found when the water content was reduced to 25%. The presence of salt gradually decreased T_p up to a salt concentration of 3%. Between 3 and 4% NaCl, T_p remained relatively constant and at the same value as was found for the starch with higher water contents.

Under the limited water environment (e.g. below 35%), small changes in water content had a dramatic impact on the thermal transition temperatures of the starch and the presence of salt reduces this impact. This is likely due to the solvation effect of NaCl which restricts initial starch swelling. With the increase in the NaCl concentration, the interaction of starch and NaCl became dominate. In the presence of NaCl (regardless of water content), the initial swelling of amorphous regions reduced due to the interaction of Na^+ with the hydroxyl groups of starch. NaCl essentially regulates the thermal transitions of starch (particularly in a limited water environment) such that the effects of variations in water content are limited at moisture contents between 25 and 35%. This essentially provides much greater processing tolerance during manufacturing starch based cereal products at low moisture content for example, grain cooking or extrusion processing for breakfast cereals. Reducing salt in the formulation could mean that the water content in the formulation needs to be more strictly controlled to ensure that starch is gelatinised during the time and temperature of processing.

4. Conclusions

In this study, we investigated the effect of NaCl on the thermal behaviour of starch in excess and limited water. The presence of salt resulted in a slight reduction in the peak viscosity of starch in excess water as measured by RVA. In addition, DSC results showed that salt shifted the thermal peaks to higher temperatures at water contents above 35%. The enthalpy associated with the M1 endotherm decreased in the presence of salt. In situ CSLM examination between 64 and 74 °C showed that 2% salt reduced the extent of granule swelling compared to when salt was absent at a moisture content of 45% but no difference was seen at 25% moisture content. This is believed to be due to the interaction between Na^+ ions and starch. The Na^+ ions inhibit the starch–water interactions, hence reducing the amount of 'bound' water absorbed by starch. As a result, the degree of starch swelling is reduced and the on-set temperature of the starch gelatinisation and crystalline melting is increased.

The most intriguing results were found when the water content was reduced below 35%. Salt appears to control the starch–water interactions and hence the thermal transition behaviour of the starch granule. It appears that the level of water (at as low as 25%) was not the limiting factor to induce changes in the starch molecular and granular structure upon heating due to limited swelling of the granule. At a salt concentration greater than 2% (w/w total), the T_p of the starch remained relatively constant at all water contents. These results are of great interest as the thermal behaviour of starch at low moisture conditions could have a significant impact on the processing of starch-based foods such as breakfast cereals. The mechanism of how salt influences the order to disorder transition of crystalline structure in the starch granule needs to be further elucidated. Studies using X-ray diffraction during heating to probe changes in starch structure in the presence of salt and limited water conditions would provide further insight into the mechanism behind salts controlling over the thermal transitions of starch.

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