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# DSC enthalpic transitions during starch gelatinization in excess water, dilute sodium chloride, and dilute sucrose solutions

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## Abstract

**Background:** Starch phase transition characteristics were studied by pre-treating starch samples in excess water, dilute sodium chloride and dilute sucrose solutions and subjecting them to differential scanning calorimetry (DSC). Unmodified maize, wheat and potato starches were held at specific temperatures between 30 and 90 °C for 30 min and promptly cooled to 25 °C. Treated samples were then analyzed *in situ* by DSC.

**Results:** It was found that the progression of the phase transition behavior differed among the three starches and was dependent on the solvent. It was also revealed that phase transition-related enthalpic changes started to occur at low temperatures and that this process involved a continuous sequence of structural changes, resulting in progressive differences in endothermic patterns from low to high temperatures.

**Conclusion:** These findings are in agreement with recent evidence suggesting that starch gelatinization occurs over a wider temperature range rather than as a sudden order–disorder transition taking place within a narrow temperature range. The phase transition mechanism is determined by starch type and solvent combination.

**Keywords:** starch, gelatinization, phase transition, DSC, sodium chloride, sucrose

## Introduction

When raw starch granules are heated in water, their semicrystalline nature is gradually eliminated, resulting in structural breakdown and starch polymer dispersion in solution. This heat-induced starch granule breakdown or the phase transition from an ordered granular structure into a disordered state in water is known as gelatinization.<sup>1,2</sup>

Although starch gelatinization has been studied by various researchers since the early 1800s, the exact nature of hydrothermal treatment-induced structural transition-related changes that take place during the process is still poorly understood. French<sup>3,4</sup> identified three distinct stages in the starch gelatinization process: (1) granular swelling by slow water absorption; (2) rapid loss of birefringence by absorption of large amounts of water by granules; (3) leaching of the soluble portion of starch into solution, transforming the granules into formless sacs. Subsequent studies by other researchers led to similar theories based on light microscopy and Kofler hot-stage microscopy with polarized light.<sup>5–8</sup> Goering *et al.*<sup>9</sup> concluded that birefringence measurement did not fully reveal starch gelatinization process-related structural changes. Using results obtained by a small-angle light-scattering technique, Marchant and Blanshard<sup>10</sup> proposed a combination of three separate processes taking place during starch gelatinization. This “semi-cooperative” theory explained starch gelatinization

as a process involving (a) water diffusion into granules, (b) loss of birefringence due to hydration-facilitated melting (also explained as solvation-assisted helix–coil transition) and (c) granular swelling after loss of birefringence. Marchant and Blanshard<sup>10</sup> suggested that starch polymer chains in amorphous regions of granules were susceptible to rearrangement under suitable conditions, thus affecting the gelatinization process. Several other explanations have been published to explain the starch gelatinization process. The water availability,<sup>11</sup> crystallite stability<sup>12</sup> and sequential phase transition<sup>13</sup> theories all explain starch gelatinization by different approaches.

Biliaderis *et al.*<sup>14</sup> suggested a three-stage (partial melting, recrystallization and complete melting) process for starch gelatinization. This theory accounted for the potential changes in starch structure during heating prior to completion of the phase transition. This explanation was closer to what was subsequently reported by other researchers.<sup>15–18</sup> The evolution of starch gelatinization theories and recent advances in starch phase transition research have been documented elsewhere.<sup>1</sup>

Most studies on starch gelatinization have been conducted using differential scanning calorimetry (DSC) as the primary experimental technique.<sup>11, 12, 19, 20</sup> Starch gelatinization theories based solely on DSC results assume that a fairly rapid direct scan from room temperature to a certain above-boiling temperature accurately represent the entire phase transition process. DSC enthalpy represents a net sum

of all endothermic processes that take place during heating. The advantage of using DSC to investigate starch gelatinization is that it permits precise control of the sample temperature while keeping the sample in a physically closed system. Salt (sodium chloride) and sugar (sucrose) are two commonly used food ingredients. It is generally known that both sodium chloride and sucrose increase the starch gelatinization temperature and decrease the degree of gelatinization,<sup>12, 21</sup> especially at low (<50 g kg<sup>-1</sup>) concentrations. Chiotelli *et al.*<sup>22</sup> investigated the starch gelatinization process by a multi-measurement (including DSC) study and reported that the effect of salt on starch gelatinization can be attributed to water-solute interactions as well as starch polymer-solute interactions. However, they did not elaborate how these processes play their individual roles simultaneously during heat treatment, although it was found that the net effect of the presence of salt was concentration-dependent. Buck and Walker<sup>23</sup> studied the effect of 10–30 g kg<sup>-1</sup> sucrose concentrations on starch gelatinization. They reported that peak temperature increased and enthalpy decreased for both wheat and maize starch phase transitions in the presence of sucrose. Almost all published DSC studies on the effects of solutes on starch gelatinization have been carried out by direct DSC scans of starch/water/solute samples, making it difficult to adequately explain temperature-dependent progressive developments or changes in starch structure during the phase transition process. A systematic, temperature-controlled comparison of starch phase transition behaviors in the presence of dilute sodium chloride and sucrose compared with excess water systems is important to understand the effects of such solutes on starch structural changes during hydrothermal processing. Despite numerous attempts by researchers, the effects of sodium chloride and sucrose on the starch gelatinization process are still not very clear.<sup>22, 24–26</sup> Understanding the effects of sodium chloride and sucrose is particularly important for food processing and similar operations where starch is subjected to various hydrothermal conditions for long periods during heat processing or cooking. By *in-situ* analysis of treated samples, in this study we have eliminated the post-treatment sample preservation steps so that specific temperature (i.e. heat treatment)-influenced enthalpic changes are better represented by the DSC scans. This experimental setup should more closely explain the starch gelatinization process that takes place during food processing and similar operations where starch-containing mixtures are held at certain temperatures for relatively long durations.

The detection of enthalpic changes during DSC scans depends on many factors, including scanning rate, moisture content, degree of starch granule hydration and equipment sensitivity. Moreover, when samples are subjected to a progressively increasing heat treatment during "direct scanning", it is impossible to detect precisely what enthalpic changes occur at specific temperatures.<sup>27</sup> To overcome this, recent studies on starch gelatinization have introduced the treatment of starch samples at specific temperatures prior to DSC analysis to detect starch changes.<sup>16, 17, 28, 29</sup> However, post-treatment sample preservation prior to analysis could considerably impact the results owing to possible starch polymer rearrangements during cooling, drying and reconstitution with water. Therefore it could be hypothesized that avoiding post-treatment preservation steps would allow more precise investigation of the starch phase transition. In this study we used DSC, which permits us to

achieve these experimental requirements. The objective of the study was to investigate the effects of sodium chloride and sucrose in dilute concentrations on progressive changes in DSC enthalpic transitions during maize, wheat, and potato starch phase transition processes.

## Materials and Methods

Unmodified native starches were used in this study. Maize starch (Cargill Gel 03424) was obtained from Cargill Inc. (Cedar Rapids, IA, USA), potato starch (Pencook 10) from Penford Food Ingredients Co. (Englewood, CO, USA) and wheat starch (Lot No. 334605-0416) from Archer Daniels Midland Co. (Olathe, KS, USA). Starch samples were used as received. Reagent grade sucrose ( $\alpha$ -D-glucopyranosyl- $\beta$ -D-fructofuranoside; Cat. No. S-9378) was obtained from Sigma Chemical Co. (St Louis, MO, USA). American Chemical Society (ACS)-certified grade sodium chloride (Cat. No. 3624-01) was obtained from J. T. Baker (Phillipsburg, NJ, USA).

### Differential scanning calorimetry

DSC experiments were conducted with three different solution combinations, namely distilled water, 20 g kg<sup>-1</sup> (2% w/w) sodium chloride in water and 20 g kg<sup>-1</sup> (2% w/w) sucrose in water. Native starch samples were hermetically sealed in large-volume high-pressure stainless steel DSC pans (Part No. 03190029, Perkin Elmer, Norwalk, CT, USA) with excess liquid (~10 mg of starch in ~55  $\mu$ L of liquid) and allowed to equilibrate at room temperature for about 1 h prior to experiments. The sample treatment and scanning using DSC are illustrated in Figure 1.

#### Step 1. Heat treatment

Sealed pans were held for 30 min at specific temperatures (from 35 to 90 °C in 5 °C intervals) in a Perkin Elmer Pyris 1 equipped with a Perkin Elmer Intracooler 1P. After heating, samples were promptly cooled (40 °C min<sup>-1</sup> cooling rate) and maintained at 25 °C for 5 min (Figure 1).

#### Step 2. Scanning

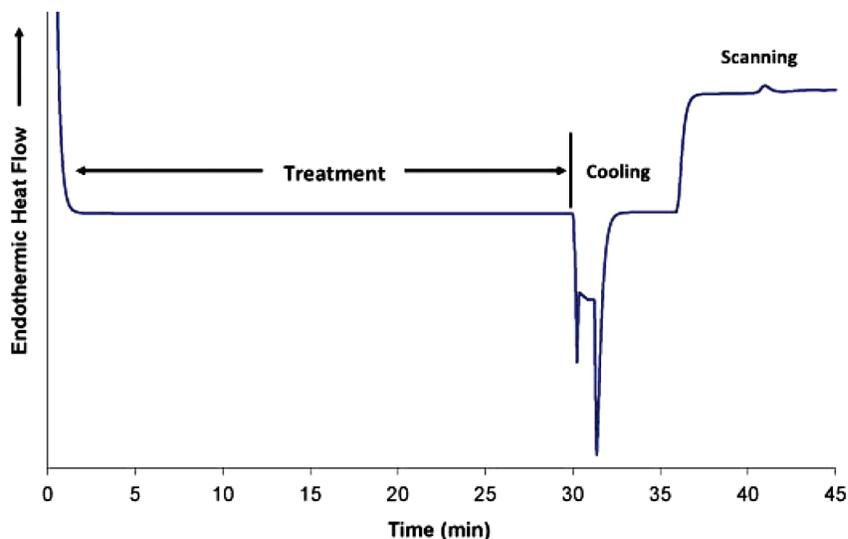
Treated samples were scanned from 25 to 120 °C at 10 °C min<sup>-1</sup> (Figure 1). Perkin Elmer Pyris Version 3.50 software was used to control the experimental conditions. The instrument was calibrated using indium as reference material. An empty sealed pan was used as reference for all experiments.

### Degree of gelatinization of starch

The degree of gelatinization was calculated as the ratio of the enthalpic transition difference between the untreated and treated samples to the enthalpy of the untreated sample as follows:

$$\text{degree of gelatinization (\%)} = [\Delta H_S - \Delta H_T] / \Delta H_S \times 100 \quad (1)$$

where  $\Delta H_S$  is the enthalpy of the untreated sample and  $\Delta H_T$  is the enthalpy of the treated sample scanned under the same experimental conditions (solid/liquid ratio, composition and scanning rate) using the same equipment. In this study the untreated starch/liquid samples ( $\Delta H_S$ ) were prepared using the same starch (maize, potato or wheat) and solution (water, sucrose or sodium chloride) as found in the treated samples. The measured DSC parameters of these untreated starch/solvent combinations are given in Table 1.



**Figure 1.** Sample treatment and scanning by DSC. Samples were treated at specific temperatures for 30 min, followed by cooling and scanning.

**Table 1.** DSC transition parameters of different untreated<sup>a</sup> starch/solvent combinations

| Starch | Solvent <sup>b</sup> | $T_o$ (°C) | $T_p$ (°C) | $T_c$ (°C) | Range, $T_c - T_o$ (°C) | Enthalpy (J g <sup>-1</sup> ) |
|--------|----------------------|------------|------------|------------|-------------------------|-------------------------------|
| Maize  | Water                | 71.95c     | 76.74c     | 81.72b     | 9.77a                   | 15.14c                        |
|        | Sodium chloride      | 78.13d     | 83.02d     | 88.51c     | 10.38a                  | 14.02bc                       |
|        | Sucrose              | 72.51c     | 77.24c     | 82.57b     | 10.06a                  | 13.39b                        |
| Wheat  | Water                | 62.32a     | 68.20a     | 75.45a     | 13.13c                  | 11.26a                        |
|        | Sodium chloride      | 68.67bc    | 74.53abc   | 81.72b     | 13.05c                  | 11.90a                        |
|        | Sucrose              | 63.08a     | 69.20ab    | 76.71ab    | 13.63c                  | 12.25ab                       |
| Potato | Water                | 66.19ab    | 72.20abc   | 79.54ab    | 13.35c                  | 17.87d                        |
|        | Sodium chloride      | 68.77bc    | 74.56b     | 81.80b     | 13.03bc                 | 17.45d                        |
|        | Sucrose              | 67.23bc    | 73.22abc   | 80.78ab    | 13.56c                  | 18.43d                        |

All results are averages of three independent replicates. Values with the same letter within a column are not significantly different ( $P > 0.05$ ) by Tukey's HSD test.

a. DSC results of "direct" scans.

b. 20 g kg<sup>-1</sup> in water mixtures.

### Data analysis

DSC data were analyzed to calculate the transition temperatures, onset ( $T_o$ ), peak ( $T_p$ ) and conclusion ( $T_c$ ), and enthalpy ( $\Delta H$ ) using Perkin Elmer Pyris Version 3.50 software. All data reported are means of three independent replicates. The experiment was conducted by completely randomizing the treatments. Means were separated by Tukey's honestly significant difference (HSD) test ( $P < 0.05$ ) using JMP Version 5.0.1.2 software (SAS Institute Inc., Cary, NC, USA).

### Results and Discussion

The patterns of transition enthalpy changes over increasing temperatures were unique to each starch source. Enthalpic transition patterns of the treated samples were also dependent on the type of solvent. The results are described in detail in the following subsections. It is important to note that DSC profiles/enthalpies indicate any changes that could contribute to an endothermic transition remaining in the sample after 30 min of treatment. In other words, this study was designed to understand "what has occurred" at a specific temperature/solvent combination by analyzing "what was remaining," as detected by DSC enthalpic transitions. The temperature ranges,

treatments and scanning conditions were selected based on previous studies.<sup>16, 27–29</sup> Elimination of post-treatment sample preservation and rehydration steps enhances the detection of actual phase transition-associated changes caused by a specific treatment combination by eliminating the potential for interferences by polymer re-association processes. In fact, the experimental conditions of this study do not permit processes such as annealing<sup>30</sup> or heat-moisture treatment<sup>30</sup> owing to the specific starch/solvent combinations and temperatures employed. Starch annealing requires much longer times at sub-gelatinization temperatures, while heat-moisture treatment requires longer times along with very-low-moisture conditions at above-gelatinization temperatures. Neither of these sets of requirements is met in the experiments of this study.

During analysis of the results it was obvious that the gelatinization patterns were determined by both starch source and solvent type. There is ample evidence in the literature<sup>16, 19, 23</sup> that granular structures, polymer arrangements, molecular characteristics (e.g. degree of polymerization and chain lengths) and phase transition characteristics are dependent on the starch source. Therefore the following part of the discussion is arranged on the basis of starch type to compare the effects of the three solvents used.

### Maize starch

In maize starch the shifting of enthalpy to higher temperatures (increasing peak temperatures  $T_p$ ) with increasing heat treatment was more prominent with water than with sodium chloride and sucrose (Figures 2G–2I). The effect of the three media in increasing the peak temperature ( $T_p$ ) of treated samples was in the order dilute sucrose < dilute sodium chloride < excess water at <70 °C treatments. Maize starch in excess water did not gelatinize completely (as indicated by the traces of enthalpies even at 85 °C pre-treatment) until it was heated to 90 °C for 30 min, but in sucrose and sodium chloride solutions it was completely gelatinized at relatively lower temperatures, i.e. at 75 and 85 °C treatments respectively (Figures 2A–2C). With excess water the small endotherms observed between 70 and 85 °C treatments had wider transition temperature ranges compared with sodium chloride as well as other starch/solvent mixtures (Figures 2M–2O, 3M–3O, and 4M–4O).

In contrast to maize starch in water, in sodium chloride and sucrose solutions it exhibited a slight decrease in transition temperature range (i.e. narrowing of enthalpies) over increasing heat treatments (Figures 2M–2O). This seems to be influenced by increasing onset temperatures ( $T_o$ ) with sodium chloride and sucrose solutions (Figures 2D–2F) rather than by changes in end temperatures ( $T_c$ ) of transition enthalpies (Figures 2J–2L). Chiotelli *et al.*<sup>31</sup> suggested that addition of sucrose increased DSC transition temperatures and the enthalpy of gelatinization of waxy maize starch using high (up to 20% w/w)-sucrose/water solvents. Perry and Donald<sup>32</sup> observed similar trends in shifting DSC enthalpies to higher temperatures with addition of sucrose (25% w/w) to waxy maize starch (40–45% w/w)/solvent mixtures. They concluded that increasing sugar concentrations did not influence the plasticizing effects of solvent (sugar solution) but shifted the DSC transition temperatures higher, indicating that the process merely required more energy rather than a change in “mechanism.” Our study showed very similar gelatinization patterns between water and 2% (w/w) sucrose solutions for maize starch (Figures 2A–2C), which disagrees with some of the previously published evidence on the effect of sucrose on starch gelatinization. The very low concentration of sucrose used in this study might be insufficient to change the maize starch phase transition to the extent detected by other researchers. Our study, however, detected a lesser degree of gelatinization with sucrose solution compared with starch/water mixture between 35 and 70 °C treatments (Figure 5, maize starch).

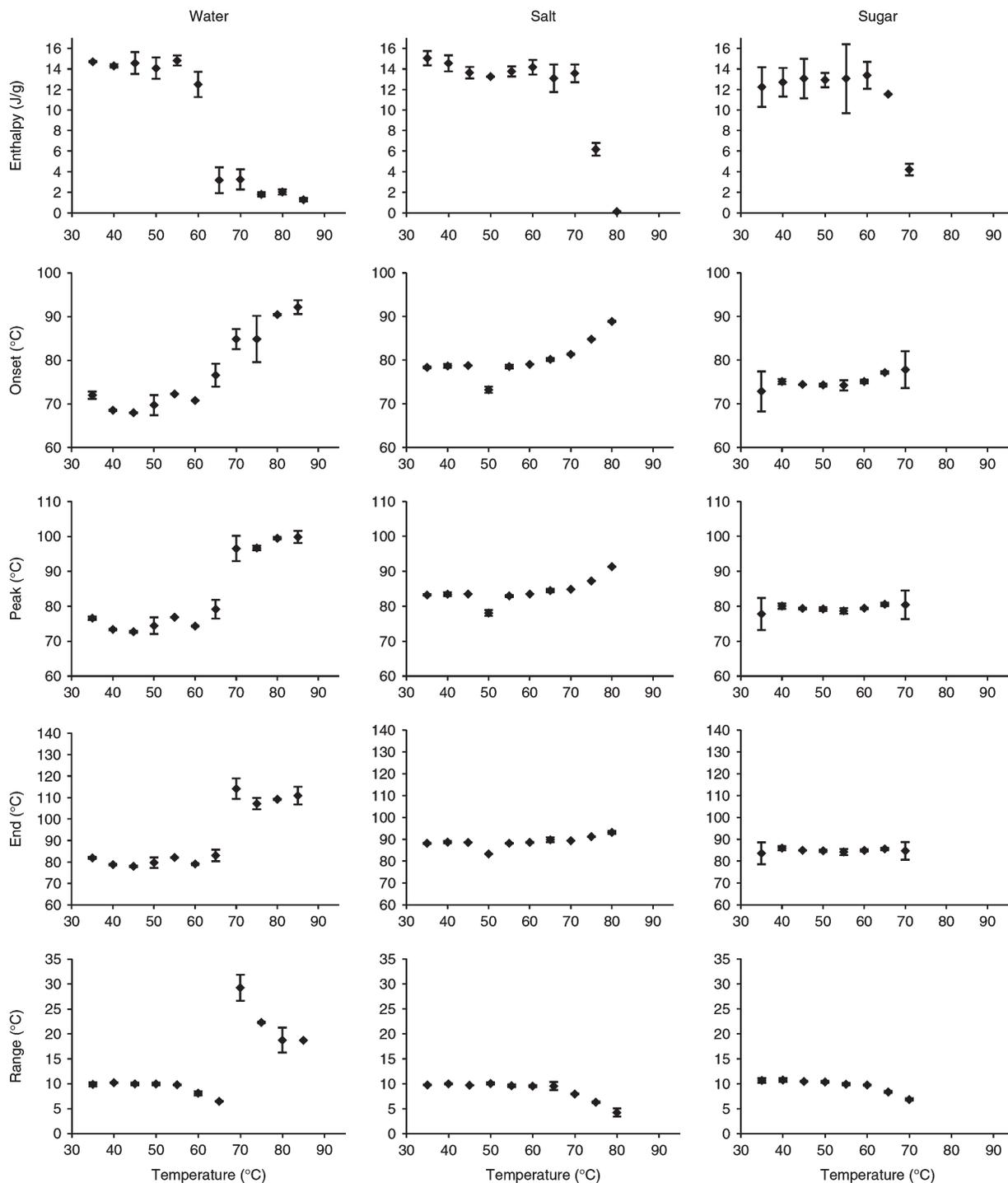
The DSC enthalpy changes observed in this study (Figure 2, water) are slightly different from those observed in our previous studies with excess water, in which the treated samples were freeze-dried and stored until analysis.<sup>16, 17</sup> Complete gelatinization occurred at 90 °C treatment with water in this study (Figure 2A), whereas the enthalpy was seen to disappear at 70 °C treatment in the previous studies. These differences could be attributed to the post-treatment structural changes taking place in the samples during preservation and rehydration in the previous analyses. Similar arguments were presented by Cooke and Gidley<sup>33</sup> regarding the analysis of pre-treated samples preserved by variable heating/cooling rates. Post-treatment drying and rehydration might eliminate some of the structural features that cause endothermic transitions during subsequent analysis by DSC.

### Wheat starch

In wheat starch the DSC endotherms shifted to higher temperatures (peak,  $T_p$ ) as the treatment temperature increased (Figures 3G–3I), indicating increased “stabilities” of non-gelatinized phases within granules. The intensities, in terms of shifting the DSC enthalpies to higher temperatures, of the effect of dispersion medium changed as water < dilute sucrose < dilute sodium chloride at >70 °C temperatures (Figure 3). None of the three dispersion media allowed wheat starch granules to “fully gelatinize”, i.e. small DSC endothermic traces were detected at 90 °C treatment (Figures 3A–3C). Wootton and Bamunuarachchi<sup>24</sup> studied the effects of sodium chloride and sucrose on wheat starch gelatinization using DSC. Their study used direct DSC scans of starch, i.e. single scans of samples, unlike this study in which DSC scans were obtained on samples pre-treated in different sodium chloride and sucrose concentrations. They reported that both sodium chloride and sucrose decreased the extent of gelatinization compared with samples gelatinized with excess water. Our study found that wheat starch does not undergo complete (100%) phase transition even after holding at 90 °C for 30 min with excess water (Figure 3A). The same was true for 2% (w/w) sodium chloride and sucrose solutions (Figures 3B and 3C). Although some of the differences could be attributed to the wheat starch source ( $T_o$ ,  $T_p$ ,  $T_c$  and  $\Delta H$  values were 50, 68, 86 °C and 19.74 J g<sup>-1</sup> for the wheat starch used in the study of Wootton and Bamunuarachchi<sup>24</sup> compared with 62.32, 68.20, 75.45 °C and 11.26 J g<sup>-1</sup>, respectively for the wheat starch used in this study), the major discrepancies might be due to the differences in experimental procedures, i.e. direct DSC scans by Wootton and Bamunuarachchi<sup>24</sup> versus post-treatment DSC scans in this study. Our results also differ from the findings of Marchant and Blanshard<sup>10</sup> that indicated a decrease in wheat starch gelatinization with increased sucrose contents. As noted above, the amount of sucrose used (20 g kg<sup>-1</sup>, i.e. 2% w/w) in water in this study is very low compared with that used in their experiments (330 g kg<sup>-1</sup>, i.e. 33% w/w).<sup>10</sup> Wootton and Bamunuarachchi<sup>24</sup> also reported restrictive effects of sucrose on starch gelatinization when sucrose was added at >15% (w/w), i.e. >150 g kg<sup>-1</sup>. When sucrose is present in high amounts, the lower water activity may reduce the available water, which acts as a diluent for the starch gelatinization process, which is evident in the analysis of the degree of gelatinization between 50 and 60 °C (Figure 5, wheat starch). The amount of sucrose used in this study is insufficient to lower the water activity to an extent that will dramatically affect the gelatinization process. Our study indicated fairly comparable effects on enthalpic transitions by excess water and 20 g kg<sup>-1</sup> sucrose in water solution on wheat starch gelatinization (Figures 3A and 3C).

### Potato starch

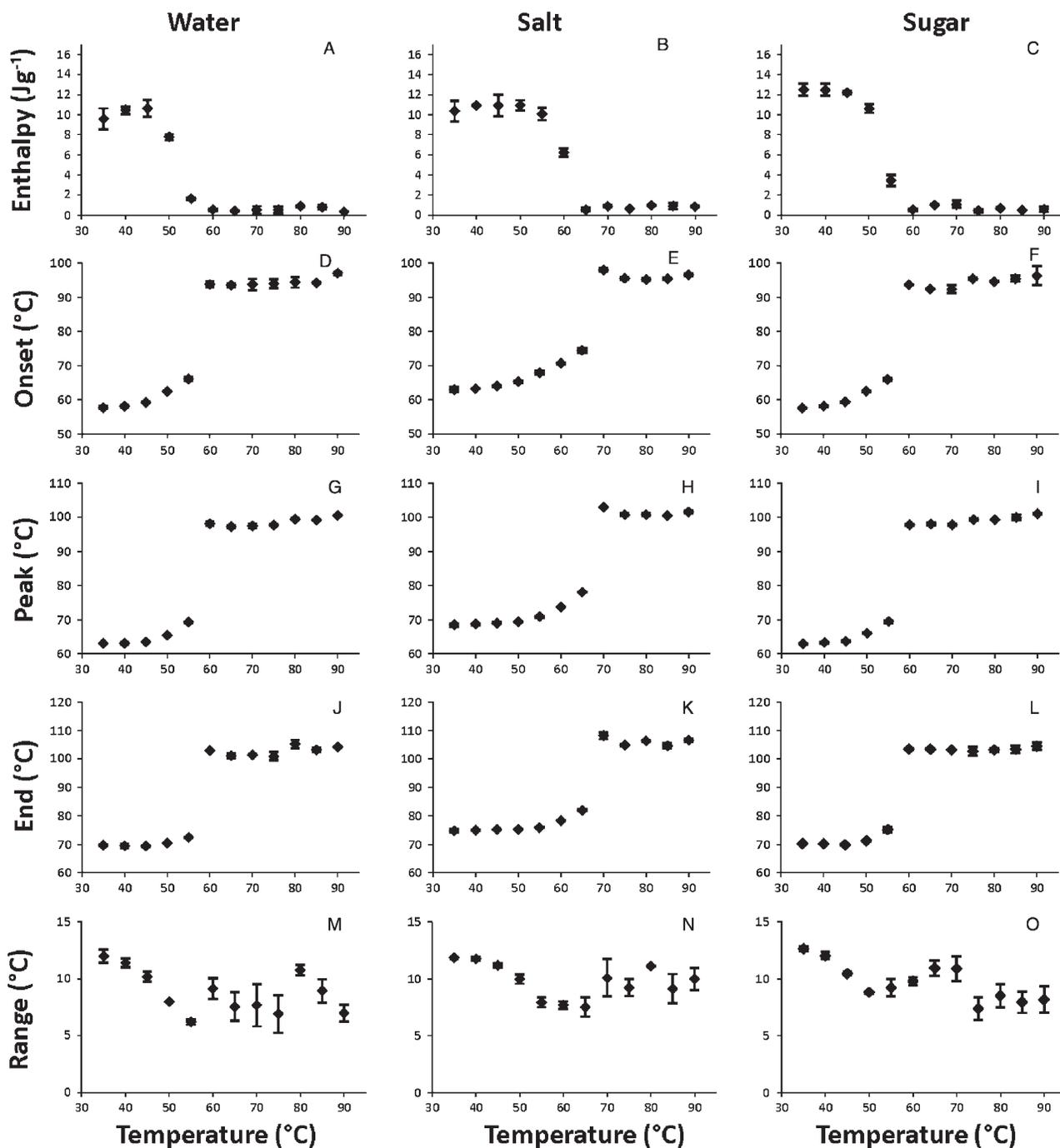
Unlike the other two starches studied, potato starch underwent complete phase transition, as indicated by the disappearance of transition enthalpies, when treated for 30 min at  $\geq 65$  °C with all three solvents (Figures 4A–4C). The patterns of DSC profile changes were almost identical for all three starch/solvent combinations. Few previously published starch gelatinization theories have been established by studying the phase transition behavior of potato starch alone.<sup>11, 12, 34</sup> It has been reported that the phase transition behaviors of different polymorphic structures are different owing to the structural variability caused by polymer and branch chain lengths<sup>35</sup> and their packing.<sup>36</sup> Shio-



**Figure 2.** DSC parameters of maize starch. All data points represent means of three independent replicates and corresponding standard deviations.

shio<sup>27</sup> studied potato starch gelatinization by treating samples in excess water at different temperatures between 54.8 and 66.5 °C for varying durations between 0 and 60 min and discovered that increasing temperature progressively increased the degree of gelatinization from 0% at 54.8 °C to 100% at 66.5 °C after 30 min incubation time. While acknowledging the differences in results potentially attributable to starch source and experimental methods, the findings of Shio<sup>27</sup> align very closely with the results we obtained in this study within the

corresponding temperature range. Shio<sup>27</sup> and Shio and Takahashi<sup>37</sup> discussed in detail the disadvantages of using faster heating rates in analyzing starch gelatinization. Using slow heating rates to analyze potato starch gelatinization, they concluded that starch gelatinization should not be characterized by onset ( $T_o$ ) and end ( $T_e$ ) temperatures of DSC profiles obtained by direct DSC scans. They also proposed that actual starch gelatinization initiated at lower temperatures than previously reported in the literature, which was confirmed by



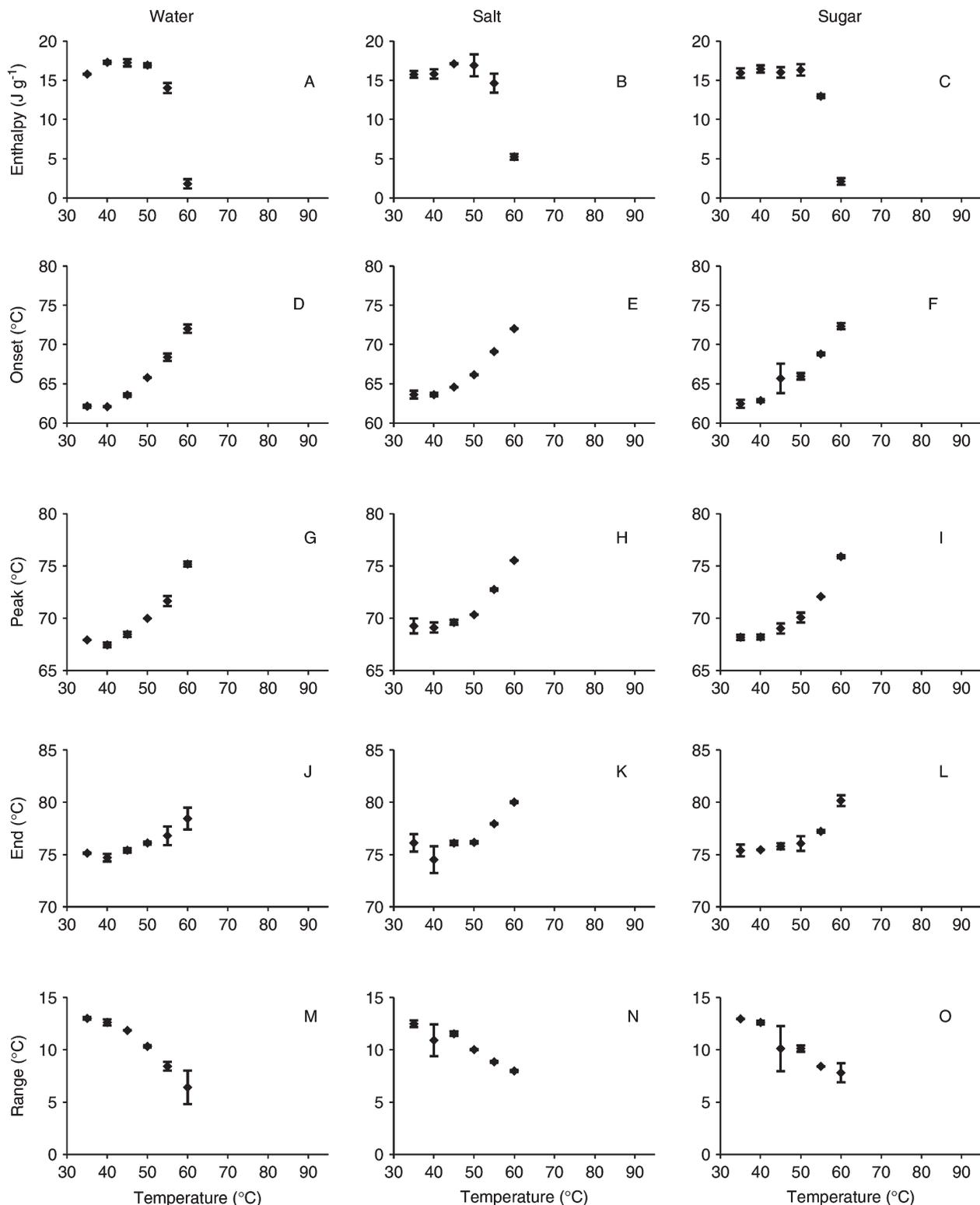
**Figure 3.** DSC parameters of wheat starch. All data points represent means of three independent replicates and corresponding standard deviations.

more recent studies as well.<sup>16–18</sup> Shiotsubo<sup>27</sup> also suggested that the degree of gelatinization of starch followed a sigmoidal pattern with increasing temperature. This observation is consistent with our results (Figure 5).

#### General discussion

Many published starch gelatinization/phase transition theories have been derived by studying just one starch type, primarily using DSC.<sup>11–13, 24, 38, 39</sup> As indicated previously, there are many advantages of using DSC to study starch phase transition, one being the ability to study the transition caused by hy-

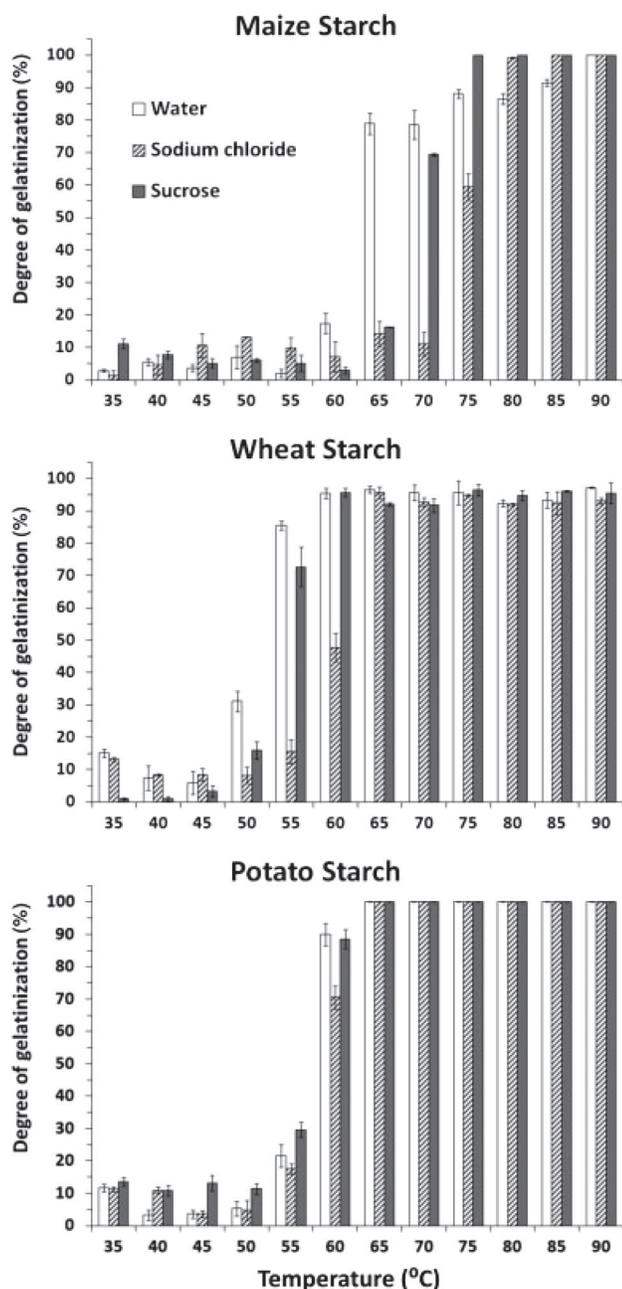
drothermal events in a physically closed system. However, using DSC to scan samples directly from room temperature (low) to a certain “above-gelatinization” temperature (high) will not reveal the full extent of temperature-specific enthalpic transitions. Apart from “dynamic” hydrothermal conditions during “direct DSC scans,” instrumentation lag, as explained by Reid,<sup>40</sup> plays a critical role in determining the experimental results. According to Reid,<sup>40</sup> such differences could be due to sample size, pan volume, uniformity of the mixture being analyzed, etc., which determine the coupling between sample and measuring system. For example, regular DSC scans of maize



**Figure 4.** DSC parameters of potato starch. All data points represent means of three independent replicates and corresponding standard deviations.

starch in excess water (Table 1) indicated  $T_o$ ,  $T_p$  and  $T_c$  values of 71.95, 76.74, and 81.72 °C, respectively. However, these values do not match with those obtained by 30 min heat treatments (Figures 1D, 1G, and 1J). They also did not correctly predict the completion of maize starch gelatinization in excess

water under isothermal conditions (Figure 5). Other methods such as X-ray diffraction require samples to be in dry form after treatments, and post-processing of samples may impact the structural changes taking place during phase transition under high-moisture conditions. Our experimental set-up permitted



**Figure 5.** Degree of gelatinization of starch/solvent combinations after treatment at specific temperatures for 30 min. All data points represent means of three independent replicates and corresponding standard deviations.

relatively “live” observations on samples during the phase transition process by eliminating the post-processing step. This study, especially the results obtained with starch/excess water mixtures, suggests that starches from different sources undergo phase transition in very different manners. This suggests that the theories derived by studying the gelatinization process of a specific starch may not be fully applicable to starches from other sources, which may have different granular and molecular characteristics.

Both solvent (diluent) and starch types were responsible for starch structural changes as observed by DSC enthalpic tran-

sitions. It appeared that holding at  $>60$  °C for 30 min caused most, if not all, DSC-detectable transitions in all three starches (Figures 2A–2C, 3A–3C, and 4A–4C), though wheat starch did not undergo complete transition even at the highest temperature (90 °C) tested.

The water activities of sodium chloride- and sucrose-containing mixtures are not affected by the small concentrations of the solutes in water. It appears that sodium chloride exerted a “protective” or “restrictive” effect on starch gelatinization, as indicated by the increasing temperatures required to decrease the enthalpies of treated samples dramatically in all three starches (Figures 2B, 3B and 4B). Jane<sup>39</sup> suggested that adding sodium chloride to water changed the water structure and electrostatic interactions between starch and ions via sodium chloride acting as a water “structure maker.” Jane’s<sup>39</sup> argument on stabilizing the water structure and its effect on protecting starch from gelatinization by charged ions such as  $\text{Na}^+$  explains the sudden drop in transition enthalpy of samples treated with dilute sodium chloride at the higher temperatures in all three mixtures (70–80 °C for maize and 55–65 °C for wheat and potato; Figures 2B, 3B, and 4B). In this study the effect of salt in restricting starch phase transition was lesser with potato starch than with maize and wheat starches. Starch source being the only variable, such differences could be attributed to the specific starch structural differences, including polymorphic composition (potato starch has B-type polymorphs, whereas the other two starches have A-type polymorphs<sup>36</sup>). Spies and Hoseney<sup>41</sup> suggested that the restriction of starch gelatinization by sugars (i.e. sucrose and glucose in amounts as high as 33% w/w) did not occur owing to the reduction in water activity but by hindering the ability of water to interact with other components in the system. This argument might be more relevant to low sucrose concentrations, such as those used in the present study, than to high sucrose concentrations, which could reduce the water activity greatly.

## Conclusions

Starch gelatinization initiates at low temperatures and the structural changes associated with starch phase transition are inconsistent with order–disorder phase transition theory, which describes the process as a sudden structural collapse taking place within a narrow temperature range. These structural changes start to occur at low temperatures and involve starch structural rearrangements prior to complete order–disorder transition.

Application of a universal theory to explain starch phase transition may not be possible owing to the granular and molecular differences attributed to the source of starch. The presence of other solutes such as sodium chloride and sucrose, even at very dilute levels, further complicates the starch phase transition process, especially the temperatures at which endothermic transitions occur during starch gelatinization. With the three solutions investigated in this study, starch gelatinization-related structural transitions occur as a continuous process starting at low (30 °C) temperatures and reaching completion at or continuing to high (65–90 °C) temperatures. The exact mechanism of starch phase transition, specifically the extent of structural changes or starch polymer interactions caused by the temperature treatment, is determined by starch type and solvent combination. This information may be applicable in food-processing operations where determination of

the degree of gelatinization of starch under specific hydrothermal conditions in the presence of other ingredients is critical. Starch gelatinization phenomena, as explained by direct DSC scans, may not represent the nature of the complete starch phase transition process, especially under time-controlled hydrothermal conditions commonly used in food-processing operations.

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