

Phase Transitions of Pea Starch over a Wide Range of Water Content

Shujun Wang* and Les Copeland*

Faculty of Agriculture and Environment, The University of Sydney, NSW 2006, Australia

ABSTRACT: The phase transitions of pea starch over a wide range of water content were investigated by differential scanning calorimetry (DSC). Swelling of starch granules increased progressively with increasing water content. The main endotherm G broadened progressively with increasing water content up to 94.5 wt % (water:starch ratio 15:1), above which it became too broad to define. The corresponding peak and conclusion temperatures and enthalpy change increased with increasing water content. Scanning electron microscopy (SEM) showed that, at a water:starch ratio of 2:1 (water content of 70.7 wt %), starch granules only swelled partially with discernible granular contours still clearly evident. The results of swelling power tests and SEM images revealed that the endotherm G obtained at a water:starch ratio of 2:1 represented only partial swelling of starch granules. The transition from a narrow to broad endotherm G was interpreted to reflect the thermal transition behavior progressing from limited swelling to maximum swelling and then partial dissolution and leaching of starch polymers from the granules.

KEYWORDS: starch, pea, *Pisum sativum*, swelling power, thermal transition, dissolution

■ INTRODUCTION

Native starch granules are composed of two types of polymers of α -D-glucopyranosyl units: amylose, an essentially linear molecule, and the highly branched amylopectin which has 2–5% of the α -D-glucopyranosyl units in α -(1–6) linkages.¹ Amylopectin is responsible for starch crystalline structures, which are distributed around an amorphous central core of the granules. Amylose occurs predominantly in the amorphous center of the granules, with some interspersed among the amylopectin molecules.^{2,3} Normal native starches contain 20–30% amylose. Pea starches have higher amylose content, mostly ranging between 30 and 40%.^{4,5} Unbranched and singly branched amylopectin chains that have more than 10 glucosyl units may form double helices, which are packed in either a monoclinic or a hexagonal crystalline unit cell, giving rise to A- or B-type X-ray diffraction (XRD) patterns, respectively.⁶ The A-type crystallites occur mainly in cereal starches, and the B-type in root, tuber, and high-amylose starches. Starches from pulses, rhizomes, and some fruits yield XRD patterns that contain both A- and B-type crystallites, and these are termed C-type. The B-type crystallites are located predominantly in the center of the pea starch granule surrounded by the peripheral A-type crystallites.^{3,7–9}

When heated in excess water, native starch granules undergo an irreversible phase transition, referred to as gelatinization, in which the highly ordered structure is lost. The changes that starch undergoes during gelatinization are major determinants of its functional properties for food processing and digestion. During gelatinization, starch granules take up water and swell, concomitant with a series of changes such as loss of birefringence, melting of crystallites, unwinding of amylopectin double helices, loss of granular morphology, and solubilization of some of the starch molecules.^{10–13} Differential scanning calorimetry (DSC), which provides a means for the quantitative analysis of thermal transition parameters, has been widely applied to monitoring starch gelatinization. Donovan first studied the influence of water content on phase transitions of potato starch using DSC,¹⁴ and subsequent studies have presented similar DSC thermograms of starch–water systems at similar water content.^{11,15,16} At around

50% water content, two overlapping endotherms (referred to as endotherms G and M1) are observed, and then at higher temperature a third endotherm is usually observed to overlap with an adjacent following exotherm. Increasing water content above 50% results in a progressive convergence of endotherms G and M1, whereas decreasing water content below 50% leads to the gradual disappearance of endotherm G and the shifting of endotherm M1 to higher temperatures. Several theoretical models have been proposed to interpret the biphasic G and M1 endothermic transitions of starch–water systems including the following: swelling-driven melting theory (melting of crystallites driven by swelling of amorphous regions and then melting of the remaining crystallites); crystallite stability theory (melting of less stable and then more stable crystallites); sequential phase transition theory (first amorphous and then crystalline regions); and a three-stage phase transition theory (partial melting, recrystallization, and total melting). An in-depth consideration of these models concluded that none gives an entirely satisfactory explanation of the mechanism of gelatinization.¹¹ A side-chain liquid crystalline model has also been put forward to explain changes in the lamellar, double-helical and crystalline order during gelatinization.¹⁷ Slow-heating DSC studies suggested that some exothermic amylopectin reassociation occurs in the later stages of gelatinization,^{18,19} but these proposed molecular events have, in general, drawn little attention. The overlapping endotherm and exotherm often observed at 95–125 °C with normal cereal starches have been related to decomplexing/dissociation/melting and then recrystallization of amylose–lipid complexes.²⁰

In our previous study, endotherm G of pea starch observed at a high water:starch ratio of 2:1 (water content 70.7 wt %) was proposed to represent only partial swelling of the granules and incomplete gelatinization.²¹ In the present study, the effect of

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water content on swelling power and DSC profiles of pea starch was investigated over a wide range of water:starch ratios to further understand the mechanism of thermal transitions as starch goes from an ordered native structure to a highly disrupted state. Such studies are relevant to explaining the effects of processing or cooking on starch gelatinization and, in turn digestibility, which is attracting increasing nutritional attention. The study of pea starch is of interest because its amylose content is higher than that of many other natural starches, and it contains a mixture of A- and B-type polymorphic structures. Moreover, peas are a source of food starch that is often consumed after domestic cooking. Although there have been previous studies of thermal transitions of pea starch at a particular water content,⁴ to the best of our knowledge, this is the first study to address the mechanism of thermal transitions of pea starch granules over a wide range of water contents (from 34.0 to 97.2 wt %). The nature of thermal transitions of starch granules is interpreted in terms of polymer swelling and dissolution theory and provides new insights into the mechanization of starch gelatinization.

EXPERIMENTAL SECTION

Materials. Pea starch was isolated from field pea variety Kasper obtained from the Plant Breeding Institute (Narrabri, The University of Sydney, NSW). The origin of the variety and the isolation and analysis of the starch, including determination of moisture content (11.8%) and amylose content (37%), are described elsewhere.⁵

Sample Preparation. To understand the swelling behavior of starch granules during the DSC heating process, the same water:starch ratios were used in the swelling power test and DSC measurements (Table 1).

Table 1. Water:Starch Ratios and Equivalent Moisture Contents Used in the Swelling Power Test and for DSC

sample no.	swelling power water/starch ($\mu\text{L}/\text{mg}$)	DSC water/starch ($\mu\text{L}/\text{mg}$)	water:starch ratio (w:w)	moisture content (% db ^a)
1	13.3:40	1.0:3	0.33:1	34.0
2	20.0:40	1.5:3	0.5:1	41.3
3	26.7:40	2.0:3	0.67:1	47.2
4	40.0:40	3.0:3	1.0:1	56.0
5	53.3:40	4.0:3	1.33:1	62.3
6	60.0:40	4.5:3	1.5:1	64.8
7	66.7:40	5.0:3	1.67:1	67.0
8	73.3:40	5.5:3	1.83:1	68.9
9	80.0:40	6.0:3	2.0:1	70.7
10	120:40	9.0:3	3.0:1	78.0
11	160:40	12.0:3	4.0:1	82.4
12	200:40	15.0:3	5.0:1	85.3
13	300:40	22.5:3	7.5:1	89.6
14	400:40	30.0:3	10:1	92.0
15	600:40	30.0:2	15:1	94.5
16	800:40	20.0:1	20:1	95.8
17	1000:40	25.0:1	25:1	96.6
18	1200:40	nd ^b	30:1	97.2

^aDry weight basis. ^bNot determined.

Swelling Power and Starch Solubility. Swelling power and solubility of pea starch were determined in triplicate according to the method described elsewhere²² as follows. Pea starch (approximately 40 mg) was weighed accurately into a 2 mL screw cap plastic test tube and water added as described in Table 1. After the lid was screwed on tightly, the starch–water mixtures were heated in a water bath at 92.5 °C for 30 min with regular shaking. The samples were cooled at 20 °C for 3 min and centrifuged at 1300g for 10 min. When a supernatant was obtained, it was transferred carefully to a glass evaporating dish, evaporated to

dryness on a steam bath, and dried for 24 h at 80 °C. The sedimented, swollen granules and dried soluble fraction were weighed to determine swelling power (g of H₂O absorbed/g of dry starch) and solubility (% of dry starch) using the following formulas:

$$\text{solubility, } S = \frac{[\text{weight of dried soluble fraction}]}{[\text{dry weight of original starch}]}$$

$$\text{swelling power, SP} = \frac{[\text{weight of sedimented granules}]}{[\text{dry weight of original starch}]}$$

Differential Scanning Calorimetry. Thermal transition measurements of starch were made over a wide range of water content using a modulated differential scanning calorimeter MDSC 2920 instrument (TA Instruments Inc., Delaware, USA) equipped with a thermal analysis data station and data recording software. Exactly 3 mg of starch was weighed into 40 μL aluminum pans. Different amounts of distilled water were added to the starch in the DSC pans with a microsyringe (Table 1). For samples with low water content (water:starch ratios of 0.33:1 and 0.5:1), a pin was used to gently mix starch with water. When larger volumes of water were added, care was taken to ensure that the starch granules were completely immersed in the water by gentle shaking. The pans were sealed and reweighed to determine the amount of water added. The sealed pans were allowed to stand overnight at room temperature before DSC analysis. An empty pan was used as a reference. The pans were heated from 30 to 120 °C at a scanning rate of 10 °C/min. The instrument was calibrated using indium as a standard. At least two thermograms were recorded at each water content, and the precision of water addition based on the weight of the sealed pans before heating was estimated to be $\pm 0.5\%$. The DSC thermograms derived from those samples without any weight loss after heating were selected for data analysis.

The Universal Analysis 2000 software was used to analyze the main endotherm of the DSC traces for start (T_s), peak (T_p), and conclusion (T_c) temperatures and enthalpy change (ΔH). The start and conclusion temperatures were defined, respectively, as the point at which the DSC trace first starts and finally ceases to deviate from a flat baseline. The peak temperature was defined as the point of maximum endothermic heat flow relative to the baseline. The ΔH was defined as the area under the line drawn from the start temperature to the conclusion temperature.

Field-Emission Scanning Electron Microscopy. To investigate the morphological changes of starch granules after the main endothermic transition, separate starch–water samples were heated to the conclusion temperature of the main endotherm (determined from DSC). After heating, the pans were cooled to room temperature and reweighed. The pans were opened carefully and left to dry overnight at room temperature (22–23 °C) before the starch samples were removed carefully with a spatula. The dried starch specimens were fixed onto the surface of double-sided, carbon-coated adhesive tape attached to an aluminum stub. The mounted samples were sputter coated with palladium/gold prior to imaging by FE-SEM (Carl Zeiss ULTRA plus, Germany). The accelerating voltage was 1.01 kV.

RESULTS

Swelling Power and Starch Solubility as a Function of Water Content. Swelling and solubility behavior of the pea starch granules are presented as a function of water:starch ratios in Figure 1 to represent the transitions more clearly. The swelling power of starch granules increased gradually from 1.0 g H₂O/g starch for native starch to 12.2 g/g at a water:starch ratio of 20:1, above which it remained essentially constant with further increases in water content (Figure 1). When the water:starch ratio was below 10:1, no supernatant was obtained on centrifugation, indicating that all of the water added to starch was absorbed into the granules and that no leaching occurred. The swelling power at these water:starch ratios was close to the theoretical value, which is the weight of starch plus absorbed

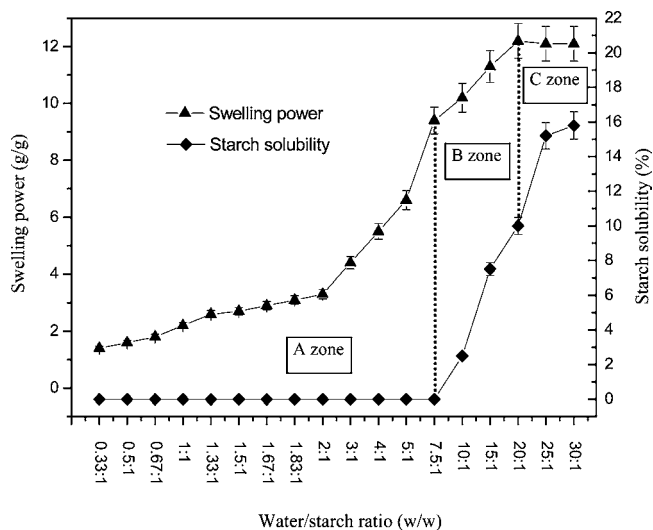


Figure 1. Effect of water:starch ratio on swelling power and solubility of starch granules. The zones marked A, B, and C correspond to the stages of swelling discussed in the text, namely: A, limited swelling without leaching; B, incomplete swelling with some leaching; C, complete swelling with continuous leaching.

water divided by the dry weight of the starch. At a water:starch ratio of 10:1, a supernatant was obtained on centrifugation and the swelling power was 10.2 g/g, which was lower than the theoretical value of 12.2 g/g. At 10:1 water:starch, about 2.5% of the starch was leached out of the granules (i.e., the starch solubility was 2.5%). The amount of material leached from the granules increased considerably at higher water content, reaching 15.2% and 15.8% at water:starch ratios of 25:1 and 30:1, respectively (Figure 1).

Thermal Transition of Starch as a Function of Water Content. Figure 2 presents the DSC thermograms of the starch–water systems at low to intermediate water contents (water:starch ratios in the range 0.33:1 to 1.83:1, or 34.0 to 68.9% moisture), whereas the thermograms of starch at high water content (water:starch ratios of 2.0:1 to 25:1, or 70.7 to

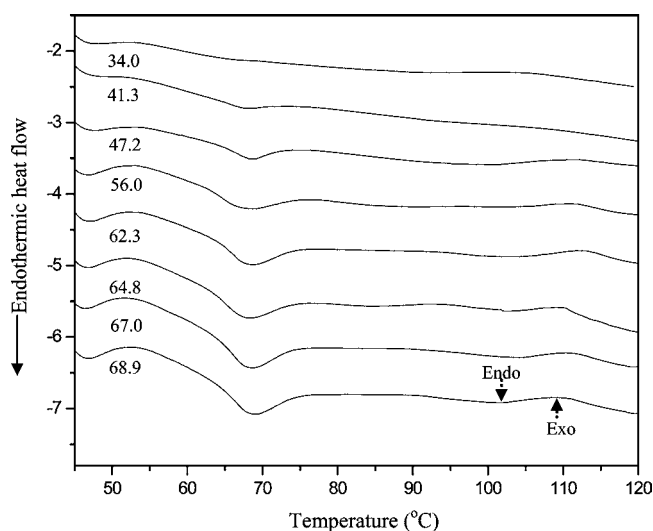


Figure 2. DSC thermograms of native pea starch in limited water (numbers under each line represent the moisture content in wt %). The arrows indicate the endothermic and exothermic transitions at high temperatures.

97.2% moisture) are presented in Figure 3. The effect of water content on endothermic transition temperatures and ΔH from

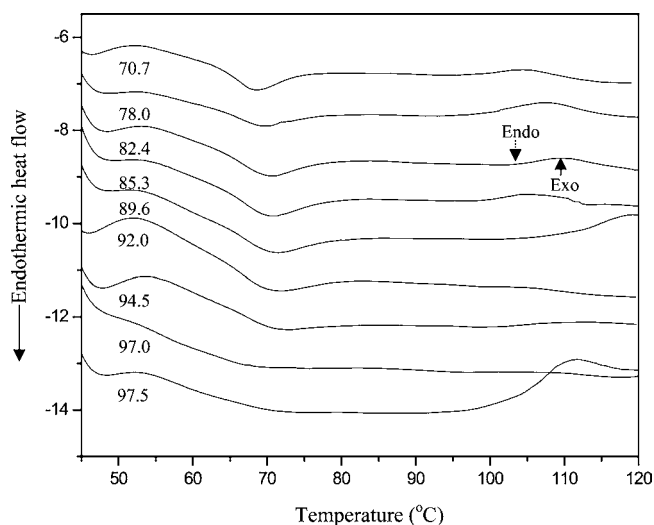


Figure 3. DSC thermograms of native pea starch in excess water (numbers under each line represent the moisture content in wt %).

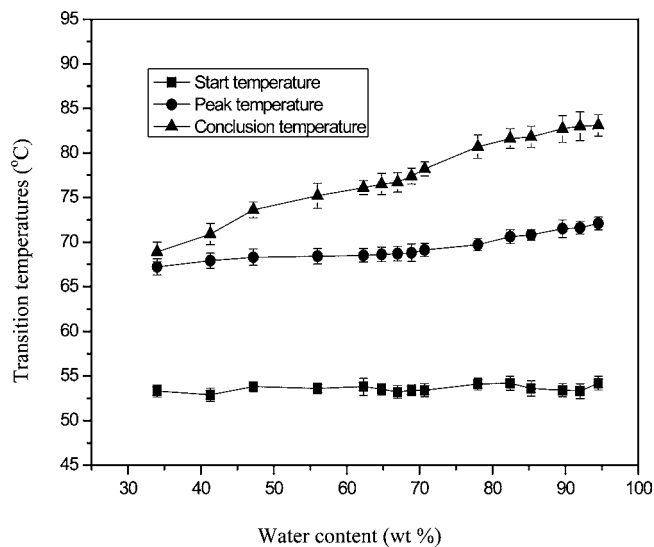


Figure 4. Effect of water content on the transition temperatures of endotherm G.

these thermograms are presented in Figure 4 and Figure 5, respectively. All the starch–water systems showed the typical endothermic transition occurring between 50 and 85 °C, with well-defined start, peak, and conclusion transition points, except for the two most dilute systems (water:starch ratios of 20:1 and 25:1), which presented an initial endothermic trend that flattened out. This typical endothermic transition is widely considered to represent the gelatinization of starch granules and is referred to as endotherm G. Apart from the endotherm G, a second shallow endotherm occurring at about 90–100 °C was observed, which overlapped with a subsequent exothermic transition (Figures 2 and 3).

The peak and conclusion temperatures and ΔH of the endotherm G increased with increasing water content (Figure 4

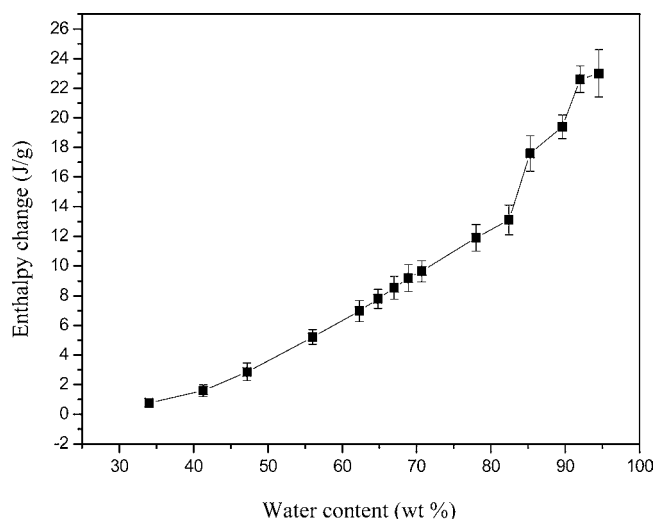


Figure 5. Effect of water content on the enthalpy of the endotherm G.

and Figure 5). At low and medium water content, the peak and conclusion temperatures of the endotherm G increased from 67.2 to 68.8 °C, and from 68.9 to 77.4 °C, respectively (Figure 4). At high water content, the peak and conclusion temperatures of endotherm G increased from 69.1 to 72.1 °C and from 78.2 to 83.1 °C, respectively (Figure 4). The enthalpy of endotherm G increased from 0.76 to 9.2 J/g across the low and medium water content ranges, and from 9.6 to 23.0 J/g in the high water content range up to 94.5 wt % (water:starch ratio of 15:1) (Figure 5). When water content was below 94.5 wt % (water:starch ratio \leq 15:1), the end point of endotherm G could be clearly identified. Above this water content the endothermic transition became too broad to accurately determine the peak temperature, conclusion temperature, and enthalpy. No significant differences were observed in the start temperature of endotherm G across the entire range of water:starch ratios (Figure 4).

Morphological Changes of Starch after DSC Heating.

The morphological changes of starch granules at different water contents after heating to the conclusion temperature of endotherm G in DSC pans are presented in Figure 6 and Figure 7, representing low and intermediate water content and high water content, respectively. At low and intermediate water content, the granular contour could be clearly made out and granular morphology was not completely lost. At a moisture content of 34.0 wt % (water:starch ratio of 0.33:1), the starch sample was observed visually not to have formed a gel after heating. Small patches seemed to have peeled off the granule surface, and some granules were deformed (Figure 6A2). All of the other starch–water mixtures were observed visually to have formed gels after DSC heating, and as the water content increased the SEM images showed a greater degree of granule swelling and coalescence, with the progressive loss of granular morphology. At moisture contents of 47.2 and 56.0 wt % (water:starch ratios of 0.67:1 and 1:1, respectively), deformed but nevertheless discrete starch granules were still observed. These granules had swelled to only a limited extent and had obvious central depressions (Figure 6B1,B2, Figure 6C1,C2). At 62.3 and 67.0 wt % moisture (water:starch ratios of 1.33:1 and 1.67:1, respectively), the starch granules had swelled and coalesced substantially, although elements of the granule form were still discernible (Figure 6D,E).

At a water:starch ratio of 2:1 (water content of 70.7 wt %), the contour of swollen granules became less pronounced (Figure

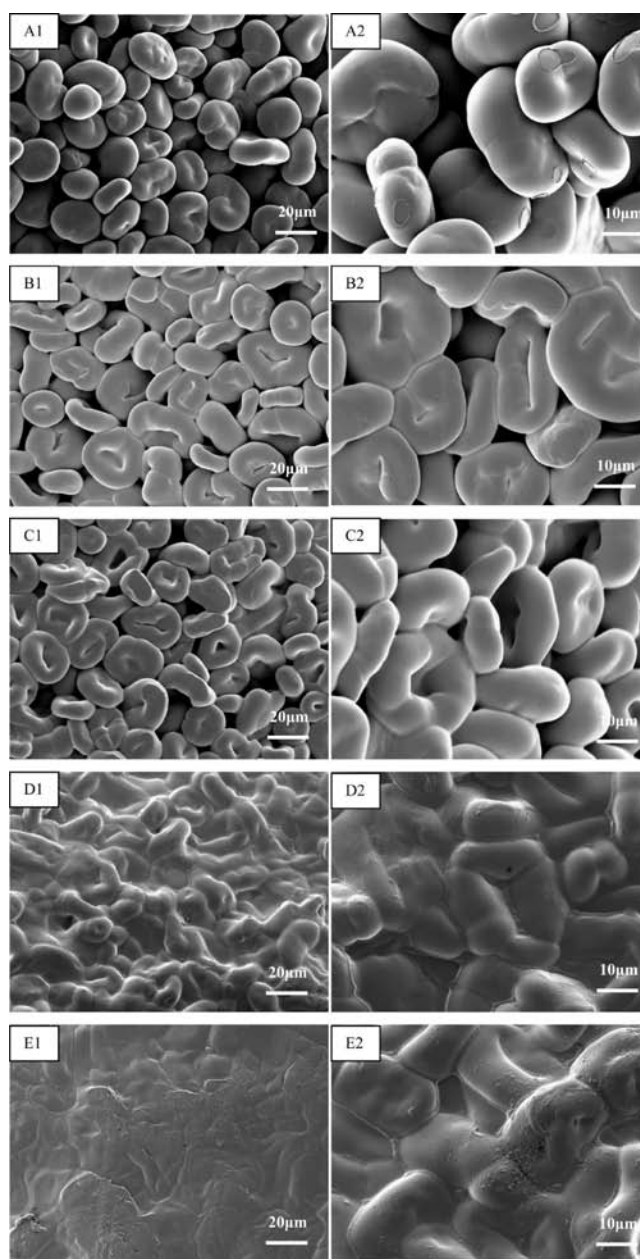


Figure 6. Scanning electron micrographs of starch after heating to the conclusion temperatures of the endotherm G at low to intermediate water contents. The panels show water:starch ratios: 0.33:1 (A1, A2), 0.67:1 (B1, B2), 1:1 (C1, C2), 1.33:1 (D1, D2), 1.67:1 (E1, E2). The scale and magnification are shown on the panels.

7F1,F2). When the gel was cut out, the exposed inner part was observed to be composed of tightly stacked swollen granules, indicating the incomplete swelling of starch granules (Figure 7G1,G2). With water content increasing further, much of the granular morphology was lost, although occasional residual granule outlines were still observed (indicated by white arrows in Figure 7H–L). At a water:starch ratio of 15:1 (water content of 94.5 wt %), the outline of the granules was essentially lost and there was evidence of a film over the granule surface. This film may be due to dried amylose molecules that were leached from the swollen granules, particularly at high water content (Figure 7M–O).

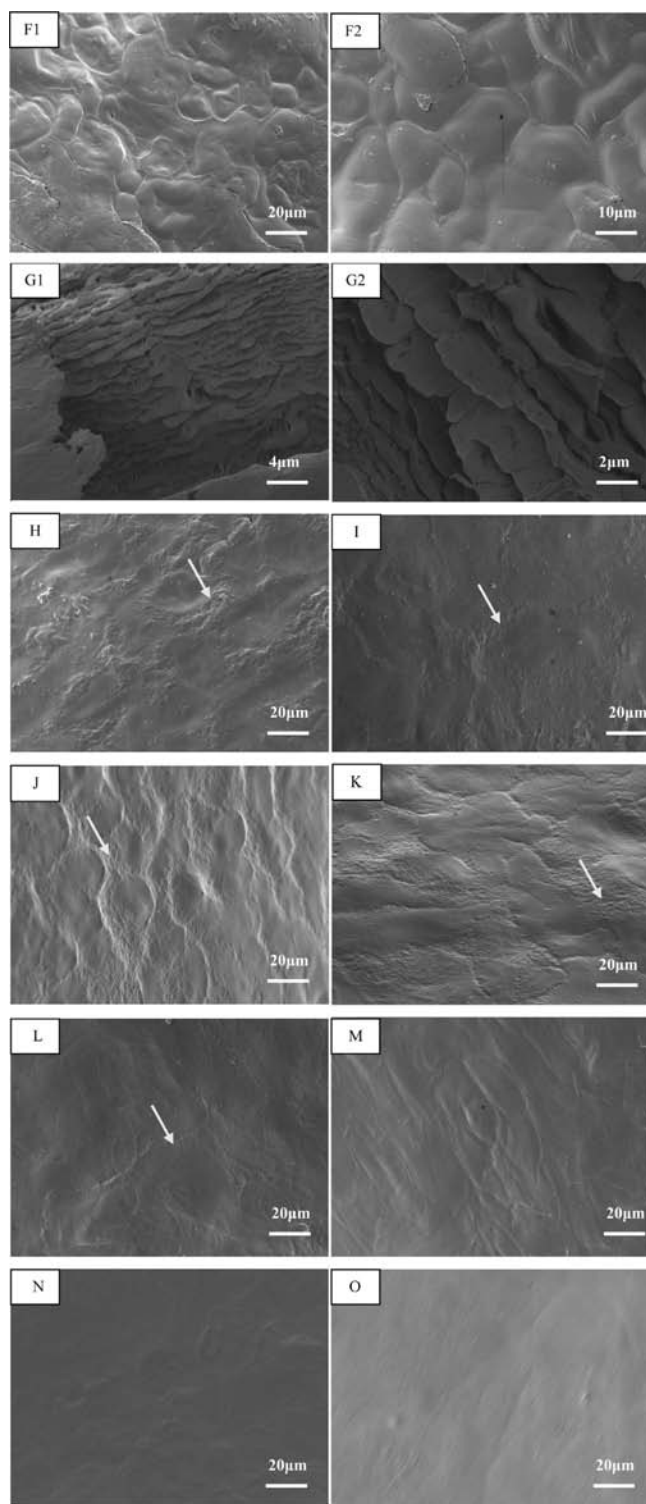


Figure 7. Scanning electron micrographs of starch after heating to the conclusion temperatures of the endotherm G at high water content. The panels show water:starch ratios: 2:1 (F1, F2), 2:1 (G1, G2), 3:1 (H), 4:1 (I), 5:1 (J), 7.5:1 (K), 10:1 (L), 2:30 (M), 20:1 (N), and 25:1 (O). The scale and magnification are shown on the panels.

DISCUSSION

Effect of Water Content on Swelling Behavior and Solubility of Native Pea Starch. The swelling behavior of pea starch granules as a function of water content can be differentiated into three stages that occur progressively: very

limited swelling without leaching, incomplete swelling with some leaching, and complete swelling with continuous leaching (Figure 1). When the water:starch ratio is below 10:1 (water content of 92.0 wt %), pea starch granules can absorb all of the water available and no supernatant separates after centrifugation. Hence, we can conclude that swelling of pea starch granules below this water content is limited and no starch polymer molecules leach out of the swollen granules. At a water:starch ratio of 10:1 (water content of 92.0 wt %), pea starch polymer molecules were leached from the granules after the swelling power test, although the starch did not swell to the maximum value. With further increases in available water, starch granules can absorb more water and swell to a greater extent, as starch polymer molecules progressively leach out of the granules. The maximum swelling of starch granules was reached at a water:starch ratio of 20:1 (water content of 95.8 wt %), at which point starch solubility was still increasing. These observations from the present study are consistent with those of studies with cereal starches.²³

Swelling behavior of starch granules is predominantly a property of amylopectin molecules.^{21–23} When starch granules are heated in excess water, the linear amylose molecules tend to swell and then dissolve, whereas highly branched amylopectin molecules only swell to a maximum without subsequent dissolution. Such behavior of starch granules has been considered to be similar to the dissolution behavior of a mixture of linear and cross-linked polymers in a compatible solvent²¹ and is consistent with the observation that starch solubility continued to increase after the granules had reached maximum swelling.

Effect of Water Content on Thermal Transitions of Starch. In the present study, endotherm G broadened progressively and peak and conclusion temperatures and ΔH increased over the full range of water content. Above water:starch ratios of 10:1 to 15:1 (water content of 92.0 to 94.5 wt %), endotherm G became progressively broader and without a clearly identified end point, which is consistent with the starch granules approaching their maximum extent of swelling. Above this water content, not all of the available water can be absorbed into the granules and starch polymer molecules start to leach into the external free water. Hence, endotherm G in the DSC thermogram is proposed to represent the water absorption and swelling behavior of starch granules, with the end point of the endotherm G corresponding to the completion of water absorption and granule swelling. Differences in the conditions used to perform the swelling power and DSC experiments may account for leaching of starch molecules starting to occur before maximum swelling has been reached, although it is possible that the processes of swelling and leaching overlap to a small extent.

A key finding of the present study is that endotherm G broadened progressively with increasing water content in the high range of water content (≥ 70.7 wt %, water:starch ratio $\geq 2:1$). The peak temperature, conclusion temperature, and enthalpy of endotherm G increased up to 94.5% of water content (water:starch ratio: 15:1), coincident with continued swelling of granules. Increasing peak and conclusion temperatures with increasing water:starch ratios at high water content have been reported in the literature but were not discussed further.^{18,24–26}

Similarly, the increase in enthalpy of endotherm G with water content increasing has also been reported without explanation for wheat starch,^{18,24–26} rice starch,²⁷ potato starch,²⁸ legume starches,²⁹ and maize starch.³⁰ Our results and those of the other studies cited seem to be inconsistent with the general assumption that the single endotherm G observed at a water:starch ratio of

around 2:1 (water content of 70.7 wt %) represents the complete gelatinization behavior of starch granules. At the water:starch ratio of 2:1, only partial swelling of starch granules had occurred, as indicated by the swelling power values and SEM images showing clearly discernible granule outlines. Hence, endotherm G obtained at this water content actually reflects partial swelling behavior of starch granules rather than the complete gelatinization, as is often assumed. This interpretation is supported by previous findings that considerable residual crystallinity and lamellar structure remain at the end of this so-called gelatinization endotherm.^{19,31–33} At water:starch ratios up to about 15:1 (water content of 94.5 wt %), when all available water can be absorbed into starch granules, endotherm G had clearly an identified end point. Further increase in water content resulted in a very broad endotherm without a well-defined end point. The sharp endothermic trend followed by gradual heat flow is generally consistent with polymer dissolution theory,³⁴ in that most of the heat input is required for the disentanglement and swelling of polymer chains, with much less heat input required for their subsequent dissolution. The preferential swelling of mainly amylopectin followed by the partial leaching of mainly amylose during starch gelatinization fits this model.

Another interesting result from the present study is the increasing peak and conclusion temperatures as well as ΔH of endotherm G with increasing water content at low and intermediate water content (below 70.7%, water:starch ratio <2:1) as well as the single endotherm G observed at intermediate water content. In the range of low and intermediate water contents, the increase in enthalpy of endotherm G with increasing water content has also been observed with potato starch,^{14,24,28} wheat starch,^{18,35–39} maize starch,^{24,30,37} waxy maize starch,^{24,30,37} sago starch,⁴⁰ rice starch,^{27,41} and legume starches.^{24,29} At intermediate water content, two overlapping endotherms are often observed, as mentioned in the Introduction. The shape of DSC thermograms of starch–water systems is influenced by the experimental conditions. For example, endotherm G observed at high water:starch ratios does not always disappear as water content is decreased,^{18,32,35,42–45} and endotherm M1 observed at intermediate water level does not always appear, especially with rapid heating rates.^{27,45–47} Heating rate plays an important role in determining the shape of DSC thermograms of starch–water systems. At intermediate water level, increasing the heating rate can result in the gradual convergence of the endotherms G and M1 and eventual disappearance of endotherm M1.^{27,45–48} In addition to water content and heating rate, the reference (empty pan or pan with water or silicon oil), types of DSC pans, and moisture equilibration time could also influence the thermograms of starch–water systems.⁴⁹

Exothermic Transition in DSC Traces of Starch–Water System. The exothermic transition occurring between about 105 and 120 °C has been reported in several DSC studies of starch–water systems.^{32,33} This exothermic transition was attributed to the recrystallization of amylose–lipid complexes, by two possible mechanisms: (a) aggregation of leached amylose–lipid complexes present in native starch into V_h orthorhombic crystalline packing and (b) in situ crystallization of amylose in the presence of available endogenous lipids.³² Since no amylose leaches out of the granules at water:starch ratios of 1.5 to 2:1 (water content of 64.8 to 70.7 wt %), the crystallization of leached amylose–lipid complexes seems implausible. Hence, the annealing of amorphous type I amylose–lipid complexes according to mechanism (b) may contribute to the exothermic

transition during DCS heating. It should be noted that the gradual development of V -amylose pattern could also be caused by the gradual disappearance of predominant crystalline diffraction peaks of native starch crystals, which may well hide the presence of V -amylose contribution in native starch.⁵⁰ In the present study, the exothermic transition could not be related to the crystallization of amylose–lipid complexes due to the tiny amount of lipid (0.04–0.08%) present in pea starch⁴ and the similar DSC thermograms between native and defatted pea starch (data not shown). Hence, another explanation for the exothermic transition observed for all of the pea starch–water systems, namely, that it represents the phase transition of water from vapor to liquid, is reasonable, given that it occurs in DSC pans that contain only water.²¹

What Is Starch Gelatinization? A long-standing problem in starch science has been to gain a clear understanding of the relationship between multiple endothermic transitions measured by DSC and starch gelatinization. Starch gelatinization has been defined as the “collapse of molecular orders within the starch granule manifested in irreversible changes in properties such as granule swelling, native crystallite melting, loss of birefringence, and starch solubilisation”.¹⁰ From this definition, three distinct changes can be identified in the starch gelatinization process: granule swelling, disruption of ordered structures (crystalline and molecular), and solubilization of starch molecules. If the definition of starch gelatinization includes solubilization of starch polymers, endotherm G obtained at water contents below which starch polymers begin to leach out of granules should not be considered as representing complete gelatinization. On the other hand, complete disruption of starch structures could occur upon heating to the end of the endotherm G at certain water contents, even though no starch polymers are leached out. In this case, starch gelatinization should be considered as being incomplete according to the above definition.

In summary, the present study answers the question why at a water:starch ratio of 1.5:1 or 2:1 (water content of 64.8 or 70.7 wt %) there are still considerable residual crystallinity and lamellar structure at the end of the so-called complete gelatinization transition. At a water:starch ratio of 1.5 or 2:1, swelling of starch granules is very incomplete and no amylose leaches out of the granules. Endotherm G broadened progressively with increasing water content over the full range of water content. The gradual transition from a sharply defined to broad endotherm G reflects the changes from very limited swelling to maximum swelling of starch granules (mainly amylopectin molecules) and partial dissolution of starch polymers (mainly amylose molecules). The high-temperature exothermic transition observed in the present study reflects the phase transition of water from vapor to liquid, although for normal cereal starches it could also represent the phase transition of amylose–lipid complexes.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shujun.wang@sydney.edu.au; edwinwa@hotmail.com (S.W.); les.copeland@sydney.edu.au (L.C.).

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The authors declare no competing financial interest.

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