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Studies on the starch–water interactions between partially gelatinized corn starch and water during gelatinization

Zong-qiang Fu[a,1], Li-jun Wang[b,1], Hui Zou[c], Dong Li[a,*], Benu Adhikari[d]

[a] College of Engineering, China Agricultural University, P.O. Box 50, 17 Qinghua Donglu, Beijing 100083, China
[b] College of Food Science and Nutritional Engineering, Beijing Key Laboratory of Functional Food from Plant Resources, China Agricultural University, Beijing, China
[c] College of Science, China Agricultural University, Beijing, China
[d] School of Applied Sciences, RMIT University, City Campus, Melbourne, VIC 3001, Australia

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ABSTRACT

The effect of moisture content on the interactions between water and partially gelatinized starch during gelatinization process was investigated. The interactions were probed using differential scanning calorimetry (DSC). The starch samples were partially gelatinized at 25 °C (*S25*), 64 °C (*S64*), 68 °C (*S68*) and 70 °C (*S70*) and the moisture contents were varied from 25% to 78% (w/w). The G endotherm was not observed and only the M1 endotherm was observed in *S64*, *S68* and *S70* in the entire moisture content range. The G endotherm was not observed and only the M1 endotherm was observed at higher peak temperature in *S25* when the moisture content was below 30% (w/w). The melting temperature of M2 endotherm in *S70* was the highest among all the samples tested in the entire moisture content range. At water content > 30% (w/w), *S68* and *S70* had lower amount of unfreezable water, while *S64* had higher amount of unfreezable water.

1. Introduction

Starch is a renewable biomass and it has been commonly used in food, chemical, textile, papermaking, medicine and many other industries (Hoover, Hughes, Chung, & Liu, 2010). Partial gelatinization of starch commonly occurs due to high hydrostatic pressure, parboiling of rice, and drying of moist cereals because of exposure to heat, high humidity and mechanical stress in production processes. Because of very poor solubility of native starch in water at ambient temperature, gelatinization of starch is essential in most production processes. The moisture content within the starch granules, the ease or difficulty with which the moisture diffuses within the starch granules and temperature of the starch–water suspension or treatment temperature determine the gelatinization behavior of starch (Hoover, 2001). Hence, a proper understanding of the role of water and its interplay with starch during thermal treatment is essential in the industrial processing and subsequent application of starch and starch-containing materials (Rolée, Chiotelli, & Meste, 2002).

Heating of an aqueous starch suspension induces a number of structural changes in the starch granules during gelatinization (Orlowska & Randzio, 2010). Differential scanning calorimetry (DSC) is now commonly regarded as one of the most suitable methods for quantifying the endothermic behavior of starch during gelatinization (Campanha & Franco, 2011; Patel and Seetharaman, 2010; Thirathumthavorn & Trisuth, 2008). When starch is heated in the presence of excess water, a single symmetric endotherm, usually denoted as G, is observed in the lower temperature region. As the amount of available water decreases, a biphasic endotherm with a tailing shoulder (M1) is observed. When water content is reduced further, the first endotherm (G) fades out and it is only possible to observe the second endotherm (M1) and the temperature shifts toward a higher region. Yet another endotherm appears at higher temperatures (M2) induced by the melting of the amylose–lipid complex (Svensson & Eliasson, 1995). Several theories have been proposed in order to explain the mechanism of starch gelatinization; however, no model has been generally or universally accepted until now (Karapantsios, Sakonidou, & Raphaelides, 2002). Starch samples having different crystalline patterns and granular structures exhibit different gelatinization behavior (Crochet and Beauxis, 2005; Jyothi, Sajeev, & Sreekumar, 2011; Tran, Piyachomkwan, & Sriroth, 2007). The understanding of the influence of the amorphous and crystalline structures and the overall granular form on the gelatinization of starch granule is a complex problem. The complexity is induced by many factors such as the interaction of water both at the interior and exterior of the granule and the role of the amorphous and crystalline domains

* Corresponding author. Tel.: +86 10 62737351; fax: +86 10 62737351.
E-mail address: dongli@cau.edu.cn (D. Li).
[1] These authors contributed equally to this work.

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within the granule (Crochet and Beauxis, 2005). Hence, it would be of practical importance to study the gelatinization of starch samples having different microstructure and which have undergone partial gelatinization. Such study can also provide better understanding of the mechanism involved in the gelatinization of starch.

Interaction between starch and water is one of the most important factors that determines the physicochemical properties of starch. The interaction between starch and water can be monitored by following the change in physical state of water within the starch (Tananuwong & Reid, 2004). The physical state of water in starch can be described as unfreezable and freezable water (Li, Dickinson, & Chinachoti, 1998). The unfreezable water is strongly bound to starch molecules and it is responsible for the stability of a starch-based product (Charles, Kao, & Huang, 2003). The water binding capacity has an important relationship with the microstructure of starch granules. Chung, Lee, & Lim (2002) studied the difference in the water binding capacity between native and gelatinized rice starch. They found that the freezable water was reduced by gelatinization due to a greater proportion of amorphous chains to interact with water. Many researchers have detected the freezable water content (Brouillet-Fourmann, Carrot, Lacabanne, Mignard, & Samouillan, 2002; Li et al., 1998; Zhong & Sun, 2005). However, there is still little insight on the interactions between water and partially gelatinized starch having different microstructure.

In these contexts, the main objective of this work was to study the effect of partial gelatinization of starch on starch–water interactions during gelatinization. The DSC was used to probe these interactions. The gelatinization thermograms were determined and the amount of unfreezable water was calculated. Information obtained from this study would provide better understanding of the mechanism of starch gelatinization, especially when it is partially gelatinized.

2. Materials and methods

2.1. Materials

Native corn starch was purchased from Hebei Zhangjiakou Yujin Food Co., Ltd. (Hebei, China). Its moisture content was 10% (w/w). The lipid content in this corn starch varied between 0.15% (w/w) and 0.20% (w/w) (as per the certificate of analysis provided by the supplier, Hebei Zhangjiakou Yujin Food Co., Ltd. (Hebei, China)).

Partially gelatinized starch *S64*, *S68* and *S70* were prepared by using the method proposed by Fu, Wang, Li, & Adhikari (2012). Corn starch dispersions (10.0%, w/w) were prepared by adding 20.0 g of pre-dried corn starch into deionized water at 24 ± 1 °C. Each batch of corn starch dispersion was thoroughly stirred at 300 rpm (in beakers) for 15 min using a thermostated water bath at 64 °C, 68 °C and 70 °C. After being preheated these partially gelatinized starch dispersions were spray dried using a bench-top spray drier (GPW120-II, Shandong Tianli Drying Equipment Inc., China). The feed rate, inlet temperature, flow rate of the air and exhaust aspiration level used in the spray drying process were maintained at 7.2 ml/min, 200 °C, 0.375 m^3/h and 95%, respectively. Partially gelatinized starch *S25* was used as a control and it was prepared by stirring corn starch dispersion for 15 min at room temperature followed by spray drying.

The degree of gelatinization of *S25*, *S64*, *S68* and *S70* samples was determined as previously reported (Fu et al., 2012). Distilled water (7.5 μl) was added with a microsyringe into partially gelatinized starch sample (2.5 mg) in an aluminum pan. This mixture of water and starch sample was then immediately hermetically sealed with an aluminum lid. Each sealed sample was equilibrated for about 3 h at ambient temperature before thermally scanning using a differential scanning calorimeter (DSC-Q10, TA Instruments, New Castle, USA). In these DSC tests, these samples were heated from 20 °C to 120 °C with a heating rate of 10 °C/min. The gelatinization enthalpy (ΔH_{gel}) was calculated. The degree of gelatinization (GD) was determined using Eq. (1) given below (Błaszczak et al., 2007).

$$GD = \{(\Delta H_{ns} - \Delta H_{it})\Delta H_{ns}^{-1}\} \times 100\% \quad (1)$$

where ΔH_{ns} and ΔH_{ts} are the melting enthalpies of native and modified starches, respectively.

2.2. The differential scanning calorimetry (DSC) analysis

The DSC measurements were performed using the same instrument as mentioned in Section 2.1 above. The DSC analyzer was calibrated using indium (melting point = 156.6 °C, melting enthalpy = 26.59 J/g) and an empty aluminum pan was used as a reference. Samples for DSC analysis were prepared using procedures similar to those described by Jang and Pyun (1996) and Maaruf, Che Man, Asbi, Junainah, and Kennedy (2001). Partially gelatinized starch samples (2.0–3.0 mg) were prepared in aluminum pans. Distilled water was added with a microsyringe into starch until all the granules were wetted and uniformly settled at the bottom of the pan. Filled pans were left to air dry until the contents reached the desired moisture level (25, 30, 40, 50, 60 and 78%, w/w) and then immediately sealed with an aluminum lid. Each sealed sample was equilibrated for 1 h at ambient temperature before thermally scanning in the DSC. The samples were then heated from −60 °C to 200 °C at 10 °C/min. The peak (T_p) of the gelatinization temperature and melting temperature of amylose–lipid complexes were quantified. The enthalpy of the frozen water of the samples was recorded.

Unfreezable water was determined using the DSC data following the method described by Ross (1978) and Zhong and Sun (2000). The same calorimetric measurements were carried out for pure water. The melting enthalpy of pure water was obtained and used as the reference enthalpy. The amount of unfreezable water was calculated using Eq. (2) given below:

$$M = \frac{m_m}{m_s} - \frac{\Delta H_1}{\Delta H_2} \quad (2)$$

where M (g water/g dry starch) is the amount of unfreezable water, m_m (g water) and m_s (g dry starch) are the amounts of moisture content and dry starch in samples, respectively. ΔH_1 (J/g dry starch) and ΔH_2 (J/g water) are the ice melting enthalpies of moisture in starch samples and pure water, respectively.

2.3. Statistical analyses

All the tests were carried out at least in triplicate and results are reported as the mean and standard derivation of these measurements. Duncan's multiple comparison tests were carried out to determine the significant effect of heating processes on the properties of starch samples at 95% ($P < 0.05$) confidence level using the SPSS statistical package (LEAD Technologies, US).

3. Results and discussion

3.1. Thermal endotherms of starch at different moisture contents

The degree of gelatinization of *S25*, *S64*, *S68* and *S70* samples was calculated and was found to be 32.30%, 47.75%, 69.40% and 96.78%, respectively. The DSC thermograms of *S25*, *S64*, *S68* and *S70* starch samples having moisture contents between 25% and 78% (w/w) are presented in Fig. 1. As can be seen in Fig. 1A, the G endotherm is observed in the case of *S25* starch sample at moisture contents higher than 40% (w/w) and this disappeared at moisture contents lower than 30% (w/w). However, G endotherm

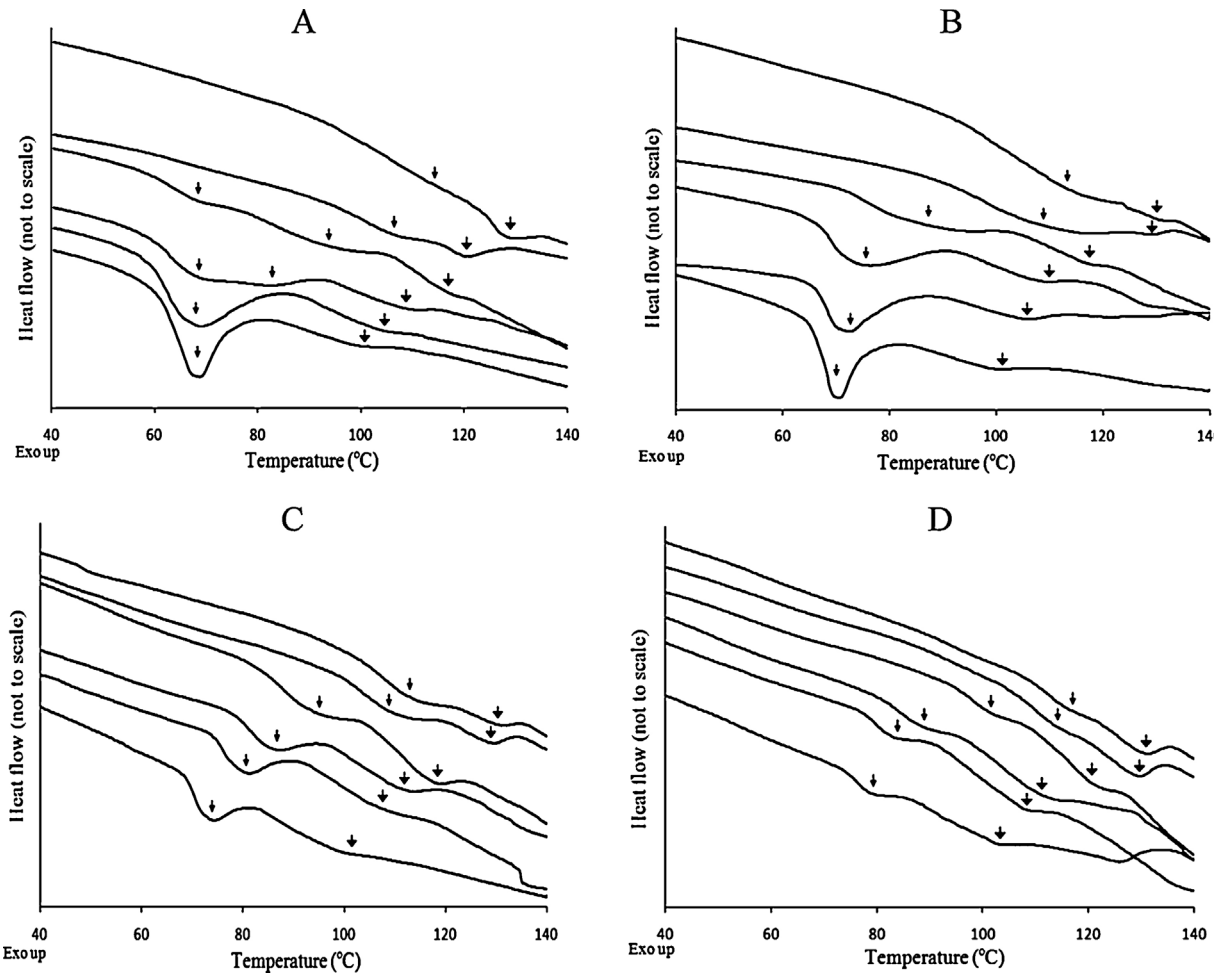

Fig. 1. The DSC thermograms of G, M1 and M2 endotherm of partially gelatinized starch having different moisture contents: (A) *S25*; (B) *S64*; (C) *S68*; (D) *S70*. (25, 30, 40, 50, 60 and 78% (w/w) from top to bottom for all the samples).

was reportedly observed in wheat starch when the moisture content was as low as 25% (w/w) (Day, Fayet, & Homer, 2013). It appears that the moisture contents at which the G endotherm can be observed depends on the nature (source) of starch used. When the moisture contents are 40% and 50% (w/w), a new endotherm (M1 endotherm) has appeared at temperatures higher than the gelatinization temperature of the G endotherm. Interestingly, only one endotherm has appeared having peak temperature less than 100 °C in the case of *S64*, *S68* and *S70* starch samples in the moisture content range of 40–78% (w/w). As the moisture content decreased from 30% to 25% (w/w), this endotherm moved to a higher peak temperature which was higher than 110 °C. Tananuwong and Reid (2004) believed that the disappearance of the M1 endotherm at the excess water could be considered as the convolution of the M1 with the G peak. They found that stopping the DSC scan near the peak temperature of the G endotherm is sufficient to eliminate the G endotherm and claimed that the small endotherm in the rescanned thermogram is the M1 endotherm. The peak temperature of G endotherm of native corn starch samples used in this study is 68.76 °C (Fu et al., 2012). Sample *S70* was gelatinized at 70 °C which is higher than the peak temperature of G endotherm (68.76 °C). Because of this reason, the first endotherm presented in Fig. 1D (the DSC thermogram of *S70*) is the M1 endotherm. *S64* and *S68* were gelatinized at the temperatures below the peak temperature of G endotherm (68.76 °C). Sample *S25* was prepared by stirring starch dispersion at room temperature followed by spray drying. The degree of gelatinization of *S25* is 32.30% which means that the starch dispersion was partially gelatinized during the spray drying process. *S64* and *S68* were gelatinized near the peak temperature of G endotherm and these samples were further gelatinized during the spray drying process. It appears that these two gelatinization processes have eliminated the G endotherm in *S64* and *S68* samples. It can be seen in Fig. 1B–D that the gelatinization behavior of *S64*, *S68* and *S70* is similar. Because of this reason the first endotherm presented in Fig. 1B–D can be assigned to be M1 endotherm.

Fig. 2 shows the endothermic peaks of G and M1 endotherms in the case of *S25*, *S64*, *S68* and *S70* starch samples at moisture contents ranging from 25% to 78% (w/w). As can be seen from this figure, the peak gelatinization temperature of G endotherm has remained the same in the case of *S25* within the moisture content range of 40–78% (w/w). As the moisture contents decreased, the melting temperature of M1 endotherm shifted toward the higher temperature for all the starch samples. We wish to point out here that the melting temperature of M1 in the case of *S25* is higher than that of *S64* within the moisture content range of 40–50% (w/w) even though there is also an endothermic peak of G endotherm in the case of *S25*. As the moisture contents decreased to a range of 25–30% (w/w), there is no significant difference ($P > 0.05$) in the melting temperature of M1 endotherms of *S25*, *S64* and *S68*. The melting temperature of M1 in the case of *S70* is always higher than those of *S25*, *S64* and *S68* in the moisture content range of 25–78% (w/w).

As can be seen in Fig. 1, there is also an endothermic peak above 100 °C which is due to melting of the amylose–lipid complexes (M2 endotherm). The melting temperatures of M2 endotherms for all

Table 1
The peak melting temperatures (T_p) of amylose–lipid complex (M2 endotherm) of partially gelatinized starch samples at different moisture contents (w/w).

Overall moisture content (%)	T_p of amylose–lipid complex (M2 endotherm, °C)			
	S25	*S64*	*S68*	*S70*
25	128.70 ± 0.53[a]	130.33 ± 0.47[b]	130.24 ± 1.14[b]	130.67 ± 0.62[b]
30	120.50 ± 1.04[a]	129.12 ± 0.19[b]	129.08 ± 0.68[b]	129.25 ± 0.48[b]
40	116.49 ± 0.38[a]	116.85 ± 0.39[a]	117.38 ± 0.38[a]	120.68 ± 0.65[b]
50	109.26 ± 0.46[a]	109.51 ± 0.40[a]	110.77 ± 0.52[b]	110.68 ± 0.48[b]
60	104.65 ± 0.44[a]	105.24 ± 0.73[a]	105.46 ± 0.49[a]	107.60 ± 0.54[b]
78	100.39 ± 0.33[a]	100.78 ± 0.38[a]	101.07 ± 0.73[a]	103.09 ± 0.77[b]

Values are mean ± standard deviation ($n = 3$). Values in the same rows having different letter in the superscripts are significantly different ($P < 0.05$).

starch samples shifted toward the higher temperatures when the moisture contents decreased from 78% to 25% (w/w). The melting temperatures of M2 endotherms of all the starch samples are presented in Table 1. The melting temperature of M2 endotherm of *S70* is higher than those of *S25*, *S64* and *S68* within the moisture content range of 40–78% (w/w). As the moisture contents decreased to 30% (w/w), there is no significant difference ($P > 0.05$) in the melting temperatures of M2 endotherms in *S64*, *S68* and *S70*.

Starch undergoes a series of thermal transitions, including gelatinization transition of starch (G endotherm), melting of starch crystals (M1 endotherm) and melting of the amylose–lipid complexes (M2 endotherm) when heated in the presence of water. The nature of these thermal transitions depends on the composition of starch, moisture content and thermal history (Zhong & Sun, 2005).

There are three classical models describing or explaining the nature of the G and the M1 endotherms in limited water (Tananuwong & Reid, 2004). In the first model (Donovan, 1979) the first peak (G endotherm) is considered to be induced by the swelling of amorphous regions of starch granules. This swelling process 'strips' the amorphous component from the surface of crystallites. The crystallites remaining after dissolution of the amorphous region are melted at higher temperatures which results into the M1 endotherm. The second model (Evans & Haisman, 1982) suggests that the G endotherm represents the melting of the less perfect (less stable) crystallites, while the M1 endotherm represents the melting of the more perfect (more stable) crystallites. The third model (Slade & Levine, 1988) suggests that the G endotherm primarily reflects the plasticization of amorphous region, while the M1 endotherm reflects the non-equilibrium melting of crystallites. A newly proposed model (Waigh, Gidley, Komanshek, & Donald, 2000) considers that the G endotherm is a result of the helix–helix dissociation, while the M1 endotherm reflects the helix–coil transition of amylopectin helices.

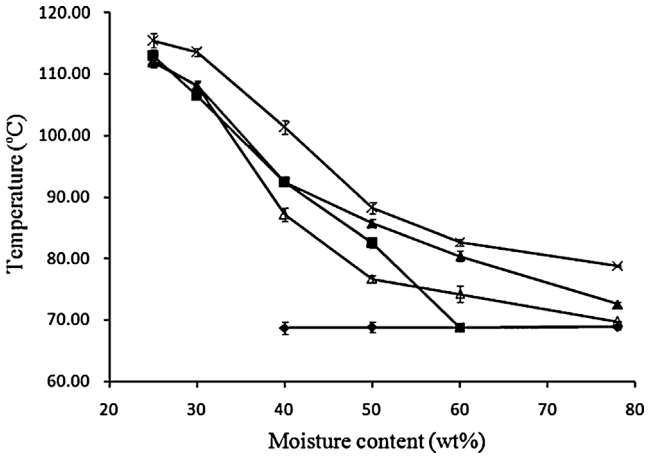

Fig. 2. Thermal properties of partially gelatinized starch against moisture content: the gelatinization (G endotherm) temperature of *S25* (♦); the melting (M1 endotherm) temperature of *S25* (■), *S64* (△), *S68* (▲) and *S70* (×).

In our experiments we only observed M1 endotherms in the case of *S64*, *S68* and *S70* samples. These results cannot be explained by the first (Donovan, 1979), third (Slade & Levine, 1988) and the newly proposed model (Waigh et al., 2000). According to the second model (Evans & Haisman, 1982), a single gelatinization peak (G endothermic) is observed when each granule absorbs water when the supply of water is not restricted. If the supply of water is limited, then the melting process becomes competitive. The granules which contain the least stable crystallites will melt first (G endotherm) and absorb free water from the ungelatinized granules. Consequently, the water content of the ungelatinized granules decreases which results into increase in the melting point (M1 endotherm). As a result, two endotherms will be observed each corresponding to different type of melting. This model can also help explain the fact that the melting temperature of M1 in the case of *S25* starch samples is higher than that of *S64* starch sample in the moisture contents range of 40–50% (w/w). However, the melting temperature of M1 in the case of *S68* and *S70* samples is higher than that of *S25* sample in the moisture contents range of 40–50% (w/w). This could be due to the fact that the crystallites which remained in *S68* and *S70*, after this higher level of gelatinization, were more stable. When the water content is further reduced, there is no enough free water to facilitate the gelatinization of the less stable crystallites. Because of the restricted supply of water, the first endotherm (G endotherm) does not appear and the second peak (M1 endotherm) moves to higher temperatures in *S25* sample. However, the *S64*, *S68* and *S70* starch samples have been preheated during the process of preparing partially gelatinized starch. The less stable crystallites have been gelatinized in that process because the gelatinization enthalpy of these samples is lower than that of native corn starch (Fu et al., 2012). As a consequence, no G endotherms were observed in *S64*, *S68* and *S70* starch samples.

The moisture contents not only affected the G and M1 endotherms, but also affected the melting temperature of M2 endotherm. As the moisture content increased from 25% to 78% (w/w), the plasticization effect of water lowered the melting temperatures of amylose–lipid complexes (M2 endotherm) (Zhong & Sun, 2005). The amylose–lipid complexes are formed during the gelatinization of starch in the presence of lipids (naturally occurring or externally introduced lipids) (Eliasson, 1985). As can be seen in Fig. 3, the melting enthalpy of amylose–lipid complexes of the *S70* is the highest compared to other samples when the moisture content is sufficiently high (78%, w/w). This observation indicates that higher extent of amylose–lipid complexes is formed when the partially gelatinized starch samples is prepared at higher temperature. Bhatnagar and Hanna (1994) found that native corn starch extruded without added lipid showed as much as 3% complexing due to the formation of complex between native lipids present in the commercial starches. These different amylose–lipid complexes are expected to melt at different temperatures due to difference in their nature (Tufvesson, Wahlgren, & Eliasson, 2003). However,

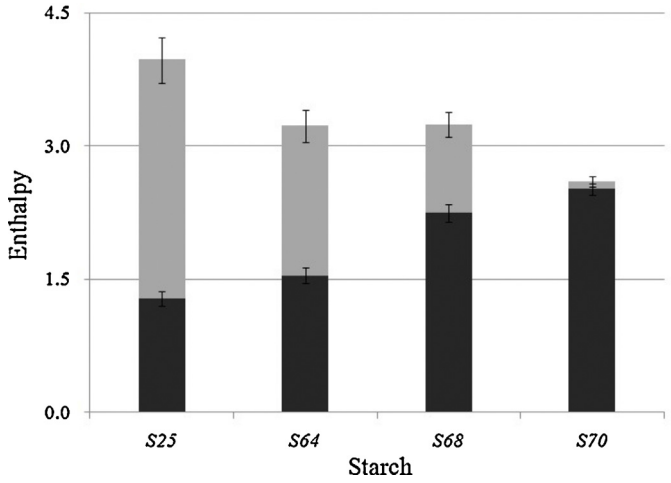

Fig. 3. The melting enthalpy of amylose–lipid complex (M2 endotherm) of partially gelatinized starch at the moisture content of 78% (w/w): J/g starch (■); J/g gelatinized starch (■).

the melting enthalpy (J/g gelatinized starch) of amylose–lipid complexes decreased as the degree of gelatinization of starch samples increased which means that the increase of amylose–lipid complexes has limitations.

3.2. Determination of unfreezable and freezable water

The amount or percentage of unfreezable water was calculated using the enthalpy of ice melting (Table 2). There was no significant difference ($P > 0.05$) in the amount of unfreezable water in these samples when the moisture content was 25% (w/w). As the moisture content increased to 30% (w/w), the amount of unfreezable water in *S70* was 0.347 ± 0.006 which was lower than that of *S64*. The amount of unfreezable water in *S64* was the highest among the samples when the moisture content was above 30% (w/w).

In a starch–water mixture, hydration of starch granules occurs toward the surface or outer part of the native starch granules (Wolfe, Bryant, & Koster, 2002). Water molecules in the hydrated part of the starch remain unfrozen at subzero temperature due to starch–water interactions (Tananuwong & Reid, 2004). As the number of available water binding sites is different in differently treated starch samples, this gives rise to the difference in the amount of unfreezable water content. The binding sites are considered to be the hydroxyl groups and the inter-glucose oxygen atom. The availability of these sites to interact with water depends on the structural (molecular arrangement, amorphous and crystalline domains) and the compositional (mainly amylose and amylopectin) differences of starches (Wootton and Bamunuarachchi, 1978). Water molecules can establish several hydrogen bonds with polar hydroxyl groups of starch and the number of hydrogen bonds increases with increase in the humidity ratio to a certain limit relative humidity. However, the total number of bonds between water and starch can only be finite and is usually increases until finite (mono molecular layers to few layers) layers of water molecules surround the starch molecules (Brouillet-Fourmann et al., 2002). As a result, the amount of unfreezable water (on solid starch basis) increased rapidly in all the samples when the moisture content increased from 25% to 30% (w/w) and subsequently leveled off. As the moisture content increased from 50% to 78% (w/w), the amount of unfreezable water of *S64* was higher than that of *S25*. This observation indicates that better hydration (better starch–water interaction) occurs in samples partially gelatinized at 64 °C than partially gelatinized at 25 °C. This is expected because much higher degree of gelatinization has occurred in *S64* than in *S25*. The gelatinization process causes disruption of the weak associative bonds in the amorphous region of the granules enabling increased hydration of starch molecules (Wootton & Bamunuarachchi, 1978). Tananuwong and Reid (2004) found that the amount of unfreezable water increased when a native starch was heated. These authors also found that the amount of unfreezable water in fully gelatinized starch samples was higher than that in partially gelatinized starch samples. Even though the degree of gelatinization of *S68* and *S70* was higher than those of *S25* and *S64*, the amount of unfreezable water in these samples is lower than those of *S25* and *S64*. This may be due to the fact that the amount of amylose–lipid complexes in *S68* and *S70* was higher than that for *S25* and *S64* (Fig. 3). Hoover and Hadziyev (1981) reported that the formation of amylose–lipid complexes resulted into significant decrease in the amount of unfreezable water content. These authors attributed the decrease in the unfreezable water content to the decrease in water binding sites due to starch–lipid interaction.

Table 2
The amount of unfreezable water in partially gelatinized starch samples having different moisture content.

Moisture content (%)	Unfreezable water ($\times 10^{-2}$ g water/g dry starch)			
	S25	*S64*	*S68*	*S70*
25	29.2 ± 0.4^{A}	29.8 ± 0.5^{A}	29.0 ± 0.2^{A}	29.5 ± 0.6^{A}
30	36.0 ± 1.0^{AB}	37.3 ± 1.8^{A}	35.7 ± 0.3^{AB}	34.7 ± 0.6^{B}
40	38.1 ± 0.5^{AB}	39.2 ± 1.0^{A}	37.8 ± 0.4^{B}	34.0 ± 0.6^{C}
50	36.0 ± 1.1^{B}	38.1 ± 1.1^{A}	36.0 ± 1.3^{B}	33.5 ± 0.5^{C}
60	38.2 ± 2.8^{AB}	40.2 ± 3.0^{A}	36.6 ± 2.8^{AB}	34.0 ± 0.6^{B}
78	36.3 ± 1.5^{B}	39.4 ± 1.3^{A}	35.8 ± 0.9^{B}	33.3 ± 1.5^{C}

Values are mean ± standard deviation ($n = 3$). Values in the same line followed by different lowercase (capital) letters in the superscript are significantly different ($P < 0.05$).

4. Conclusions

The effect of moisture content (25–78%, w/w) on the peak melting temperature of starch, amount of unfreezable water, peak melting temperature of amylose–lipid complex, melting enthalpy of amylose–lipid complex were investigated. When the moisture content was higher than 60% (w/w), there was only G endotherm in the case of *S25* starch sample. When the moisture content decreased, M1 endotherm was observed at higher peak temperature. The G endotherm was not observed when the moisture content was below 40% (w/w). There was no G endotherm and only M1 endotherm was observed in the case of *S64*, *S68* and *S70* starch samples in the entire moisture content range of 25–78% (w/w). The peak gelatinization temperature of G endotherm did not change in the case of *S25* starch sample, while the melting temperatures of M1 endotherm shifted toward higher temperatures in all the starch samples when the moisture contents decreased. The melting temperature of M2 endotherm of *S70* was higher than those of *S25*, *S64* and *S68* starch samples within the moisture content range of 40–78% (w/w). The melting enthalpies of M2 endotherm of *S68* and *S70* were higher than those of *S25* and *S64* at the highest moisture content (78%, w/w) tested.

The amount of unfreezable water was not different ($P > 0.05$) in all the starch samples at the moisture content of 25% (w/w). As the moisture content increased to 40% (w/w), the percentage of unfreezable water in the case of *S70* was the lowest. At the moisture contents > 40% (w/w) the amount of unfreezable water in *S25* and *S64* samples was higher than those in *S68* and *S70* samples.

Acknowledgments

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