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Phase transitions of maize starches with different amylose contents in glycerol–water systems

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ABSTRACT

The phase transitions of maize starches with different amylose contents (3.4–82.9%) were systematically studied by DSC with stainless steel high-pressure pan under temperature scanning from 30 up to 200 °C. The results show that the distinct pattern of multiphase transitions of maize starch was not only determined by the amylose content, but also by glycerol–water mixture content (50 and 70%) and glycerol/water ratio (0/100, 10/90, 50/50, 90/10, and 100/0). Moreover, a big exothermic transition could be observed within the range of about 95–135 °C for all four maize starches mixed with pure glycerol, which was mainly due to the glycerol–starch –OH binding reaction and was greatly affected by the granular structure and molecular characteristics of maize starch (starch type). It has been shown that high temperature, adequacy of glycerol, and long storage time all favour the reaction of glycerol with starch molecules.

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1. Introduction

Starch is a natural polymer with particular properties unlike those of traditional polymers. As a heterogeneous material: it has macromolecular structures bound in a granular superstructure; it normally has both linear (amylose) and branched (amylopectin) molecules; and it contains both amorphous and crystalline regions within its granules (French, 1984). When raw starch granules are heated in water, their semi-crystalline nature is gradually eliminated, resulting in structural breakdown and starch polymer dispersion in solution. This heat induced starch granular breakdown or the phase transition from an ordered granular structure into a disordered state in water is known as “gelatinisation” (Ratnayake & Jackson, 2008). The gelatinisation process is essential in that it determines the proper conversion of starch in the processing of foods and emerging biodegradable starch-based materials.

Since Stevens and Elton (1971) first utilised differential scanning calorimetry (DSC) to measure gelatinisation and retrogradation of starch in 1971, it has become widely accepted as one of the most suitable techniques for the evaluation of starch thermal behaviours (Liu, Xie, Yu, Chen, & Li, 2009). Many studies have shown that starch with water could experience complex multiphase transitions during DSC temperature scanning. For starch with excess water, a single gelatinisation endotherm (usually denoted G) can be usually observed in the low temperature range (54–73 °C) (Donovan, 1979; Evans & Haisman, 1982; Russell, 1987; Wootton & Bamunuarachchi, 1979; Zobel, 1984). By reducing the water content (<64%) in starch, another endotherm, M1, which occurs at higher temperature and overlaps with G transition, can be observed (Donovan, 1979; Russell, 1987). Based on the assumption that amylopectin molecules have a structure similar to that of a branched side-chain liquid-crystalline polymer of a smectic or nematic type, Waigh, Gidley, Komanshek, and Donald (2000) proposed that the first stage of gelatinisation (G) is related to the transition from smectic to nematic phase for B-type starches, and from smectic to isotropic phase for A-type starches. Swelling of the starch granules begins after completion of the first stage of gelatinisation. Further heating leads to the helix–coil transition associated with the unwinding of amylopectin double helices and loss of the starch granular birefringence, which is reflected as M1 endotherm in DSC results. However, at excess water conditions, both transitions involved in the two-stage mechanism occur either at the same temperature range, or the first stage of gelatinisation is a slow process that overlaps with the fast helix–coil transition. As a result, a single endothermic effect was observed on the calorimetrical traces. Besides G and M1, more endothermic peaks have also been observed at even higher temperature: M2, considered to be the phase transition within an amylose–lipid complex (Biladeris,

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Abbreviations: T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔT, temperature range, i.e. $T_c - T_o$; ΔH, enthalpy.

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Page, Slade, & Sirett, 1985; Jovanovich & Añón, 1999; Raphaelides & Karkalas, 1988) and Z, attributed to the annealing of amylopectin crystallites during heating (Maurice, Slade, Sirett, & Page, 1985; Russell, 1987). Furthermore, a weak exothermic process has been reported between two endothermic peaks at low temperature scanning rates (Randzio, Flis-Kabulska, & Grolier, 2002; Vermeylen et al., 2006). This exothermic effect has been associated with the formation of novel hydrogen bonds with added water between unwounded amylopectin helices (Waigh et al., 2000) or between amylose and outer branches of unwounded amylopectin helices (Vermeylen et al., 2006).

Among a variety of starch cultivars, maize starch has been of particular scientific interest since this kind of starch with different amylose/amylopectin ratios can be directly provided by the nature/agriculture. Much work has been done on the thermal transitions of various maize starches and it has been found that the endothermic pattern can be greatly affected by the amylose content (Russell, 1987; Shogren, 1992; Stevens & Elton, 1971; Takahashi, Shiraai, & Wada, 1982; Von Eberstein, Hopcke, Konieczny-Janda, & Stute, 1980). By utilising a new DSC technique using high pressure stainless-steel pans, which allows temperature scanning of starch with high water content (~75%) and at high temperature (~360 °C) without loss of moisture, Liu, Yu, Xie, and Chen (2006) in our group systematically studied the phase transitions of maize starches with different amylose/amylopectin ratios. They found that the number of endotherms and enthalpies depended on the amylose/amylopectin ratio and the moisture and lipid contents, and the gelatinisation enthalpy of the amylopectin-rich starch was higher than that of the amylose-rich starch.

During the processing of starch-based foods and the preparation of thermoplastic starch (TPS), glycerol is frequently utilised with water or alone as a plasticiser due to its abilities of lowering mass viscosity during melting and improving the strength and flexibility of final products (Liu et al., 2009). Besides, the low vapour pressure of glycerol makes the processing of starch more stable than pure water. There have been limited reports dealing with the thermal behaviours of maize starch in the presence of glycerol. For example, using simultaneous SAXS and WAXS and DSC to study the gelatinisation of waxy starch, Perry and Donald (2000, 2002) concluded that the glycerol concentration will not change the temperature range and enthalpy of gelatinisation peak although the endotherm is systematically shifted upwards; only the properties of the solution as a whole are of importance in determining gelatinisation behaviour. However, in a study of the gelatinisation of maize starches with different amylose contents over a range of water–glycerol concentrations, Tan, Wee, Sopade, and Halley (2004) revealed that the addition of glycerol increased the gelatinisation onset temperature with an extent that depended on the water content in the system; besides, the addition of glycerol promoted starch gelatinisation at low water content (0.4 g water/g dry starch) and the enthalpy of gelatinisation varied with glycerol concentration (0.73–19.61 J/g dry starch) depending on the water content and starch type. All of the past studies, however, concentrated on the single gelatinisation transition (G) with scanning temperature up to 150 °C at most. Since various, especially high-amylose, maize starches were widely used in the preparation of biodegradable starch-based materials in the presence of glycerol using various processing techniques at high temperature (~200 °C) (Liu et al., 2009), the understanding of the thermal multiphase transitions of maize starches under such conditions is of obvious interest.

The present work aimed to systematically study the phase transitions of maize starches with different amylose contents during scanning up to 200 °C as functions of glycerol–water mixture content and glycerol/water ratio using DSC. The effect of storage time on the thermal behaviours of maize starches in pure glycerol was also investigated. The role of glycerol in the phase transitions of starch will be discussed here.

2. Experimental

2.1. Materials

Four commercial maize starches with different amylose contents (waxy, 3.4%; regular, 24.4%; Gelose 50, 56.6%; and Gelose 80, 82.9%) were obtained from Penford Australia Limited (Lane Cove, NSW, Australia) and were used as model materials in the experimental work. Their amylose contents were determined previously (Tan, Flanagan, Halley, Whittaker, & Gidley, 2007). The original moisture contents of these starches were 9–11%. Before use, starch samples were dried in a vacuum oven at 60 °C for first 24 h and then at 110 °C for another 24 h to the moisture content level less than 1% (as determined by the weight loss). Glycerol, purchased from Taishan Yueqiao Reagent Plastic Co., Ltd. (China), was analytical grade at 99.5% purity.

2.2. Sample preparation

Glycerol was mixed with distilled water in various ratios: 0/100, 10/90, 50/50, 90/10, and 100/0 (glycerol/water, w/w). Then, dried starch samples were mixed with the glycerol–water mixture at specific percentages (70% and 50%, dry basis) in a glass vial, and sealed and stored for at least 24 h for the equilibrium of the solvents. After that, the samples (about 7 mg, dry basis) were accurately weighed in high-pressure stainless steel pans (PerkinElmer No.: B0182901) for DSC measurements.

2.3. Differential scanning calorimetry (DSC)

A PerkinElmer Diamond DSC with an internal coolant (Intercooler IP) and nitrogen purge gas was used in the experimental work. Melting point and enthalpies of indium and zinc were used for temperature and heat capacity calibration. The slow heating rate of 5 °C/min was used to minimise any temperature lag due to the large mass of the steel pan (Yu & Christie, 2001). Samples were subjected to a heating scan from 30 °C to 200 °C at 5 °C/min. Each run was repeated at least twice to ensure the repetition of the results.

2.4. Microscopy

A polarisation microscope (Axioskop 40 Pol/40 A Pol, ZEISS) was used to observe phase transition of starch samples with pure glycerol. After DSC scanning to specific temperatures, the starch samples were rapidly cooled to room temperature by DSC program to stop further changes. The starch sample was taken out of DSC pan and then dispersed using water. Then, starch suspension was sealed between two microscope glass slides using silicon adhesive. The same field was photographed under both normal and polarised lights. The magnification was 500 (50 × 10). At least three replicates were performed for each sample to ensure the consistent results.

3. Results and discussion

3.1. Endothermic phase transitions of maize starches in glycerol–water systems

Waxy maize starch is especially interesting since it contains mainly amylopectin molecules. The knowledge of thermal behaviours of waxy starch in the presence of glycerol can help us understand the phase transitions of other maize starches with high content of amylose in the same environment. Fig. 1 shows the DSC

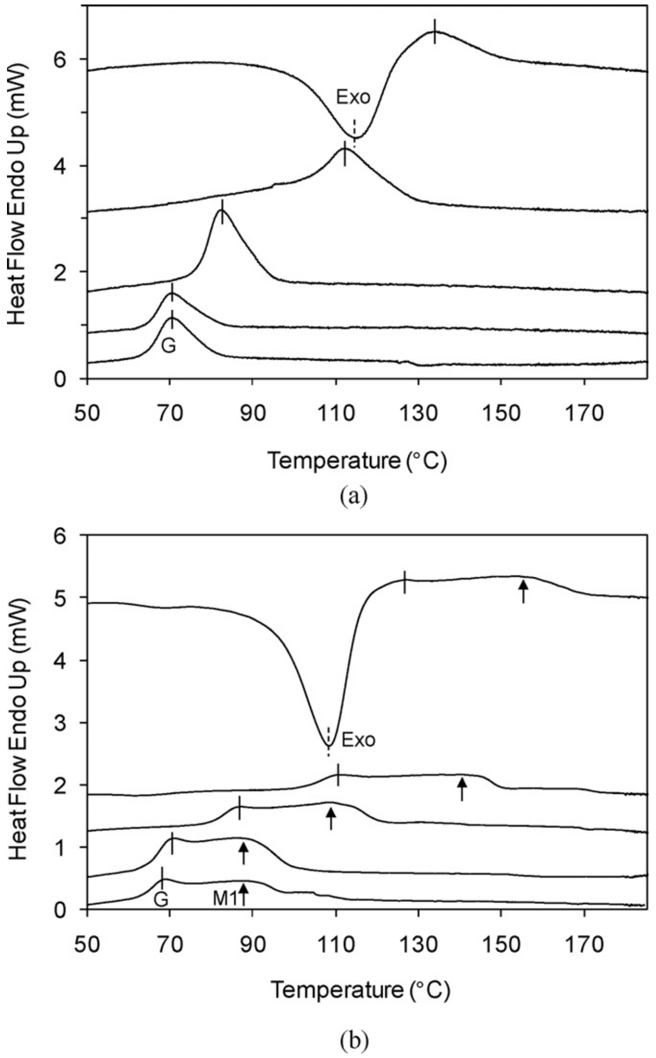


Fig. 1. DSC results of waxy starch with 70% (a) and 50% (b) glycerol–water mixture content, respectively (glycerol/water ratio: 0/100, 10/90, 50/50, 90/10, and 100/0, from bottom to top).

results of waxy starch with both 70% and 50% glycerol–water mixture contents. For each fixed mixture content, the glycerol/water ratio was varied in order to understand its effect on the thermal behaviour of waxy starch. It can be observed in Fig. 1a that there was a single endothermic peak (G), attributed to the gelatinisation of amylopectin (Liu et al., 2006; Perry & Donald, 2000, 2002; Tan et al., 2004), for waxy starch with 70% mixture content, with its position moving towards higher temperature with increasing glycerol concentration. When the glycerol concentration increased to 100% (glycerol/water ratio: 100/0), there was only an exothermic peak observed instead, which will be discussed in detail later. When the glycerol–water mixture content was lower (50%), the gelatinisation endothermic peak was split into two overlapping with each other (see Fig. 1b). In this case, the G endotherm reflects the smectic-isotropic phase transition, and the additional endotherm (M1) at higher temperature reflecting the helix–coil transformation (Waigh et al., 2000). Table 1 lists the detailed data describing the endothermic transitions in Fig. 1. It can be noted in Table 1 that, when the mixture content was 70%, with glycerol/water ratio varying from 0:100 to 90:10, the onset (T_o), peak (T_{p1}), and conclusion (T_c) temperatures and the enthalpy (ΔH) all moved to higher values. In addition, the thermal transition temperature range ($\Delta T = T_c - T_o$) also had an increasing trend, although the increments were small for 0/100, 10/90, and 50/50 (glycerol/water, w/w) samples. When the mixture content was 50%, T_o, T_{p1} (G), T_{p2} (M1), T_c, and ΔT also increased to higher values with increasing glycerol/water ratio. However, the maximum value of ΔH (G + M1) emerged at 10/90 glycerol/water ratio (see Table 1).

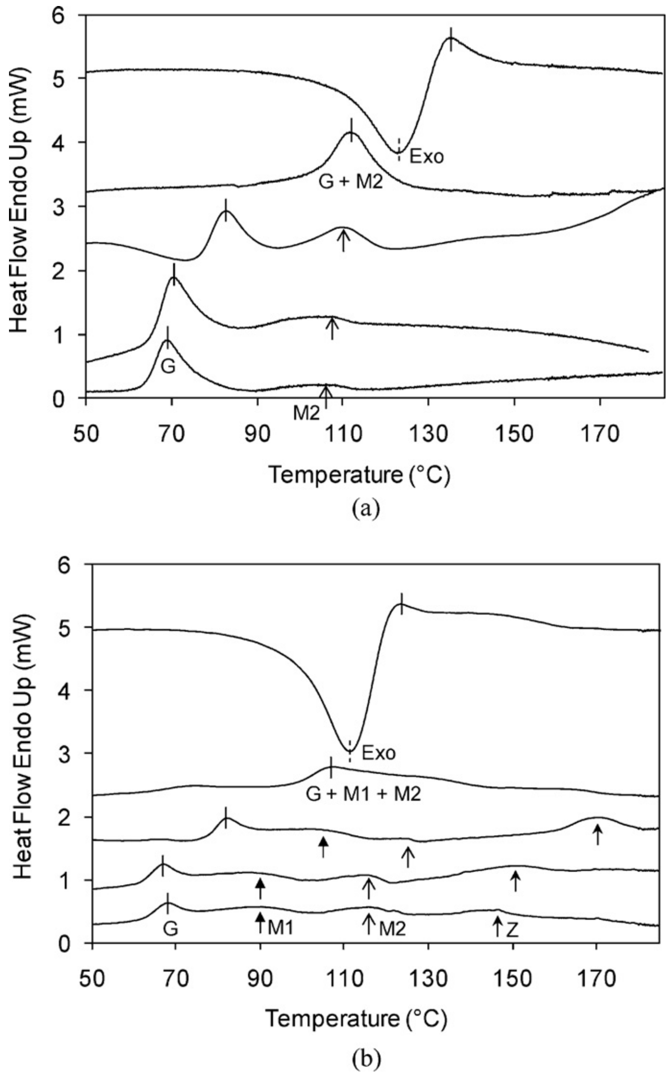
Though the effect of glycerol concentration on the gelatinisation parameters has been studied before, the results were not consistent. Some researchers (Evans & Haisman, 1982; Perry & Donald, 2000, 2002; van Soest, Bezemer, de Wit, & Vliegenthart, 1996) reported that increasing the concentration of glycerol solution only shift the gelatinisation endotherm upwards to higher temperature without affecting ΔT and ΔH. However, an increase of ΔH with increasing glycerol concentration was observed in another study (Gunaratne, Ranaweera, & Corke, 2007). Moreover, others (Habitante, Sobral, Carvalho, Solorza-Feria, & Bergo, 2008) reported a decreased ΔH with increased glycerol concentration measured by micro-DSC. On the other hand, there have also been discrepancies over the explanations of the effect of glycerol on starch gelatinisation. The main theories are: (1) glycerol has an “anti-plasticiser” behaviour and it hinders the gelatinisation process by diminishing the effectiveness of moisture contents of the starch to aid gelatinisation (Evans & Haisman, 1982; Nashed, Rutgers, & Sopade, 2003); (2) glycerol–water solution as a whole affect the gelatinisation behaviour—lower molecular weight, lower viscosity and higher hydroxyl group density of the solution can improve starch gelatinisation (Li, Sarazin, & Favis, 2008; Perry & Donald, 2000, 2002); and (3) glycerol increases the gelatinisation temperature by increasing the stability of starch amorphous regions (Gunaratne et al., 2007) or the activation energy (van Soest et al., 1996).

It can be noticed in Fig. 1 that, with 70% mixture content, only one endothermic peak (G) was observed regardless of the glycerol/water ratio, while the starch with 50% mixture content showed separated but partially overlapped transitions (G and M1) irrespective of the glycerol/water ratio. If water is the sole gelatinisation agent, and glycerol has an “anti-plasticiser” behaviour acting preferentially to bind water and reducing the amount of water available to starch for gelatinisation, M1 transition should appeared at high glycerol/water ratio with 70% mixture content. This phenomenon, however, was not observed in Fig. 1; thus, glycerol should behave as a co-agent for starch gelatinisation. Besides, it can be noticed in Fig. 1 that, at each glycerol/water ratio (0/100; 10/90; 50/50; or 90/10), T_o and T_{p1} showed little changes with varying mixture contents (70% and 50%). Similar phenomenon was observed in the study of starch gelatinisation with pure water, where the

Table 1
Phase transition data of waxy starch with 70% and 50% water–glycerol mixture contents.

Glycerol/water ratio	G (70% mixture content)					G + M1 (50% mixture content)					
	T_o (°C)	T_{p1} (°C)	T_c (°C)	ΔT (°C)[a]	ΔH (J/g)	T_o (°C)	T_{p1} (°C)	T_{p2} (°C)	T_c (°C)	ΔT (°C)[a]	ΔH (J/g)
90:10	101.4	122.4	125.6	24.2	25.82	101.8	111.1	144.4	148.3	46.5	15.29
50:50	76.3	82.4	93.6	17.4	21.39	79.4	85.9	108.4	120.3	40.9	19.81
10:90	64.2	70.6	82.1	17.9	17.59	63.5	71.0	89.1	96.8	33.3	22.18
0:100	64.0	70.6	80.8	16.7	15.37	62.5	68.7	89.7	97.0	34.5	17.92

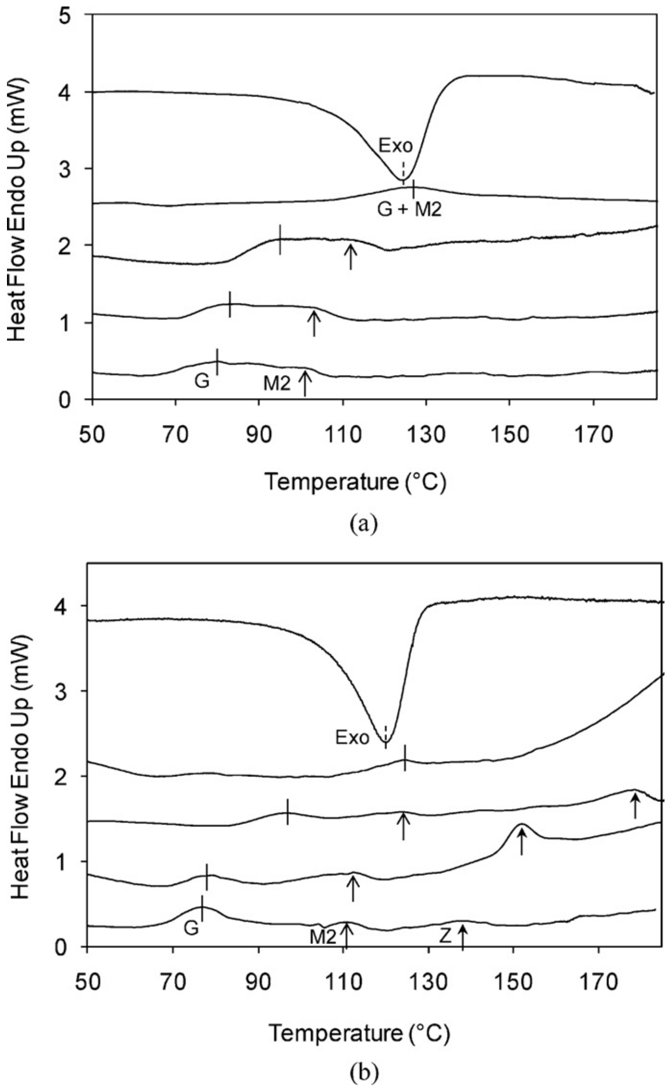
[a] $\Delta T = T_c - T_o$.



(a)

(b)

Fig. 2. DSC results of regular maize starch with 70% (a) and 50% (b) glycerol–water mixture content, respectively (glycerol/water ratio: 0/100, 10/90, 50/50, 90/10, and 100/0, from bottom to top).



(a)

(b)

Fig. 3. DSC results of Gelose 80 with 70% (a) and 50% (b) glycerol–water mixture content, respectively (glycerol/water ratio: 0/100, 10/90, 50/50, 90/10, and 100/0, from bottom to top).

endotherm of G was shift to higher temperature only when the water content was at least below 52% (Liu et al., 2006). As a result, both 70% and 50% mixture content can be considered to be "abundant" for the smectic-isotropic phase transition of amylopectin double helices (G) in the current study. As mentioned before, with 70% mixture content, T_o, T_{p1}, T_c, and ΔT all increased to higher values with increasing glycerol/water ratio. Thus, glycerol is considered not as effective as water for the G transition of starch due to its higher molecular weight and viscosity. However, higher temperature can enable glycerol to facilitate helix–coil transition and unwinding of amylopectin double helices to a greater extent, as evidenced by the increase of ΔH with higher glycerol/water ratio. However, for waxy starch with 50% mixture content, the higher glycerol/water ratios (50:50 and 90:10) resulted in broader ΔT and lower ΔH, suggesting the impediment and limitation of the helix–coil transition (M2).

Fig. 2 shows the DSC results of regular maize starch with 70% and 50% glycerol–water mixture contents. With 70% mixture content, there were two endothermic peaks at 0/100 glycerol/water ratio, which were designated as G and M2 (Liu et al., 2006). M2 has been considered as the phase transition within amylose–lipid complex (Biladeris et al., 1985; Jovanovich & Añón, 1999; Liu et al., 2006; Raphaelides & Karkalas, 1988). When the glycerol/water ratio increased until 50/50, the G and M2 endotherms were shifted to higher temperatures, while ΔT was not changed. For enthalpy, the total ΔH (G + M2) was also increased, which was due to greater ability of glycerol at higher temperature to facilitate such transitions. When the glycerol/water ratio was further increased to 90:10, the G and M2 endotherms were considered to be merged as indicated by the broader ΔT (data not shown). Moreover, the enthalpy of M2 was increased with increasing glycerol/water ratio, suggesting that higher glycerol concentration was favourable for the phase transition within amylose–lipid complex. On the other hand, with 50% mixture content, there was an additional endotherm at 146 °C at 0/100 glycerol/water ratio, which was resulted from the annealing of the amylopectin crystallites during heating (Liu et al., 2006; Maurice et al., 1985; Russell, 1987). When the glycerol/water ratio was increased to 50/50, G, M1, M2, and Z were shifted upwards and the ΔT value was increased; when the glycerol/water ratio was further increased to 90/10, G, M1 and M2 were merged as indicated by the broader ΔT, and Z disappeared in the experimental temperature range. Regarding to the enthalpy, the maximum value of ΔH (G + M1 + M2) occurred at 10/90 glycerol/water ratio, suggesting greater phase transitions at this level. Besides, the enthalpy of

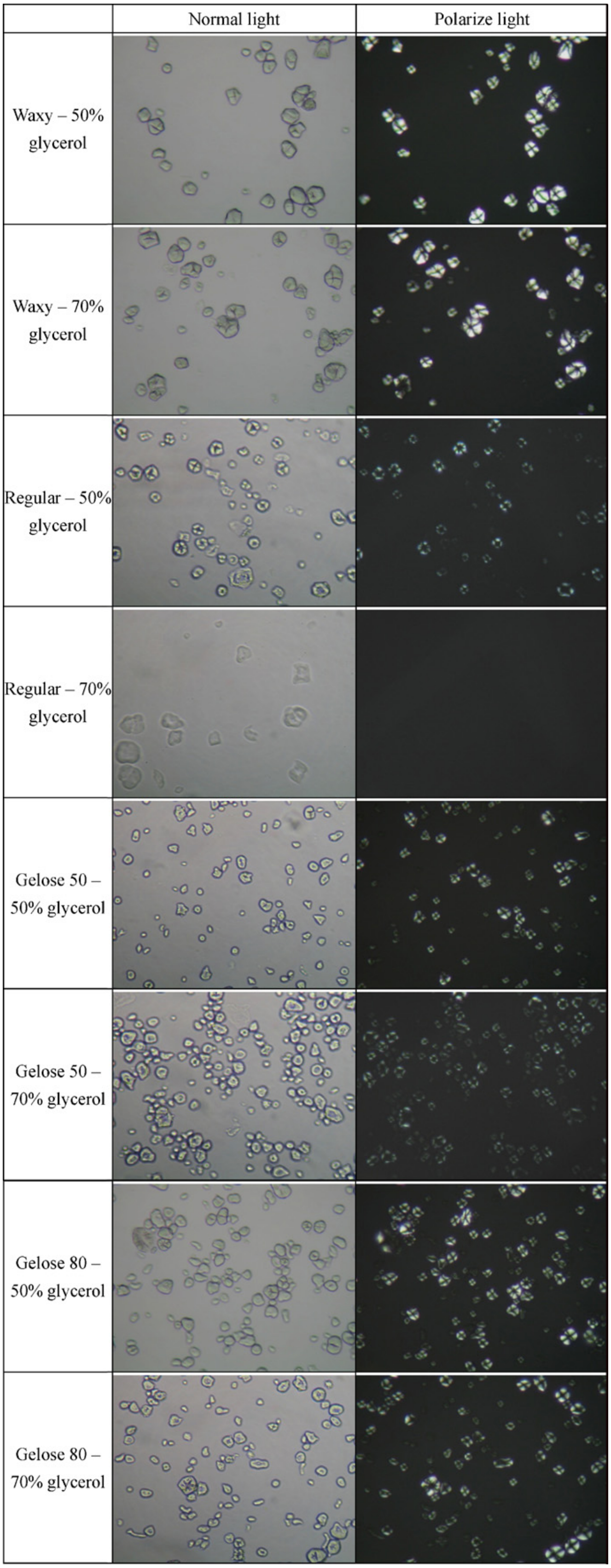


Fig. 4. Microscopic images of different maize starches with pure glycerol after heated to specific temperatures: 125 °C for waxy with 70% glycerol content; 115 °C for waxy starch with 50% glycerol content; 130 °C for regular maize with 70% glycerol content; 120 °C for regular maize with 50% glycerol content, 135 °C for Gelose 50 and Gelose 80 with 70% glycerol content; and 125 °C for Gelose 50 and Gelose 80 with 50% glycerol content.

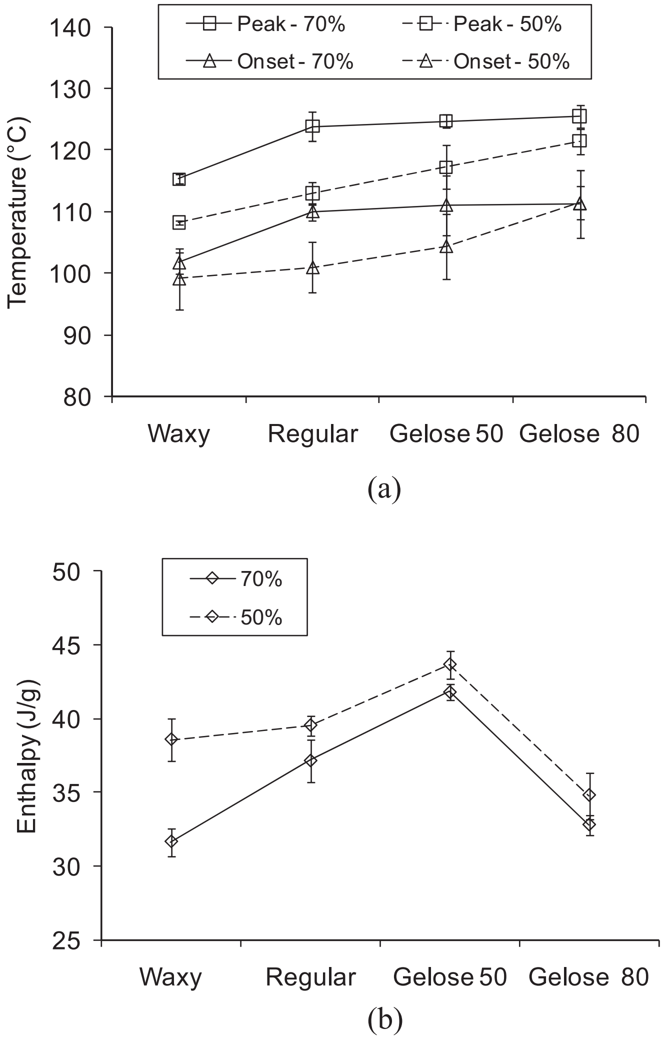


Fig. 5. The effects of starch type on the DSC exothermic parameters: onset and peak temperature (a) and enthalpy (b) (70%: starch with 70% glycerol content; 50%: starch with 70% glycerol content).

Z also increased with increasing glycerol/water ratio, suggesting that glycerol favours the annealing of amylopectin crystallites during heating. In both cases, the greatest enthalpy of G endotherm was observed at 90/10 glycerol/water ratio. In all, the distinct pattern of thermal transitions of regular maize starch was determined by the glycerol–water mixture content. Higher glycerol/water ratio tended to shift upwards and even merge the multiple thermal transitions.

Fig. 3 demonstrates the DSC results of Gelose 80 with 70% and 50% glycerol–water mixture contents. With 70% mixture content, there was a broad endotherm, which was composed of the G and M2 transitions (Liu et al., 2006). Higher glycerol/water ratio (up to 50/50 glycerol/water ratio) moved this shoulder upwards to higher temperature, but total ΔH (G + M2) and ΔT was stable. Finally the G and M2 endotherms were merged at 90/10 glycerol/water ratio. On the other hand, for Gelose 80 with 50% mixture content, Z transition emerged. Besides, G, M2, and Z were shifted to higher temperatures with the increase of glycerol/water ratio, but ΔT and ΔH were stable. When the glycerol/water ratio was increased to 90/10, only a weak G endotherm remained. For Gelose 80, higher glycerol/water ratio could not only shift the multiple thermal transitions upwards to higher temperature, but also suppress various thermal transitions. Similar thermal behaviours were observed for Gelose 50.

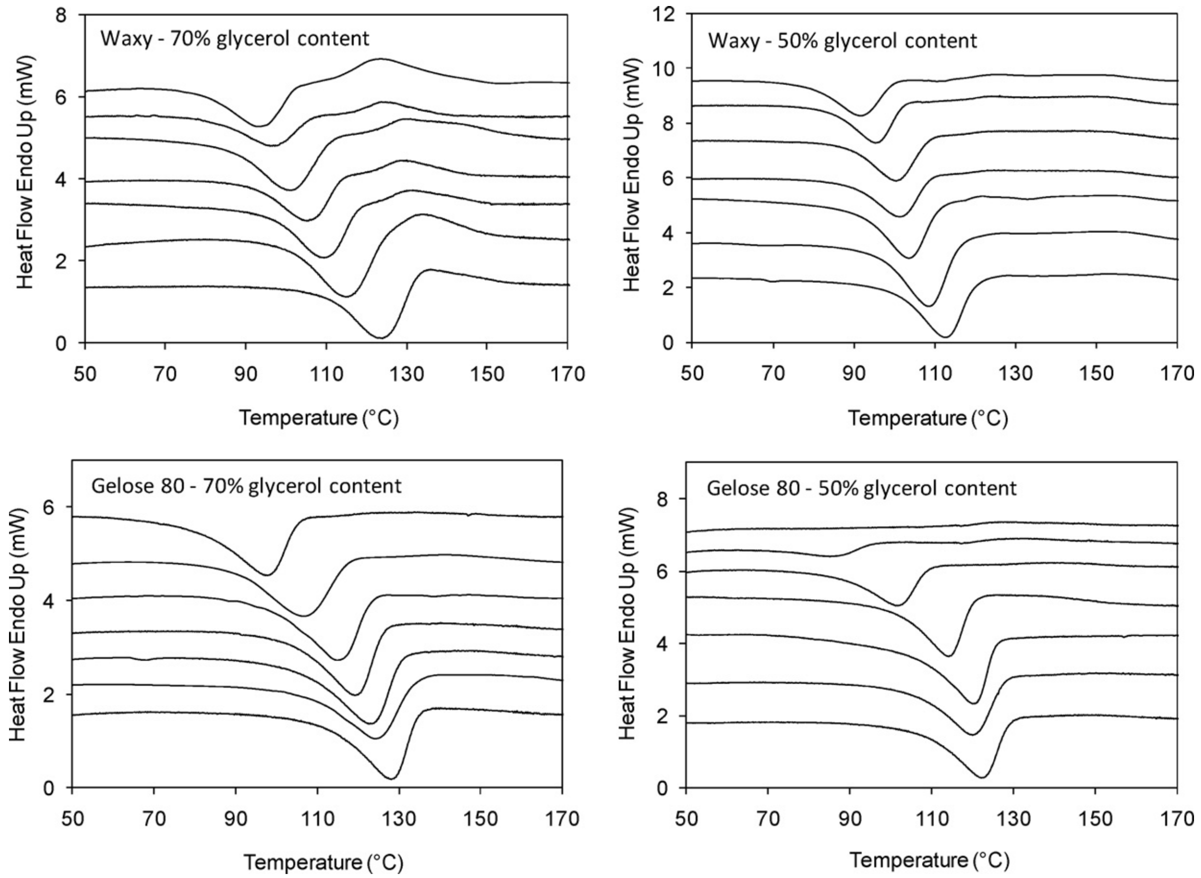


Fig. 6. DSC results of waxy starch and Gelose 80 with 70% and 50% glycerol contents after storage for different times.

3.2. Exothermic phenomena of maize starches with pure glycerol

As mentioned before, the DSC results of maize starches with pure glycerol (100/0 glycerol/water ratio) show a big exothermic peak (see Figs. 1–3). This exothermic phenomenon has also been observed in previous studies of starch with high concentration of glycerol (Habitante et al., 2008; Perry & Donald, 2000; van Soest et al., 1996). van Soest et al. (1996) proposed that this exothermic peak was due to the starch–glycerol "interaction". Perry and Donald (2000) suggested that self-assembly upon solvation of plasticiser like glycerol transforms the disordered structure of dry starch into an ordered smectic-like lamellar system with pronounced crystallinity, which is an exothermic reaction and can be greatly accelerated by increasing temperature; with water acting as the solvent, lamellar assembly and crystallisation can occur effectively and instantaneously at room temperature since water can easily penetrate the starch granules and effectively increase the free volume of amorphous regions. In this study, considering the exothermic peak is much bigger than the endothermic transitions (gelatinisation process), it could be proposed that the exothermic phenomenon for starch with high glycerol concentration is a combined result from both the starch–glycerol interaction and the solvation-assembly process in amylopectin structure. The former happens by the formation of –OH bonds between free –OH groups (which is not involved in the formation of starch–starch –OH binding) in starch molecules (both amylose and amylopectin) and –OH groups in glycerol molecules, releasing much more heat that the latter. The former could be the prerequisite of the latter and takes place during "solvation of plasticiser".

In order to understand if there was any gelatinisation process during the exothermic transitions for maize starches with pure glycerol, the samples were heated until the exothermic peak was concluded (but before, if any, following endothermic transitions) and then immediately cooled down to room temperature by DSC program, followed by microscopic observation. The results were shown in Fig. 4. It is clearly demonstrated that, in all cases except regular maize starch with 70% glycerol content, the granular morphology were basically not changed and the Maltese crosses were still maintained, which means gelatinisation process did not happen during the exothermic transition. For regular maize starch with 70% glycerol content, the granules partially swelled and the Maltese crosses disappeared, which means regular maize starch could be gelatinised simultaneously with the exothermic transition.

Fig. 5 illustrates the characteristic data of the exothermic peak of maize starches with different amylose contents with both 70% and 50% glycerol contents. It can be noticed in Fig. 5 that, the starch with 70% glycerol content generally showed an exothermic peak at higher temperature but a smaller enthalpy than that with 50% glycerol content. The reason could be that higher glycerol content (70%) could benefit starch–glycerol interaction (and subsequent self-assembly of starch crystallites) at room temperature during sample equilibrium (24 h storage); however, with more –OH group in the starch molecules bound with the –OH groups of glycerol, the remaining –OH binding reaction in the starch molecules should be more difficult due to the steric hindrance, and could only be initiated at higher temperature with such glycerol content level. On the other hand, with more limited content of glycerol (50%), small proportion of starch–glycerol –OH binding reaction happened before DSC temperature scanning, with remaining large proportion of reaction that required lower temperature to be started. These results demonstrate that both temperature and adequacy determine the activity of glycerol in the reaction with starch molecules.

Fig. 5 also shows that the starch type (amylose content) had some effect on the temperature (onset and peak) and the enthalpy of the exothermic peak. With the increase of amylose content, the exothermic peak was shifted to higher temperature. Generally, the high-amylose maize starch granules have a more compact microstructure than that of low-amylose maize starches, which makes the former more solvent-resistant and thermally stable (Chen, Yu, Kealy, Chen, & Li, 2007; Liu et al., 2006). It has also been revealed by confocal laser scanning microscopy (CLSM) (Chen et al., 2009) that there are many large channels connecting the border and the cavities at the hilum in low-amylose maize starch (waxy and regular maize starch) granules, while such channels do not exist for high-amylose maize starch (Gelose 50 and Gelose 80) granules. These could result in the less permeability of high-amylose maize starch that makes glycerol molecules less easy to penetrate into starch granules for starch–glycerol interaction. On the other hand, the change of exothermic enthalpy with amylose content did not see a simple trend. As illustrated in Fig. 4, the exothermic enthalpy of Gelose 50 was higher than both those of waxy maize starch Gelose 80. According to the data reported by Tan et al. (2007), Gelose 50 has less double helix and crystallinity and more amorphous region than waxy maize starch, thus it contains more free –OH groups available for starch–glycerol –OH binding reaction. Besides, as discussed before, the more permeability of waxy maize starch made it easy for starch–glycerol –OH binding reaction; thus, more starch–glycerol interaction took place for waxy maize starch at room temperature before DSC measurement. However, compared with those of Gelose 50, Gelose 80 has relative larger proportion of V-type polymorph and lower proportion of amorphous regions (Tan et al., 2007), which results in less free –OH groups of Gelose 80 available for starch–glycerol –OH binding reaction.

The equilibrium of starch with plasticiser like glycerol after blending is a common practice in the production of starch-based foods and thermoplastics. Considering that the storage time may also affect the starch–glycerol –OH binding reaction and self-assembly of amylopectin crystallites, the effect of time on the thermal transitions of maize starches was also investigated in this study. The typical results are shown in Fig. 6. It can be seen in Fig. 6 that the longer the storage time was, the lower both the temperature and the enthalpy of the exotherm were. For waxy starch samples with 70% and 50% glycerol contents, the exothermic peak still existed even after 4 weeks' storage. Besides, a small gelatinisation transition was developed with time for waxy starch samples with 70% glycerol content, which was due to the self-assembly of crystallites. This result demonstrates again that the exothermic transition was mainly due to the starch–glycerol –OH binding reaction. On the other hand, for Gelose 80 with 50% glycerol content stored for the same period of time, the exothermic peak disappeared. This could mean that the starch–glycerol –OH binding reaction could be completed for Gelose 80 sample with 50% glycerol content after 4 weeks' storage; for Gelose 80 sample with more glycerol content, more starch–glycerol –OH binding reaction could take place even after the same period of time.

4. Conclusion

Each maize starch with different amylose content showed distinct pattern of multiphase transitions, which could be greatly affected by glycerol–water mixture content and glycerol/water ratio. Higher glycerol/water ratio tended to shift upwards and even merge the multiple thermal transitions. Glycerol behaved as a co-agent with water for starch gelatinisation. Higher temperature enabled glycerol to facilitate phase transitions of maize starch to a greater extent if abundant plasticiser was present. For maize starch with higher amylose content, this "abundant" level of plasticiser content could be higher.

For all maize starches mixed with pure glycerol, a big exothermic transition could be observed within the range of about 95–135 °C, which was mainly due to the glycerol–starch –OH binding reaction and was greatly affected by the inherent granular structure and molecular characteristics of maize starch. The higher the amylose content of maize starch, the higher temperature was required to initiate the bulk starch–glycerol interaction. During the exothermic transition, gelatinisation process had not started for all four maize starches except regular maize starch with 70% glycerol content. Besides, both temperature and glycerol content determine the activity of glycerol in the reaction with starch molecules. This exothermic peak could also be affected by storage time, with its temperature and enthalpy of Gelose 80 decreased to a greater extent than those of any other maize starches.

The results from this work have confirmed some previously reported results, and also addressed some earlier confusion. The better understanding of the phase transition of starch could be instructive to the thermal processing of starch-based foods and thermoplastics.

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