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Investigation of the starch gelatinisation phenomena in water–glycerol systems: application of modulated temperature differential scanning calorimetry

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Abstract

The use of modulated temperature differential scanning calorimetry (MTDSC) has provided further insight into the gelatinisation process since it allows the detection of glass transition during gelatinisation process. It was found in this work that the glass transition overlapped with the gelatinisation peak temperature for all maize starch formulations studied. Systematic investigation on maize starch gelatinisation over a range of water–glycerol concentrations with MTDSC revealed that the addition of glycerol increased the gelatinisation onset temperature with an extent that depended on the water content in the system. Furthermore, 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. The validities of published gelatinisation models were explored. These models failed to explain the glass transition phenomena observed during the course of gelatinisation and failed to describe the gelatinisation behaviour observed over the water–glycerol concentrations range investigated. A hypothesis for the mechanisms involved during gelatinisation was proposed based on the side chain liquid crystalline polymer model for starch structure and the concept that the order–disorder transition in starch requires that the hydrogen bonds (the major structural element in the granule packing) to be broken before the collapse of order (helix–coil transition) can take place.

Keywords: MTDSC; Gelatinisation; Maize starch; Glass transition; Glycerol

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1. Introduction

Starch is of interest as a raw material for biodegradable plastics due to its low cost, its availability as a renewable resources and its thermal processability using conventional plastics processing equipment such as injection moulding, film blowing, thermoforming and extrusion (Kaplan, 1998; Mohanty, Misra, & Hinrichsen, 2000; Seindenstucker & Fritz, 1998; Shah, Bandopadhyay, & Bellare, 1995). Starch can be converted into thermoplastic material (TPS) through destructurisation in the presence of plasticisers under specific extrusion conditions. Water and glycerol are the most widely used plasticisers in TPS materials (Van Soest, Bezemer, De Wit, & Vliegenthart, 1996). Unlike synthetic thermoplastic polymers, however, starch exists as semi-crystalline granules with complex internal supramolecular packing (Buleon, Colonna, Planchot, & Ball, 1998; Donald, Kato, Perry, & Waigh, 2001). This packed structure gives rise to the characteristic endothermic first order transition known as gelatinisation during the transformation of granular starch into thermoplastic starch (Hulleman, Janssen, & Feil, 1998).

Starch gelatinisation can be generally defined as an irreversible order–disorder transition, which involves the disruption of molecular organization within the starch granules upon heating in the presence of plasticisers. A wide range of techniques have been employed to investigate the gelatinisation process (Cooke & Gidley, 1992; Derby,

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Miller, Miller, & Trimbo, 1975; Donovan, 1979; Jenkins & Donald, 1998; Liu, Charlet, Yelle, & Arul, 2002; Sopade, 1990; Stevens & Elton, 1971) and depending on the measurement techniques, events such as granules swelling, loss of crystallinity (birefringence and its X-ray diffraction pattern), uptake of heat, increased viscosity and solubilisation of amylose have been noted to occur during gelatinisation (Cooke & Gidley, 1992; Donovan, 1979; Garcia, Buleon, Colonna, Della Valle, & Lourdin, 1994; Jenkins & Donald, 1998; Maaruf, Man, Asbi, Junainah, & Kennedy, 2001; Sopade, 1990; Stevens & Elton, 1971). Many models have been proposed to describe the mechanism of gelatinisation (Biliaderis, Page, Maurice, & Juliano, 1986; Blanshard, 1987; Donovan, 1979; Evans & Haisman, 1982; Liu et al., 2002; Waigh et al., 2000) and these can be broadly classified into three approaches.

The first approach views gelatinisation as water-mediated melting of starch crystallites where water is considered as the sole gelatinising medium for starch (Donovan, 1979; Liu et al., 2002; Maaruf et al., 2001). This classical view was mainly supported by the observation that starch gelatinisation was strongly influenced by the water content in the system (Biliaderis, Maurice, & Vose, 1980; Donovan, 1979). Based on this viewpoint, when low molecular weight solutes such as sugars or glycerol are added into starch–water systems, hypotheses such as reduction of water availability due to the moisture binding by solutes, reduction in water activity and inhibition of granular hydration, are adopted to explain the increase in gelatinisation onset temperature (Derby et al., 1975; Evans & Haisman, 1982; Nashed, Rutgers, & Sopade, 2003; Sopade, 1990; Wootton & Bamunuarachchi, 1979).

The recognition of starch as partially crystalline polymer led researchers to consider gelatinisation as similar to melting process in synthetic semi-crystalline polymers, where the crystallite melting is controlled by pre-requisite plasticisation (‘softening’) of the amorphous regions of the native starch granule (Slade & Levine, 1988). According to this second viewpoint, a glass transition of the amorphous regions will precede the melting of crystallites and gelatinisation is controlled by the molecular mobility in the amorphous phase surrounding crystallites (Biliaderis, 1992; Blanshard, 1987; Roos, 1995). Accordingly, the increase in gelatinisation onset temperature by the addition of glycerol resulted from an increase in the activation energy of starch crystallites melting due to the higher glass transition temperature of the amorphous phase and higher interaction forces between starch and glycerol (Van Soest et al., 1996). A large amount of research has been performed to investigate the existence of glass transition prior to gelatinisation (Liu & Lelievre, 1991; Noel & Ring, 1992; Slade & Levine, 1988; Yost & Hoseney, 1986), but with no conclusive findings and the precise temperature of the transition remains unknown (Lelievre & Liu, 1994). Although some researchers have reported the occurrence of incremental change in heat capacity prior to the melting endotherm (Slade & Levine, 1988), the glass transition is obscure for most granular starch, presumably due to the heterogeneous nature of the amorphous phase in granular starch and limitations of analytical methods (Biliaderis, 1992; Blanshard, 1987).

From extensive study using dynamic small and wide angle X-ray scattering (SAXS/WAXS), scanning X-ray micro-diffraction, small angle neutron scattering (SANS), and ^{13}C CP/MAS NMR, a chiral side chain liquid crystalline polymeric (SCLCP) model has been proposed to describe the structure and physical properties of starch (Donald et al., 2001; Jenkins, Cameron, & Donald, 1993; Waigh et al., 2000; Waigh, Perry, Riekel, Gidley, & Donald, 1998). This third approach views gelatinisation in analogy with the SCLCP model, where gelatinisation is due to the inter-play between self-assembly and the breakdown of structure during heating (Waigh et al., 2000). It was postulated that the plasticisation of the double helical regions, to permit them to come into registry and exhibit the familiar 9 nm repeat lamellar assembly, is a necessary pre-requisite for gelatinisation to occur (Perry & Donald, 2002). During gelatinisation, the structural phase transitions included three order parameters (helical ordering, lamellar ordering and the number helices; Waigh et al., 2000) and involved two main stages, namely slow helix–helix dissociation and fast helix to coil transition (Waigh, Gidley, Komanshek & Donald, 2000). The increase in gelatinisation onset temperature with increasing glycerol content was due to the fact that glycerol was less effective in plasticising the starch granule compared to water, hence more thermal energy would be required to achieve the total plasticisation, and consequently gelatinisation will proceed at higher temperature (Perry & Donald, 2002; Perry & Donald, 2000). Nevertheless, although the evolution of SAXS peak in starch–glycerol system with increasing temperature was a clear evidence of the self-assembly of periodic lamellar structure, there is hardly any evidence proving that starch granules are in plasticised state prior to gelatinisation. Consequently, further investigations on this aspect become particularly important to validate this approach.

Hence, despite advances in research on starch gelatinisation, conflicting views and disagreements regarding the mechanism of gelatinisation still remain. This further complicates the understanding of the role of plasticisers on gelatinisation during processing of starch into TPS. Issues such as whether water is the only starch gelatinising medium, the existence of glass transition and plasticisation of starch granules prior to gelatinisation, the role of plasticisers (water and glycerol) on gelatinisation require further examination. This demands systematic investigations using a robust scientific technique that enables the detection of any glass transition event during the course of gelatinisation process or state of plasticisation prior to gelatinisation.

Conventional differential scanning calorimetry (DSC) was pioneered for gelatinisation studies by Stevens and Elton (1971) but its use is limited in detecting the glass transition event during gelatinisation (Blanshard, 1987) and glass transition is usually masked by the large gelatinisation endotherm (Yost & Hoseney, 1986). With modulated temperature DSC (MTDSC), the sample experiences a sinusoidal modulation (oscillation) overlaid on the conventional linear heating or cooling ramp, hence the total heat flow signal is separated into its heat capacity (reversible thermal event) and kinetic components (irreversible event) (Lai & Lii, 1999; T.A. Instruments, 1996). Thus, MTDSC has improved capabilities compared to conventional DSC, namely the measurement of heat capacity and heat flow in a single experiment, separation of complex transitions into more easily interpreted components, increased sensitivity for detection of weak transitions and increased resolution of transitions without loss of sensitivity (Cuq & Icard-Verniere, 2001; De Meuter, Rahier, & Van Mele, 1999; Lai & Lii, 1999; T.A. Instruments, 1996; Wunderlich, Boller, Okazaki, & Ishikiriyama, 1997).

Therefore, using MTDSC as the analytical tool, this study investigates starch gelatinisation in glycerol–water systems of various concentrations and aimed to: (i) examine the validity of the three models outlined above; (ii) provide clarifications of some issues in gelatinisation such as existence of glass transition, plasticisation of starch granules prior to gelatinisation; (iii) elucidate the role of water and glycerol on gelatinisation. Four types of maize starches of differing amylose content will be investigated to explore any differences in the gelatinisation behaviour between these starches.

2. Materials and method

2.1. Materials

Four maize starches with different amylose content (Table 1) were obtained from Penford Australia Limited (Lane Cove, NSW 2066). Moisture content was determined using standard oven-method procedures (Association of Official Analytical Chemists, 1990).

2.2. Sample preparation

Three levels (0.4, 1.0 and 4.0 g water/g dry starch) of water content and five levels (0, 0.2, 0.4, 0.6 and 0.8 g glycerol/g dry starch) of glycerol content were prepared for each maize starch type. The composition of these starch–water–glycerol mixtures is outlined in Table 2. About 2 g of the starch was mixed with the required amount of solvents (glycerol and water) and left to equilibrate on a slow roller overnight at room temperature. Test samples were carefully weighed (<20 mg) into aluminium pans and hermetically sealed.

Table 1
The amylose and moisture contents (%) of the maize starches studied

Starch type	Amylose[a] (%)	Moisture (%)
Waxy maize	0	10.5±0.23
Regular maize	28	10.5±0.02
High amylose maize—Gelose 50	55	14.6±0.45
High amylose maize—Gelose 80	85	11.5±0.26

[a] Manufacturer's specifications.

2.3. Calorimetry

A TA 2920 Modulated Temperature DSC (from TA Instruments Inc., New Castle, DE 19720) was used to investigate the gelatinisation process. The scan intervals were 30–140 °C for normal and waxy maize starch, and 30–180 °C for the high amylose starches. A heating rate of 5 °C/min was chosen and the modulation was set at ±1 °C for every 60 s. These conditions were selected to minimize error that may result from incomplete modulation of the sample volume (Wunderlich et al., 1997). Temperature, enthalpy and heat capacity calibrations were performed with zinc, tin, mercury, indium, and sapphire. The Universal Analysis™ software was used to obtain the gelatinisation enthalpy, gelatinisation temperatures (onset, peak and end) and glass transition temperature. The gelatinisation enthalpy and temperatures were obtained from the non-reversible heat flow while the glass transition temperature was computed from the reversible heat flow. At least duplicate analysis was conducted for all formulations and the mean value was used since the coefficient of variation was less than 7%.

3. Results and discussion

3.1. Elucidation of glass transition phenomena during gelatinisation

Fig. 1 shows a typical thermogram from the modulated temperature DSC and reveals that the glass transition occurred after the onset gelatinisation temperature. The heat capacity change occurred within the gelatinisation endotherm, as demonstrated in Fig. 1, and the glass transition temperature essentially overlapped with the peak gelatinisation temperature (Fig. 2). Similar course of transitions were observed irrespective of starch types and formulations. Hence, this observation that glass transition occurred after the gelatinisation onset temperature is contrary to what would have been expected if gelatinisation is analogous melting of semi-crystalline polymers where gelatinisation is controlled by previous softening of the amorphous regions, as advanced by the second viewpoint (Biliaderis, 1992; Roos, 1995; Slade & Levine, 1988).

Nevertheless, the glass transition phenomena discerned within the gelatinisation endotherm could possibly be an

Table 2
The relative weight composition of starch–water–glycerol mixtures prepared for the gelatinisation study

Water content (g water/g dry starch)	Glycerol content (g glycerol/g dry starch)	Composition [% (w/w)]			Total solvent content (g solvent/g dry starch)	Glycerol concentration (%, g glycerol/g total solvent)
		Starch	Water	Glycerol		
0.4: 1	0.0	70.0	30.0	0.0	0.4	0
	0.2	61.1	26.2	12.8	0.6	33
	0.4	54.7	23.5	21.8	0.8	50
	0.6	49.3	21.1	29.6	1.0	60
	0.8	44.9	19.2	35.9	1.2	67
1: 1	0.0	50.0	50.0	0.0	1.0	0
	0.2	45.3	45.3	9.5	1.2	17
	0.4	41.7	41.7	16.6	1.4	29
	0.6	38.4	38.4	23.1	1.6	38
	0.8	35.7	35.7	28.6	1.8	44
4: 1	0.0	20.0	80.0	0.0	4.0	0
	0.2	19.2	76.8	4.0	4.2	5
	0.4	18.5	74.1	7.4	4.4	9
	0.6	17.9	71.4	10.7	4.6	13
	0.8	17.2	69.0	13.8	4.8	17

implication of structural changes involved during gelatinisation. Glass transition could be qualitatively interpreted as the onset temperature of long-range, coordinated molecular motion, which does not occur below T_g due to the immobilisation of molecules within the solid state (Roos, 1995; Sperling, 1992). It was reported that the uptake of water by the amorphous background is of prime importance prior to the peak temperature of the DSC endotherm (T_p) and after this point there is a progressive loss of crystalline packing of the double helices within the crystalline lamellae (Jenkins & Donald, 1998). Therefore, as the crystalline packing was lost, the polymer chains in double helical conformation (which were initially constrained by hydrogen bond) undergo helix to coil transition (Waigh, Gidley, et al., 2000). Consequently, the polymer chains became more mobilised where long-range molecular motions of the polymer chains were possible. This was reflected as the heat capacity change or glass transition event detected during the course of gelatinisation. It is important to note that heat capacity is a temperature derivative of an integral characteristic (i.e. of enthalpy) and hence any temperature-induced change of state would be

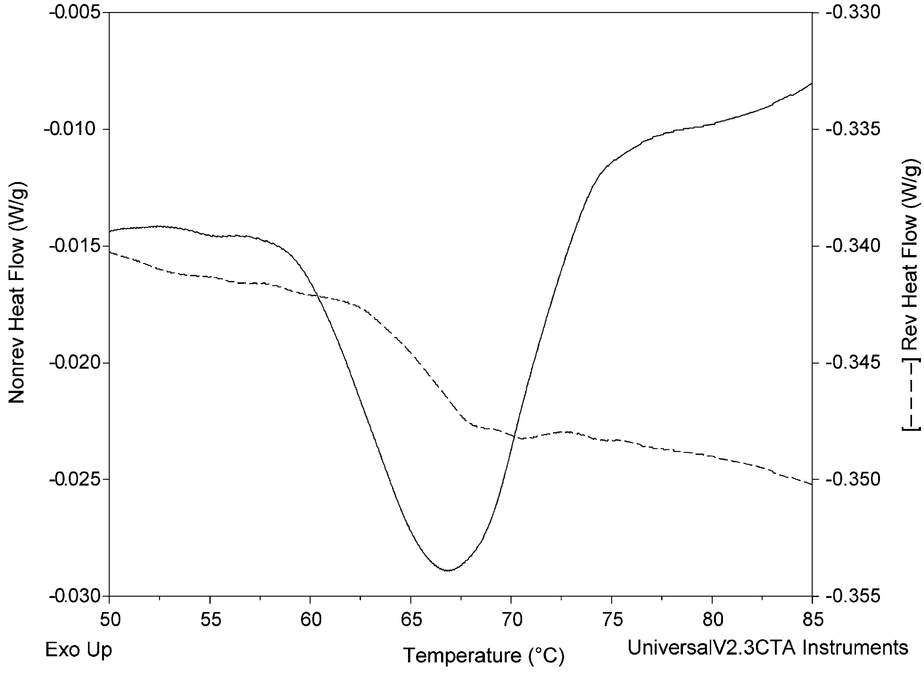

Fig. 1. Gelatinisation of normal maize starch at 4.0 g water/g dry starch as measured by modulated temperature DSC, which allowed the separation of the reversible thermal event (glass transition) and non-reversible thermal event (gelatinisation) in a single experiment.

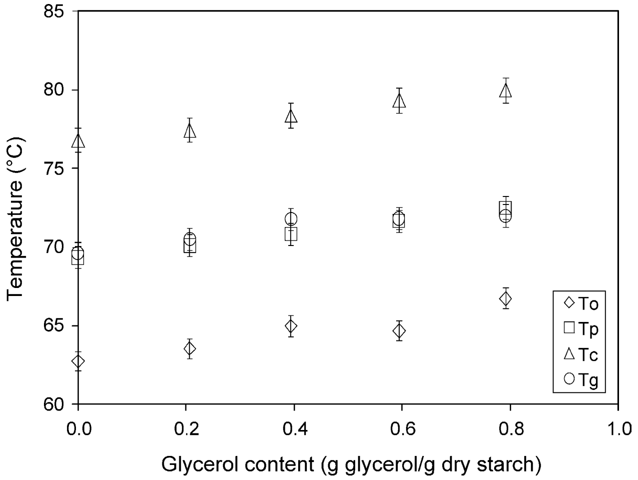

Fig. 2. The gelatinisation and glass transition temperatures for waxy maize starch at 4.0 g water/g dry starch and different levels of glycerol (g glycerol/g dry starch). T_o, gelatinisation onset temperature (◇); T_p, gelatinisation peak temperature (□); T_c, gelatinisation conclusion temperature (△); T_g, glass transition temperature (○).

reflected as well in the heat capacity curve (Privalov, 1979). Therefore, the heat capacity change observed is more accurately described as due to a change in state of the starch polymers from being highly constrained in the granular packing to entangled polymers of amylose and amylopectin systems (order–disorder transition).

3.2. Gelatinisation: theory of water-mediated melting of starch crystallites?

To explore the validity of the viewpoint that defines gelatinisation as water-mediated melting of starch crystallites, a range of starch–water–glycerol concentrations was investigated. Generally for all starch, no gelatinisation endotherm was observed at 0.4 g water/g dry starch. Interestingly, however, as glycerol was added, the gelatinisation endotherm became more pronounced with increasing glycerol concentration in the system (Fig. 3). Since the glycerol was essentially dry (negligible moisture) and did not have any freezable water (unpublished study), there are three major deductions from this observation:

1. Glycerol aids gelatinisation at limited water level and this is contrary to published inferences that glycerol competes with starch for water (Evans & Haisman, 1982; Nashed et al., 2003).
2. Water is not the only gelatinising medium for starch, and glycerol could have contributed its –OH bonds to enhance the gelatinisation process. Blanshard (1987) noted that solvents such as liquid ammonia, alkali and dimethyl sulphoxide can ‘gelatinise’ starch.
3. Glycerol shows anti-plasticisation behaviour and needs not be referred to as a plasticiser from the starch gelatinisation standpoint.

Furthermore, normal maize starch can be gelatinised in the presence of pure glycerol and the trend in enthalpy with glycerol content was qualitatively similar to that observed in water systems (Tan, Sopade, & Halley, 2004). This clearly shows that water is not the sole gelatinising medium for starch, other solvents such as glycerol can also gelatinise starch. Therefore, the first viewpoint (Donovan, 1979; Liu et al., 2002; Maaruf et al., 2001) that gelatinisation is a water-mediated melting of starch crystallites, is inconsistent with our observations.

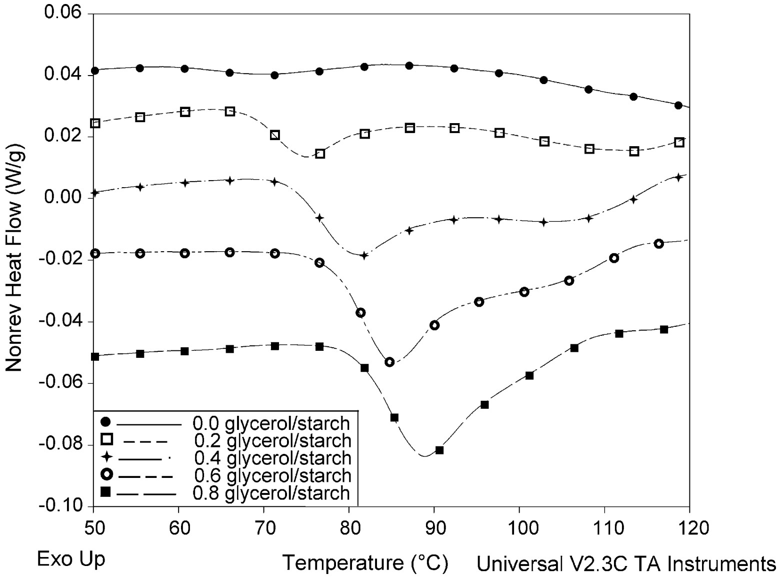

Fig. 3. Gelatinisation of normal maize starch at 0.4 g water/g dry starch with varying glycerol content (g glycerol/g dry starch). Thermograms are arranged vertically with increasing glycerol concentration from top to bottom (0.0, 0.2, 0.4, 0.6 and 0.8 g glycerol/g dry starch).

3.3. Gelatinisation: theory of lamellar assembly and structural breakdown in analogy to SCLCP model?

The third viewpoint considers gelatinisation as a structural breakdown in analogy to the SCLCP model where there is a requirement for critical degree of plasticisation, as indicated by the self-lamellar assembly (Perry & Donald, 2002). This total degree of plasticisation can be induced both by the input of plasticising solvent and thermal energy and the different influence of glycerol and water on gelatinisation onset temperature was explained to be due to the ineffectiveness of glycerol to plasticise starch granules compared to water (Perry & Donald, 2000). The existence of glass transition phenomena in the vicinity of the exothermal transition (as an indicative of granular plasticisation due to lamellar self-assembly) upon heating starch–glycerol mixtures was explored with modulated temperature DSC and no glass transition was detected anywhere close to the exothermal transition (Tan et al., 2004). Nevertheless, the exothermal transition was a clear evident of the self-lamellar assembly process (Perry & Donald, 2000) and rather than due to granular plasticisation, the assembly process was considered as a mere consequence of solvent diffusion into the granules, acting as lubrications between amylopectin polymer chains to allow the smectic like ordering (Tan et al., 2004).

3.4. Gelatinisation: theory of granular structural breakdown, an extension of SCLCP structural breakdown theory

In this paper, we wish to propose an extension of gelatinisation theory of SCLCP structural breakdown by considering the concepts proposed by Stevens and Elton (1971) and the SCLCP model of starch structure (Donald et al., 2001; Waigh, Gidley, et al., 2000; Waigh et al., 2000; Waigh et al., 1998). Gelatinisation is an order–disorder process, which involves the diffusion of solvents into the granules to bring about the lamellar self-assembly process, granular swelling and finally the structural (supra-macromolecular packing) breakdown. The disruption of such molecular packing during gelatinisation would thus involve three main steps:

1. The cleavage of existing hydrogen bonds between starch molecules.
2. The formation of new hydrogen bonds between starch and solvent.
3. The unwinding helix–coil transition of the amylopectin helices to give a less ordered structure.

When viewing starch as a structural analogue to a chiral side chain liquid crystalline polymer, the breakdown of the starch granular structure during gelatinisation would involve two steps, i.e. the amylopectin helix–helix dissociation (as a result of the first two steps) and then the unwinding helix to coil transition (Waigh et al., 2000). The macromolecules are mainly held together by hydrogen bonding to pack into such a dense granule, ca. 1500 kg/m^3 (Buleon et al., 1998), with complex supramolecular structure (Donald et al., 2001; Jenkins et al., 1993; Waigh, Hopkinson, & Donald, 1997). Thus, the structural breakdown of the granules requires that these hydrogen bonds holding the macromolecules together be broken. The temperature at which the thermal energy becomes sufficient to break these large amounts of hydrogen bonds is so high that the starch granules decompose even before this temperature is achieved (Nashed et al., 2003). When starch is heated in the presence of water, however, the structural breakdown (usually known as gelatinisation) becomes possible as aided by the presence of water contributing its –OH bonds and hence the gelatinisation is highly dependant on the moisture content (Donovan, 1979; Maaruf et al., 2001; Sopade, 1990). Therefore, we hypothesise that the structural breakdown during gelatinisation would possibly be due to available solvent(s) acting to disrupt the starch–starch hydrogen bonds (between amylopectin helices) and then form starch–solvent hydrogen bonds simultaneously. This causes the amylopectin helices to dissociate before the unwinding helix–coil transition can take place. The diffusion and ingress of solvents into the granules is an important preliminary step before the cleavage of starch–starch hydrogen bonds by the solvents (water or glycerol) could take place (Perry & Donald, 2002; Perry & Donald, 2000). Thus, the solvent's properties such as its ingress rate or diffusivity, viscosity, molecular size and hydrogen bonding capacity would determine its effectiveness to gelatinise starch. The influence of solvent effectiveness on starch gelatinisation behaviour will be outlined in Sections 3.4.1 and 3.4.2, by exploring the effect of varying water and/or glycerol concentration on gelatinisation parameters.

3.4.1. The effect of water and/or glycerol on gelatinisation temperature

Fig. 4 demonstrates that the addition of water resulted in the reduction of the gelatinisation onset temperature (T_o) and this observation agrees with those reported by earlier workers (Donovan, 1979; Evans & Haisman, 1982; Maaruf et al., 2001). However, the opposite effect was observed with the addition of glycerol. Generally, for all starch types, the addition of glycerol increased the gelatinisation onset temperature (Fig. 5), and this was consistent with previous observations (Blanshard, 1987; Evans & Haisman, 1982; Nashed et al., 2003; Perry & Donald, 2002; Van Soest et al., 1996). Additionally, it was demonstrated that the extent of increase in the onset temperature (T_o) with glycerol addition depended on the water content in the system, and the most pronounced increase was observed in systems with the lowest water content, i.e. 0.4 g water/g dry starch. It is important to note that in our study, increasing the glycerol content at particular water content corresponds to increasing the total amount of gelatinising solvents (Table 2). Fig. 6(a) plots the variation in the onset gelatinisation temperature with the total solvent content and glycerol concentration

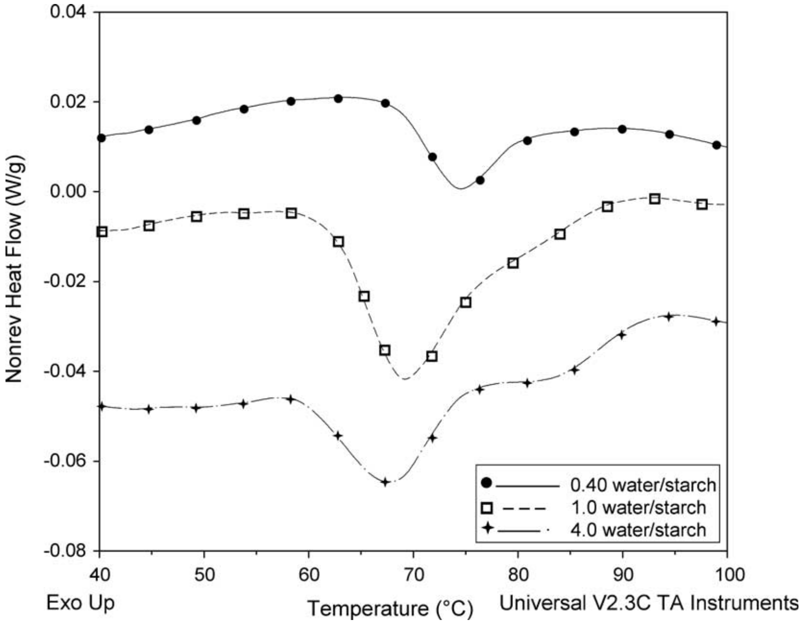

Fig. 4. Gelatinisation of normal maize starch at 0.2 g glycerol/ g dry starch with increasing water content, from top to bottom—0.4, 1.0, and 4.0 g water/g dry starch.

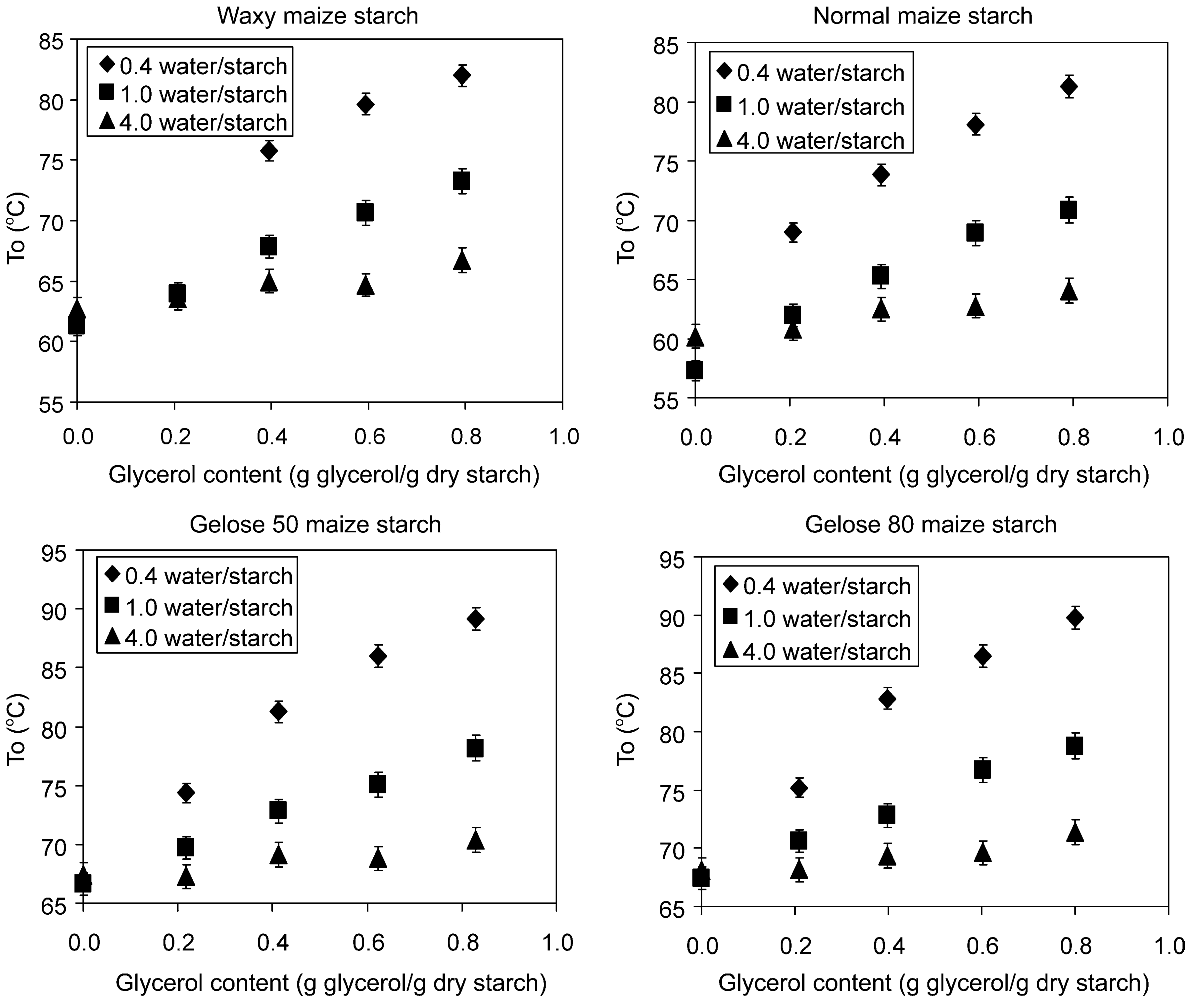

Fig. 5. Variation in gelatinisation onset temperature (T_o) for waxy, normal, Gelose 50 and Gelose 80 maize starches as a function of glycerol content (g glycerol/g dry starch) at three different water contents (0.4, 1.0 and 4.0 g water/g dry starch).

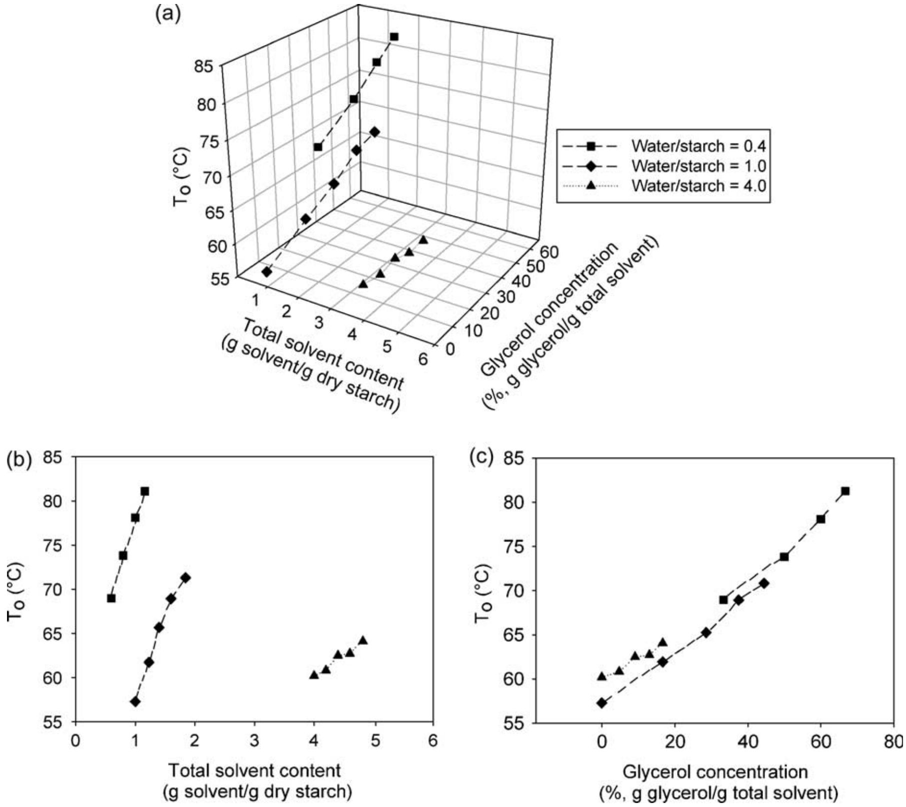

Fig. 6. Variation in the onset temperature (T_o) with total solvent content and glycerol concentration (over total solvent) for normal maize starch. (a) Three dimensional plot of the gelatinisation onset temperature (T_o) versus total solvent content (g solvent/g dry starch) and glycerol concentration (%). (b) Variation in the onset temperature (T_o) plotted against total solvent content (g solvent/g dry starch). (c) Variation in the onset temperature (T_o) plotted against the glycerol concentration (%).

relative to the total solvent for normal maize starch in a three-dimensional plot. According to the plasticisation theory of self-lamellar assembly, increasing the input of solvent would reduce the requirement of heat input and hence lowering the gelatinisation onset temperature (Perry & Donald, 2002). Such change is observed in Fig. 6(b), which demonstrates that the onset temperature is generally higher at low water content (0.4 g water/g dry starch) than at intermediate water content (1.0 g water/g dry starch). However, it is interesting to note that although the total solvent content are the same for some samples (note for samples with total solvent content of 1.0 and 1.2), the onset temperature is still higher at low water content than at intermediate water content. This is most likely due to the difference in glycerol concentration between these samples (Table 2). For the same amount of total solvent, system with low water content would have higher glycerol concentration relative to the total solvent. Higher glycerol concentration would mean higher viscosity and lower diffusivity (Ternstrom, Sjostrand, Aly, & Jernqvist, 1996). This consequently resulted in lower solvent ingress rates into the granules and thus elevation in gelatinisation onset temperature. Hence, this appears to indicate the significance of the transport properties of the solvent mixtures (which is affected by the glycerol concentration in this case) in determining the gelatinisation onset temperature. This is further supported by the observation that the onset temperature generally increases with glycerol concentration, as shown in Fig. 6(c). Therefore, it is evident from these results that not only the availability of solvent is important in determining the gelatinisation onset temperature but the solvent's transport properties (such as viscosity, diffusion and ingress rates) are also important. However, it should be stressed that the likelihood of an increase in viscosity (and hence, diffusivity) of water–sugar mixtures does not entirely explain starch gelatinisation behaviours in solutions of mono- and disaccharides (Sopade, Halley, & Junming, 2004). Other solvent properties such as the molecular sizes, number of hydrogen bonds could also influence the gelatinisation onset temperature (Tan et al., 2004).

The changes in glass transition temperature with the glycerol and/or water content (Fig. 7) were similar to the trends observed with the gelatinisation onset temperature. This further confirmed that the glass transition is an event related to gelatinisation where long-range molecular motions of the polymer chains become possible as soon as the granular structure collapse.

3.4.2. The influence of water and/or glycerol on gelatinisation enthalpy

The significance of the endothermic enthalpy value is that it represents the amount of thermal energy involved during

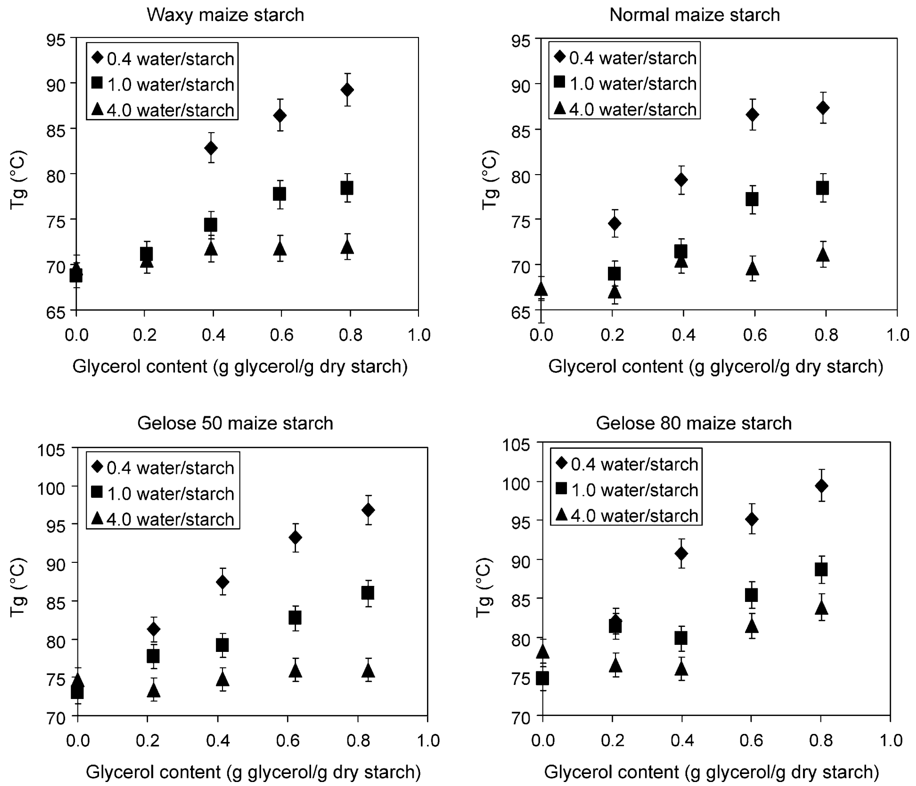

Fig. 7. Variation in glass transition temperature (T_g) for waxy, normal, Gelose 50 and Gelose 80 maize starches as a function of glycerol content (g glycerol/g dry starch) at three different water levels (0.4, 1.0 and 4.0 g water/g dry starch).

gelatinisation (Stevens & Elton, 1971). Since we proposed that gelatinisation is a three-step process, the endothermic nature of gelatinisation would be the resultant of thermal energy from the three processes (Stevens et al., 1971; Waigh, Gidley, et al., 2000):

1. Cleavage of existing starch–starch –OH bonds (Endothermic).
2. Formation of starch–solvent –OH bonds (Exothermic).
3. The unwinding helix–coil transition of amylopectin helices (Endothermic).

The cleavage of starch–starch hydrogen bonds by the solvent and subsequent formation of starch–solvent hydrogen bonds would occur simultaneously before the unwinding helix–coil transition process. Since the starch–starch hydrogen bonds are stronger than starch–solvent hydrogen bonds, the result of the first two steps would be endothermic and the magnitude (ΔH_{OH}) would depend on the number of starch–starch hydrogen bonds disrupted (which equals to the number of starch–solvent hydrogen bonds formed). Thus, the magnitude of ΔH_{OH} is an intrinsic property of the starch type since to completely gelatinise that particular starch, the same amount of hydrogen bonds would be disrupted regardless of the type of solvent(s) used. So, the ΔH_{OH} value from complete gelatinisation of normal maize starch would be the same for gelatinisation both in glycerol and water systems. However, the gelatinisation enthalpy for normal maize starch is higher in excess glycerol (~7.3 J/g dry starch) compared to that in excess water (~3.2 J/g dry starch; Tan et al., 2004). This indicates the significance of contribution from the thermal energy due to amylopectin unwinding helix–coil transition (ΔH_{HC}). The helix–coil unwinding transition of amylopectin helices possibly occurred with more difficulty with glycerol compared to water because glycerol has larger molecular size and less effective –OH bonding capacity compared to that of water. Thus, the magnitude of ΔH_{HC} would be larger for gelatinisation of the same starch in glycerol than in water, giving rise to a higher total enthalpy in glycerol system as observed in previous work. As a result, the ΔH_{HC} value would depend on the effectiveness of solvent(s) in terms of its hydrogen bonding capacity that would determine the ease of amylopectin helix–coil unwinding transition. Therefore, the gelatinisation enthalpy is the additive sum of thermal energy involved, ΔH_{OH} and ΔH_{HC}, which are influenced by the starch type and the 'gelatinising' solvent(s) used, respectively.

While determining the effectiveness of a pure solvent (in terms of its hydrogen bonding capacity) is rather straightforward, estimating how effective the hydrogen bonding capacity of a particular solvent mixture (in this case water and glycerol) gelatinises starch is complicated by the interactions that may exist between water and glycerol. Different concentrations of aqueous glycerol mixture would be expected to have different nature of interactions. In glycerol-rich systems, x_G (glycerol molar fraction) >0.8, the addition of water disrupts the inherent structures of glycerol and water without sufficient compensation by binding the water to the glycerol (Marcus, 2000). On the other hand, water self-interactions persist in water-rich mixtures and a fairly high glycerol interactions would be required to break them, leading to a maximal mutual interactions (water–glycerol interactions) near $x_G = 0.60$ (Marcus, 2000). Since the glycerol concentration (of the total solvent) in our study was closer to the range of water-rich mixture systems, the water binding action by glycerol did not take place in our systems while noting that some form of water–glycerol interactions did exist to different extent at different glycerol–water composition (Marcus).

Fig. 8 demonstrated that the enthalpy of gelatinisation for normal maize starch varies with the addition of glycerol and the variation depended on the water content. At high water content (4.0 g water/g dry starch), the gelatinisation enthalpy was essentially constant even though the glycerol concentration was varied. Possibly, at 4.0 g water/g dry starch, sufficient water was available to cleave hydrogen bonds between amylopectin helices and form starch–solvent –OH bonds. Thus, in this excess water system, the amount of –OH bonds disrupted would be pretty much constant for all glycerol concentrations and the unwinding transition would take place at around the same level of difficulty, and consequently the overall enthalpy value would be virtually constant regardless of the glycerol content. It is obvious that insufficient solvent was available at intermediate water content (1.0 g water/g dry starch) and the addition of glycerol may result in more cleavage of starch–starch –OH bonds, which consequently resulted in an increase in the enthalpy value. However, on adding glycerol, the enthalpy increased significantly to values higher than those of high water content systems (Fig. 8). The increasing contribution of glycerol in ‘gelatinising’ starch, which was less effective than water, caused the unwinding transition to occur with more difficulty and increased the ΔH_{HC} value, contributing to an overall increase in gelatinisation enthalpy. Accordingly, we observed the most significant increase in the enthalpy values with glycerol addition at low water content (0.4 g water/g dry starch), as demonstrated in Fig. 8, due to the high contribution of glycerol in gelatinising starch.

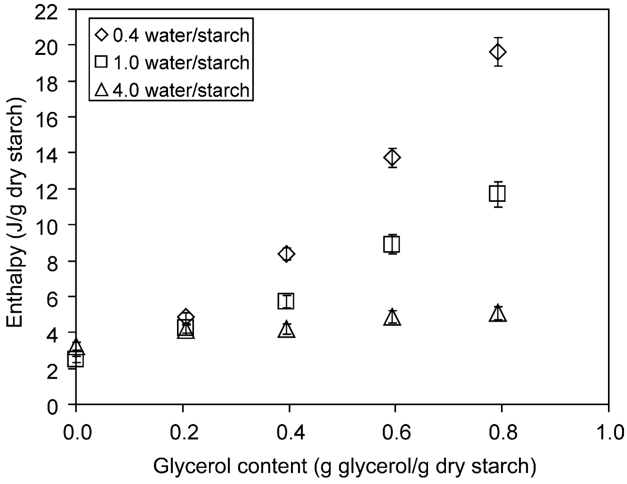

Fig. 8. Gelatinisation enthalpy of normal maize starch upon variation in glycerol content (g glycerol/g dry starch) at different water content (0.4, 1.0 and 4.0 g water/g dry starch).

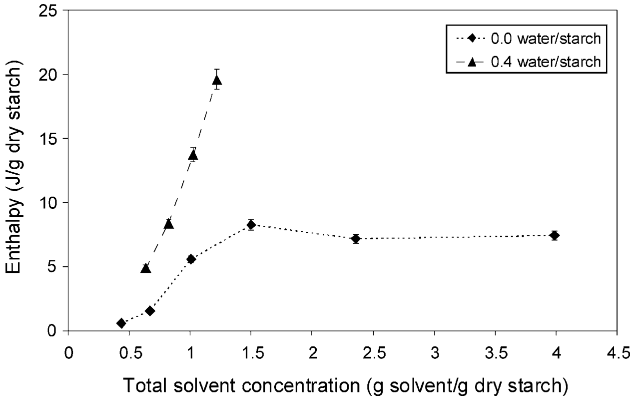

Fig. 9. Enthalpy values of normal maize starch gelatinisation plotted against total solvent (water and glycerol) concentration for systems where glycerol is the dominant ‘gelatinising’ solvent, i.e. at low water content, 0.4 g water/g dry starch and in pure glycerol system (data taken from Tan et al., 2004).

It is worth noting that the enthalpy values for normal maize starch at low water content were significantly higher than its enthalpy in pure glycerol systems. Fig. 9 compares the enthalpy values of normal maize starch gelatinisation in these two systems, plotted against the total solvent concentration. It is clearly shown that on adding glycerol, the enthalpy increases more rapidly in systems with low water content than in pure glycerol systems. This may suggests that the water–glycerol interactions were significant in low water content systems, thus affecting the solvents mixture’s effectiveness to gelatinise starch and caused the unwinding transition to occur with more difficulties, giving rise to a higher overall enthalpy of gelatinisation.

Similarly, it was demonstrated that for the gelatinisation of waxy maize starch at high water content (4.0 g water/g dry starch), the enthalpy was fairly constant on adding glycerol (Fig. 10). Then at intermediate water content (1.0 g water/g dry starch), the enthalpy increased to values higher than those of high water content, attributable to higher ΔH_{HC} as more glycerol contributed its –OH bonds to gelatinise starch. At low water content (0.4 g water/g dry starch), the gelatinisation endotherm was only observed at 0.4 g glycerol/g dry starch and the enthalpy increased as glycerol content was increased further. However, the extent of increase in enthalpy value was lower than the enthalpy increase in intermediate water content, which is contrary to that observed in normal maize starch. Since waxy maize starch possesses a higher double helical order than normal maize starch (Gidley & Bociek, 1985) and hence more starch–starch hydrogen bonds, more solvent(s) would be required to provide more –OH bonds to bring about the same

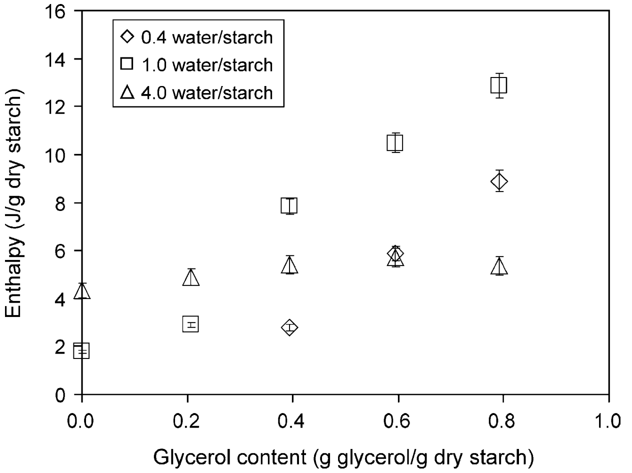

Fig. 10. Gelatinisation enthalpy of waxy maize starch upon variation in glycerol content (g glycerol/g dry starch) at three levels of water content (0.4, 1.0 and 4.0 g water/dry starch).

structural changes as in normal maize. Therefore, the disparity in the enthalpy trend with glycerol at low water content is possibly due to the different intrinsic property (in particular the amount of hydrogen bonds) of the two starch types. So it would be expected that on increasing the glycerol content above 0.8 g glycerol/g dry starch, the enthalpy would continue to increase to values higher than those in intermediate water content, as observed in normal maize starch.

A rather different trend, however, was observed for gelatinisation enthalpy variation of high amylose maize starches with water and glycerol concentration (Fig. 11). For both high amylose maize starches, the enthalpy decreased with glycerol content at high water content (4.0 g water/g dry starch), while at low and intermediate water content the values increased on adding glycerol. Hence, the above hypothesis for waxy and maize starch could not be applied in these high amylose maize starches. This is perhaps due to the fact that the amylopectin structures in high amylose maize starches are quite different from those of waxy and normal maize starch. The maize mutant amylose-extender (ae) is commonly used to generate commercial high amylose maize starches (Evans, McNish, & Thompson, 2003). Characterisation of the macromolecules from these starches revealed the existence of some intermediate materials and anomalous amylopectin with reduced degree of branching and longer average chain length (Kasemsuwan, Jane, Schnable, Stinard, & Robertson, 1995; Pan, 2000; Wang, White, Pollak, & Jane, 1993). As a result, the amylopectin structures and consequently the macromolecules packing could be different in high amylose starches. Furthermore, the association of amylose and amylopectin in each of these maize starches would be somewhat different and hence there exist variations such as transition of crystallinity type from A to B (Cheetham & Tao, 1998), increasing crystalline lamellar size (Jenkins & Donald, 1995) with increasing amylose content. Hence to consider high amylose starches in analogue with SCLCP model may not be appropriate due to the effect of high amylose content inside the granules in a way that is not yet fully understood. Moreover, the fact that the exact conformation of amylose inside starch granules and the precise amylopectin double helical packing in lamellar assembly of high amylose maize starches are still unclear, makes it difficult to understand the gelatinisation behaviour in high amylose starches.

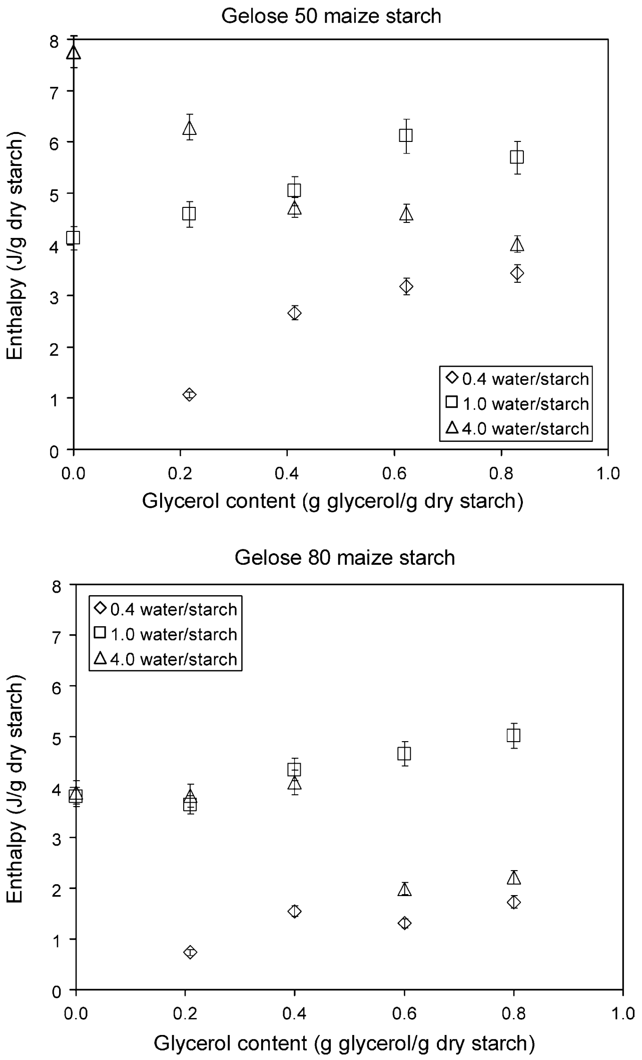

Fig. 11. Variation in the enthalpy of gelatinisation for high amylose maize starches (Gelose 50 and Gelose 80) with glycerol concentration (g glycerol/g dry starch) at three levels of water content (0.4, 1.0 and 4.0 g water/g dry starch).

Therefore, further clarification on the supramolecular structure in high amylose maize starches would be vital before we could extend the hypothesis for high amylose starches. Additionally, further information on the changing dynamic state of starch chains will elucidate the progressive changes in chain dynamics of the amylose component, the rigid and mobile amylopectin components in the semi-crystalline lamellae and amorphous growth ring, respectively, as gelatinisation proceed. Moreover, changes in the solvent microscopic distribution within the granules during gelatinisation will provide further information on solvent's penetration into granules to bring about the breakage of starch–starch –OH bonds, formation of starch–solvent –OH bonds, and finally the unwinding helix–coil transition. Thus, our future works will emphasise on the investigation of changes in chain dynamic states of starch components (amylose and amylopectin) and solvent microscopic distribution within the granules during gelatinisation of the different starch types using NMR relaxometry. Comparative NMR studies between different starch types with varying amylose content will be conducted to extend the hypothesis, incorporating the influence of amylose/amylopectin ratio and their molecular properties such as degree of branching, chain length distribution, on the granular structures.

4. Conclusion

The application of MTDSC to investigate starch gelatinisation has provided clarification on the glass transition phenomena during the course of gelatinisation process. Plasticisation of the granules prior to gelatinisation was not observed and it was found that the glass transition temperature essentially overlapped with the gelatinisation peak temperature. The heat capacity change accompanying gelatinisation, which has been deemed as due to glass transition, is in fact due to a change in state of the starch macromolecules from being highly restrained within the granular packing to entangled macromolecules as the order to disorder transition occurs. The addition of glycerol promoted starch gelatinisation in systems with a low water content. It was postulated that the same structural changes occurred in these systems regardless of the solvents used and that the major structural element within starch, i.e. hydrogen bonds, has to be broken to bring about the gelatinisation process. The abundant hydrogen bonds present within the granules necessitate the presence of solvent(s) with some hydrogen bonding capacity to allow gelatinisation to proceed at a temperature lower than the decomposition temperature. So, as the starch–solvent(s) system was heated, the solvent would penetrate into the granules and act to disrupt the starch–starch hydrogen bonds to bring about the amylopectin helix–helix dissociation and subsequently the unwinding helix to coil transition. Hence, any solvent with hydrogen bonds would be able to gelatinise starch and its effectiveness highly depends on properties such as molecular size, number of –OH bonds, viscosity, diffusivity and hydrogen bonding capacity. The solvent properties such as viscosity, diffusivity and molecular size would determine solvent ingress into the granules and hence affect the onset gelatinisation onset temperature.

The gelatinisation enthalpy is the additive sum of thermal energy involved due to the breakage of starch–starch –OH bonds (endothermic), formation of starch–solvent –OH bonds (exothermic) and unwinding helix–coil transition (endothermic). Hence, the thermal energy due to the disruption of starch–starch –OH bonds and formation of starch–solvent –OH bonds (ΔH_{OH}) would depend on the amount of –OH bonds disrupted, while the thermal energy due to helix–coil transition (ΔH_{HC}) depends on the ease and readiness of the unwinding helix–coil transition. Consequently, the magnitude of ΔH_{OH} would be an intrinsic property of the starch type and ΔH_{HC} value would be highly dependent on the effectiveness on the solvent(s) used in terms of its hydrogen bonding capacity.

The high amylose maize starches exhibited a distinct trend in the variation of gelatinisation enthalpy with glycerol and water content. Possibly, the supramolecular packing in these high amylose maize starches was quite different from that of the SCLCP. Although the structural breakdowns of these starches do require the breaking of starch–starch –OH bonds in a similar way as in waxy and normal maize starches (which is illustrated in the same trends observed for gelatinisation onset temperature variation with glycerol and water content for all maize starches studied), the unwinding of amylopectin chains from helix to coil may proceed quite differently due to the existence of anomalous amylopectin, some intermediate materials as well as the presence of higher amylose content thus resulting in distinct granular packing of these starches. Consequently, further investigation on the structural characteristics and granular packing in these high amylose maize starches would be essential to extend the hypothesis to cover trends of a whole range of starch with varying amylose content. Moreover, investigation on the changing dynamic states of starch chain components and solvent microscopic distribution within the granules during gelatinisation will provide further information and verification on our hypothesis. Nevertheless, the results of this study has provided information on the glass transition event, which has been quite a controversy in starch research, as well as further insight into the role and influence of glycerol on starch gelatinisation.

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