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Gelatinisation of starch in mixtures of sugars. II. Application of differential scanning calorimetry[☆]

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Abstract

Differential scanning calorimetry was used to investigate the effect of mixtures of glucose and fructose, and five types of honeys on starch gelatinisation. At a 1:1 starch:water ratio, glucose generally increased the enthalpy (ΔH_{gel}) and temperatures (T_{onset}, T_{peak} and T_{end}) of gelatinisation more than fructose. Upon mixing, ΔH_{gel} of the low-temperature endotherm decreased in comparison to the sole sugars, but was fairly constant (7.7 ± 0.33 J/g dry starch). ΔH_{gel} of the high-temperature endotherm increased with the fructose content. For both endotherms, the gelatinisation temperatures were unchanged ($CV \leq 3\%$) for the mixtures. With the honeys (moisture, 14.9–18.0%; fructose, 37.2–44.0%; glucose, 28.3–31.9%) added at 1.1–4.4 g per g dry starch, the enthalpy and temperatures of gelatinisation did not vary significantly ($CV \leq 6\%$). Typical thermograms are presented, and the results are interpreted in the light of the various proposed mechanisms for starch gelatinisation in sugar–water systems, total sugar content and possible sugar–sugar interactions. The thermograms were broader in the presence of the sugars and honeys, and a biphasic character was consistently exhibited. The application of an exponential equation to the gelatinisation temperatures of the starch–honey mixtures revealed an opposing influence of fructose and glucose during gelatinisation. The mechanism of starch gelatinisation may be better understood if techniques could be perfected to quantify breakage and formation of hydrogen bonds in the starch granules, and suggested techniques are discussed.

Keywords: DSC; Glucose; Fructose; Honey; Low-temperature endotherm; Enthalpy of gelatinisation

1. Introduction

Gelatinisation is a key physicochemical transformation that starch granules undergo when they are subjected to heat treatment in the presence of water, although pressure, shear, other solvents (liquid ammonia, alkali and dimethyl sulphoxide), and milling can achieve the same end (Abd Karim, Norziah & Seow, 2000; Blanshard, 1987; Fukuoka, Ohta & Watanabe, 2002; Lai & Kokini, 1991; Olkku & Rha, 1973). Gelatinisation induces a number of changes in the starch granules, and changes such as loss of order (birefringence, X-ray crystallinity), swelling, exudation of amylose, improved digestibility, granule disruption, enhanced solubility, and increased viscosity have been reported (Alavi, 2003; Blanshard, 1987; Karapantsios, Sakonidou, & Raphaelides, 2002). The progression of events during starch gelatinisation depends on the measuring techniques, which are many, varied and diverse (Blanshard, 1987; Jenkins & Donald, 1998; Lai & Kokini, 1991; Liu, Charlet, Yelle & Arul, 2002; Olkku & Rha, 1973; Steven & Elton, 1971). Calorimetry, specifically, differential scanning calorimetry (DSC), appears to be the most widely used technique, where the heat flow changes associated with both first and second order transitions of polymeric materials can be detected, and these can be studied across a wider range of moisture and temperature than most techniques (Biliaderis, Maurice & Vose, 1980;

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Donovan, 1979; Fukuoka et al., 2002; Lelievre, 1976; Wootton & Bamunuarachchi, 1979a,b, 1980). From DSC studies, gelatinisation is resultantly an endothermic process, although it could involve the following two stages (Steven & Elton, 1971):

> Cleavage of existing hydrogen bonds (endothermic).
> Formation of new bonds (involving water) to give a less ordered structure (exothermic).

This opinion has been corroborated by, among others, Fourier transform infra-red (FTIR) studies, which show that below the gelatinisation temperature no interactions between starch and water are apparent but as temperature increases, intensity of some bands (1640 cm^{-1}) increases with a new peak at 1020 cm^{-1} (Liu et al., 2002). This suggests rupturing of most inter- and intra-hydrogen bonds and hydrophobic bonds of the starch, while an increase in absorbance after a critical temperature indicates sol formation due to exchange of hydrogen bonds between starch and water.

For many of its applications, starch is usually combined with various additives, and sugars are common for food applications in baked goods, breakfast cereals, snacks, and ready-to-eat (RTE) foods. These additives play a role and, consequently, influence molecular changes that starch experiences during gelatinisation. The influence of sugars on starch gelatinisation has been extensively studied for many decades, and various mechanisms (Table 1), extensively discussed elsewhere, have been proposed to explain why sugars increase gelatinisation temperature, decrease the resulting viscosity and de- or in-crease the heat (enthalpy) of gelatinisation (Ahmad & Williams, 1999; Bean, Yamazaki & Donelson, 1978; Eliasson, 1992; Hester, Briant & Personius, 1956; Maaurf, CheMan, Asbi, Junainah & Kennedy, 2001a; Perry & Donald, 2002; Savage & Osman, 1978; Spies & Hoseney, 1982; Wootton & Bamunuarachchi, 1980). However, despite advances in understanding the behaviour of sugar–water–starch systems, no single mechanism explains the influence of di- and mono-saccharides across the entire spectrum of sugars or, generally, solutes. This could be because of inherent differences in the physicochemical characteristics of these materials. Using DSC and X-ray diffraction techniques, Perry and Donald (2002) proposed a mechanism for gelatinisation in sugar and glycerol systems, however, they admitted that their results did not agree with other findings (e.g. Eliasson, 1992) possibly because of differences in the concentrations of starch–water–sugar systems studied. Moreover, previous studies have concentrated on single sugar systems, despite the possibility of mixtures of these sugars being used for various formulations. Formulations exist in the food industry, particularly where honeys, natural mixtures of sugars, are used for their health and nutritional benefits (Anon, 2002; Babacan, Pivarnik & Rand, 2002; Busserolls, Gueux, Rock, Mazur & Rayssiguier, 2002; Cardetti, 1997). Honey essentially consists of water, 13–23%, glucose, 27–44% and fructose, 22–40% (White, 1978), and the authors of this paper are unaware of any calorimetric study on starch gelatinisation in mixtures of sugars. We have recently commenced investigations in this direction, and reported the rheological behaviours and properties of starch–honey systems (Sopade, Halley & Junming, 2004). This paper is a continuation of our studies in this area, with the primary objective of investigating gelatinisation in mixtures of fructose and glucose, as well as in honeys.

Table 1
Broad classification of selected mechanisms of the effects of sugars (solutes) on starch gelatinisation[a]

Physical interaction	Chemical interaction
Reduction of water activity	Higher affinity for water
Boiling point elevation	Free and bound water
'Antiplasticisation' by sugar–water co-solvent	Sugar–starch interactions
Increase in free volume resulting in less plasticising effect of sugar–water solvent	Delayed swelling
Rate of penetration of sugar molecules into the interior of the starch granules	Change in conformation of the starch polymer
Molecular weight issue	Decrease in translational and rotational mobility
Increased viscosity	
Slow rates of diffusion	
Reduction in water polarization	

[a] Some mechanisms can apply to both interactions.

2. Materials and methods

2.1. Materials

Wheat starch, traded as Wheaten cornflour™ (Penford Aust. Ltd, NSW 2066), and five honeys (Bloodwood, Gumtop, Leatherwood, Stringybark NT, and Yapunyah), products of Capilano Honey Ltd, Richlands, QLD 4077, were used. The moisture content of the starch was about 12.3% as determined by oven-drying method (AOAC, 1990), while Table 2 shows the water, glucose and fructose contents of the honeys. Fructose and glucose of analytical grade, additionally dried over P_2O_5, were used. Millipore Q™ water (ultrapure) was used for all dilutions, solutions and pastes.

2.2. Methods

2.2.1. Formulations

Appropriate solutions of fructose and glucose were prepared and added to the starch to give 1:1 starch:water ratio with the sugars being 0.26–0.86 g/g dry starch. The solutions, rather than sugar crystals, were used in order to prevent dissolution of the sugar crystals during the DSC measurements, which could introduce erroneous peaks

Table 2
Selected composition of the Australian honeys[a]

Honey	Botanical name	Code	Moisture (%)	Fructose (%)	Glucose (%)
Bloodwood	*Eucalyptus intemedia*	Bwood	16.3	44.0	30.9
Gumtop	*Eucalyptus moluccana*	GumTop	17.0	43.8	31.9
Leatherwood	*Eucryphia lucida*	Lwood	14.9	38.9	31.2
Stringybark NT	*Eucalyptus tetradonta*	STBark	18.0	40.3	28.3
Yapunyah	*Eucalyptus ochrophloia*	Yap	15.8	37.2	29.8

[a] Adapted from Sopade et al. (2001).

(Eliasson, 1992; Maaurf et al., 2001a). At 0.86 g sugar/g dry starch, fructose–glucose mixtures were prepared to make 30:70, 50:50 and 70:30 mixtures. Five formulations per honey were prepared to give moisture levels (g/g dry starch) of 0.34–0.80. About 5–10 g of each formulation was prepared and thoroughly mixed manually with a spatula before leaving (not less than 12 h) on a slow roller at room temperature to equilibrate. We have observed the need to allow even moisture distribution throughout the sample in order to prevent localised wetting prior to DSC analysis.

2.2.2. Calorimetry

The TA 2920 Modulated DSC (TA Instruments Inc. New Castle, DE, USA) was used at 10 °C min^{-1} from 30 to 180 °C with an empty pan as the reference. The DSC is routinely calibrated for temperature and enthalpy using indium (T_m = 156.6 °C, ΔH = 28.5 J g^{-1}), mercury (T_m = −38.9 °C, ΔH = 11.4 J g^{-1}), tin (T_m = 231.9 °C, ΔH = 60.6 J g^{-1}), and zinc (T_m = 419.5 °C, ΔH = 108.0 J g^{-1}). Samples were weighed (≈10 mg) into aluminum pans and hermetically sealed prior to analysis. The Universal Analysis™ software was used to obtain the onset, peak and end temperatures as well as the enthalpy of gelatinisation. Not less than duplicate analysis was done per sample, and results are presented as means since coefficient of variation (100×standard deviation/mean), CV, was found to be less than 7%.

3. Results and discussion

3.1. Effect of moisture content

The gelatinisation behaviour of the starch in different concentration of water (0.43–2.34 g water/g dry starch) is shown in Fig. 1. The trend described in Fig. 1 follows published studies that under limited water, gelatinisation and melting of starch crystallites occur (Biliaderis et al., 1980; Donovan, 1979). Perry and Donald (2002) have suggested that as the relative amount of solvent becomes limited, the first part of gelatinisation occurs by the same process as in excess solvent. Once all the available solvent that is external to the granule has been exhausted, the cooperative plasticisation process is arrested, and further gelatinisation depends upon increased levels of molecular mobility and granular swelling that are initiated and enhanced by heat. This demands heating to higher temperatures than in excess solvent, and consequently, two endotherms (low-temperature, LTE, and high-temperature, HTE) evolve, with the later decreasing in intensity and temperature as the starch fraction decreases (Fig. 1). Table 3 contains the gelatinisation parameters of the starch–water systems, and it can be observed that the temperature of the HTE increases with starch concentration, while that of the LTE is relatively unaffected. Moreover, while the span of the gelatinisation process, ΔT_{gel} ($=T_{\text{end}}-T_{\text{onset}}$), is relatively constant with the LTE (11.9–12.7 °C), it varies more with the HTE (8.7–12.7 °C) as moisture content increases. Conflicting reports exist in the literature on the trend of the gelatinisation span with water and/or solutes possibly because of differences in starch genotypes and concentrations studied (Eliasson, 1992; Maaurf, CheMan, Asbi, Junainah & Kennedy, 2001b; Perry & Donald, 2002).

We observed an increase in the enthalpy of gelatinisation with an increase in moisture content (Table 3) for the LTE, while the reverse occurs with the HTE. The trend displayed by the LTE is in agreement with that of Maaurf et al.

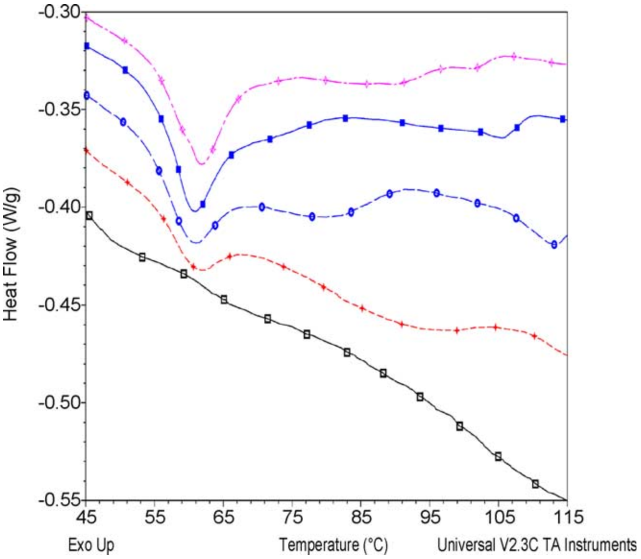

Fig. 1. Starch gelatinisation at different water levels (from bottom per g dry starch—0.43, 0.67, 1.01, 1.50, 2.34 g water). All thermograms are vertically displaced for clarity, and this applies to all the figures.

Table 3
The gelatinisation parameters of the starch–water–sugar formulations (per g dry starch)

Mixture	Concentration		Enthalpy (J/g dry starch)	Onset (°C)	Peak (°C)	End (°C)
Starch–water	Water in g		Low temperature endotherm			
	0.43		nd[a]	nd	nd	nd
	0.67		1.4	56.1	61.9	68.7
	1.01		3.1	56.0	60.8	67.9
	1.50		4.5	55.3	60.6	67.2
	2.34		6.3	54.4	60.3	67.1
			High temperature endotherm			
	0.43		3.5	164.0	168.7	172.7
	0.67		2.1	117.2	122.3	127.2
	1.01		1.2	107.0	113.1	119.7
	1.50		nd	nd	nd	nd
	2.34		nd	nd	nd	nd
Starch–water–fructose (1 g water per g dry starch)	Fructose in g		Low temperature endotherm			
	0.26		4.9	59.8	65.8	74.9
	0.43		5.3	63.7	69.8	77.5
	0.60		5.6	67.3	73.3	80.3
	0.86		12.2	72.0	78.9	95.6
			High temperature endotherm			
	0.86		2.3	110.7	120.9	126.1
Starch–water–glucose (1 g water per g dry starch)	Glucose in g		Low temperature endotherm			
	0.26		3.9	61.5	67.3	73.9
	0.43		4.1	66.7	71.3	79.6
	0.60		6.3	69.2	75.5	83.8
	0.87		14.1	75.7	82.1	99.4
			High temperature endotherm			
	0.87		1.9	114.3	123.0	127.9
Starch–water–fructose–glucose (1 g water per g dry starch)	Fructose in g	Glucose in g	Low temperature endotherm			
	0.26	0.60	7.6	75.0	80.8	88.0
	0.44	0.43	8.1	74.6	80.3	88.2
	0.60	0.26	7.4	73.9	80.0	87.1
			High temperature endotherm			
	0.26	0.60	1.4	114.3	121.6	126.4
	0.44	0.43	1.3	115.2	121.1	125.8
	0.60	0.26	2.0	106.4	120.8	126.8

[a] nd = Not detected.

(2001b), but these authors did not obtain a distinct HTE despite studying a fairly concentrated (< 1 g water per g dry starch) system. If according to Steven & Elton (1971) gelatinisation is about breakage (endothermic) and formation (exothermic) of hydrogen bonds in the starch, it is reasonable to accept that there would be more breakage of intramolecular bonds with more water, which penetrates and swells the amorphous region thereby increasing mobility. However, the presence of more water would also increase formation of intermolecular hydrogen bonds, perhaps with less difficulty and possibly less energy. The overall energy would be endothermic, and this is expected to increase with water content. The HTE is a much more heat-driven process, and its intensity would be expected to be inversely related to the water level because the available water would have been associated with the water-driven LTE.

3.2. *Effect of fructose and glucose*

Figs. 2 and 3 show the effect of fructose and glucose on the gelatinisation characteristics of the starch. Generally, both sugars delayed the gelatinisation process, and the delay increased with the concentration of the sugars. These results are in agreement with published studies, and some of the mechanisms proposed for such an effect have been itemised above. Comparatively, glucose was more effective in delaying gelatinisation (Table 3), but fructose yielded a higher ΔH_{gel} at low concentrations (< 0.6 g/g dry starch). Although sugars generally have higher affinity for water than starch, from the gelatinisation temperatures obtained, it can be inferred that they possibly did not substantially reduce the available water for gelatinisation until at a concentration of about 0.86 g per g dry starch or about 46%

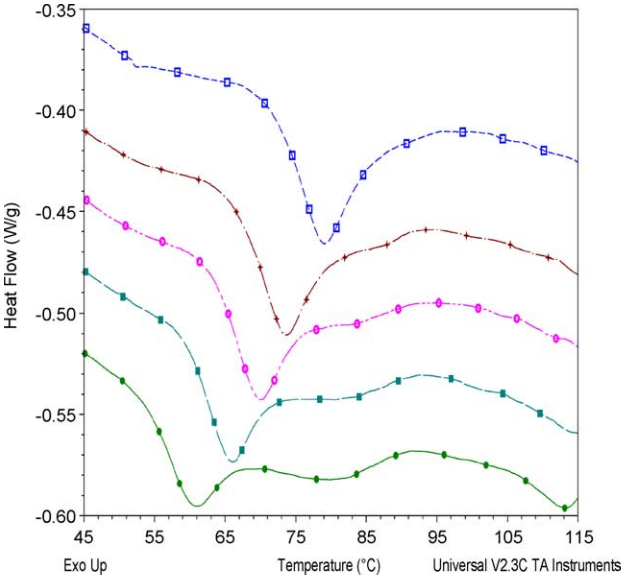

Fig. 2. Gelatinisation in starch–fructose–water systems (from bottom per g dry starch—0; 0.26; 0.43; 0.60; 0.86 g fructose).

sugar solution. This is because, at concentrations below this, only one endotherm was evident with the starch–water–sugar systems. At the highest concentration of the sugars studied, the temperatures of the high-temperature endotherm are identical to those of 0.67 g water per g dry starch (Table 3). However, the temperatures of the LTE at the highest concentrations of the sugars are higher than the corresponding ones for the 0.67 g water per g dry starch formulation. This, in a way, shows that the delay in starch gelatinisation by sugars is not entirely through the mechanism of available water ('limiting water'), but this does not infer that literature reports have chosen this as the sole mechanism. To a certain extent, this observation agrees with the deductions from Perry and Donald (2002), who opined that solutes generally delay the threshold of gelatinisation, and once that is passed, gelatinisation occurs as if in excess water. They went further to suggest that the presence of solutes does not broaden the gelatinisation process, nor introduce a biphasic 'limiting water' character. This is probably understandable because neither they, Eliasson (1992) nor Maaurf et al. (2001a) reported both the LTE and HTE that we observed at about 46% sugar solution in the present studies, which suggest a biphasic character. Also, we observed slight broadening ($\Delta T_{\mathrm{gel}} = 12.4$–$15.1$ °C) of the gelatinisation process below about 38% sugar solution, and substantial broadening ($\Delta T_{\mathrm{gel}} = 24$ °C) at 46% sugar solution for the LTE. Moreover, $\Delta T_{\mathrm{gel}} = 13.6$–$15.4$ °C for the HTE for both sugars, and this is higher than the range reported above for 0.43–1.01 g water per g dry starch. With these observations, gelatinisation in these sugar solutions could not have strictly proceeded as if in excess water even after overcoming the gelatinisation threshold.

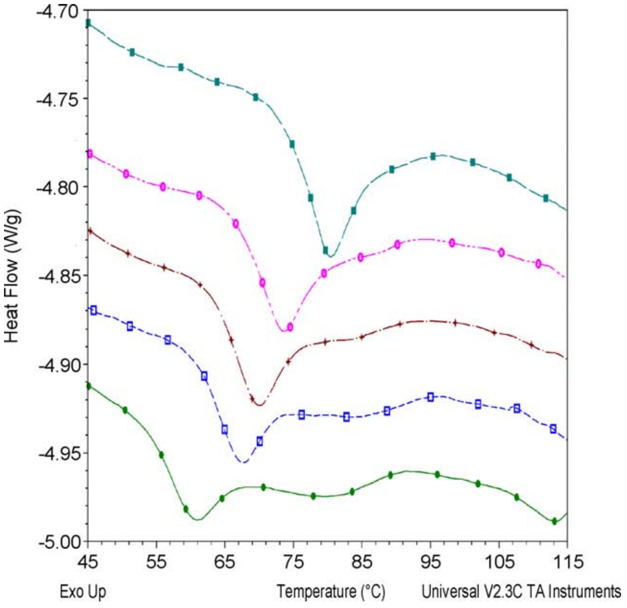

Fig. 3. Gelatinisation in starch–glucose–water systems (from bottom per g dry starch—0; 0.26; 0.44; 0.60; 0.87 g glucose).

Similar to the trend with water content, the enthalpy of gelatinisation increases with an increase in either fructose or glucose (Table 3); a result that agrees with that of Eliasson (1992), who worked with sucrose. However, some studies have reported it to increase, decrease or not affected at all by sugars (Maaurf et al., 2001a). Through their hydroxyl groups, sugars are expected to form strong bonds with water, alter its chemical characteristics and possibly decrease its rate of ingress into the amorphous region to break the existing hydrogen bonds in the starch. Huang, Tang, Swanson, Cavinato, Lin and Rasco (2003) have noted that the presence of solutes in hydrocolloid systems can induce changes in the hydrogen bonding within water molecules, and consequently alters the shape and position of water bands in the near-infrared region to suggest modifications of water-water and water–colloid interactions. With starch–water–sugar systems, such sugar-induced modifications could alter the swelling behaviour of starches in the presence of sugars. Changes to the swelling ability of starches in the presence of sugars have been reported (Ahmad & Wlliams, 1999), although it seems that the relationship between swelling and sugar concentration is not linear; an increase at low concentrations followed by a decrease at high concentrations. However, using the proposal of Steven and Elton (1971), one could deduce that, since sugars could modify certain chemical characteristics of water, more energy would be required in breaking the hydrogen bonds in the starch than in forming such bonds in the presence of sugars. Hence, enthalpy of gelatinisation (relative to dry starch) should possibly increase with an increase in sugar concentration. Singh, Singh, Kaur, Sodhi, and Gill (2003) suggested that gelatinisation enthalpy gives an overall measure of crystallinity (quality and quantity), and it is an indication of the loss of molecular order within the granules. The ease at which this order is lost is expected to be influenced by the composition of the liquid phase in which the starch is, and the extent of interactions between the starch and solutes in the solution. Although FTIR studies did not show pronounced starch-water interactions prior to onset temperature, nuclear magnetic resonance (NMR) studies indicated starch–sugar interactions before the onset of gelatinisation, and the interaction sites for sucrose have been identified as the G1, G5 and G6 (G-glucose), and F1 and F6 (F-fructose) carbon atoms (Ahmad & Williams, 1999; Liu et al., 2002). Although it is a mathematical exercise, the applications of the linear or non-linear form of the Flory–Huggins equation to the temperature-solvent data of starch–water–sugar systems have also shown a form of interaction between these components (Blanshard, 1987; Farhat & Blanshard, 1997; Maaruf et al., 2001b). However, we did not extensively apply the equation to our data because its suitability in describing starch–water–sugar systems has been well demonstrated, but from our data and some published ones, T_m^o, the true melting point of the undiluted starch, is generally higher in starch–water–sugar systems than in starch–water systems.

3.3. Effect of fructose–glucose mixtures

At 0.86 g sugar per g dry starch in a starch–water system of 1 g water per g dry starch solution, concentrations of fructose and glucose were varied in mixtures of these monosaccaharides. Gelatinisation of the starch was delayed to about the same extent as either of the sugars, the biphasic character was maintained, the gelatinisation process was narrowed for the LTE ($\Delta T_{gel} = 13–13.6$ °C) and widened for the HTE ($\Delta T_{gel} > 15$ °C), and while ΔH_{gel} for the LTE was substantially reduced, that for the HTE was effectively unchanged in comparison to either of the sugars (Table 3). The gelatinisation temperatures of the fructose–glucose mixtures did not depend on the composition of the mixtures, and they fall within the range for the sugars (Fig. 4). This shows that when these sugars are mixed, gelatinisation will proceed as if in one of the sugars, but will be concluded at a slightly lower temperature with less energy. The relative reduction in ΔH_{gel} for the LTE is indicative of changes to the demand for thermal energy for the breakage and formation of hydrogen bonds within the starch granule. Remarkably, the resulting ΔH_{gel} from the mixtures is comparable to that with water. If fructose and glucose could singly modify the characteristics of water to yield higher enthalpy of gelatinisation in the present study, it appears that when they exist together, the interactions between them possibly leave the water (chemically) unaffected as to pose no substantial effect on the energy required for gelatinisation. The detailed chemistry behind this observation demands further investigation, but simply fructose is a ketose sugar, while glucose is an aldose sugar. The positions of the hydroxyl groups in these sugars are expected to influence hydrogen bonding with water and/or starch, and sugar–water interactions. Both fructose (levorotatory) and glucose (dextrorotatory) exhibit opposite tendency during light polarization, and it is unknown to what extent these chemical differences or opposites could have influenced the trend with, and define the mechanisms behind the enthalpy of gelatinisation in mixtures of these sugars. We are interested in the situation with total concentrations other than 0.87 g sugars per g dry starch, coupled with polarimetry studies on such solutions. The applications of temperature-modulated DSC (MDSC) to such mixtures of glucose, fructose and other sugars (sucrose, maltose, etc.) should contribute to the understanding of gelatinisation in these systems. This is because reversible and non-reversible reactions can be separated and, possibly, better quantified (Coleman & Craig, 1996; Gill, Sauerbrunn & Reading, 1993; Höhne, 1999; Lai & Lii, 1999; Micard & Guilbert, 2000).

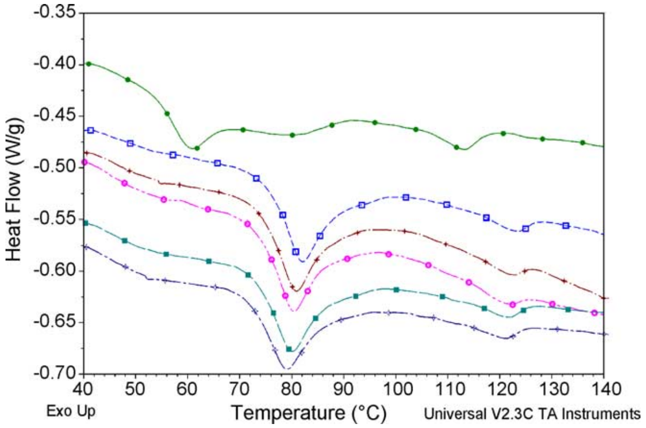

Fig. 4. The gelatinisation thermograms of the starch–fructose–glucose mixtures (from top per g dry starch—no sugars, 0.86 g glucose, 0.26 g fructose 0.60 g glucose, 0.43 g fructose 0.43 g glucose, 0.60 g fructose 0.26 g glucose, 0.86 g fructose).

3.4. Gelatinisation in starch–honey systems

As highlighted above, both fructose and glucose are the main sugars in honeys, and Figs. 5 and 6 show the typical thermograms for gelatinisation of starch in the honeys, and when the concentration of a type of honey was varied. As expected, the honeys delayed the gelatinisation process, but when gelatinisation started, it did not proceed as if in excess water because $\Delta T_{gel} = 17.4–34.6$ °C (LTE) and 4.5–16.3 °C (HTE), and these are ranges that are greater than in excess water systems (3.1). Furthermore, the following can be deduced from Table 4:

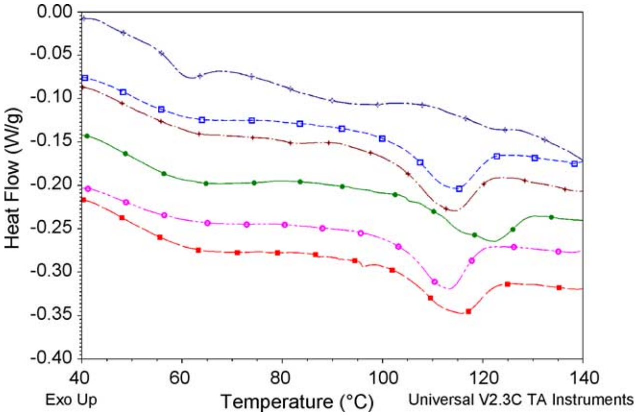

Fig. 5. The gelatinisation thermograms of starch–honey systems at 0.68 g water per g dry starch (from top, starch; Bwood, GumTop, Lwood, STBark, Yap).

a. Gelatinisation was initiated at temperatures close to 100 °C.
b. All the formulations exhibited a biphasic character.
c. The gelatinisation process was generally broader than in the starch–water or starch–water–sugar systems for both endotherms.
d. The gelatinisation temperatures are effectively unaffected by the quantity of honey because water, fructose and glucose (and other components) changed with the amount of honey added.
e. The gelatinisation enthalpy for the LTE is higher than that for the fructose–glucose mixtures, but comparable to that for either of the sugars, and is unaffected by the amount of honey.
f. Generally, the gelatinisation enthalpy for the HTE is about the same as for the fructose–glucose mixtures, and are unaffected by the quantity of honey.

Hence, from these observations, it can be inferred that the breakage and formation of hydrogen bonds in the starch–honey systems occurred with an overall energy that is more than in excess water. The development of the biphasic character is akin to a ‘limited water’ scenario for all the formulations, and we have explained above that this mechanism is not entirely applicable at all concentrations. As can be seen in Fig. 7, at a water level of about 0.34 g water per g dry starch (25% water), no distinct gelatinisation endotherm was obtained in a starch–water mixture before 160 °C, while starch–honey mixtures were gelatinised within this temperature (90–140 °C). If the sugars in the honey reduced the available water for starch gelatinisation, there would have been no endotherm within this temperature range, and the mixtures would have had to be heated to a much higher temperature (>160 °C) than required to gelatinise the 75% starch dispersion. Or, perhaps the honeys contributed more water for the gelatinisation process. Working with glycerol, Nashed, Rutgers and Sopade (2003) have used the sorption behaviours of starch and glycerol to explain and model the gelatinisation temperature. While this was successfully done, subsequent studies (unpublished) in our laboratory with maize starches have shown that when glycerol (up to 0.8 g per g dry starch) was added to 75% starch dispersions, distinct gelatinisation endotherms were obtained as against none without glycerol (Wee, 2002). Again, if glycerol preferentially ‘withdrew’ water from the starch–water system, gelatinisation would not have occurred within the temperature range of 70–100 °C. Therefore, using the water availability argument to explain the delay in gelatinisation across sugar or glycerol formulations has gross limitations.

From our previous studies on the physical properties of the honeys, there was no evidence to suggest that the honeys had freezable, free or unbound water in them because of the absence of melting or crystallisation peak when the honeys were cooled to or heated from −130 °C (Sopade, Bhandari, Halley, D’Arcy & Caffin, 2001). We chose undiluted honeys for this study in order to nullify the role of free water during gelatinisation in the starch–honey systems. Hence, the water in the honeys was bound, but it was made available for gelatinisation once the threshold had been surmounted. Spies and Hoseney (1982) investigated the role of bound water on gelatinisation temperature, but concluded that bound water is not directly involved in controlling the temperature at which starch gelatinises. It seems that despite having sugars, the honey provided the liquid phase, and the hydroxyl groups in its components would have participated in the hydrogen bonds with the starch. Since we consistently obtained a biphasic character in the starch–water–sugar (or honey) systems, the suggestion that such character is not prominent or does not have a molecular undertone in starch–water-solute systems needs to be re-examined. It seems that no single mechanism is suitable for all formulations, and a combination of mechanisms might be a feasible approach if the objective is to cater for all scenarios, in view of differences in specific physicochemical effects, as well as molecular organisations and structures of starches.

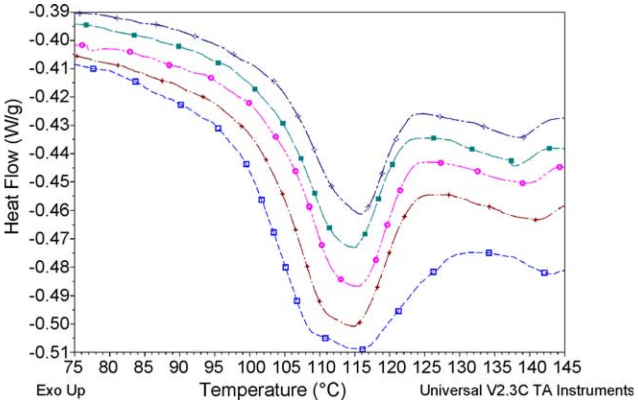

Fig. 6. The gelatinisation thermograms of Bwood-starch systems (from bottom, g per g dry starch; 1.23, 1.94, 2.64, 3.34, 4.04).

Table 4
The gelatinisation temperatures of the starch–honey formulations

Honey	Component (g/g dry starch)				Low-temperature endotherm				High-temperature endotherm			
	Honey	Water[a]	Fructose	Glucose	ΔH_{gel} (J g^{-1})	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	ΔH_{gel} (J g^{-1})[b]	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)
Bwood	1.23	0.34	0.54	0.38	15.9	99.1	109.9	131.6	0.1	143.6	146.0	148.1
	1.94	0.46	0.85	0.60	15.4	102.1	112.8	126.2	0.9	132.2	141.1	145.5
	2.64	0.57	1.16	0.81	15.5	103.7	114.3	124.7	2.6	130.6	138.7	144.3
	3.34	0.68	1.47	1.03	15.0	103.5	114.4	124.5	1.4	133.6	138.1	143.2
	4.04	0.80	1.77	1.25	15.3	104.4	115.6	124.5	1.6	129.7	138.8	144.7
					(15.4±0.3)[c]	(102.6±2.1)	(113.4±2.2)	(126.3±3.1)		(133.9±5.6)	(140.5±3.2)	(145.2±1.8)
GumTop	1.19	0.34	0.52	0.38	14.3	97.2	108.0	130.8	1.0	138.6	144.5	149.0
	1.86	0.46	0.81	0.59	15.6	101.1	110.8	124.6	1.1	130.6	140.5	145.0
	2.53	0.57	1.11	0.81	15.3	102.4	112.4	124.2	1.4	128.3	139.1	143.9
	3.20	0.68	1.40	1.02	16.0	102.6	114.0	123.3	1.2	129.8	137.9	143.0
	3.87	0.80	1.70	1.24	16.8	103.1	114.5	124.6	1.0	131.6	137.5	143.6
					(15.6±0.9)	(101.3±2.4)	(111.9±2.6)	(125.5±3.0)		(131.8±4.0)	(139.9±2.8)	(144.9± 2.4)
Lwood	1.35	0.34	0.53	0.42	14.1	103.3	113.7	132.0	0.3	141.4	145.0	149.4
	2.12	0.46	0.82	0.66	15.5	106.3	117.8	130.9	0.6	132.3	142.3	147.1
	2.89	0.57	1.12	0.90	13.1	108.7	121.3	130.2	0.2	140.0	141.2	145.5
	3.65	0.68	1.42	1.14	14.9	108.5	121.9	130.8	0.6	132.9	139.4	144.4
	4.41	0.80	1.72	1.38	14.9	109.3	122.6	131.5	0.7	133.2	140.4	144.9
					(14.5±0.9)	(107.2±2.5)	(119.5±3.7)	(131.1±0.7)		(136.0±4.4)	(141.6±2.2)	(146.3±2.0)
STBark	1.12	0.34	0.45	0.32	13.5	98.0	108.0	132.6	0.8	136.6	145.6	149.4
	1.75	0.46	0.71	0.50	15.3	100.9	111.0	124.7	1.4	131.9	141.4	146.3
	2.39	0.57	0.96	0.67	15.1	102.1	111.7	122.0	1.6	128.1	139.2	144.3
	3.02	0.68	1.22	0.85	14.9	103.1	113.2	123.4	1.9	128.3	138.5	143.9
	3.65	0.80	1.47	1.03	15.1	103.8	113.2	121.2	0.1	128.3	131.9	134.2
					(14.8±0.7)	(101.6±2.3)	(111.4±2.1)	(124.8±4.6)		(130.6±3.7)	(139.3±5.0)	(143.6±5.7)
Yap	1.28	0.34	0.48	0.38	14.5	98.6	108.8	129.5	0.8	135.8	145.0	148.8
	2.00	0.46	0.74	0.60	15.6	101.7	111.5	125.1	1.2	129.1	141.0	145.4
	2.72	0.57	1.01	0.81	15.0	103.7	113.9	125.2	1.4	128.9	140.1	144.4
	3.44	0.68	1.28	1.03	14.7	104.1	115.5	125.4	1.0	131.1	138.7	144.1
	4.16	0.80	1.55	1.24	15.0	104.5	116.2	125.6	1.5	127.7	138.9	143.0
					(15.0±0.4)	(102.5±2.4)	(113.1±3.0)	(126.1±1.9)		(130.5±3.2)	(140.7±2.5)	(145.1±2.2)

[a] The total water content, and it includes water from the starch.

[b] The coefficient of variation for the enthalpy of the high-temperature endotherm is $>10\%$.

[c] Values are means ± standard deviations for the five formulations per honey.

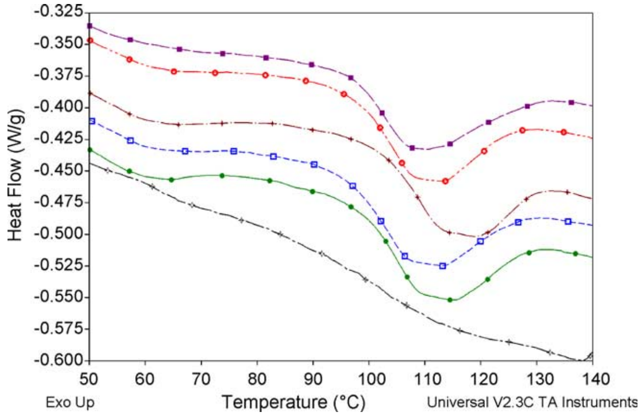

Fig. 7. The gelatinisation thermograms of starch-water and starch–honey systems at about 0.34 g water per g dry starch (from bottom-no honey, Bwood, GumTop, Lwood, Yap, STBark).

Although component–component interactions are well established, it is important to clarify, and possibly quantify these as such might hold the key to understanding gelatinisation in multi-component systems.

It is noteworthy that the gelatinisation temperatures that we obtained in the DSC study for the starch–honey systems are identical to the derived temperatures from our rheological studies (Sopade et al., 2004), even though both techniques measured different properties of the gelatinising starch. In the rheological studies, the contributions of water and the monosaccharides in the honeys to the gelatinisation temperatures were investigated using an exponential model:

$$T_{\text{onset}};\ T_{\text{peak}};\ T_{\text{end}} = A \exp\left(\sum_{i=1}^{n} BiXi\right) \qquad (1)$$

where A, B, constant, X, the fraction of the component relative to dry starch. Table 5 shows the parameters of the non-linear multiple regression analysis, which generally shows that for both the LTE and HTE, the glucose content of the honey increases the gelatinisation temperatures, while the total water present in the starch–honey mixtures decreases it. For the LTE, the more the fructose in the honey, the lower are the temperatures, while for the HTE, it can be generally inferred that an increase in the fructose content of the honey elevates the gelatinisation temperatures. The trend with water is consistent with the well-known gelatinisation mechanism in varying water content, but the trend exhibited by fructose for the LTE, which is opposite to that of glucose, negates the widely held view on the effect of sugars on gelatinisation as discussed above. It can be seen from Table 5 with the analysis of the rheological behaviour of the starch–honeys systems that fructose displays the unexpected trend (also water), while glucose consistently maintains the expected relationship. When it is realised that both viscometry and calorimetry measure different properties and scales of the gelatinising mass, these results possibly confirm that fructose and glucose oppositely influence gelatinisation when they are mixed. We speculated on this possibility above (Section 3.3), even when fructose and glucose were physically mixed. Thus, the major outcome of this study is that, in mixtures of fructose and glucose, the gelatinisation temperatures are as if one of the sugars is present in a concentration that approximates the total for the sugars, but the enthalpy of gelatinisation would be much lower than that for one of the sugars, as the sugars possibly counteract each other.

4. Conclusions

Starch gelatinisation in mixtures of fructose and glucose revealed parameters that are different from the single sugar systems. There could be interactions between the sugars thereby modifying their sole effects, but the total amount of sugars appeared to be the critical gelatinisation factor. With honeys, the gelatinisation temperature was effectively unaffected by increasing the honey content, as the influences

Table 5
The constants in the exponential model

Parameter	A	Water	Fructose	Glucose	r^{2a}
Low-temperature endotherm					
T_{onset}	99.9	−0.13	−0.10	0.26	0.6876
T_{peak}	111.7	−0.25	−0.11	0.34	0.7671
T_{end}	139.1	−0.40	−0.08	0.28	0.6529
High-temperature endotherm					
T_{onset}	149.6	−0.49	0.07	0.11	0.5013
T_{peak}	152.9	−0.26	−0.02	0.11	0.8136
T_{end}	157.6	−0.30	0.01	0.09	0.7213
Parameters from rheological studies[b]					
T_{onset}	93.1	0.20	−0.17	0.24	0.7967
T_{peak}	100.3	−0.0031	−0.14	0.27	0.7258
T_{end}	99.8	0.36	−0.21	0.19	0.5737

[a] r^2 = Coefficient of determination, and all values are significantly ($P < 0.01$) different from zero.

[b] Adapted from Sopade et al. (2004), and included here for comparison purposes.

of water and the monosaccharides on gelatinisation seemed to counteract each other. Other components (sucrose, maltose, turanose, acid, etc.) of the honey could have played a role in the gelatinisation process, however, the water in the honeys, which is non-freezable played a major role in the process. Consistently, a biphasic character was exhibited by the mixtures during gelatinisation, and the width of the gelatinisation endotherm for these formulations showed that the process did not proceed as if in excess water. The concepts of ‘limiting water’, water availability and preferential water sorption by certain solutes, do not explain variations in gelatinisation in these solutes at all the concentrations. Some other proposed mechanisms for gelatinisation in sugars (or solutes) are discussed, but no single one appeared suitable for all the formulations. We have introduced temperature-modulated DSC (MDSC) into our starch research to enable the separation of reversible (e.g. glass transition) and non-reversible (e.g. gelatinisation) reactions, and this should help to quantify the extent of glass transition during the gelatinisation process, and contribute to our understanding of the process.

The gelatinisation enthalpy results from breakage and formation of hydrogen bonds in the starch granules, and it is expected that the environment (water, solutes) in which the granules are, will influence such. Techniques (e.g. infra-red spectroscopy) that reasonably measure existence or non-existence of appropriate bonds in gelatinised or non-gelatinised starch with or without solutes will contribute to the understanding of the gelatinisation process. Huang et al. (2003) have noted that infrared spectroscopy is yet to be fully applied to study polymer gelling temperatures or physicochemical properties of hydrocolloids used in foods, despite its success in polymer science. Dual techniques such as rheo-NMR, rheo-FTIR and DSC-FTIR, where possible with measurable and reproducible signals, will offer opportunities to probe physicochemical changes during gelatinisation, and significantly contribute to the understanding of the process. Some studies on dual techniques are available (Jenkins & Donald, 1998). Gelatinisation in mixtures of sugars offers a new challenge or frontier in clarifying the gelatinisation process because formulations exist in practical, industrial or commercial situations where two or more sugars are mixed (physically or naturally) for desirable product characteristics. The results of this study provide fundamental information of what can occur in such case.

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