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# The effect of sugars on the gelatinisation of starch

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**Abstract**

It is well-known that the addition of sugars and other polyols to starch–water systems elevates the starch gelatinisation temperature, with the elevation being greater the higher the concentration of the aqueous solution and the larger the molecular weight of the added solute. Small angle X-ray scattering combined with wide-angle X-ray scattering and DSC are used to study the effects which aqueous solutions of low molecular weight sugars and other polyols have on starch gelatinisation. It is shown that adding sugars is not equivalent to moving into a regime of limiting water, with no broadening or splitting of the gelatinisation endotherm being observed, other than in limiting solution conditions. The results are interpreted within a phenomenological model of gelatinisation, based on the concept of a continuous plasticisation curve, with a degree of internal plasticisation and self-assembly being required before gelatinisation can proceed. © 2002 Published by Elsevier Science Ltd.

*Keywords*: starch; gelatinisation; solute; sugars; plasticisation

## 1. Introduction

Gelatinisation of starch in pure water is generally thought of as a swelling-driven process. In this formulation, stress, applied to the semi-crystalline lamellae due to the expansion of the amorphous growth ring, results in crystallite disruption (Donovan, 1979). In excess water, the degree of swelling and resulting disruption is sufficient to gelatinise the granule fully. It was proposed by Donovan that upon reducing the amount of water, a point is reached at which the limited extent of swelling is insufficient to disrupt the granule completely. Further double helical order is disrupted at a higher temperature by a more conventional melting transition. The relative amounts of swelling-driven disruption and higher temperature melting are dependent upon the amount of water present and the extent to which the amorphous regions are plasticised (Donovan, 1979; Blanshard, 1987; Zobel, Young & Rocca, 1988; Liu, Lelievre & Ayong-Chee, 1991; Jenkins & Donald, 1998). Gelatinisation is therefore thought of as varying from all swelling-driven in excess water, to all (higher temperature) melting at very low levels of water.

Recently it has been proposed that the processes of lamellar assembly and gelatinisation are distinct stages in a continuous progression of increasing plasticisation and molecular mobility (Perry & Donald, 2000; Waigh, Gidley & Komanshek, 2000). Initially, the increasing molecular mobility induced by a combination of solvent and thermal plasticisation produces increased order, lamellar assembly and crystallisation. The input of further thermal energy leads to a level of molecular mobility which is sufficient to disrupt lamellar structure and crystallinity, leading to the production of an amorphous paste which gels upon cooling. In this formulation, the structure of starch is considered to be analogous to that of a side chain liquid–crystalline polymer (Donald & Windle, 1992; Waigh, Perry, Riekel, Gidley and Donald, 1998; Waigh, Kato, Donald, Gidley, Clarke and Riekel, 2000) and gelatinisation is seen as a process which is critically based upon the degree of plasticisation and mobility of the amorphous regions within the starch granule. As well as extending the work of Waigh and co-workers, the concept of starch structure and functionality being governed by plasticisation and molecular mobility builds upon the pioneering water and glass dynamics work of Slade and Levine (Levine & Slade, 1988; Slade & Levine, 1993).

It has been shown in earlier work (Perry & Donald, 2000) that at room temperature a dry granule is less well ordered than when hydrated. The characteristic 9 nm spacing, seen in the small angle X-ray scattering (SAXS) curves of wet slurries is absent when the starch is dry. The change in packing from the dry to hydrated state, shown in Fig. 1, is equivalent to a nematic–smectic transition for the lamellar crystals comprised of double helices of the amylopectin side chains (Waigh, Jenkins & Donald, 1996; Waigh et al., 1998, 2000). Also shown is the further breakdown of packing that occurs as

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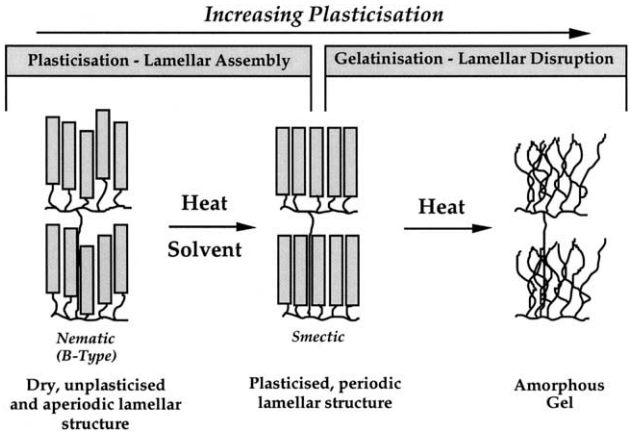


Fig. 1. A schematic representation of the progression of heat and solvent induced changes in B-type starch granule structure. The unplasticised state in A-type starch is more isotropic in character.

the side chains in the double helices unwind, eventually leading to an amorphous gel. The progression shown is for B-type starch: the unplasticised state in A-type starch is more isotropic in character (Waigh, Gidley et al., 2000).

It is proposed that lamellar assembly occurs within the starch granule when the degree of plasticisation—induced by an appropriate combination of solvent and heat—exceeds a certain minimum level. This minimum level of plasticity is that which is necessary to produce mobility within the amorphous lamellar regions of the granule, sufficient to allow smectic-like ordering within the crystalline lamellae, and is thus related to mobility of the sections of the branches which attach the helix-forming regions to the backbone of the amylopectin molecule. In the parlance of liquid crystals, these regions are known as 'flexible spacers'. Subsequently, gelatinisation comes about when the degree of plasticisation and mobility within the amorphous growth rings exceeds a certain maximum level: below this maximum mobility level the smectic-like lamellar structure is stable and amylopectin double helices are intact, while above it the starch granule swells and lamellar and double helical order is irreversibly lost, along with the integrity of the granule as a whole.

To investigate the validity of the concept and the nature of the continuous plasticisation curve for starch granules, the plasticisation state must be controllable. In this paper we explore the effects of selective variation of the combination of plasticising solvent and temperature. This is done by examining the effects of sugars on gelatinisation, as pure water is replaced with aqueous solutions of low molecular weight sugars and polyols, upon the structure and thermal behaviour of starch.

Discussion of the response of starch in aqueous solutions of sugars and other polyols will be divided into two regimes, dependent upon the solution concentration. These concentration regimes will be termed semi-dilute and concentrated. The semi-dilute regime covers the range of concentrations which are of interest when the effects of added sugars on the gelatinisation behaviour of starch is considered. Issues of plasticisation and lamellar assembly and starch–plasticised interactions in model thermoplastic starch materials are covered by the concentrated solution regime, which naturally feeds into pure non-aqueous solvents. It must be noted that the distinction between the two regimes is drawn on the basis of variations in structure and thermal behaviour rather than on concentration, hence more precise definition of these regimes must await the presentation of results below.

The addition of sugars and other polyols to starch–water systems elevates the starch gelatinisation temperature. A number of possible explanations for this effect have been proposed. These possible explanations fall into two categories, with aqueous solutions being considered from two different compositional viewpoints. These viewpoints are that aqueous solutions are equivalent to:

1. water with added higher molecular weight neutral solutes; solutes play a separate role from that of the sole major plasticiser, water;
2. mixtures of two plasticisers of the starch granule; solutes serve to plasticise the starch granule structure, as well as water.

The first viewpoint covers arguments based upon direct starch–solute interactions and the impositions of limiting water conditions, whilst the second viewpoint encompasses explanations based upon the variations of thermodynamic properties and kinetics. Based upon the continuous plasticisation framework discussed above, the second viewpoint is that which is favoured here. In accord with the original ideas of Slade and Levine (1989), it is proposed that sugars and other polyols serve to plasticise the starch granule, but are less effective than pure water. The reduced level of solvent plasticisation, resulting from the addition of solutes to the pure water system, requires a greater level of thermal energy input (heating to higher temperatures) before the starch granule can swell and begin to gelatinise. In this paper the validity of this hypothesis is tested, and a distinction sought between the two compositional viewpoints described.

## 2. Experimental

### 2.1. DSC

A Perkin Elmer DSC-7, equipped with an Intracooler II was used with heating rates between 0.5 and 10°/min. Temperature and enthalpy parameters were calibrated using the melting transition of indium ($T_0 = 156.60$°C, $\Delta H = 28.45$ J/g). An empty sample pan was used as a reference in all cases. Samples were made up as starch slurries of varying composition and were then samples in one of two forms of sample pan. The solutes studied were glycerol, glucose and sucrose. Glycerol (propanetriol) is a common plasticiser for a wide range of biological and synthetic polymers, whilst glucose and sucrose are typical examples of a

monosaccharide and disaccharide respectively, two common additives to starch based food products.

For samples which were not heated above approximately 100°C, in which the risk of solvent loss was usually low, scans were performed using standard aluminium 40-μl sample pans. Pans were weighed before and after running to check for solvent loss. Those indicating mass loss were remade and the runs were repeated. In cases in which the temperature of interest passed beyond this point, Perkin Elmer large volume capsules (LVD) were used. The LVCs had an internal volume of 60-μl and could withstand internal pressures of up to 240 atm, hence the possibility of water loss, even at elevated temperatures, was significantly reduced. Analysis of the data was carried out with the Perkin Elmer system software, with temperature and $\Delta H$values from at least three separate sample runs being collected for each value quoted. Sample masses were within the range 10–25 mg.

### 2.2. SAXS/WAXS

The simultaneous SAXS/WAXS experiments described in this study were performed on Station 8.2 at the Synchrotron Radiation Source at the Daresbury Laboratory, UK. All experiments described were carried out with the small angle detector camera length set between 1.5 and 3.5 m. These provide (with CuK$\alpha$ wavelength radiation) a range $q$ values from 0.02 to 0.500 and 0.009 to 0.230 $\text{Å}^{-1}$, respectively. These $q$ values correspond to $d$-spacings of 12–289 and 28–674 Å. The incident radiation on Station 8.2 has a wavelength of 1.52 Å. The flux of photons is equal to $4 \times 10^{10}$ photons/s. The small angle gas filled quadrant detector is multi-wire, and produces powder averaged diffraction data. The wide angle Inel detector measures powder averaged scattering using a single delay line.

Samples were made up as starch slurries of approximately 40–45% (w/w) starch. Most of the experiments were carried out on waxy maize starch, a gift from National Starch. Potato starch, a gift from Dalgety Food Technology Centre Cambridge, was also used. Solutions of glycerol and ethylene glycol were made up with simple stirring while solutions of other, crystalline solutes (glucose and sucrose) were made by combining stirring and heating. Samples were investigated in aluminium DSC pans, supplied by TA instruments. These pans were modified in an attempt to avoid strong absorption of X-rays by aluminium. Circular holes were punched in the pan tops and mica was fixed onto the inside of the pan, covering the hole, with Araldite epoxy. Mica was used as the window material due to its effective transparency to X-rays. Aluminium rings of depth 0.25 mm were inserted into the pan bottoms to standardise the pathlength of the samples. The pans were inserted into a Linkam hot stage, with thermal contact being maintained between the pan and heater element by the use of steel spring. Additional details about the design of the pan and beamline can be found elsewhere (Bras, Derbyshire & Devine, 1995).

All SAXS/WAXS data were reduced as described previously (Cameron & Donald, 1992; Jenkins, Cameron & Donald, 1994; Jenkins & Donald 1998). The fitting of the SAXS data uses the three-phase model presented earlier, in which the key parameters are the electron density differences between the amorphous lamellae and the amorphous background regions ($\Delta\rho$). The other parameters in the model are the number of lamellae in the semicrystalline stack (N), the average repeat distance between crystalline lamellae (d), the fraction of this repeat distance that is crystalline ($\phi$) and a parameter defining the distribution of lamellar sizes ($\beta$). Fitting procedures to extract these parameters from the SAXS curves have been fully discussed elsewhere (Cameron & Donald, 1992). Note that in all SAXS data the values of $\Delta\rho$ have been normalized, with the first frame value in each case being set equal to unity and the values in all subsequent frames being scaled accordingly. $\Delta\rho_u$ values have been scaled according to the $\Delta\rho$ values, and subsequently displaced vertically for clarity. The values of other structural parameters were not altered during the model fitting of elevated temperature scattering patterns, as in previous work (Cameron & Donald, 1993a,b). The WAXS data has been analysed using the Wakelin method (Wakelin, Virgil & Crystal, 1959) to describe the crystallinity index, as described previously (Jenkins et al., 1994; Jenkins & Donald, 1998).

## 3. Results

Fig. 2(a) shows the effects of varying the concentration of glycerol and glucose solutions on the peak temperature of the gelatinisation endotherm (determined by DSC) from waxy maize starch. Fig. 2(b) shows examples of the DSC traces recorded during the gelatinisation of maize starch in glycerol and sucrose solutions. In each case the gelatinisation onset temperature is found to be the only parameter which changes upon varying the solute or the concentration of the solution. The width of the gelatinisation temperature range (breadth of the endothermic transition) and the enthalpy change associated with gelatinisation are not significantly affected, at least over this concentration range (the study by Eliasson, 1992 which showed a narrowing of the peak, dealt with more concentrated starch solutions). Although data for other starches and solutes is not shown, the elevation of gelatinisation temperature (or more correctly the gelatinisation temperature range) is found to be qualitatively the same whatever the starch cultivar or added polyol. Variations in starch cultivar only result in differences in the absolute magnitude of the temperature elevation associated with each solution.

Fig. 2(a) shows that variations in the effects produced by the different solutes investigated in this work are affected by the solute's size, molecular weight and plasticising ability. The greater the molecular weight of the solute, and hence the less effective it would be expected to be at plasticising

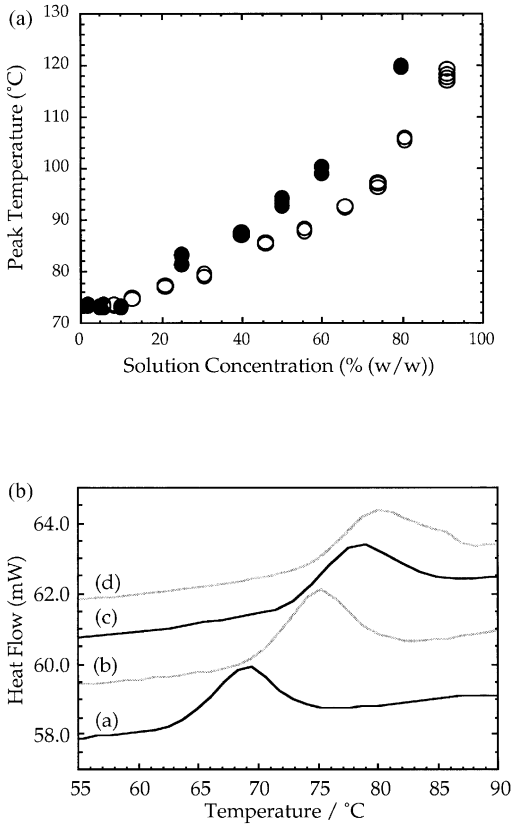


Fig. 2. (a) Peak temperature of waxy maize starch (in 1:3 starch:solution) gelatinisation as function of glycerol and glucose solution (open circles, glycerol; filled circles, glucose); (b) DSC traces (vertically offset) from maize starch in 1:3 starch:solution at a heating rate of 10°C/min. Starch heated: (a) pure water; (b) 25% glycerol; (c) 25% sucrose; (d) 40% glycerol.

the starch granule (according to free-volume theory Young & Lovell, 1991), the greater the temperature elevation at any given concentration. For example (not all data are shown), at a concentration of 40% (w/w), sucrose ($M_w = 342.3$ g mol$^{-1}$) has a greater effect on the gelatinisation temperature than glucose ($M_w = 180.2$ g mol$^{-1}$), which in turn has a greater effect than glycerol ($M_w = 92.1$ g mol$^{-1}$). Correspondingly, the DSC trace for gelatinisation in 25% (w/w) sucrose is shown to be almost identical to that observed in 40% (w/w) glycerol. It must be noted that glycerol, glucose and sucrose all have a high density of hydroxyl groups (a large number of —OH groups per carbon). With starch–starch and starch–solvent hydrogen bonding being of great importance in determining granule structure and plasticisation, the observed relationship between molecular weight and gelatinisation temperature may only hold, to the extent shown, if the —OH group density is kept reasonably constant. It should be kept in mind that reducing the hydroxyl group density, or altering the size of a molecule at constant molecular weight may also affect gelatinisation behaviour.

Knowing the general effect of low molecular weight solutes on gelatinisation, specific aspects can be examined in turn. It is found that for any given starch, at a fixed relative starch–solution composition, the gelatinisation temperature increases with increasing solution concentration. However, by varying the solution concentration at a fixed starch:solution ratio, the values of both the starch:-water and starch:solute ratios are being varied. To explore this effect, three sample compositions were investigated using DSC. In each case shown, the starch cultivar used was waxy maize and the solute was glycerol. Results from waxy maize starch are shown here for two main reasons: to tie in to the greatest extent with the scattering data presented later, where the high intensity of scattering from waxy maize starch makes it an ideal choice, and due to its model, amylose-free structure. The behaviour of other starches investigated was qualitatively identical. Glycerol was used due to the fact that a whole range of solution concentrations (up to pure glycerol) could be formulated; for glucose and sucrose the maximum aqueous solution concentrations which could be produced without precipitation were found to be of the order of 60% (w/w).

Two groups of samples were made with fixed starch:glycerol ratios of 1:1 and 1:3 by weight. In these cases, the solution concentration was varied by changing the starch:water ratio. The other group of samples was made, as in the examples shown previously, with a fixed starch:solution ration of 1:3. In this latter case, both starch: water and starch:glycerol ratios varied. By comparison of the three data sets the effects of varying values of starch: solute and starch:water ratios can be isolated, and the

Table 1
A comparison of the relative weight compositions of mixtures prepared with fixed starch:glycerol and fixed starch:solution ratios

| Solute concentration [% (w/w)] | Starch:glycerol:water compostion | | |
|---|---|---|---|
| | Fixed 1:1 Starch:glycerol | Fixed 1:3 Starch:glycerol | Fixed 1:3 Starch:solution |
| 10 | 1:1:9 | 1:3:27 | 1:0.3:2.7 |
| 25 | 1:1:3 | 1:3:9 | 1:0.75:2.25 |
| 35 | 1:1:1.86 | 1:3:5.57 | 1:1.05:1.95 |
| 50 | 1:1:1 | 1:3:3 | 1:1.5:1.5 |
| 60 | 1:1:0.66 | 1:3:2 | 1:1.8:1.2 |
| 70 | 1:1:0.43 | 1:3:1.29 | 1:2.1:0.9 |
| 80 | 1:1:0.25 | 1:3:0.75 | 1:2.4:0.6 |

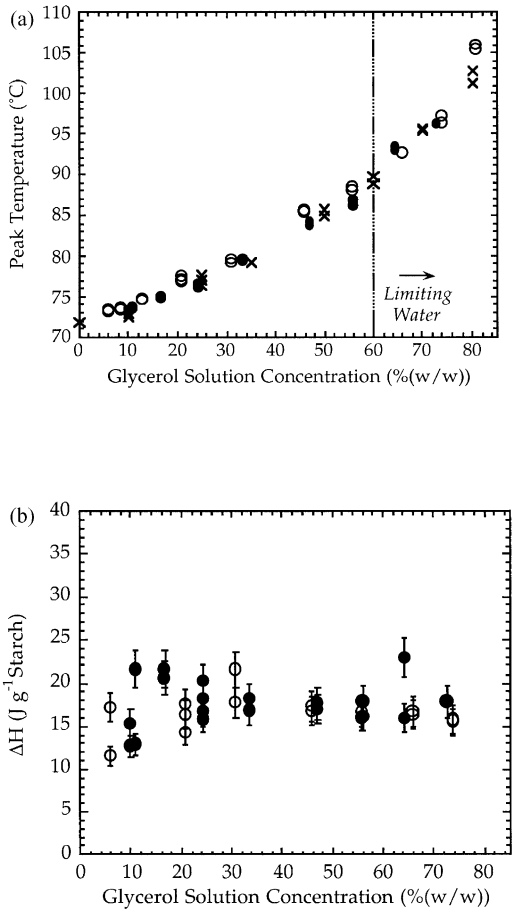


Fig. 3. (a) The effects of sample composition of the glycerol solution concentration dependence of the peak temperatures of the gelatinisation endotherm for waxy maize: filled circles,, 1:1 starch:glycerol; ×, 1:3 starch:glycerol; ○ 1:3 starch:solution. (b) The effects of sample composition on the glycerol solution concentration dependence of the enthalpy of the gelatinisation endotherm for waxy maize: filled circles,, 1:1 starch: glycerol; open circles, 2:3 starch:glycerol.

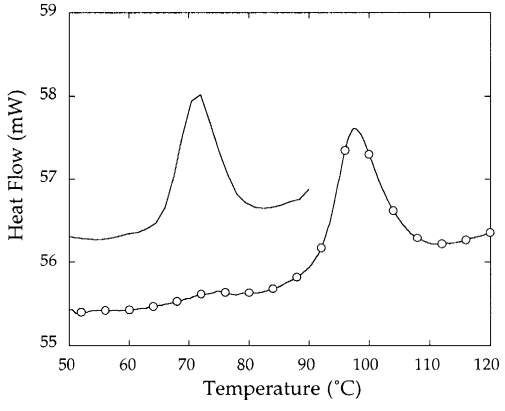


Fig. 4. DSC traces showing the gelatinisation of waxy maize starch in pure water at a fixed starch:solvent composition of 1:3 (solid line) and in an 80% (w/w) glycerol solution at a fixed starch:glycerol composition of 1:1 (open circles). Traces are displaced vertically for clarity.

relative impact of both can be assessed. A comparison of system compositions is shown in Table 1.

The thermal behaviour of these samples was investigated using DSC, with a heating rate of 10°C/min. Fig. 3 shows the variation in peak temperature of the gelatinisation endotherm with increasing glycerol concentration of each of the samples. Also shown is the variation in the enthalpy change, $\Delta H$, associated with the gelatinisation process for the two fixed starch:glycerol samples. $\Delta H$ is determined directly from the area below the DSC endotherm and is expressed in units of J $g^{-1}$ of starch.

Fig. 3 shows clearly that the gelatinisation behaviour of waxy maize starch is not dependent, to any significant extent, upon the starch:glycerol or the starch:solution ratios. The peak temperature and the enthalpy change associated with the gelatinisation endotherm can be seen to be the same whatever the sample composition for any given glycerol solution concentration. Only the overall concentration of the glycerol solution determines the temperature for gelatinisation. This finding lead to a number of conclusions. Firstly, it would seem probable that if direct, specific starch–solute interactions were the cause of gelatinisation temperature elevation, then the effect would become more pronounced as the relative amount of solute compared to starch increased. In this case a disparity between the gelatinisation behaviour of the fixed 1:1 and fixed 1:3 starch:glycerol systems would be anticipated. This does not turn out to be the case: changing the starch:glycerol ratio does not alter gelatinisation behaviour in any significant way. This implies that starch–solute stabilizing interactions are not the cause of temperature elevation.

Secondly, a similar conclusion is reached with respect to the role of water in gelatinisation and the importance of the starch:water ratio. As well as the relative amount of starch and solute not being important, it is also clear that the relative amount of water does not influence gelatinisation behaviour. Table 1 illustrates that each of the three sample compositions, at almost all glycerol solution concentrations, has a different value of the starch:water ratio. Despite these differences there is no corresponding variation in the peak temperature of the gelatinisation endotherm or the enthalpy change associated with it, as Fig. 3 shows.

It is very interesting to note that gelatinisation behaviour is not altered when the starch:water ratio reaches a level at which the sample is effectively in ‘limiting water’ (the boundary of ‘limiting water’ conditions in the fixed 1:1 starch:glycerol system is marked by the dotted line in Fig. 3(a). When the mass of water in the system drops below the mass of starch, a condition which in the absence of glycerol would lead to ‘limiting water’ behaviour (defined by the appearance of two endothermic DSC peaks and a broadening of the gelatinisation temperature range, Donovan, 1979; Donovan & Mapes, 1980) gelatinisation occurs as if in excess water. Even at a glycerol solution concentration of 80% (w/w), at which the starch:water ratio ranges from 1:0.25 to 1:0.75, there is no broadening of the DSC

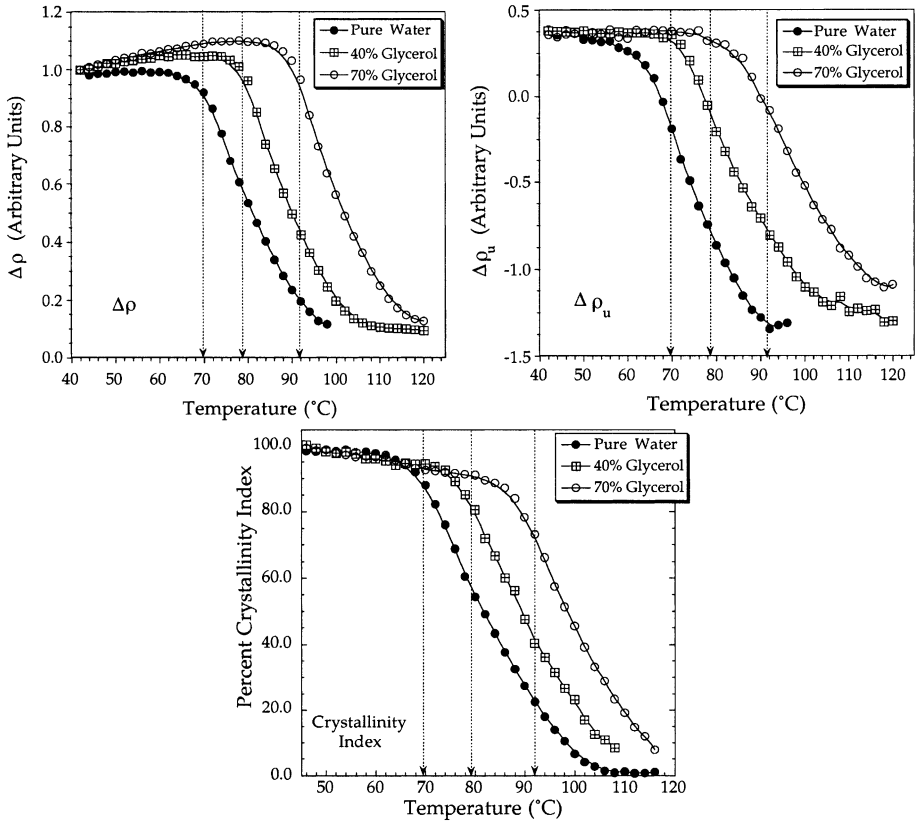


Fig. 5. The effects of glycerol concentration on the decay of $\Delta\rho$, $\Delta\rho_u$ and crystallinity index in waxy maize starch, heated at 2°C/min. Dotted lines indicate the peak temperature of the DSC endotherm from (from left to right) pure water, 40 and 70% (w/w) glycerol solutions.

endotherm and no appearance of a second peak. This is illustrated in Fig. 4, where the DSC traces recorded during gelatinisation in pure water, at a system composition of 1:3 starch:water, and in 80% (w/w) glycerol, at a system composition of 1:1 starch:glycerol, are compared. No qualitative difference is found in gelatinisation behaviour over the whole of the concentration range.

Simultaneous small and wide angle X-ray scattering (SAXS/WAXS) was carried out on Station 8.2 at the Synchrotron Radiation Source at the Daresbury Laboratory, in an attempt to elucidate the effects of sugars on the loss of lamellar and crystalline order occurring during gelatinisation. Dynamic data were collected during the heating of waxy maize starch samples mixed with pure water (as a control) and a range of semi-dilute aqueous solutions. Variations in electron density differences between the three regions of the granule (crystalline and amorphous lamellae and amorphous growth rings) were determined from the best-fits to the experimental SAXS patterns, with starch being modeled as a three phase 1-D paracrystalline lamellar stack, as described in earlier papers (Cameron & Donald, 1992, 1993a,b). Results from these earlier studies have allowed structural changes represented by variations in $\Delta\rho$, $\Delta\rho_u$ and crystallinity index to be identified. The onset of variation in $\Delta\rho_u$ marks the onset of swelling within the amorphous growth ring regions of the starch granule. Swelling and water ingress in these regions reduces the value of $\rho_u$ (the electron density of the amorphous growth ring) and hence, with the amorphous lamellae remaining unaffected, $\Delta\rho_u$ decreases. The onset of swelling and decay in $\Delta\rho_u$ is found always to precede the onset of change of lamellar structure, as reflected in changes in $\Delta\rho$. The onset of reduction in $\Delta\rho$ correlates with the onset of change in crystallinity index: crystallinity loss is initiated at the point at which lamellar disruption commences. In excess water $\Delta\rho$, $\Delta\rho_u$ and crystallinity index all decay in a continuous one step process.

In 'limiting' water [~65% (w/w) starch] the decrease in $\Delta\rho$, $\Delta\rho_u$ and crystallinity is initiated at the same temperature as in excess water, but the rate of decrease is much slowed. Each of these parameters decays over a temperature range which is greatly increased from that found in excess water. Reduction of $\Delta\rho_u$ is found also to occur in a two-step process: an initial rapid drop is followed by much slower reduction at higher temperatures. The point at which this change in rate is observed is assigned as being the point at which all available water external to the granule is exhausted and swelling slows. The studies here investigate whether the addition of sugars and other polyols induce variations in the mechanism or chronology of processes constituting gelatinisation, and if there is any evidence to suggest that the presence of non-aqueous solutes imposes

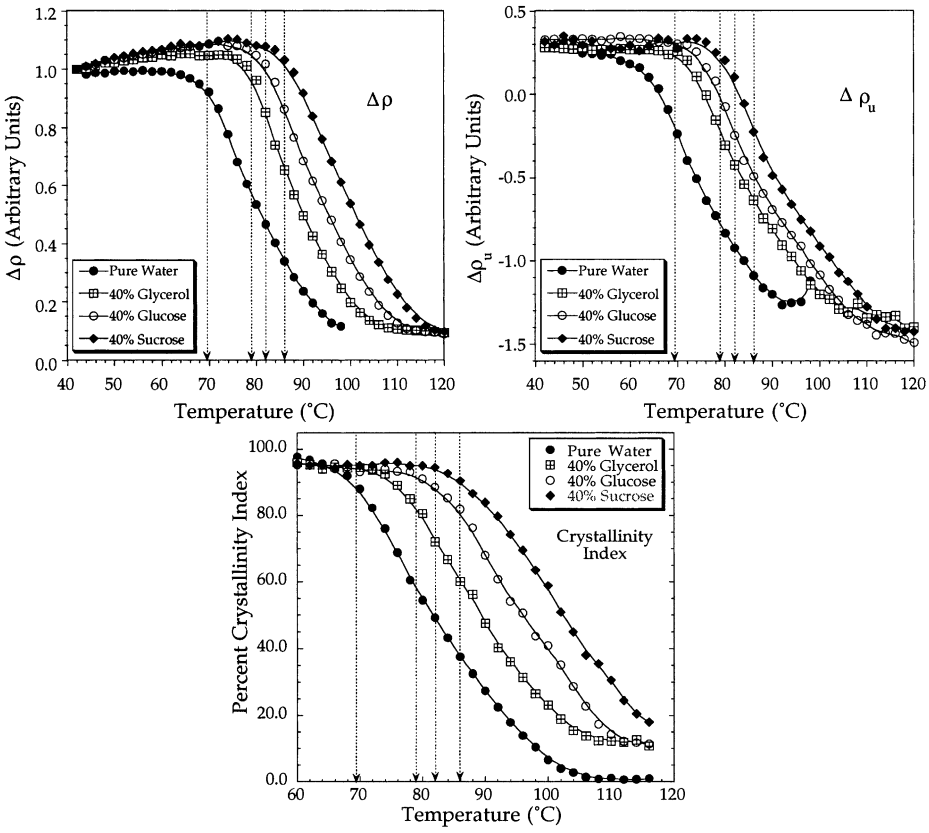


Fig. 6. The effects of 40% (w/w) solutions and water on the decay of $\Delta\rho$, $\Delta\rho_u$ and crystallinity index on waxy maize starch heated at 2°C/min. Dotted lines indicate the peak temperature of the DSC endotherm from (from left to right) pure water, 40% (w/w) glycerol, glucose and sucrose.

'limiting water' behaviour, as would be indicated by the broadening of $\Delta\rho$ and $\Delta\rho_u$ curves or the appearance of a two stage decay process.

The effects of increasing glycerol solution concentration on $\Delta\rho$ and $\Delta\rho_u$ variation during the gelatinisation of waxy maize starch [40% (w/w) starch] are shown in Fig. 5. Waxy maize starch was predominantly used in this study for the reasons given earlier; however, other starch cultivars investigated (results not shown) were found to exhibit qualitatively similar trends). Comparing 40 and 70% (w/w) glycerol to the pure water control, as shown in Fig. 5, it can be seen that the initiation of granule swelling (as represented by reduction in $\Delta\rho_u$), and the onset of lamellar and crystallite disruption (as represented by the decay in $\Delta\rho$ and crystallinity index, respectively) occur at a higher temperature than in pure water. Swelling of non-lamellar regions and lamellar/crystallite disruption are shifted to the same extent, as shown by the relation of each curve to the peak temperatures of the DSC endotherms (shown by arrows), with swelling still preceding the onset of disruption by the same extent. The low temperature slight increase in $\Delta\rho$ (before the onset of gelatinisation) has previously been seen for pure water (Jenkins & Donald, 1998), although the effect for waxy maize is less marked than in these glycerol solutions. The interpretation proposed for this rise (Jenkins & Donald, 1998; Jenkins, 1995) is that some slight tangential expansion of the amorphous lamellae occurs, due to enhanced mobility within these regions. Fig. 6 also shows that the decay curves for starch in each glycerol solution are effectively parallel to each other, and to the pure water control. There is no indication of any temperature broadening of the gelatinisation process, or the introduction of any biphasic 'limiting water' character in the decay curves obtained during gelatinisation in glycerol solutions with concentrations of up to 70% (w/w).

The effects of glucose and sucrose on waxy maize starch gelatinisation have been followed in the same way as with glycerol. Fig. 6 shows that in the presence of glucose and sucrose, the same behaviour as was found with glycerol is observed. There is no evidence of any temperature broadening, 'limiting water' behaviour, specific complex formation or altered mechanism. The onset of gelatinisation on all structural levels is retarded to the same extent, with the sequence of structural changes remaining unaltered. Granule swelling still precedes, and is inferred to directly lead to, lamellar and crystallite disruption.

In all cases the values of the best-fit structural parameters determined from the modeling of the SAXS patterns did not vary significantly between samples. The addition of solutes to water does not lead to any significant variations in peak position, lamellar repeat distance, fractional lamellar crystallinity $\phi$, or degree of paracrystallinity, $\beta$. As an

Table 2
Structural parameters determined from the modeling of SAXS patterns recorded at 40°C from waxy maize starch in pure water and 70% (w/w) glycerol solution

| | Pure vater | 70% Glycerol |
|---|---|---|
| d ($Å^{-1}$) | 90 ± 2 | 89 ± 3 |
| N | 22 ± 1 | 21 ± 1 |
| $\phi$ | 0.36 ± 0.01 | 0.36 ± 0.01 |
| $\beta$ | 0.71 ± 0.01 | 0.71 ± 0.02 |

example of this the best-fit values from the modeling of the scattering patterns recorded at 40°C from waxy maize starch in pure water and 70% (w/w) glycerol are shown in Table 2.

All the evidence indicates that in the presence of glycerol, glucose and sucrose, starch gelatinisation is not altered in any way other than the temperature at which it is initiated. The whole gelatinisation process appears to be simply translated further up the temperature axis with increasing solute concentration, with all structural changes after the onset of gelatinisation being the same as in pure water.

The one structural level which could not be examined fully using waxy maize starch was that of inter-helical crystalline ordering, as represented by the 100 (5.5° $2\theta$) inter-helix reflection in B- and C-type starches, since in the A-type polymorph this reflection is systematically absent in the WAXS pattern. In order to explore this, potato starch was examined. The effects of glycerol, glucose and sucrose on disruption within the crystalline lamellae of potato starch was examined, by charting the loss of the 100 inter-helix peak during gelatinisation. As with the 9 nm lamellar repeat peak, the 100 peak decreases in intensity during gelatinisation, due to a reduction in the degree of crystallinity.

To obtain quantitative data, the 100 peak from potato starch was modeled as Gaussian using the *xfit* data analysis program supplied by the Daresbury Laboratory. Normalised peak heights (the peak height in the initial frame being set equal to unity) for potato starch heated in pure water and 25 and 40% (w/w) glycerol and sucrose solutions are shown in Fig. 7. This figure shows that on this structural level too, added solutes act only to delay the onset of gelatinisation. After initiation of structural change the loss of order on all length scales proceeds as in excess pure water.

To explore more fully the distinction between the effects of added solutes and 'limiting water' behaviour, the gelatinisation of waxy maize starch in 'excess' and 'limiting' pure water and 'excess' and 'limiting' 40% (w/w) glycerol solution (based on the assumption of a direct equivalence with pure water) was compared. 'Excess' systems were composed of 40% (w/w) starch and 'limiting' systems 63% (w/w) starch. Results are shown in Fig. 8. This figure clearly shows the overlaying of two distinct effects on gelatinisation behaviour. The gelatinisation onset temperature is elevated, due to the presence of solutes, and the temperature range over which gelatinisation occurs is significantly broadened (greater than 10°C in each case), due to the imposition of 'limiting solvent' conditions. $\Delta\rho_u$ can also be seen to decay in a two stage process in 'limiting solvent' just as in 'limiting water'. All signs indicate that the mechanism of gelatinisation of the starch granule is the same, no matter what the gelatinizing medium or the relative starch:solvent composition.

## 4. Discussion

All the evidence presented here shows that, whatever the solute concentration, or whether water is present at all, the basic parameters of gelatinisation remain unchanged, although the endotherm is systematically shifted upwards. It is proposed here that gelatinisation is initiated at the point at which the degree of molecular mobility within the amorphous growth ring regions of the starch granule reaches a critical level. Molecular mobility in these regions is in turn controlled by the total degree of plasticisation, induced both by the input of plasticising solvent and thermal energy. One indirect signature of the enhanced mobility due to solvent

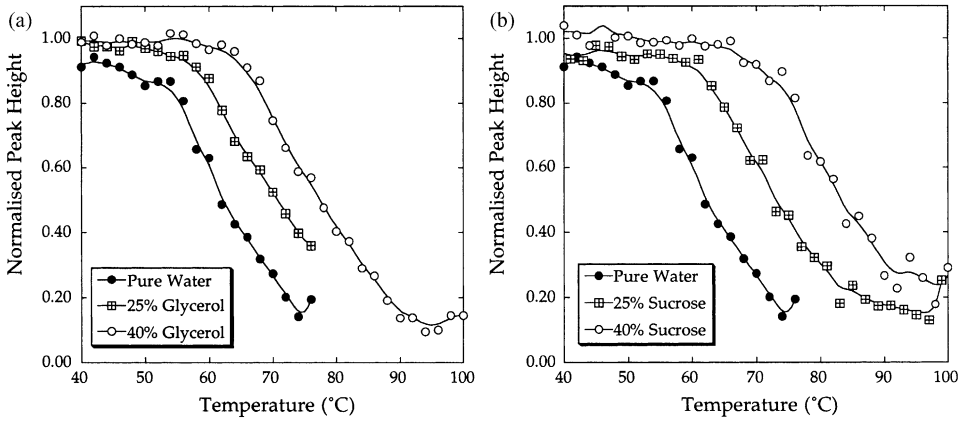


Fig. 7. Decay upon heating (2°C/min) of the 100 inter-helix peak from potato starch in pure water and 25 and 40% (w/w) solutions of glycerol (a) and sucrose (b).

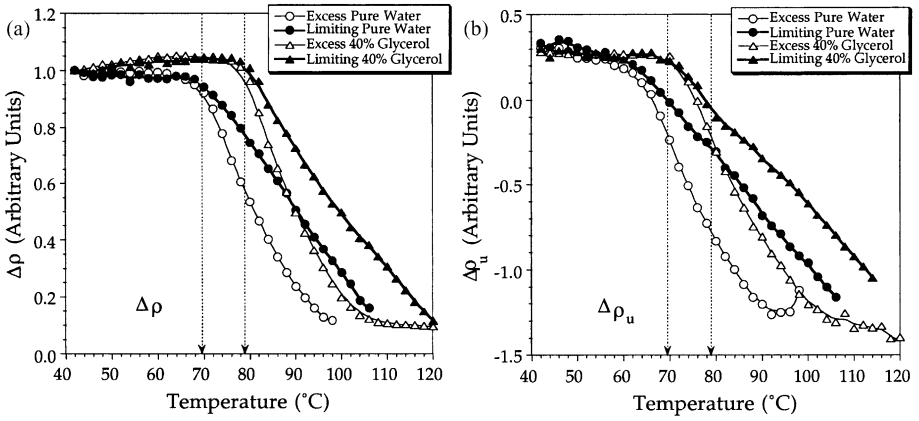


Fig. 8. Variation in $\Delta\rho$, $\Delta\rho_u$ for waxy maize starch heated in 'excess' and 'limiting' pure water and 40% (w/w) glycerol solution. Dotted lines indicate the peak temperature of the DSC endotherm in excess pure water (left) and excess 40% (w/w) glycerol (right).

ingress and subsequent plasticisation can be seen in the slight increase in $\Delta\rho$ observed in Figs. 5 and 6 before the onset of gelatinisation. Such an increase, when seen in pure water, has previously been attributed to the onset of mobility (Jenkins, 1995) causing a slight lateral increase in the amorphous lamellae, and this interpretation fits in exactly with what is proposed here for solute containing systems. The point at which gelatinisation is initiated can be thought of as the stability apex of plasticisation curve. At this apex, the mobility and swelling of the amorphous growth ring regions reaches a maximum level, beyond which native granular structure is irreversibly altered. The uptake of solvent upon swelling of the amorphous growth rings leads to a co-operative cycle of increasing plasticisation, molecular mobility and structural disruption.

It is proposed that the critical degree of plasticisation, molecular mobility and swelling which are necessary to initiate gelatinisation are the same no matter what the plasticising solvent; what matters is the effectiveness of the solvent at plasticising the granule. Those less effective will require a greater amount of thermal plasticisation to bring the total level of molecular mobility within the amorphous growth rings to the stability apex of the plasticisation curve. This hypothesis can be considered as an amalgamation and extension of the ideas of Waigh et al. (1998), Slade and Levine (1989), Donovan (1979), Jenkins et al. (1994) and Perry and Donald (2000).

In 'excess solvent', co-operative swelling and solvent uptake results in the complete disruption of lamellar and crystalline order by the swelling-driven crystallite disruption mechanism proposed by Donovan (1979) and Jenkins (1995). The *G* endotherm observed in DSC traces is due to granular disruption brought about by the co-operative combination of increasing solvent and thermal plasticisation and the molecular mobility and swelling which this induces.

As the relative amount of solvent is reduced to 'limiting solvent' levels, the first part of gelatinisation occurs by the same process as in excess solvent. However, once all of the available solvent external to the granule has been exhausted, the co-operative plasticisation process is arrested. Further gelatinisation is now dependent upon increased levels of molecular mobility and granular swelling which can only be brought about by the input of thermal energy. Samples must therefore be heated to higher temperatures than in the presence of excess solvent, leading to the biphasic nature of gelatinisation in 'limiting solvent' and the broadening of the gelatinisation temperature range. In this formulation the *M* endotherm arises at the point at which all solvent external to the granule is exhausted and swelling and granular disruption occur due to the sole influence of increasing thermal plasticisation and thermally induced mobility.

At very low solvent levels, the stability apex of the plasticisation curve, necessary to induce swelling and granular disruption, can only be reached by the input of thermal energy, with the amount of solvent being insufficient to produce significant molecular mobility. In this case the initiation of gelatinisation is shifted a long way up the temperature axis. It is proposed that in the complete absence of solvent, gelatinisation may still occur upon heating to greatly elevated temperatures, however thermal degradation of the starch polymers occurs at a temperature below the solvent-free gelatinisation temperature.

However, if solute is present, what happens is shown not to be the same as 'limiting water' conditions. Gelatinisation in glycerol solutions proceeds as in excess water even in the presence of only a token amount of water. The glycerol is clearly entering the starch granule and taking an active part in plasticisation and the gelatinisation process. It is meaningless to talk of the water and solute components of such solutions, as all that is of importance is the concentration of the solution as a whole. Glycerol has been shown to be able to facilitate the gelatinisation of the starch granule as effectively as water, albeit at a higher temperature. This confirms the combined plasticising action of water and glycerol, as reported by other workers (Kirby, Clark & Parker, 1993; Sala & Tomka, 1993; Forssel, Mikkila & Moates, 1997) including in instances of non-food uses, such as thermoplastic starch. The results also support the claim made by

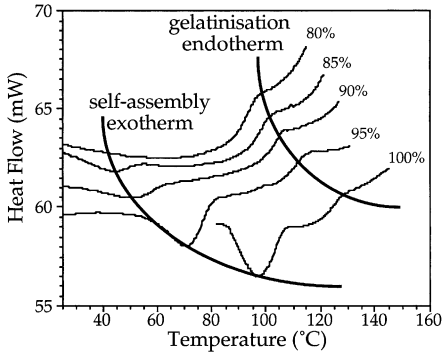


Fig. 9. DSC traces, vertically offset, for waxy maize heated at 10°C $min^{-1}$ in aqueous glycerol solutions with concentrations marked (% glycerol). The arcs indicate the temperature/concentration dependence of the lamellar self-assembly exotherm and the gelatinisation endotherm (after Perry & Donald, 2000).

Slade and Levine (1988), that there is no chemical requirement for water molecules, just a requirement for mobility, imparted by the presence of a low molecular weight plasticiser. These results also eliminate the concept of water being the sole major gelatinising medium in aqueous solutions, with added solutes acting only to bind water (and hence reduce water availability) or to bind directly to starch chains (and hence stabilize the granule).

In sugar solutions, all the results presented here indicate that what matters is the ease with which the plasticising solution can enter the granule, and in particular enter the amorphous growth ring. Their effect is in no way analogous to the role of limiting water conditions. This conclusion concerning plasticisation runs parallel to the role of solvent ingress and plasticisation in the self-assembly of the lamellar crystals themselves, reported earlier (Perry & Donald, 2000). The plasticisation of the double helical regions, to permit them to come into registry and exhibit the familiar 9 nm repeat, is a necessary pre-requisite for gelantinisation to occur, in the sense that a lower level of plasticisation is required for this step and therefore it must occur first. That this is so is demonstrated by Fig. 9, which shows how for starch slurries in glycerol/water mixtures, both the exotherm associated with the self-assembly of the lamellae and the gelatinisation endotherm systematically move up as the amount of water in the mixture is reduced. The two thermal events in these low water systems indicate the successive stages in the ingress of the plasticising solvent. The rationale for the steady increase in gelatinisation temperature with solute size and concentration can therefore be identified as the increasing difficulty these conditions impose on ingress of the plasticiser. However, if the combination of heat and plasticiser is sufficient, destabilization of the granule will occur in exactly the same way as in pure water. However, as well as the relative inability (when compared to water) of non-aqueous solutes to plasticise the starch granule, which is proposed here as the major cause of temperature elevation, variations in the rates of diffusion of aqueous solutions may also be of possible importance. It is considered that the higher viscosity and slower diffusion rates of sugar solutions, as compared to pure water could also contribute as a cause of gelantinisation temperature elevation, although the proposal here is that the reduced plasticising ability is dominant. In this context it is also the case that thermodynamic factors could be of some relevance at the local level. For free chains the presence of solutes are known to affect order–disorder transitions (Cioci & Lavecchia, 1998), but it is unclear that this would be relevant for the supramolecular structures present within a starch granule. Nevertheless, experiments at different rates might be illuminating in demonstrating the relative magnitudes of kinetic and thermodynamic factors.

## 5. Conclusion

DSC, combined with simultaneous SAXS/WAXS, has shown that the onset of gelatinisation, as measured on all length scales, is shifted to higher temperatures with the addition of sugars and glycerol. Once gelatinisation is initiated, it is found to progress in a way identical to that found in pure water, with the nature of plasticising solvent not affecting the mechanism of starch gelatinisation, only the temperature at which it occurs. The entire gelatinisation process is simply translated further up the temperature axis. The greater the mean molecular weight of the solvent (the molecular weight being increased by increasing the solution concentration or the molecular weight of the individual solute molecules), the greater is the extent to which gelatinisation is shifted. Such variations in gelatinisation temperature appear to be caused not by specific starch–solute or solute–water interactions, but by non-specific variations in thermodynamic and kinetic properties, which affect the ability of the granule to swell.

It is also concluded that the consideration of gelatinisation in semi-dilute solutions in terms of water and solute components is meaningless. Only the properties of the solution as a whole are of importance in determining gelatinisation behaviour. To talk about gelatinisation in terms of water availability is to be too restrictive. Talk should instead be of solvent availability and ‘excess solvent’ and ‘limiting solvent’ conditions. Allied to this point, it is also concluded, based upon the fact that gelatinisation proceeds in systems in which there is only a token amount of water just as in excess water, that glycerol as well as water can effectively plasticise the starch granule and facilitate gelatinisation.

Despite the fact that a great deal of the experiments reported here investigated the behaviour of waxy maize starch with glycerol, it is not considered that this is in any way a unique starch–solute combination. With the same trends being exhibited by other starch cultivars, such as potato and maize, and with other solutes, such as glucose and sucrose, it believed that all of the conclusions drawn are applicable to the whole range of commonly encountered starches and low molecular weight solutes.

These conclusions support the initial hypothesis, that it is the reduced level of solvent plasticisation, resulting from the addition of non-aqueous solutes to the pure water system, which results in the elevation of the gelatinisation temperature. A reduced level of solvent plasticisation of the amorphous growth ring regions requires that a greater level of thermal energy be input before the starch granule can swell and begin to gelatinise. A universal model has been proposed of gelantinisation in pure water and aqueous semi-dilute solutions, based upon the concept of a continuous plasticisation curve.

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## References

Blanshard, J. M. V. (1987). In T. Galliard, *Starch: Properties and potential* (pp. 17–78). Wiley.

Bras, W., Derbyshire, G. E., & Devine, A. (1995). The combination of thermal analysis and time-resolved X-ray techniques—a powerful method for materials characterisation. *J. Appl. Cryst.*, *28*, 26–32.

Cameron, R. E., & Donald, A. M. (1992). A SAXS study of the annealing and gelatinisation of starch. *Polymer*, *33*, 2628–2635.

Cameron, R. E., & Donald, A. M. (1993a). A SAXS study of starch gelatinisation in excess and limiting water. *J. Poly. Sci. Phys. Ed.*, *31*, 1197–1204.

Cameron, R. E., & Donald, A. M. (1993b). A SAXS study of the absorption of water into the starch granule. *Carb. Res.*, *244*, 225–236.

Cioci, F., & Lavecchia, R. (1998). Thermostabilization of proteins by water-miscible additives. *Chem. Biochem. Eng. Q*, *12*, 191–199.

Donald, A. M., & Windle, A. H. (1992). *Liquid Crystalline Polymers*, CUP Cambridge.

Donovan, A. M. (1979). Phase transitions of the starch water system. *Biopolymers*, *18*, 263–275.

Donovan, J., & Mapes, C. (1980). Multiple phase transitions of starches and Nägeli amylodextrins. *Starch*, *32*, 190–193.

Eliasson, A. -C. (1992). A calorimetric investigation of the influence of sucrose on the gelatiniazation of starch. *Carb. Poly.*, *18*, 131–138.

Forssel, P. M., Mikkila, J. M., & Moates, G. K. (1997). *Carbohydrate Polymers*, *34*, 275.

Jenkins, P. J. (1995). *X-ray and neutron scattering studies of starch granule structure*. Cambridge University.

Jenkins, P. J., & Donald, A. M. (1998). Gelatinisation of starch: a combined SAXS/WAXS/SANS study. *Carb. Res.*, *308*, 133–147.

Jenkins, P. J., Cameron, R. E., & Donald, A. M. (1994). In situ simultaneous small and wide angle X-ray scattering: a new technique to study starch gelatinisation. *J. Poly. Sci. Phys. Ed.*, *32*, 1579–1583.

Kirby, A. R., Clark, S. A., & Parker, R. (1993). *Journal of Materials Science*, *28*, 5937.

Levine, H., & Slade, L. (1988). In J. M. V. Blanshard & J. R. Mitchell, *Food structure: Its creation and evaluation* London: Butterworths.

Liu, H., Lelievre, J., & Ayong-Chee, W. (1991). A study of starch gelatinisation using differential scanning calorimetry. *X-ray and birefringence measurements. Carbohydrate Research*, *210*, 79–87.

Perry, P. A., & Donald, A. M. (2000). The role of plasticisation in starch granule assembly. *Biomacromols.*, *1*, 424–432.

Sala, R., & Tomka, I. (1993). In J. M. V. Blanshard & P. J. Lillford, *The glassy state in foods* Nottingham: Nottingham University Press.

Slade, L., & Levine, H. (1988). In J. M. V. Blanshard & J. R. Mitchell, *Food structure—Its creation and evaluation* (p. 115). London: Butterworths.

Slade, L., & Levine, H. (1989). In R. P. Milane, J. N. Bemiller & R. Chandrasekaran, *Frontiers in carbohydrate research—1: food applications* London: Elsevier Applied Science.

Slade, L., & Levine, H. (1993). In J. M. V. Blanshard & P. J. Lillford, *The glassy state in foods* Nottingham: Nottingham University Press.

Waigh, T. A., Jenkins, P., & Donald, A. M. (1996). Quantification of water in carbohydrate lamellae using SANS. *Far. Disc.*, *103*, 325–337.

Waigh, T. A., Perry, P. A., Riekel, C., Gidley, M. J., & Donald, A. M. (1998). Side chain liquid crystalline properties of starch. *Macromols.*, *31*, 7980–7984.

Waigh, T. A., Gidley, M. J. Komanshek, B. U., & Donald, A. M. (2000). The phase transformations in starch during gelatinisation: a liquid crystalline approach. *Carb. Res.*, *328*, 165–176.

Waigh, T. A., Kato, K. L., Donald, A. M., Gidley, M. J., Clarke, C. J., & Riekel, C. (2000). Side-chain liquid crystalline models for starch. *Stärke*, *52*, 450–460.

Wakelin, J. H., Virgil, H. S., & Crystal, E. (1959). Developments and comparison of two X-ray methods for determining the crystallinity of cotton cellulose. *J. Appl. Phys.*, *30* (11), 1654–1662.

Young, R. J., & Lovell, P. A. (1991). *Introduction to polymers*, London: Chapman and Hall.

Zobel, H. F., Yong, S. N., & Rocca, L. A. (1988). Stach gelatinisation: an X-ray diffraction study. *Cereal Chemistry*, *65*, 443–446.