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A study of the heat capacity of starch/water mixtures*

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ABSTRACT

The heat capacity of starch/water mixtures was investigated as a function of temperature and composition by differential scanning calorimetry. For amorphous amylopectin/water mixtures, the polysaccharide made the major contribution to the observed heat capacity increment at the glass-transition temperature of the mixture. In the glass, the apparent partial specific heat capacity of the water was comparable to that of liquid water. The heat capacity increment observed on gelatinisation of maize and potato starches was compared to that observed on melting and dissolution of highly crystalline A and B polymorphs of short-chain amylose. The role of melting and glass transitions in starch gelatinisation is discussed.

INTRODUCTION

The thermal processing of starch is influenced by the melting of crystalline fractions and the glass-transition behaviour of amorphous regions. The thermal degradation of dry starch precludes the direct determination of melting (T_m) and glass-transition (T_g) temperatures. From measurements[1] on the effect of a diluent (water) on the melting of A- and B-type crystalline polymorphs of amylose, average d.p. 15, it was possible to obtain, by extrapolation, a T_m for dry crystals of 530 K. Similarly[2], by extrapolation of the T_g values of dry malto-oligosaccharides, it was possible to estimate a high molecular weight limit for T_g of 500 K. For polymeric materials, a transition from brittle to rubbery behaviour occurs at T_g. Calorimetric measurements provide a convenient means of determining T_g, from the sharp increase in heat capacity, with a heat-capacity increment (ΔC_p), which occurs at T_g. The heat capacity change (ΔC_p) reflects changes in rotational, translational, and configurational contributions to heat capacity, as these motions are "frozen" on vitrification. Although the experimentally observed transition is influenced by kinetics, a theoretical approach due to Couchman[3,4] considers that an underlying second-order phase transition is present. The glass-transition temperature of a binary mixture (T_{gm}) is predicted from the T_g and the ΔC_p of the individual components; thus,

$$T_{gm} = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}}$$

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where w is the mass fraction of the component. This relationship was found to predict successfully the composition dependence of T_g for a mixture of compatible synthetic polymers[3,4] and for a polymer–diluent mixture[5]. The prediction of the effect of water as a diluent on the glass-transition behaviour of amylopectin and malto-oligosaccharides was less good[2]. More particularly, the depression of the T_g of the carbohydrate by water was underestimated.

The primary aim of this paper is to consider in more detail the glass-transition behaviour of starch/water systems, more particularly the composition dependence of heat capacity (C_p) and the ΔC_p at T_g, and the origins of the differences between observed and predicted behaviour.

A secondary aim is to consider the origins of heat capacity changes which occur during starch gelatinisation. Granular starch is a partially crystalline solid. Currently, there are two views of gelatinisation. In one [6–9], it is considered as a melting process, the gelatinisation temperature being influenced by the thermal stability of the starch crystallites. In the other[10], gelatinisation is considered to be influenced primarily by the plasticisation of amorphous regions of the granule and that once the T_g of these regions is exceeded, gelatinisation can proceed. Evidence for the latter view comes from calorimetry studies[10] of the heat capacity changes which occur during gelatinisation. The two views are not mutually exclusive, as the glass transition must precede crystallite melting; what is at issue is the dominant transition which affects the observed gelatinisation behaviour.

RESULTS AND DISCUSSION

Glass transition behaviour. — Fig. 1 shows a plot of specific heat capacity in $J.g^{-1}.K^{-1}$ as a function of temperature, in the range 280 to 343 K, for dry amylopectin and samples containing 14 and 17% (w/w) of water. In this range, the specific heat capacity of dry amylopectin increased linearly from 1.12 to 1.37 $J.g^{-1}.K^{-1}$. For the sample containing 14% of water, there was a relatively sharp increase in heat capacity corresponding to a glass transition, spanning 30 K, with a mid-point (T_g) at 312 K; for the sample containing 17% of water, the mid-point occurred at 304 K. The T_g for these mixtures was consistent with other published work on the effect of water as a diluent on the T_g of amylopectin[2]. The heat capacity increment at T_g for these mixtures was 0.44 and 0.42 $J.g^{-1}.K^{-1}$ for the 14 and 17% mixtures, respectively. The ΔC_p of mixtures can be predicted from the separate contributions to ΔC_p from the individual components, assuming that ΔC_p is independent of temperature and that heat capacity effects due to mixing are similar both above and below T_g. The validity of these assumptions has been demonstrated[3,5].

Glassy amorphous forms of water have been prepared by several methods[11–13] and undergo a glass-to-liquid transition, as indicated by a sharp change in heat capacity, in the region of 120–134 K, the precise value depending on the thermal history and the experimental timescale of measurement. Over the measured range of 90–124 K, the heat capacities of a vapour-deposited glass[11] and a low density amorph[13] are similar and a

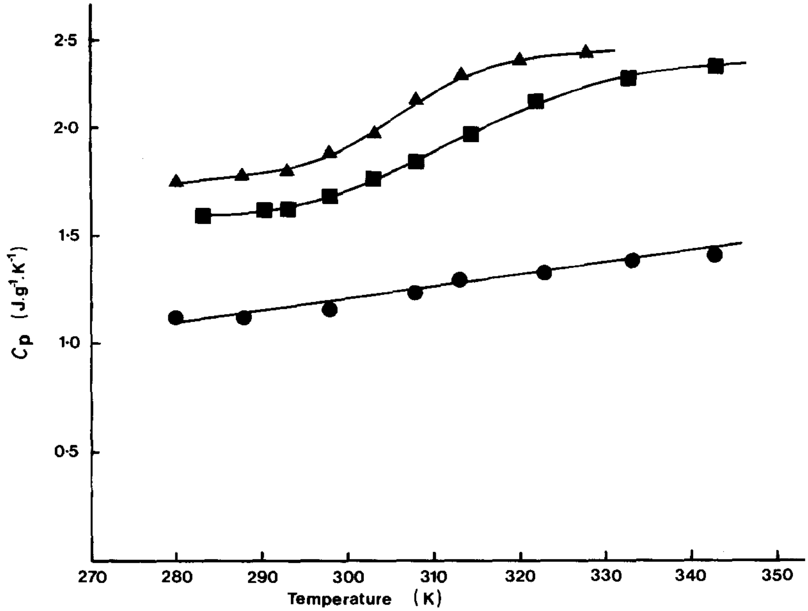

Fig. 1. Specific heat capacity as a function of temperature for dry amylopectin (●), and for amylopectin with 14% (■) and 17% (w/w) of water (▲).

little higher (0.039 J.g^{-1}.K^{-1}) than the heat capacity of hexagonal ice[11]. There is less agreement on the ΔC_p at T_g; thus 1.94 J.g^{-1}.K^{-1} was obtained[11] for a vapour-deposited glass and 0.092 J.g^{-1}.K^{-1} for a liquid-quenched material[12]. Estimates of the ΔC_p for water have also been obtained from extrapolation of data of binary aqueous mixtures; these values range from 1.06 to 1.39 J.g^{-1}.K^{-1} for electrolyte/water mixtures[14], and values of 0.93 and 1.39 J.g^{-1}.K^{-1} were obtained for D-galactose/water and polyvinylpyrrolidone/water mixtures, respectively[15].

The ΔC_p for dry malto-oligosaccharides has been determined[2]; for maltohexaose, it was 0.49 J.g^{-1}.K^{-1}. From extrapolation of the malto-oligosaccharide data, it was possible to obtain a high molecular weight limit for ΔC_p of 0.47 J.g^{-1}.K^{-1}. The ΔC_p at T_g for the amylopectin/water mixtures and for maltohexaose/water mixtures containing up to 21.3% (w/w) of water is shown in Table I. For these mixtures, the calculated contribution from the carbohydrate substantially accounts for the observed ΔC_p of the mixture. A separate contribution from the water of between 0.93 and 1.94 J.g^{-1}.K^{-1} is not consistent with the data obtained, although smaller contributions (< 0.3 J.g^{-1}.K^{-1}) from water to the ΔC_p of the mixture cannot be ruled out from the present data.

From the data of Fig. 1, it was possible to calculate an apparent partial specific heat capacity for the water in the amylopectin/water mixtures. Below the glass-transition temperature T_g, the contribution of amylopectin to the total heat capacity was calculated from the heat capacity of the dry glassy amylopectin. Above the glass-transition temperature, an additional allowance was made for the ΔC_p at T_g for the now rubbery amylopectin. The calculated apparent partial specific heat capacity of water in

TABLE I

Glass transition data for amylopectin/water and maltohexaose/water mixtures

Water content (% w/w)	T_g *(K)*	ΔC_p *($J.g^{-1}.K^{-1}$)*	$\Delta C_p^{carbohydrate}$ *($J.g_{mixture}^{-1}.K^{-1}$)*
Amylopectin			
Dry	500[a]	0.47[a]	
14.0	312	0.44	0.404
17.0	304	0.42	0.390
Maltohexaose			
Dry	448	0.49	
2.9	391	0.41	0.47
5.5	356	0.45	0.46
6.1	351	0.38	0.46
9.6	325	0.42	0.44
14.1	288	0.52	0.42
15.8	281	0.44	0.41
21.3	269	0.42	0.370

[a] Values obtained by extrapolation of data for malto-oligosaccharides[2].

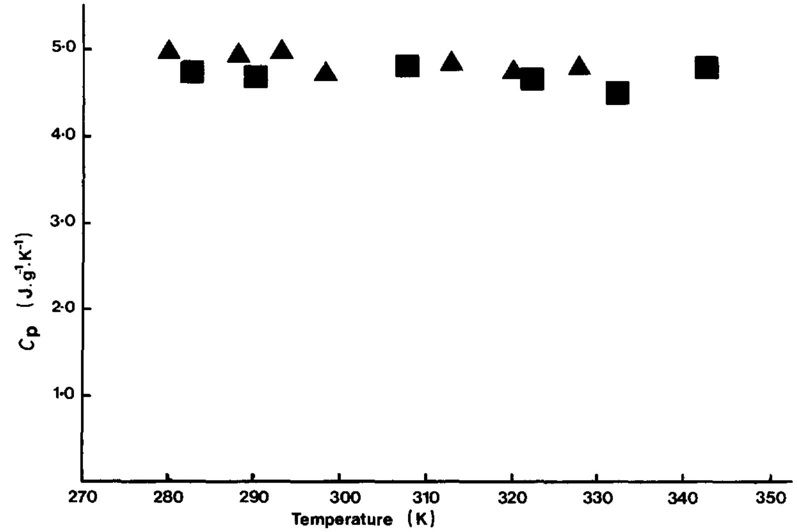

Fig. 2. Apparent specific heat capacity of water as a function of temperature for amylopectin/water mixtures: 86% (■) and 83% w/w (▲).

these mixtures was 4.84 ±0.11 $J.g^{-1}.K^{-1}$ for the 17% water mixture, and 4.68 ±0.11 for the 14% water mixture, over the temperature range 280–345 K (Fig. 2). There was no sharp change in the apparent partial specific heat capacity of water in the region of the glass transition. In the amylopectin/water glasses, the heat capacity contribution from the water was typical of liquid water (4.1796 $J.g^{-1}.K^{-1}$ at 298 K) and much higher than for solid forms of water, such as hexagonal ice (2.1 $J.g^{-1}.K.^{-1}$ at 273 K) or, by inference, water in a glassy form.

It can be argued that the observed apparent heat capacity of water contains contributions arising from the non-ideality of mixing. For dilute aqueous solutions of malto-oligosaccharides with d.p. 2–6, these effects were relatively small at 25°[16]. As a further test, the specific heat capacity of amylopectin/water mixtures in the range 0–43.5% (w/w) of water was measured at 298 K, (Fig. 3). The specific heat capacity of the mixture increases with increasing concentration of water from 1.16 $J.g^{-1}.K^{-1}$ for the dry amylopectin to 2.76 $J.g^{-1}.K^{-1}$ for the sample containing 43.5% of water. At water contents in the region of 20%, the heat capacity data show a discontinuity consistent with a glass transition occuring at this moisture content at 298 K. If the apparent partial specific heat capacity of the water is plotted as a function of water content, allowing for the contribution of glassy and rubbery forms of the amylopectin, the apparent partial specific heat capacity of the water increases continously from 4.16 ± 0.08 $J.g^{-}1.K^{-1}$ at a water content of 43.5% to 4.74 ± 0.22 $J.g^{-1}.K^{-1}$ at a water content of 14.0% (Fig. 4). In the transition from a rubber to a glass, there is no sharp change in the apparent partial specific heat capacity of the water. The results indicate that the excess terms for the heat capacity of mixing are small and positive at high concentrations of polysaccharide and

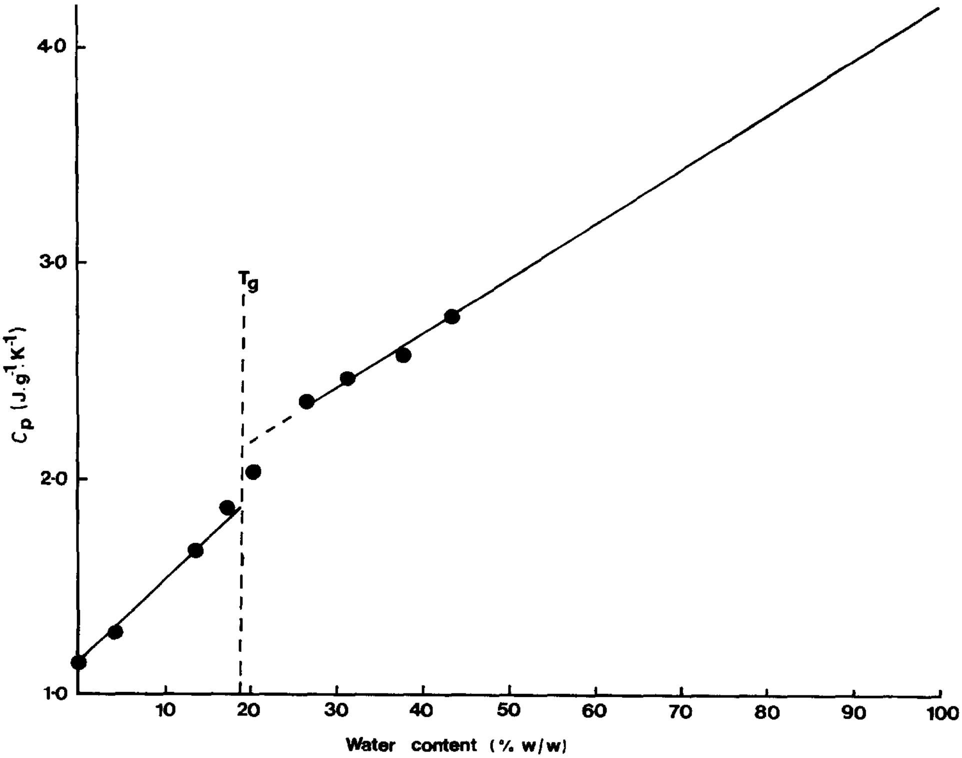

Fig. 3. Specific heat capacity as a function of water content for amylopectin/water mixtures.

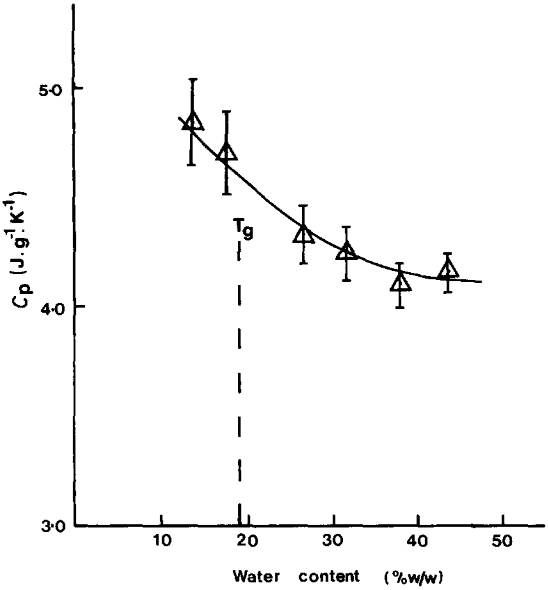

Fig. 4. Apparent specific heat capacity of water as a function of water content for amylopectin/water mixtures.

confirm that, in the glassy form, the apparent heat capacity of the water is similar to the heat capacity of liquid water at this temperature, rather than solid forms of water. The observation implies that the water is mobile within a glassy matrix of the polysaccharide. Similar conclusions have been reached in recent n.m.r. studies of diluent motion in glassy matrices. Phosphate ester diluents in glassy, synthetic polymer matrices were found to have a degree of rotational mobility, characteristic of a liquid, at tempertures below the calorimetric glass-transition temperature[17]. Similarly, in a study of the motion of water sorbed onto starch granules under conditions of temperature and water content where the amorphous regions of the granule would be glassy, it was found that the sorbed water was highly mobile and reorientated anisotropically[18].

Crystal melting and gelatinisation. — From the controlled crystallisation of short-chain amylose (average d.p. 15) from water, it is possible to prepare highly crystalline spherulites of the A- and B-type crystalline polymorphs of starch. This material gives very sharp, intense, powder-type X-ray diffraction patterns, indicating a very high level of crystallinity. Fig. 5 shows a plot of differential heat input as a function of temperature, on initial scanning and re-scanning, for a sample of the B-type crystalline polymorph of short-chain amylose in the presence of excess water. On the first scan, the B-form gave a broad endothermic transition spanning 45 K with a peak temperature of 350 K and an enthalpy change for the transition of 31.2 $J.g^{-1}$. On rescanning after quench-cooling, the sample showed an increased heat capacity below the melting temperature and a smaller endotherm that indicated a partial recrystallisation of 22%. After making an allowance for this recrystallisation, the specific heat capacity change at

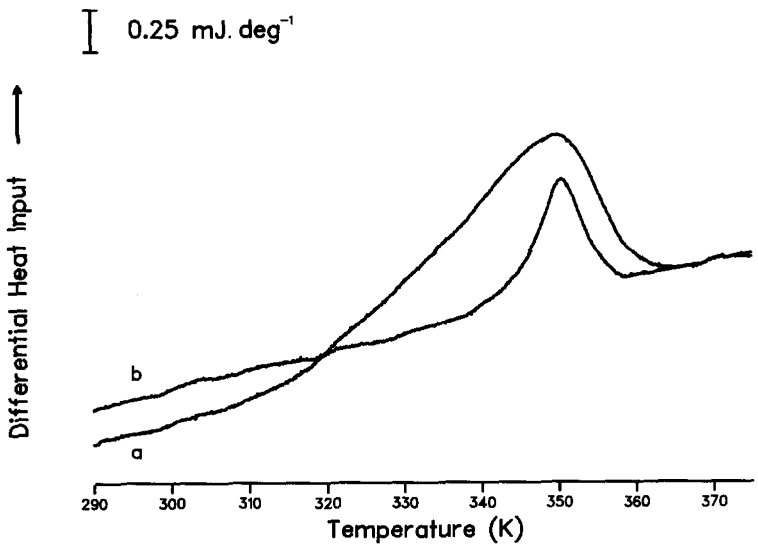

Fig. 5. Endothermic heat flow as a function of temperature during the melting and dissolution of B-spherulites (a) and on rescanning (b).

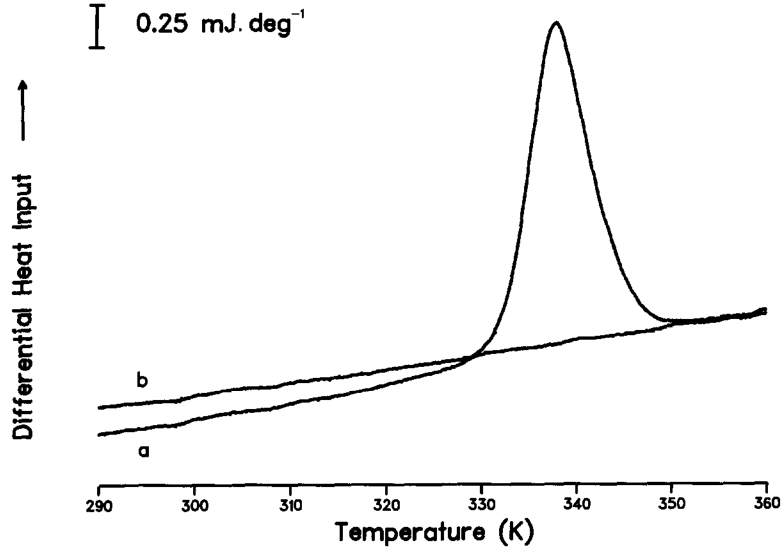

Fig. 6. Endothermic heat flow *versus* temperature for the gelatinisation of potato starch (a) and on rescanning (b).

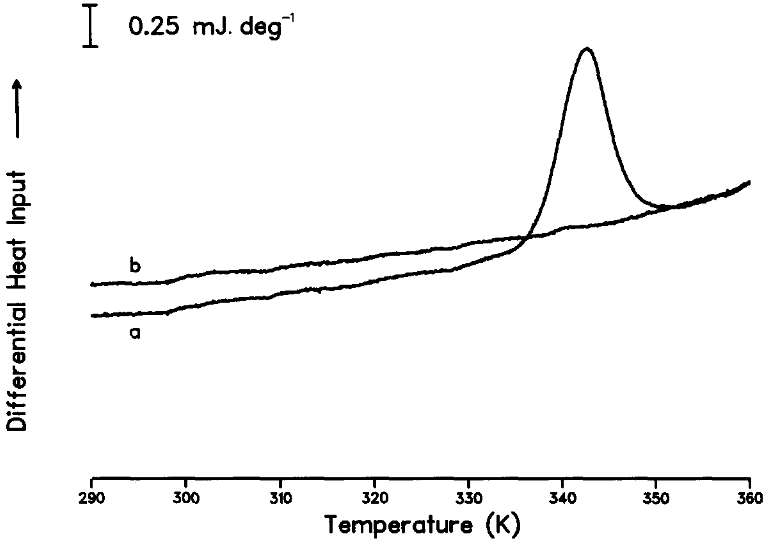

Fig. 7. Endothermic heat flow *versus* temperature for the gelatinisation of maize starch (a) and on rescanning (b).

298 K between the aqueous crystalline suspension and the amylose in solution was 0.28 J.g^{-1}.K^{-1}. For highly crystalline material of the A-type crystalline polymorph of starch, the dissolution peak temperature was 370 K, the dissolution endotherm was 32 J.g^{-1}, and the specific heat capacity difference at 298 K, between aqueous crystalline suspensions and the aqueous solution, was 0.5 J.g^{-1}.K^{-1}.

The gelatinisation endotherms of maize and potato starch, in the presence of excess water, are shown in Figs. 6 and 7, respectively. The peak temperature and enthalpy change on gelatinisation for maize was 343 K and 10.6 J.g^{-1}, and for potato 337 K and 16.1 J.g^{-1}. At 298 K, the difference in specific heat capacity between the aqueous granular and gelatinised suspensions was 0.15 J.g^{-1}.K^{-1} for potato starch and 0.17 J.g^{-1}.K^{-1} for maize starch. After gelatinisation, the difference in heat capacity between the initial scan and the rescan was not significant. The percentage of crystalline material in whole starches is generally not greater than 50%. In the present study, comparison of the endotherms obtained on gelatinisation and dissolution of highly crystalline material permits an assessment of granular crystallinity. For potato starch, both the gelatinisation endotherm and the heat capacity difference at 298 K are approximately half that of the very crystalline material. For maize starch, the estimated level of crystallinity from calorimetry is ~ 33%, giving a predicted specific heat capacity change at 298 K of 0.17 J.g^{-1}.K^{-1}, which is comparable to that observed experimentally. In both cases, an extra contribution to heat capacity difference arising from a glass transition involving amorphous regions of the granules is not observed.

These results suggest that, in these experiments, the amorphous regions of the granule were plasticised at the onset of gelatinisation; the observed gelatinisation behaviour was therefore dependent on the melting and dissolution of starch crystallites as proposed[6–9]. This situation will be influenced by non-equilibrium and equilibrium factors. Non-equilibrium factors include crystallite size, perfection, and the timescale of the process. Equilibrium factors include diluent content, the type of crystalline polymorph present, and the chain length of the amylopectin branch participating in the crystallite. In the present study, the A-type starch (maize) gelatinised at a higher temperature than the B-type starch (potato), and the crystalline polymorphs of short-chain amylose showed comparable behaviour[1]. In this case, the dissolution temperature of the A-form was substantially higher (20 K) than that of the B-form. Dissolution will also depend on the length of chain, forming the amylose double helix, which participates in the crystalline array; the longer the chain length the greater the dissolution temperature. In a recent study[19], amylopectin chain length was correlated with the crystalline structure of the starch granule. A-type starches have amylopectins with shorter short chains than the B-type starches. Experiments on the dependence of the dissolution temperature of highly crystalline polymorphs on chain length would be of use in the further investigation of starch gelatinisation and may provide a means of relating gelatinisation behaviour to molecular structure, and will also help the assessment of the relative importance of equilibrium and non-equilibrium factors in gelatinisation.

GENERAL DISCUSSION

In this study, we have examined the heat capacity changes which occur on starch gelatinisation, and on the glass transition of an amylopectin/water mixture. On starch gelatinisation, the observed heat capacity change is consistent with that observed for crystallite melting and indicates that, at the onset of gelatinisation, the amorphous regions of the granule are plasticised. More surprising are the results obtained on the amylopectin/water glasses. The calculated apparent specific heat capacity of water in the glass is comparable to that of liquid water, and implies that the water is mobile. N.m.r. experiments on water sorbed onto starch granules indicate that, at low water contents, the water has a high degree of rotational mobility[18]. Further research is needed to confirm this observation and to determine the translational diffusion of water in these glassy mixtures.

EXPERIMENTAL

Materials. — Maltohexaose was obtained from the Sigma Chemical Company Ltd. Potato starch was isolated by an aqueous extraction procedure. Samples of waxy maize starch (Amioca) and maize starch were obtained from Laing National (Manchester). To prepare non-granular amylopectin, waxy maize starch was dissolved in aqueous 90% Me_2SO, and the amylopectin was precipitated by the addition of 10 vol. of ethanol at 25°. The gelatinous precipitate was thoroughly washed with ethanol and dried *in vacuo* at 40°. Amylose of d.p. ~ 15 was prepared from potato starch by acid hydrolysis and the product isolated as described previously[1,20]. Highly crystalline spherulites of the

B-type crystalline polymorph of starch were prepared from concentrated aqueous solutions (20% w/w) of d.p. 15 by cooling from 80° to 0° at a rate of $5°.h^{-1}$. A-type spherulites were prepared in a similar way by crystallisation from aqueous 30% ethanol[1].

Calorimetry. — Studies were performed using a heat-flux Setaram Micro-DSC (Lyons, France) and a power compensation Perkin–Elmer DSC2. Heat capacity measurements of amylopectin/water mixtures were determined using the Setaram Micro-DSC scanning 1° at a heating rate of $1°.h^{-1}$. Experiments were performed on 30–50 mg of carbohydrate. Materials were dried *in vacuo* at 70° over fresh P_2O_5 for 24 h prior to rehydration; at this stage, they had reached constant weight and were considered to be dry. Dry samples were allowed to hydrate in an atmosphere saturated with water vapour until the required level of hydration was achieved. If required, the hydrated samples could be stored for a limited period of time (1–2 days) as glasses; storage of amylopectin/water rubbers leads to difficulties in the reliable measurement of heat capacity, as a result of time-dependent changes arising from the slow crystallisation of the amylopectin. Before and after scanning, a steady baseline was obtained and the heat capacity was determined by integration of the excess heat flow over the temperature interval. Allowance was made for the small differences in heat capacity of matched cells in the calculation of sample heat capacity. An empty matched cell was used as a reference. Data were logged and analysed by computer. The dry weight of sample was determined by drying at 70° *in vacuo* over P_2O_5. Determination of the T_g and ΔC_p of maltohexaose/water mixtures was performed as described[2], using a Perkin–Elmer DSC2. Thermal studies of starch gelatinisation and crystal melting were carried out using the Perkin–Elmer DSC2. Samples of starch or crystalline material, typically a few mg, were carefully weighed into aluminium sample pans and an excess amount of water (>70% w/w) was added. The sample pans and a reference pan containing air were sealed airtight. The sample and reference were scanned at 10 $K. min^{-1}$. over the temperature interval 273 K to 393 K. The cells were then rapidly cooled to the starting temperature and rescanned. The instrument was calibrated for heat capacity measurements with a sample of artifical sapphire (C_p 0.775 $J.g^{-1}.K^{-1}$ at 298 K). Temperature calibration was achieved using the melting of indium (T_m 429.6 K) and naphthyl ethyl ether (T_m 300.5 K). The dry weight of the samples was determined by piercing the sample pan and drying as before. For the Setaram microcalorimeter, heat capacity could be determined to better than 0.5 $mJ.K^{-1}$; together with the error in weighing, this led to an overall error in heat capacity determination of better than 1%. For the Perkin–Elmer instrument, duplicate determinations of the heat capacity differences between initial scanning and on rescanning of gelatinised samples were within 10%.

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