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EFFECT OF HYDROSTATIC PRESSURE ON STARCH GELATINISATION

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ABSTRACT

Samples of wheat and potato starches, mixed with water to four concentrations were subjected to preselected hydrostatic pressures (in the range 200–1500 MPa) and temperatures. Subsequent examination in a polarising microscope revealed that the effect of high hydrostatic pressure was to lower the gelatinisation temperature. With the exception of the low water content samples, the samples did not appear to be greatly affected in any other way by hydrostatic pressure (as evidenced by staining behaviour, appearance in the polarising microscope and subsequent gelatinisation behaviour at ambient pressure). Reduction in gelatinisation temperature was a non-linear function of pressure, being greatest at high pressure. The effect was also more pronounced at the higher water contents. The significance of these results with respect to thermodynamic models of starch gelatinisation is discussed.

INTRODUCTION

The Effect of Pressure on the Gelatinisation of Starch

It has long been known that during the milling of wheat, some starch granules may be 'damaged', and resemble gelatinised granules not only in appearance but also in lacking birefringence, staining with dyes such as Congo red, and being rapidly digested by enzymes (Jones, 1940). It has been shown that both shear and compression can produce damaged granules (on the surface and in the interior of endosperm particles passing between mill rollers, respectively), as can a careful application of pressure on a mixture of starch and water trapped between a microscope slide and coverslip (Jones, 1940). The only published quantitative studies of the effect of pressure on

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starch involve the subjection of wheat, maize and potato starch to a crushing action by means of a piston (Mercier *et al.*, 1968) which produced features, such as cracks and fissures, uncharacteristic of starch granules damaged by milling, and the subjection of dilute suspensions (0·4%) of potato starch to hydrostatic pressures up to 250 MPa at selected temperatures (Thevelein *et al.*, 1981).

More recently, extrusion of starch products has become widespread. Pressures of up to 30 MPa (0·3 kbar or 4351 psi) have been developed (van Zuilichem, 1979), and yet little is known of how this could affect the starch-containing material being extruded.

The purpose of this investigation is to study the affect of hydrostatic pressure on wheat and potato starches, and in particular to find the gelatinisation temperature of the starches as a function of pressure and water content.

EXPERIMENTAL

Materials

Starch granules, extracted from wheat (Manitoba) and potato (Record) were kindly supplied by M. O. Ahmed. Extraction of starch from wheat followed the method of Adkins & Greenwood (1966). Separation of potato starch granules from the cellular material was achieved by kneading blended potatoes in a chiffon bag using mercuric chloride to prevent enzyme attack; subsequently protein was removed by shaking the starch in an aqueous saline-toluene mixture (Ahmed, 1981). The extracted starches were freeze dried and stored at room temperature and humidity.

Mixtures of starch and water (containing 0·01% thiomersal to inhibit microbial growth) were prepared at concentrations of 15, 35 and 85% water by weight. The moisture contents of the starches were determined by oven drying at 125°C and found to be 11·3 and 14·6% for wheat and potato starches respectively. Thus, expressed as anhydrous starch-water mixtures, the above percentages become 44·5 and 87·2% water for 35, 85% potato starch-water mixtures respectively, and 24·6, 42·3 and 86·7% water for 15, 35 and 85% wheat starch-water mixtures. The 15 and 35% water mixtures were prepared two weeks in advance, which in addition to mechanical mixing should ensure uniform water concentration.

Method

The experiments were performed using a piston and cylinder apparatus at the High Pressure Laboratory, STL, Harlow, Essex. A PTFE cell (capacity 0·6 ml) was filled with the starch-water mixture and inserted in a closely fitting heater coil, which was then immersed in the pressure medium (castor oil) in the cylinder. The temperature was measured by means of a chromel-alumel thermocouple, wedged between the heater coil and the sample cell, using an ice-water reference.

The pressure was raised at a rate of 0·139 MPa s^{-1} (1/12 kbar min^{-1}), which was sufficiently slow to ensure isothermal conditions. When the desired pressure was reached, the sample was heated to the desired temperature at a rate of ~5°C min^{-1}. The temperature was then maintained to within 0·3°C of the desired temperature for 30 min. A check showed that the temperature in the centre of the sample would certainly have reached the temperature on the outside of the cell after 5 min. Thereafter the heater was turned off, and the pressure reduced to ambient in 10–20 min.

The starch samples were removed, and microscope slides prepared using water, 1% Pontamine sky blue 5BX or 0·2% Congo red as media. The degree of gelatinisation that had occurred, as indicated by loss of birefringence, was determined from an examination in a polarising microscope. Samples subjected to different temperatures at ambient pressure (prepared by immersion of the starch–water mixtures, sealed in glass tubes in a water-bath for 30 min) were similarly assessed.

The gelatinisation behaviour of some of the samples which had not been appreciably gelatinised by the pressure treatment was studied using the small angle light scattering (SALS) temperature jump technique (using jumps of ~2°C) details of which are described elsewhere (Marchant & Blanshard, 1978). The samples for use with the SALS apparatus consisted of 3 mg of moist starch sediment (obtained by decanting a settled slurry of the pressure treated samples) and 8 μl water.

In addition, the starch samples were examined by differential scanning calorimetry (DSC). Since thiomersal attacks the aluminium sample pans, the samples to be used for DSC were first washed in distilled water and freeze dried. The DSC measurements were then made on a Perkin-Elmer DSC II, using 10 μl samples of an 80% water-starch slurry, a heating rate of 10°C min^{-1} and an empty pan as reference. The dry weight (used to calculate enthalpies) was determined after each run by piercing the pan lid and drying for 1 h in a 125°C oven.

RESULTS

The extent of gelatinisation revealed in the 'post-mortem' inspection of the samples is given in Tables 1–5. The method of determining the degree of gelatinisation has the following limitations:

(1) For potato starch at high degrees of gelatinisation, the gelatinised granules cannot be individually recognised, so that it is not possible to count them.

(2) Especially for samples of low water content, individual granules are apparently often partially gelatinised. For wheat starch, such granules are stained but still weakly birefringent; for potato starch (where staining was not used), partially gelatinised granules can be seen to be composed of birefringent and isotropic regions. Granules can be found at all intermediate states of gelatinisation. In potato starch with 44·5% water, the 'gelatinised' granules still display weak birefringence.

TABLE 1
Percentage of granules of wheat starch (13·3%)/water (86·7%) system gelatinised by subjecting to specified temperatures and pressures

Temperature, °C	*Pressure, MPa*				
	0·1	200	300	375	450
20					100
24			0	95	
28			0·1		
30		0			
35			50		
45	0	5	70		
49	0·1				
52	30		99·9		
53	40	50			
58	95				
61	100				

TABLE 2
Percentage of granules of potato starch (12·8%)/water (87·2%) system gelatinised by subjecting to specified temperatures and pressures

Temperature, °C	*Pressure, MPa*				
	0·1	450	600	700	800
20				95	
22					100
23		0	8		
28			30		
35			35		
45		5	95		
50	0·1				
54	25				
58	90	95			
62	99·5				

TABLE 3
Percentage of granules of wheat starch (57·7%)/water (42·3%) system gelatinised by subjecting to specified temperatures and pressures

Temperature, °C	*Pressure, MPa*			
	0·1	375	600	800
17				50
40			60	
65	2	70		
84	90			
90	99·5			

TABLE 4
Percentage of granules of potato starch (55·5%)/water (44·5%) system gelatinised by subjecting to specified temperatures and pressures

Temperature, °C	*Pressure, MPa*	
	0·1	800
70		2
75	30	
81	95	
89	100[a]	

[a] Ghosts are birefringent.

TABLE 5
Percentage of granules of potato starch (75·4%)/water (24·6%) system gelatinised by subjecting to specified temperatures and pressures

Temperature, °C	*Pressure, MPa*	
	0·1	1500
70		0·5
95		5
110	0	
130	50	
145	90	
150	95	

Nevertheless, the figures in the tables give at least a semiquantitative measure of the degree of gelatinisation, and the method of observation of birefringence does provide an unambiguous determination of the onset and end point of gelatinisation.

The main features which emerge are:

(a) Other than changing the temperature at which gelatinisation occurred, high hydrostatic pressure did not affect the appearance of the granules in the polarising microscope, or their staining behaviour.

(b) The temperature at which gelatinisation takes place is reduced at high hydrostatic pressure. The reduction is greatest for wheat starch, and for high water content. The effect is nonlinear, large pressures having a disproportionately large effect.

(c) The range of temperature over which gelatinisation takes place is broadened (see Table 1, 300 MPa and Table 2, 600 MPa, which are plotted in Figs 1 and 2).

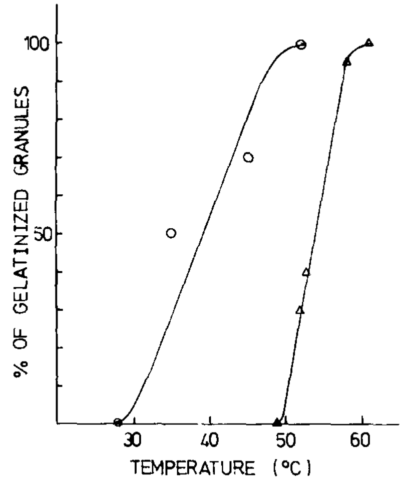

Fig. 1. Gelatinisation curves of wheat at 0·1 MPa (atmospheric, △) and 300 MPa, ○.

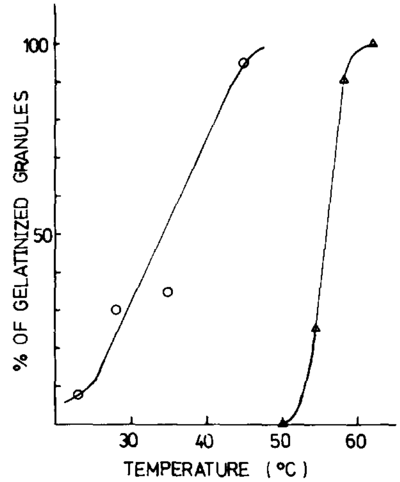

Fig. 2. Gelatinisation curves of potato starch at 0·1 MPa (atmospheric, △) and 600 MPa, ○.

In order to check the first feature, the gelatinisation behaviour (at ambient pressure) of those samples which were not significantly gelatinised by the pressure treatment was studied. The SALS technique was only used for wheat starch samples. The interpolated temperature at which 50% of the birefringence had been lost and the summed response time index were calculated from H_V (i.e. crossed polar) light intensity measurements, which were recorded as a function of time and temperature. The *summed response time index* is the sum over all the temperature jumps of the product of the time constant (τ_{B_i}) of the slow response to jump i and the fraction of total birefringence lost $B_i/\Sigma_j(A_j + B_j)$ by the slow process as a consequence of jump i. Thus it is the average time constant of the whole process, fast and slow, weighting each term by the fraction of birefringence lost. It therefore reflects the degree of slowness of gelatinisation kinetics (Bhuiyan & Blanshard, 1980). The results are given in Table 6.

The figures in Table 6 are the averages of at least two runs. For the control sample (i.e. no pressure treatment) four runs were made; the standard deviation for temperature was 1·8°C while that for the summed response time index was 20 s. It is apparent that the samples of wheat starch (86·7% water) subjected to 300 MPa and 23°C and 28°C do not significantly differ from the control. However, the sample subjected to 1500 MPa at 70°C with a water content of 24·6% has both a low temperature of loss of birefringence and a low response time index. This sample had suffered 0·5% gelatinisation during the pressure treatment, but was otherwise unchanged in appearance and staining behaviour.

For the wheat starch samples studied by SALS (Table 6) and for some potato starch samples, gelatinisation behaviour was studied by DSC. The definition of peak

TABLE 6
The effect of pressure treatment on temperature of loss of 50% birefringence and on the summed response time index of wheat starch samples

Sample	*Temperature of loss of 50% birefringence (°C)*	*Summed response time index (s)* $\sum_i \tau_i B_i / \sum_i (A_i + B_i)$
No pressure treatment	54·3	451
Subjected to 300 MPa, 23°C with 86·7% water	53·5	442
Subjected to 300 MPa, 28°C with 86·7% water	54·3	436
Subjected to 1500 MPa, 70°C with 24·6% water	51·1	357

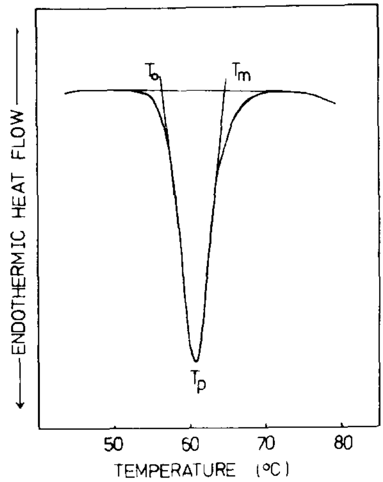

Fig. 3. Typical DSC thermogram showing manner of determination of T_0, T_p and T_m.

onset (T_0), peak (T_p) and peak end (T_m) temperatures are given in Fig. 3. Three runs were performed for each sample; the mean temperatures and enthalpies are given in Table 7. The standard deviations were of the order of 0·5°C for the temperatures and 0·15 cal g^{-1} for the enthalpies.

The two samples of wheat starch showing little apparent gelatinisation after pressure treatment nevertheless have a significantly higher T_0, the sample showing 0·1% gelatinisation also showing a modest increase in enthalpy. The sample of wheat starch subjected to 1500 MPa, 70°C with 24·6% water has significantly lower gelatinisation temperatures and enthalpy.

The sample of potato starch subjected to 450 MPa, 23°C with 87·2% water shows a decrease in gelatinisation temperatures and enthalpy – the opposite effect to that observed for the wheat starch samples of high water content.

TABLE 7
Temperature ranges and enthalpies of gelatinisation as measured by DSC

Sample	*% Gelatinised by pressure treatment*	T_0	T_p	T_m	*Enthalpy cal/g anhydrous starch*
Wheat starch, no pressure treatment	0	53·0	59·5	64·5	2·27
Wheat starch, subjected to 300 MPa, 23°C with 86·7% water	0	57·0	61·0	64·5	2·35
Wheat starch, subjected to 300 MPa 28°C with 86·7% water	0·1	57·5	61·5	65·0	2·52
Wheat starch, subjected to 1500 MPa 70°C with 24·6% water	0·5	50·5	57·5	64·0	1·93
Potato starch, no pressure treatment	0	54·0	61·0	66·0	3·72
Potato starch, subjected to 450 MPa 23°C with 87·2% water	0	52·0	56·5	61·5	3·13
Potato starch, subjected to 800 MPa 70°C with 44·5% water	2	56·0	61·0	66·0	2·26

The results shown in Tables 6 and 7 thus show that even when the apparent degree of gelatinisation is small, the starch samples are significantly affected by the hydrostatic pressure treatment. However, it is possible that these changes, which are not gross, are caused by partial ,'annealing' (Marchant & Blanshard, 1978), freeze drying (Eliasson *et al.*, 1981) or self-hydrolysis (Palasinski & Schierbaum, 1971). They do not invalidate the contention that hydrostatic pressure merely facilitates gelatinisation, which occurs in the normal way but at lower temperatures, for the samples with high water content.

As the first results obtained indicated a simple reduction of gelatinisation temperature, it was hoped that from a single experiment (revealing the percentage gelatinised at a particular temperature and pressure) the gelatinisation end point could be extrapolated, using knowledge of the percentage of granules gelatinised at ambient pressure as a function of temperature. In practice samples subjected to such extrapolated gelatinisation end points were only partially gelatinised, such experiments leading to the establishment of feature (c) above.

DISCUSSION

Gelatinisation Temperature

The results of this study are complementary to those of Thevelein *et al.* (1981) which were published after the completion of our experimental work. They report a small increase in the gelatinisation temperature of potato starch up to 150 MPa (when the increase is 4°C) and no further change thereafter, up to the maximum pressure used of 250 MPa. Our results show there is a subsequent fall in gelatinisation temperature at higher pressures.

In previous studies of the gelatinisation of starch granules, it has proved helpful to consider gelatinisation as a melting of polymer crystallites with subsequent hydration and dissolution of the polymer molecules. The dependence of the temperature at which $\Delta G = 0$ for such a transition on pressure is given by the Clapeyron equation:

$$\frac{\mathrm{d}T}{\mathrm{d}P} = \frac{\Delta V}{\Delta S} = \frac{T\Delta V}{\Delta H}$$

where ΔV is the volume change when 1 g of crystallites dissolve in an infinite reservoir of the starch-water mixture and ΔS, ΔH are the corresponding changes of entropy and enthalpy. The value of ΔH at ambient pressure can be estimated from DSC studies of starch gelatinisation. No exact knowledge of the degree of crystallinity is available, but assuming a value of ~25% (Zobel, 1981) ΔH is ~9 cal g^{-1} for wheat starch crystallites and ~15 cal g^{-1} for potato starch crystallites. The apparently lower value for wheat starch may be due to a lipid complex formation exotherm superimposed on the gelatinisation endotherm (Zobel, 1981). There is considerably more doubt about the value of ΔV at ambient pressure. Comparison of the partial specific volume of dissolved starch with the volume of immersion of starch granules in water leads to the conclusion that $\Delta V = 0$ within an experimental error of $\pm 0{\cdot}01$ g cm^{-3} (French, 1981). The results of Thevelein *et al.* (1981) may be used to infer the value of ΔV for potato starch crystallites by using the Clapeyron equation in the form

$$\Delta V = \frac{\Delta H}{T}\frac{\mathrm{d}T}{\mathrm{d}P}$$

Thus from their results $\mathrm{d}T/\mathrm{d}P \sim 4{\cdot}8 \times 10^{-8}$ deg Pa^{-1} at atmospheric pressure, whence $\Delta V = 0{\cdot}009$ $\mathrm{cm}^3\,\mathrm{g}^{-1}$ (remembering to convert calories to joules). Noting that the same (uncertain) factor of degree of crystallinity applies to both ΔV and ΔH, this result may be expressed in a more definite manner as predicting an expansion of 0·0022 cm^3 when 1 g of potato starch is gelatinised in excess water, well within the experimental errors given in the measurements quoted by French (1981).

The Flory equation for the depression of the melting point of a polymer by a diluent has been used to interpret the dependence of starch gelatinisation temperature on water content (Lelievre, 1973; Donovan, 1979; Biliaderis *et al.*, 1980; Donovan & Mapes, 1980; Hoover & Hadziyev, 1981; Zobel, 1981). The work of Donovan (1979) on potato starch yielded a value of 83 cal g^{-1} for ΔH_{F} (the latent heat of fusion per gramme of crystallites) and $3{\cdot}5 \pm 2{\cdot}3$ cal cm^{-3} for the interaction parameter B (which equals $\chi RT/V$), the enthalpy change when 1 cm^3 solvates an infinite quantity of dry molten starch. These values are incompatible with the measured enthalpy of starch gelatinisation; in particular the value of B seems quite unrealistic since a considerable amount of heat is evolved when starch absorbs water up to a moisture content of 40% (French, 1981). The strong hydrogen bond interactions prevalent in the starch-water system are no doubt responsible for the failure of the simplistic interpretation of B. Furthermore, if we attempt to reconcile the high value of ΔH_F with the measured ΔH by pointing to an exothermic hydration of the molten polymer, the observed decrease in the DSC measurements of ΔH with water content (Donovan, 1979) is contrary to expectation.

Even greater problems arise when the pressure dependence of starch gelatinisation temperature is compared to the pressure dependence of the melting point of synthetic polymer-organic diluent systems. Thus the observed non-constancy of $\mathrm{d}T/\mathrm{d}P$ for the starch-water system must be caused by a large pressure dependence of either ΔV or ΔS (or both). In contrast, an almost linear dependence of melting point on pressure is generally found for synthetic polymer-organic diluent systems (Karasz & Jones, 1967; Miyata *et al.*, 1976), indicating relatively small changes of ΔS and ΔV with pressure. Moreover, $\mathrm{d}T/\mathrm{d}P$ is invariably positive for these systems. It appears, therefore, that at present the thermodynamic theories of polymer physics can shed little light on the complex hydrogen bonding system of interest here.

However, the effect of pressure on the starch-water system shows remarkable similarities to that found for other biopolymer-water systems. Thus for denaturation of proteins under pressure, $\mathrm{d}T/\mathrm{d}P$ is generally very small but positive for pressures up to 100-300 MPa when it becomes large and negative (Hawley, 1971; Suzuki & Taniguchi, 1972). Hawley found a satisfactory fit to his data (for the reversible denaturation of chymotrypsinogen) by assuming ΔV, ΔS to be functions of pressure but taking $T(\partial S/\partial T)_P$, $(\partial V/\partial T)_P$, $(\partial S/\partial T)_T$ and $(\partial V/\partial P)_T$ to be constant. According to this fit, the form of the dependence of $\mathrm{d}T/\mathrm{d}P$ on pressure is due to a linear decrease of ΔV from a positive value at atmospheric pressure (changing sign at ~150 MPa) and a pressure dependence of ΔH which falls from a large positive value at atmospheric pressure to zero at ~350 MPa.

Molecular models have been invoked to explain the unusual pressure dependence of ΔH and ΔV for biopolymer transitions (Suzuki & Taniguchi, 1972; Zipp & Kauzmann, 1973; Li *et al.*, 1976; Williams *et al.*, 1979). In one model the importance of hydrophobic groups on the protein is stressed, because the transition of hydrophobic groups from the hydrophobic interior of (for example) a globular protein to an aqueous environment should involve a negative ΔV. However, it is also expected that ΔV should fall to zero at ~200 MPa and since this is in contradiction to all results on protein denaturation (which indicate a negative ΔV of significant amplitude at much higher pressures) the model is clearly inadequate (Suzuki & Taniguchi, 1972; Zipp & Kauzmann, 1973).

In another model, the importance of hydrogen bonds is stressed; in particular, the changing stabilities with pressure of interbiopolymer hydrogen bonds and water-biopolymer hydrogen bonds. A possible cause of the shift in these relationships is a change of water structure with pressure. The fact that the lyotropic series of anions has the same effect in reducing the temperature of starch gelatinisation as that of protein denaturation (Takahashi *et al.*, 1980; Zobel, 1981) adds support to the view that changes in water structure are significant. The basis for this effect is that when water structure is reduced, whether by pressure, temperature or structure-breaking solutes, the hydrophilic character of the solvent is increased owing to the increased proportion of open OH groups (Luck, 1973), so that it will be a better solvent for hydrogen bonded substances. The effect of pressure on the solubility of the hydrogen bonded compound diketopiperazine in water has been explained in this manner (Suzuki *et al.*, 1970). The solubility of this substance initially decreases with pressure, but at 450 MPa reaches a minimum and subsequently increases. This was explained by a decrease in (and ultimate change of sign of) ΔV, caused by increased strength in the diketopiperazine-water interactions at high pressure; ΔH also decreased but remained positive (Suzuki *et al.*, 1970; Suzuki & Taniguchi, 1972). While this explanation is attractive, it has some difficulties. thus above 200 MPa water behaves in other ways as an unstructured liquid (Horne, 1969); furthermore the pressure at which dT/dP changes sign varies considerably with the substance in question, so that consideration of water structure alone is insufficient.

It is of great interest that wheat and potato starch show different pressure dependencies of gelatinisation temperature. The reason may lie either in a difference in the pressure dependence of their partial specific volumes and water interaction enthalpies, or in different compressibilities ($\partial V/\partial P$) and thermal expansivities ($-\partial S/\partial P$) of their crystallites. Since the crystal structures of wheat and potato starch, from the X-ray evidence, are different, the latter possibility seems more likely. However, the possibility that the above solution properties of the starches do differ cannot be ruled out, since there are significant differences in their molecular structure, e.g. the existence of phosphate groups on the potato starch amylopectin.

Gelatinisation Range

A broadening of the temperature range of the transition at elevated pressure has been observed both for the denaturation of proteins (Hawley, 1971) and for the melting of synthetic polymers (Wunderlich, 1980).

According to the classical equations of thermodynamics, the equilibrium constant K of a two-state reversible reaction is related to the standard free energy change by

$$-RT \ln \mathrm{K} = \Delta G^0 = \Delta H^0 - T\Delta S^0$$

where ΔG^0 is the free energy change when the reactant in its standard state is completely converted to the product in its standard state. When pressure is a variable, it is convenient to allow the standard free energy to be a function of both temperature and pressure. Thus 'standard' refers only to composition.

Hence $(d \ln \mathrm{K})/(d\, 1/T) = -\Delta H/R$ using the Gibbs-Helmholtz relation. If we replace K by $\theta/(1-\theta)$ (where θ is the extent of transition) and evaluate the derivative at the transition midpoint ($\theta = \frac{1}{2}$) we obtain

$$\Delta H^0 = 4RT^2 \left.\frac{\mathrm{d}\theta}{\mathrm{d}T}\right|_{\theta=\frac{1}{2}}$$

It follows that if ΔH^0 is reduced (for example by the application of pressure) then the transition range will be broadened. This argument would explain the results for the reversible denaturation of chymotrypsinogen.

For many systems it is found that the van't Hoff value calculated as above (which may be denoted ΔH_{VH}) is much greater than the directly measured ΔH (cal mol^{-1}). This is caused by a degree of cooperativity in the transition, i.e. the particles interact, so that the state to which their neighbours belong exerts considerable influence. Cooperativity is characterised by a sharp transition between the states. $\Delta H_{\mathrm{VH}}/\Delta H$, the cooperative unit, is a measure of the extent of cooperativity (Stankowski & Gruenwald, 1980). Since starch gelatinisation is irreversible, these notions are not quantitatively applicable (although we can make a formal calculation of $\Delta H_{\mathrm{VH}} = 5{\cdot}91 \times 10^4$ cal mol^{-1} from the SALS birefringence versus temperature curve, corresponding to a cooperative unit of 160 monomer units). Nevertheless, the notion may be qualitatively applied. Starch gelatinisation can be expected to be at least a partially cooperative process – firstly because of the crystalline nature and secondly because of the interaction between different crystallites (Marchant & Blanshard, 1978; French, 1981). If the degree of the cooperativity is unaltered by pressure, a broadening may be to reduce the degree of cooperativity.

The reason for the broadness of melting transitions observed in synthetic polymers is not clearly resolved (Bauer, 1980). Some people stress the importance of surface effects and imperfections which destabilise the first crystallites to melt. Others stress the importance of the molecules which traverse both crystalline and amorphous regions, which results in a dependence of the entropy of the amorphous regions on the degree of crystallinity. Thus the melting of the first crystallites is accompanied by a greater entropy increase than the last. The first possibility implies ΔH for the first crystallites would be smaller, and hence $\mathrm{d}T/\mathrm{d}P$ would be larger for them – the observed effect for starch gelatinisation. The second possibility would apparently imply the reverse, since ΔS is bigger – i.e. the crystals most easily melted are less affected by pressure. While this fits with the broadening of the melting range of synthetic polymers ($\mathrm{d}T/\mathrm{d}P > 0$) it is opposite to that observed for starch-water ($\mathrm{d}T/\mathrm{d}P < 0$).

An additional possibility is that the kinetics of annealing could be much slower at high pressure, so that at high pressure a truer reflection of the different stabilities of the crystallites is obtained. If this were the case, it might be possible to find such a broadening by very rapidly heating samples to different temperatures at atmospheric pressure, and observing the degree of gelatinisation achieved. By plunging samples sealed between coverslips into a water bath, the temperature is raised in 5 s from room temperature. However, in preliminary experiments, no broadening of gelatinisation range has been revealed. The discussion above supposes that the 'equilibrium' degree of gelatinisation is a fairly well defined function of temperature; Thevelein *et al.* (1981) have rather considered that the gelatinisation rate is a well defined function of temperature. Studies by, for example, Marchant & Blanshard (1978) have shown that both representations have elements of truth. The study of the time dependence, as opposed to the temperature dependence, of gelatinisation is of great interest and we are pursuing it further.

CONCLUSIONS

The effect of pressure on starch gelatinisation is similar to the pressure dependence of the denaturation temperature and solubility of other biopolymers in water. The marked difference between the results for wheat and potato starch probably reflect differences in crystallite structure, since the molecules themselves are substantially similar and should not differ greatly in their water interaction or partial specific volumes. Alternatively, the solution properties of the macromolecules may in fact significantly differ due to the presence of such entities as phosphate groups on the potato starch amylopectin.

It is evident that very large hydrostatic pressures would be necessary to gelatinise starch of low water content at ambient temperature. While such pressures could be produced during milling, the question remains open as to whether shear stress (i.e. 'mechanical damage') could be a more important factor in producing damaged starch.

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