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A model of starch gelatinization linking differential scanning calorimetry and birefringence measurements

Hua Liu* & John Lelievre

Department of Food Science, Acadia University, Wolfville, NS, Canada BOP 1XO

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Suspensions of wheat, corn or rice starch, containing 5% polymer, were heated to temperatures in the range 20-145°C in a differential scanning calorimeter (DSC). Once the desired temperature was reached, the sample was immediately cooled at a rate of 320°C min^{-1} to room temperature. The numbers of native and gelatinized granules in the sample were then determined by microscopy. The variation in the fraction of gelatinized particles with temperature was found to follow a normal distribution function. A mathematical model based on this function was developed in an attempt to understand the DSC traces. The model predicts the shape of the gelatinization endotherm and accounts for the fact that the temperature band over which the endotherm takes place is broader than that for the birefringence loss. The model also suggests that the heat flow into an individual granule decreases as gelatinization proceeds therein.

INTRODUCTION

When heated, an aqueous suspension of starch granules undergoes an order-disorder transition known as gelatinization. This process can be monitored by differential scanning calorimetry (DSC). Single or double endothermic peaks are obtained depending on the water concentration. The molecular events responsible for the DSC traces are uncertain but entail melting (Donovan, 1979; Evans & Haisman, 1982; Biliaderis *et al.*, 1986; Zeleznak & Hoseney, 1987; Slade & Levine, 1988; Liu & Lelievre, 1991; Liu *et al.*, 1991). Possible mechanisms have been discussed in detail in a recent review (Biliaderis, 1990).

It is well established that in any given starch sample, some granules gelatinize at higher temperatures than others. Microscopy suggests that in excess water systems, the gelatinization range for the granule population is about 10°C, whereas in limited water mixtures a wider range is apparent (Ghiasi *et al.*, 1982; Burt & Russell, 1983). This heterogeneity influences the course of the overall transition (Evans & Haisman, 1982; Liu & Lelievre, 1992). For example, DSC studies suggest that in restricted water situations, the first granules to undergo transformation alter the environment in which the more stable particles gelatinize by changing the effective water concentration (Liu & Lelievre, 1992). This effect is not significant at low starch levels when water is in excess.

The temperature range over which the order-disorder change occurs within an individual granule is uncertain. Birefringence studies indicate this range is about 1°C in excess water systems, suggesting a cooperative process may take place (Biliaderis, 1990). However, a recent investigation based on X-ray studies indicates the loss of order may occur over a 10°C interval (Liu *et al.*, 1991). In limited water situations the range may be wider.

There are relatively few quantitative models of starch gelatinization. Equations based on chemical kinetics, and on stoichiometry, have been derived so far (Lund, 1984; Wang *et al.*, 1991). The present paper develops a quantitative model that considers the relationship between the temperatures at which individual granules undergo the transition and the shape of the DSC trace for the sample population. The model was used to assess the range over which individual

*Present address: Department of Food Science, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2.

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granules lose crystallinity. In addition, the question was addressed as to whether gelatinization takes place uniformly within a given particle as the temperature increases. The case where excess water is present was considered to avoid the effect of diluent restriction on gelatinization.

MATHEMATICAL MODELS OF STARCH GELATINIZATION

Suppose that in a population of starch granules, the number of particles starting to gelatinize as a function of temperature has a normal distribution. Accordingly a few granules will start to gelatinize at relatively low and at relatively high temperatures, while most will gelatinize at intermediate values in the region of the mean. The order-disorder transition within each granule is not completed instantly but takes place over a temperature interval. Assume this temperature interval is fixed, hence the granules leaving the gelatinization process will also have a normal distribution. This situation can be represented mathematically as follows,

$$S(T) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(T - T_s)^2}{2\sigma^2}\right) \quad (1)$$

$$F(T) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(T - T_f)^2}{2\sigma^2}\right) \quad (2)$$

where T is the temperature, $S(T)$ and $F(T)$ are the starting, and finishing, temperature distribution functions respectively, while T_s and T_f are the corresponding mean temperatures. σ is the standard deviation. Equation (1) and (2) are shown diagrammatically in Fig. 1. The two distribution functions have different means but the same standard deviation.

DSC measures the rate of heat flow as the temperature of the sample is raised. Assume, in the first instance, that the heat absorption rate is the same for each granule undergoing gelatinization irrespective of the temperature. The rate of heat absorption for a population of starch particles is then directly proportional to the number undergoing the transition. In other words, the derivative of the heat flow rate with respect to temperature is proportional to the difference in the number of the granules starting and leaving the gelatinization process, i.e.

$$\frac{d}{dT}\left(\frac{dH}{dt}\right) \propto Y(T) \quad (3)$$

where

$$Y(T) = S(T) - F(T) \quad (4)$$

H is the enthalpy (if we overlook the external work done by the system), and t the time. For any temperature τ, substitution of eqn (4) into eqn (3), integral tranformation and rearrangement gives,

$$\frac{dH}{dt} = C\int_{-\infty}^{\tau} Y(T)dT = C\int_{\tau - \Delta T}^{\tau} S(T)dT \quad (5)$$

where C is a proportionality constant and $\Delta T = T_f - T_s$. The integral in eqn (5) gives the total number of the granules undergoing the transition at τ. This equals the total number of granules that have started the transition in the period from $(\tau - \Delta T)$ to τ. Equation (5) provides a mathematical description of DSC traces for starch gelatinization in an idealized situation.

In practice, starch particles have various sizes and the heat absorption may increase with granule mass. The number of different sized granules in a population may be described by a distribution function $R(r)$, where r is the granule radius. Since there is no relationship between the granule size and transition temperature, except in the case of wheat where a bimodal size distribution exists (Meredith *et al.*, 1978), at any temperature the granules starting to gelatinize have various sizes and follow the same distribution function $R(r)$. It can easily be demonstrated that eqn (5) still holds in this case.

It is also possible that the rate of heat absorption by a single granule is not constant and depends on the stage of gelatinization of the particle, but not the absolute temperature at which the transition occurs. For example, the absorption may be greater when gelatinization just starts. Such variation can be taken into account by introducing an empirical variable as follows,

$$Z = \frac{T - \tau}{\Delta T} + 0{\cdot}5$$

This variable has values from $-0{\cdot}5$ to $0{\cdot}5$ when T varies from $(\tau - \Delta T)$ to τ. Its usefulness can be seen in the following example.

Suppose that the heat absorption rate for a granule decreases linearly during the course of its gelatinization as shown in Fig. 2. In this case the constant C in eqn (5) needs to be replaced by a term which takes different

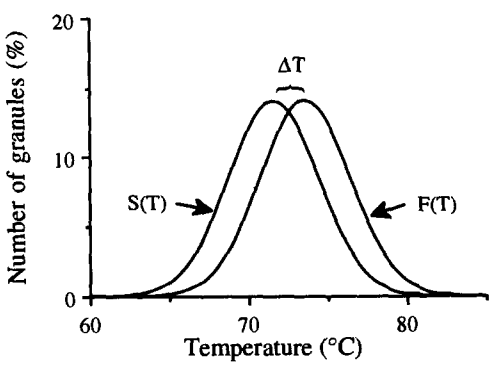

Fig. 1. Number of starch granules beginning and ending the gelatinization transition as a function of temperature.

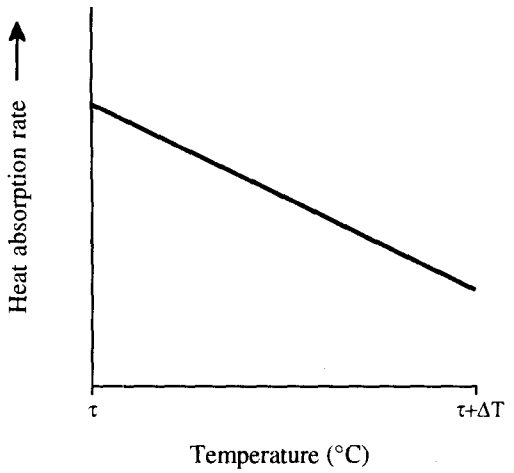

Fig. 2. The case where the heat absorption rate during gelatinization of an individual granule decreases linearly as a function of temperature.

values at different stages of gelatinization. By using the empirical variable introduced above, and noting that at τ the number of granules undergoing the transition is equal to the total that have started to gelatinize in the period $(\tau - \Delta T)$ to τ, the heat flow rate can be expressed as

$$\frac{dH}{dt} = \int_{\tau - \Delta T}^{\tau} S(T)(k + qZ)dT \qquad (6)$$

where k and q are constants. The bracketed term $(k + qZ)$ in the integral of eqn (6) has a minimum $(k - 0{\cdot}5q)$ at $(\tau - \Delta T)$ and a maximum $(k + 0{\cdot}5q)$ at τ. Its value depends on the temperature relative to τ in the interval from $(\tau - \Delta T)$ to τ but not on the absolute temperature. Cases where different heat absorption profiles occur in individual granules can be studied by substituting the relevant terms in place of $(k + qZ)$ in eqn (6).

MATERIALS AND METHODS

Starch was isolated from rice, wheat and corn as described elsewhere (Liu *et al.*, 1991). A sample of large starch granules was obtained from the wheat starch sample by sedimentation (Meredith *et al.*, 1978) and used for further study. About 25 mg 5% starch suspension was sealed in a DSC pan. Samples were heated to a temperature within the range 20–145°C, at a rate of 10°C min^{-1}, using a Perkin-Elmer DSC-2C. The experimental procedure was the same as that reported previously (Liu *et al.*, 1991). Once the desired temperature was reached, the sample was immediately cooled to ambient temperature at a rate of 320°C min^{-1}. The sample pan was then opened and the unmodified fraction determined by counting the birefringent and gelatinized granules using a polarizing microscope. The granules which had partially lost birefringence were counted in the gelatinized category. To facilitate the microscopic measurements, samples were stained by Congo red dye.

RESULTS AND DISCUSSION

Figure 3 shows that for a 5% wheat suspension the temperature at which birefringence is completely lost is much lower than that where the DSC peak ends, although the temperature recorded at the start of gelatinization by the two methods are about the same. This pattern was found for all the starch varieties studied. The difference is not an artifact caused by lack of control of temperature in the DSC instrument (Yost & Hoseney, 1986; Liu & Lelievre, 1991). A similar trend is evident in the results for 33% starch suspensions reported by Ghiasi *et al.* (1982).

In the mathematical model section, the number of starch granules going to the gelatinization transition as a function of temperature was assumed to have a normal distribution (eqn (1)). Figure 4 shows a typical variation of the birefringent granules with temperature on a probability chart, indicating that this is indeed the case. The parameters in eqn (1) can thus be estimated from Fig. 4 (Freund, 1973) and the results are summarized in Table 1 for rice, wheat and corn. As a comparison, parameters estimated from previous birefringence measurements obtained in isothermal experiments (Liu *et al.*, 1991) are also included. The standard deviation values are essentially the same. This reflects the fact that both samples are in dilute suspension (Ghiasi *et al.*, 1982). However in all instances, the means of the distribution functions for the DSC samples are shifted to higher temperatures. Considering the difference in the thermal treatments given to the samples, this would be expected (Shiotsubo & Takahashi, 1984).

Figure 5(a) gives an experimental DSC peak at dilute starch concentration. Figure 5(b) shows dH/dt as a function of temperature, calculated using eqn (5) and the parameters in Table 1 for rice starch, and assuming ΔT = 2°C. 2°C is used since it is about the range over

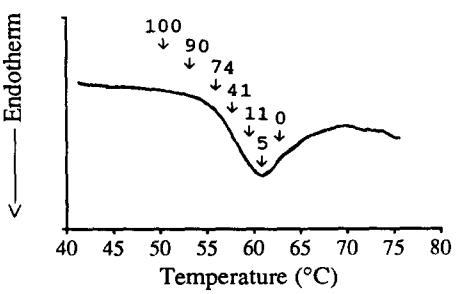

Fig. 3. DSC trace of a 5% aqueous wheat starch suspension. The numbers above the curve are % birefringent granules at the temperatures indicated.

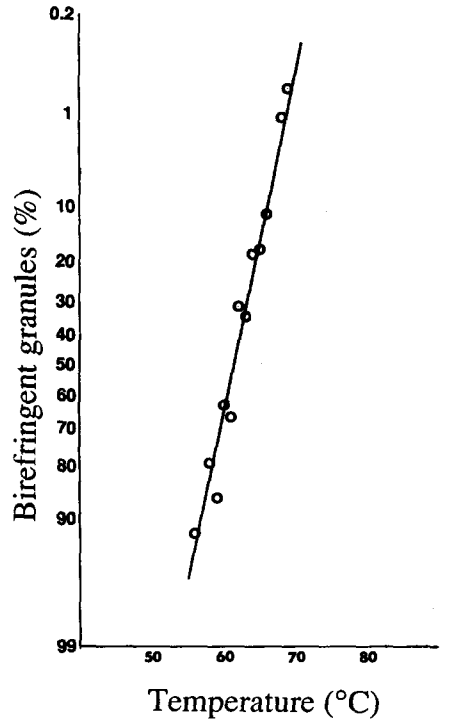

Fig. 4. Number of birefringent granules in a 5% aqueous corn starch suspension as a function of temperature plotted on a probability scale.

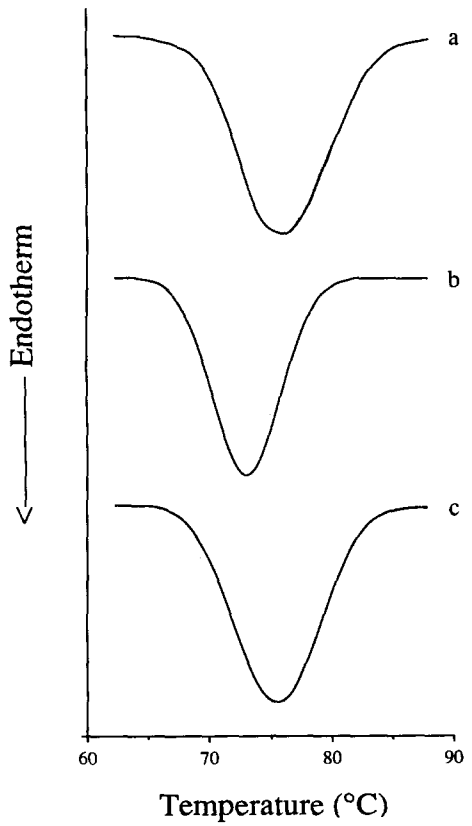

Fig. 5. (a) Experimental DSC trace for a 5% aqueous rice starch suspension. The curve has been corrected by subtracting the sloping baseline. (b) Theoretical curve calculated according to eqn (5) with $\Delta T = 2°C$. (c) Theoretical curve calculated according to eqn (5) with $\Delta T = 7°C$.

Table 1. Summary of the parameters of the normal distribution function for starch gelatinization in 5% aqueous suspensions

	σ(°C)	T_s(°C)
Rice	2·7 (2·8)[a]	72·1 (71·0)
Wheat	2·5 (2·3)	56·8 (55·5)
Corn	3·6 (3·5)	61·4 (60·5)

[a]Values in brackets are from a previous study (Liu *et al.*, 1991) in which 2% aqueous starch suspensions were gelatinized in isothermal experiments.

which the birefringence of a starch granule is lost. The shapes of the two curves are similar, however, comparison of the peak widths, and the temperature ranges at half peak height, shows that these parameters do not match those for the experimental DSC trace. This suggests that the temperature range over which a given granule melts may be greater than the range over which it loses birefringence. For a normal distribution function, nearly 99% of the peak area is within $\pm 2{\cdot}5\sigma$ of the mean (Freund, 1973). The peak width of the calculated thermal profile is therefore $(5\sigma + \Delta T)$, see Fig. 1. From the peak width of DSC traces measured in this study, ΔT can be estimated to be about 7°C. Figure 5(c) shows the thermal profile calculated when $\Delta T = 7$. A closer match to the experimental DSC trace is evident.

The DSC output can be studied further by using the first derivative of the curves. The derivative trace has two characteristic peaks, corresponding to the maximum increase and decrease in the rate of heat absorption during gelatinization, see Fig. 6. The figure shows that the height of the lower temperature peak in the first derivative trace of the experimental DSC curve is

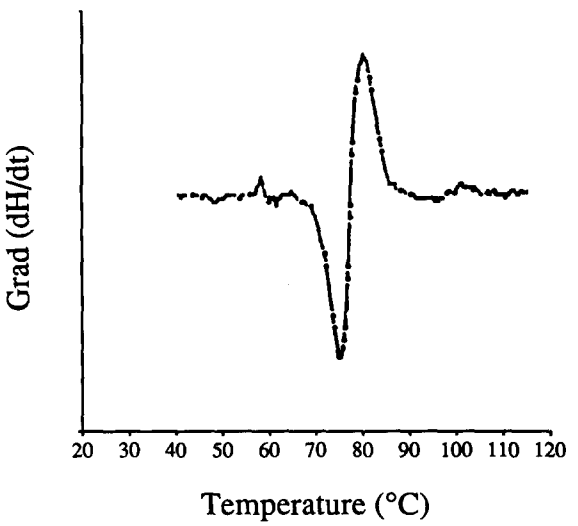

Fig. 6. The first derivative curve of the experimental DSC trace for a 5% aqueous rice starch suspension as a function of temperature.

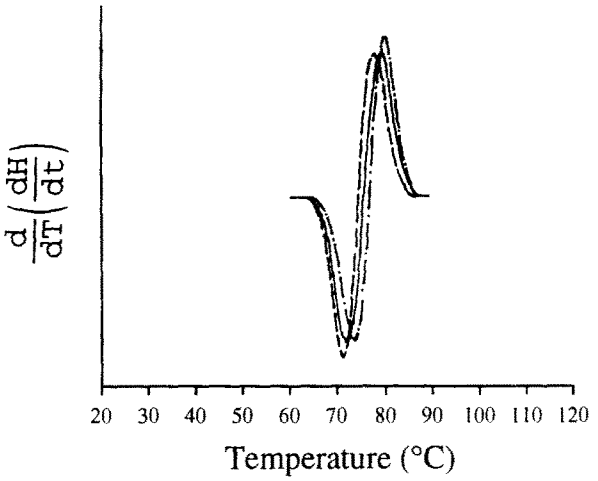

Fig. 7. The first derivative traces of heat flow rate with respect to temperature calculated using the proposed models with $\Delta T = 7°C$. (a) The rate of heat absorption is constant during gelatinization of the granule (——). (b) The rate of heat absorption decreases linearly by 10 fold during gelatinization of the granule (- - - -). (c) The rate of heat absorption increases linearly by 10 fold during gelatinization of the granule (— · — · —).

greater than that of the higher temperature. The reverse situation was found by Biliaderis *et al.* (1986) but this is not unexpected given the difference in starch concentrations used. The derivative trace can be modelled using eqn (3), see Fig. 7(a). It can be demonstrated that the difference in peak heights detected in the present study is not caused by the sloping baseline in the DSC trace, nor does the baseline displacement (Slade & Levine, 1988; Liu & Lelievre, 1991) cause a peak difference of the magnitude shown. Calculations according to eqn (6) show that an asymmetric peak will result if the heat absorption rate in single granules is not constant during their transition, see Figs 7(b) and 7(c). Comparison of the model with the experimental results suggests that the heat flow into an individual granule decreases as gelatinization proceeds.

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