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Kinetics of gelatinization of potato starch studied by non-isothermal DSC

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The kinetics of gelatinization of potato starch (starch:water weight ratio, 1:1) were investigated using differential scanning calorimetry (DSC). In the first stage, two isoconversional (Ozawa–Flynn–Wall and Friedman) methods were applied. It was found that the value of the activation energy (E) changes with $0 < \alpha < 1$ from approximately 75 to 138 kJ/mol. Further analysis using non-linear regression methods revealed that the best fit was found for a competitive double-step reaction, whereby the first step was attributed to the ''n-order reaction'' scheme and the second step was described by three-dimensional diffusion of Jander's type. The first step was attributed to the gradual formation of interchain and intrachain hydrogen bonding which restricts chain mobility and led at elevated temperature to the second diffusion-based rate-limiting step. For this model function, a spherical shape for the reacting bodies is the best stereogeometrical approximation; this corresponds well with observations concerning starch alignment at different microstructural levels and its behaviour during gelatinization. © 1998 Elsevier Science Limited. All rights reserved.

INTRODUCTION

Studies on the starch gelatinization process have been carried out both to answer fundamental questions and to obtain a better technological use of this major carbohydrate in animal and human nutrition (Bean *et al.*, 1973; Glover *et al.*, 1986; Slade *et al.*, 1991; Kim *et al.*, 1992; Wolters *et al.*, 1992; Riva *et al.*, 1993; Svensson *et al.*, 1995). The course of gelatinization depends on the structure of starch which is composed of two kinds of molecules, the essentially linear molecule, amylose, and the branched molecule, amylopectin. Amylopectin molecules are oriented perpendicular to the growth rings and to the outer surface of the granule. That is, they are aligned along an imaginary axis extending from the hilum of the granule radially towards the edge of the granule. Portions of those long, branched molecules are in crystallites, which are perpendicular to the rings. It is the regular orientation of the amorphous and crystalline regions that give the granule its characteristic birefringent pattern, known as the maltese cross (French, 1984). The non-crystalline regions contain the amylose molecules and sections of amylopectin molecules not involved in crystallites (Paredes-Lopez *et al.*, 1991). Recent studies on the structure of starch by small-angle neutron scattering (SANS) revealed that starch granules can be described as containing three regions, namely semicrystalline stacks containing alternating crystalline and amorphous lamellae, which are embedded in a matrix of amorphous material (Jenkins *et al.*, 1996).

Such a complex microstructural arrangement strongly influences the course of gelatinization which for a starch–water system is described by an endothermic transition, as observed by differential scanning calorimetry (DSC) (Donovan, 1979; Donovan *et al.*, 1980). At low water–starch ratios, water penetrates the amorphous regions and the granules start to swell. The swelling of the amorphous regions of the granule by imbibed water, strip starch chains from the surface of the ordered crystallites, effectively tearing the crystallites apart in the process known as gelatinization, giving rise to the first endotherm. At this temperature of gelatinization the granules lose their birefrigence and X-ray diffraction pattern, and material from the granules start

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to diffuse into the water. If sufficient water is present, all the crystallites can be pulled apart by the swelling, leaving none to be melted at higher temperatures. If the water–starch ratio is high, the low temperature endotherm is the only one observed. At a water content lower than a certain ratio, the remaining crystallites melt at significantly higher temperatures and a shoulder peak forms a second endotherm which shifts to a higher temperature as the water–starch ratio decreases (Larsson *et al.*, 1991). The gelatinization characteristics can be altered by different factors, such as heat–moisture treatment (Lund, 1984) or annealing time (Krueger *et al.*, 1987).

The objective of this study is to perform a kinetic analysis of the gelatinization of potato starch to gain a deeper knowledge of this process. Kinetic parameters—the activation energy, pre-exponential factor and model function—will be calculated on the basis of a novel analysis of the DSC data and the model can be utilized for the optimization of some industrial-scale processes.

EXPERIMENTAL

Materials

Potato starch was manufactured by Potato Enterprise in Trzemeszno, Poland.

Technique

DSC measurements were performed on a Netzsch DSC 200, operating in a dynamic mode, with the following conditions: sample weight ~5 mg, heating rate = 2.5, 5, 10 and 20 K/min, atmosphere of argon (30 cm^3/min), sealed aluminium pan. The calorimeter was carefully calibrated with indium (ΔH fusion 28.58 J/g, melting point 156.6°C) prior to use; an empty aluminium pan was used as a reference.

Starch samples were weighed directly into DSC pans and deionized water (starch:water weight ratio = 1:1) was added with a Hamilton microsyringe to make the desired solid suspension. After sealing, the pan was left to equilibrate for 1 h. The measurements were run in triplicate.

Kinetic analysis was carried out using in-house software and a Netzsch Thermokinetic program (v. 6.65) on a Hewlett-Packard HP 486 Vectra computer.

KINETIC ANALYSIS

In recent years, the kinetic analysis of complex reactions has received much attention (Sestak, 1984; Bradner *et al.*, 1992; Vyazovkin *et al.*, 1996). The aim was to extract the maximum relevant information from the thermal analysis data in order to gain a deeper look into the reaction mechanism and to make some predictions concerning extrapolated values of degree of extent of reaction.

In general, the rate of reaction can be described in terms of two functions: $k(T)$ and $f(\alpha)$, thus:

$$d\alpha/dt = k(T)f(\alpha) \qquad (1)$$

By substitution of the Arrhenius equation ($k(T) = A\exp(E/RT)$) the following equation results:

$$d(\alpha)/dt = A\exp(-E/RT)f(\alpha) \qquad (2)$$

After introduction of the constant heating rate $\beta = dT/dt$ and rearrangement, one obtains:

$$d(\alpha)/f(\alpha) = (A/\beta)\exp(-E/RT)dT \qquad (3)$$

where α is the degree of conversion, T the temperature in degrees kelvin, $f(\alpha)$ the kinetic model, $k(T)$ the rate constant, E the activation energy, A the pre-exponential factor, and R the gas constant.

Integration of Eq. (3) leads to:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)dT \qquad (4)$$

which cannot be expressed by a simple analytical form since its right-hand side corresponds to a series of infinite gamma functions. Taking logarithms gives:

$$\ln G(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln\beta + \ln p(x) \qquad (5)$$

when the exponential integral $p(x)$ is introduced

$$p(x) = \frac{e^{-x}}{x} - \int_\infty^x \frac{e^{-x}}{x}dx$$

where

$$x = \frac{E}{RT}$$

Using an approximation of the exponential integral $p(x)$ in the form proposed by Doyle (Doyle, 1962):

$$\ln p(x) = -5.3305 + 1.052x \qquad (6)$$

it is possible to determine the activation energy of the thermal process by following the change of heat flux from the system at several different heating rates (Ozawa, 1965; Flynn *et al.*, 1966):

$$\ln\beta = \ln(AE/R) - \ln G(\alpha) - 5.3305 + 1.052x \qquad (7)$$

Eq. (7) generates a straight line when $\ln(\beta)$ is plotted against $1/T$ for isoconversional fractions, the slope of the line being equal to $1.052E/R$ during a series of measurements with a heating rate of $\beta_1 ... \beta_j$ at a fixed degree of conversion of $\alpha = \alpha_k$. The temperatures T_{jk} are those at which the conversion α_k is reached at a heating rate of β_j.

Another isoconversional procedure, introduced by Friedman (Friedman, 1965), uses as its basis the following relationship:

$$\ln(d\alpha/dt) = \ln f(\alpha) + \ln A - E/RT \qquad (8)$$

which makes it possible to find the activation energy value from the slope of the line ($m = -E/R$) when $\ln(d\alpha/dt)$ is plotted against $1/T$ for isoconversional fractions.

Table 1. Definition of symbols in basic kinetic models

Model	Symbol	$f(\alpha)$
Random nucleation. Unimolecular decay law	F1	$(1-\alpha)$
Reaction *n*th order	Fn	$(1-\alpha)^n$
Sestak–Berggren	SB	$\alpha^m(1-\alpha)^n$
Johnson–Mehl–Avrami	JMA	$n(1-\alpha)[\ln(1-\alpha)^{1-1/n}]$
Two-dimensional growth of nuclei (Avrami equation)	A2	$2(\ln(1-\alpha)^{1/2})(1-\alpha)$
Three-dimensional growth of nuclei (Avrami equation)	A3	$3(\ln(1-\alpha)^{2/3})(1-\alpha)$
One-dimensional diffusion	D1	$1/2\alpha$
Two-dimensional diffusion	D2	$1/(\ln(1-\alpha))$
Three-dimensional diffusion (Jander equation)	D3	$(3(1-\alpha)^{2/3})/(2(1-(1-\alpha)^{1/3}))$
Three-dimensional diffusion (Ginstling–Brounshtein)	D4	$3/2((1-\alpha)^{-1/3}-1)$

In Eq. (1) term $f(\alpha)$ represents the mathematical expression of the kinetic model. Some of the most frequently cited basic kinetic models are summarized in Table 1.

The course of thermal reaction depends on many internal and external factors. Among the most important internal factors are:

(1) the energy state of the initial material and products of the reaction;
(2) mobility of structural elements of the space lattice, which depends on the geometry of the lattice, charge of the elements, etc.;
(3) activation energy, which depends on the nature of the reacting substances and the region of realization of the process;
(4) the dispersion state of the initial materials, which influences the surface energy and the mobility of the lattice elements;
(5) lattice defects;
(6) irregularities in the biopolymer chain (internal unsaturations, branches, oxidation structures, etc.);
(7) structural similarity (or dissimilarity) of the initial materials and products.

The most important external factors are:

(1) the temperature, which is decisive for the mobility of lattice elements and influences not only the course of a chemical reaction, but also the space and surface diffusions;
(2) the duration of the process;
(3) the pressure and composition of the gas phase;
(4) catalysts, the role of which can be played by impurities in the initial material or by the products of its reaction (Pysiak *et al.*, 1994).

Non-isothermal curves of a thermal reaction must satisfy the kinetic equations developed for the kinetic analysis of "*n*-order reactions", even if they follow a quite different mechanism. Results of the comparative studies lead to the conclusion that the actual mechanism of a thermal process cannot be discriminated from the kinetic analysis of a single DSC trace (Criado *et al.*, 1988; Opfermann *et al.*, 1992). Both the activation energy and the pre-exponential factor in Eq. (2) are mutually correlated through an expression $\ln A = a + bE$, where a and b are constants. Any change in the activation energy is therefore compensated by the change in "ln A". As a consequence of this correlation any DSC curve can be described by an apparent kinetic model instead of the appropriate one for a certain value of apparent activation energy. Therefore, the kinetic analysis of DSC data cannot be successful unless the true value of the activation energy is known (Sestak *et al.*, 1993).

RESULTS AND DISCUSSION

DSC curves of potato starch recorded at different heating rates are shown in Fig. 1.

From the thermal parameters, summarized in Table 2, in can be seen that the characteristic temperature of gelatinization (T_{peak}) increases with an increase of heating rate, except of the highest rate which may be influenced by certain delay of the calorimetric response. For the value of gelatinization enthalpy an opposite tendency can be observed.

Results of the Ozawa–Flynn–Wall (Fig. 2) and Friedman (Fig. 3) analysis show that the E value changes during the process (Fig. 4). This means that it is not possible to determine directly a single-step kinetic model which could be

Table 2. Gelatinization temperatures and enthalpies of potato starch in the presence of water (starch:water weight ratio, 1:1) as measured by DSC at a heating rate of 2.5, 5, 10 and 20 K/min

Heating rate [K/min]	T_{onset} [°C]	T_{peak} [°C]	T_{end} [°C]	ΔH [J/g]
2.5	57.6	82.1	92.2	− 701.4
5.0	69.8	95.7	107.7	− 626.8
10.0	52.8	103.1	139.3	− 620.3
20.0	64.8	101.0	122.1	− 381.2

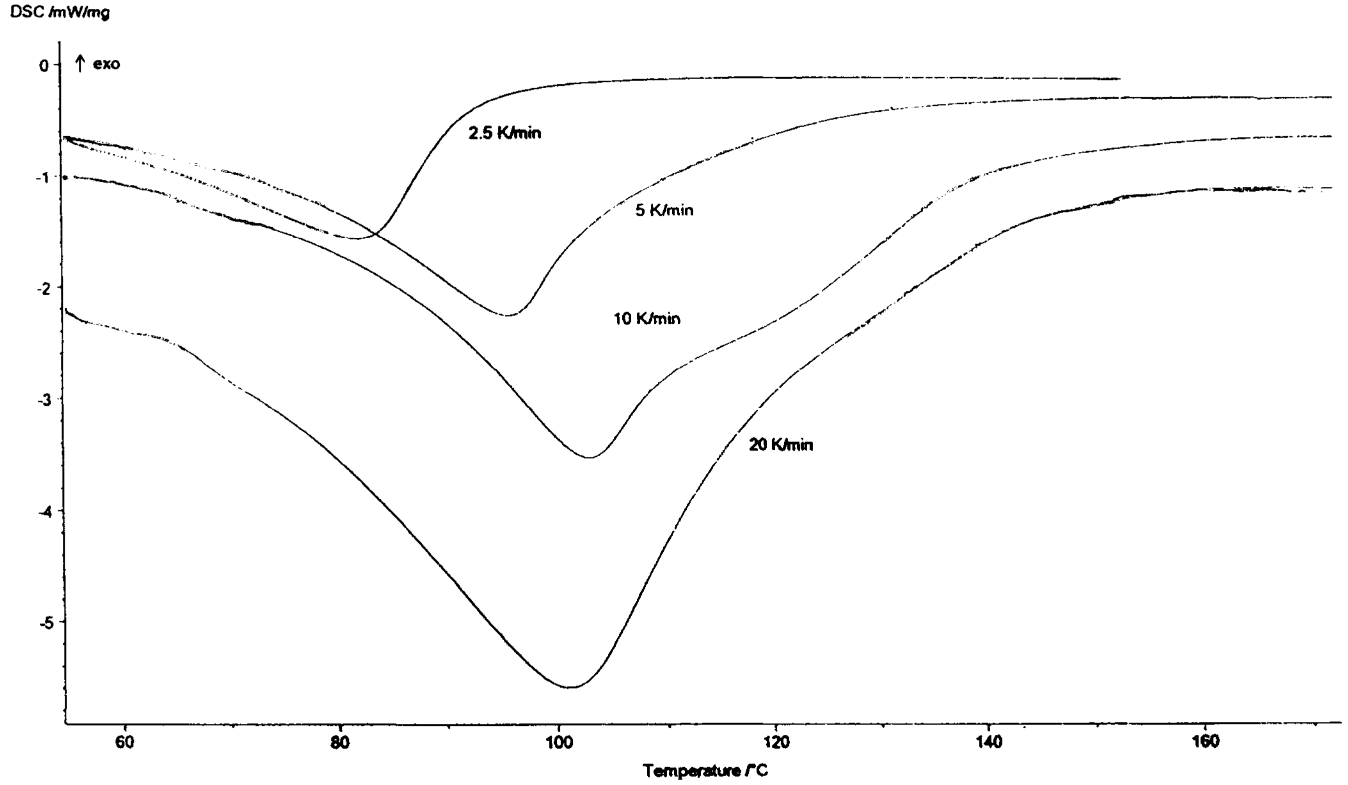

Fig. 1. DSC scans at 2.5, 5, 10 and 20 K/min of potato starch–water system (weight ratio, 1:1).

regarded as prevailing during the reaction. A change in E with an increasing degree of conversion indicates a complex reaction mechanism. For its description a multi-step kinetic scheme should be employed.

Among different models tested by non-linear regression statistics, the best fit in terms of F_{exp} parameter (as shown in Table 3) was found for a competitive double-step reaction, whereby the first step was attributed to the nth order reaction scheme ($\log A = 16.67$ s) and the second step was described by the three-dimensional diffusion of Jander's type, with the $\log A$ value equal to 12.43 s.

On the basis of the obtained kinetic parameters a prediction of the thermal behaviour of the system in an extrapolated temperature or time range can be performed (Figs. 5 and 6).

Kinetic analysis can be a valuable tool for both fundamental and applied studies. In our work the best fit of a double-step reaction (nth order scheme and three-dimensional diffusion Jander's type) indicate that at the beginning of gelatization process reaction of nth order is a rate-limiting step. It may be connected with a gradual formation of interchain and intrachain hydrogen bonding which in turn restrict chain mobility thus leading at elevated temperature to the second kinetic step, namely three-dimensional diffusion. The Jander equation proposed for the description of heterogeneous reactions running in multi-phase systems provides information about the change of system dimensionality, due to the interface growth controlled by the parabolic law of diffusion. In view of morphological arrangement in terms of characteristic dimensions (usually the longest particle length), interface (average boundary line) and volume (mean section area) the spherical shape of reacting bodies can be considered as the best stereogeometrical approximation; this corresponds well with observations concerning starch alignment on different microstructural levels (French, 1984). On the other hand, the distribution of water in the system is not regular since the crystal domains are of different area—this considerably influences the E value within the broad range of α.

CONCLUSIONS

On the basis of kinetic analysis by means of isoconversional methods it was possible to determine properly the value of

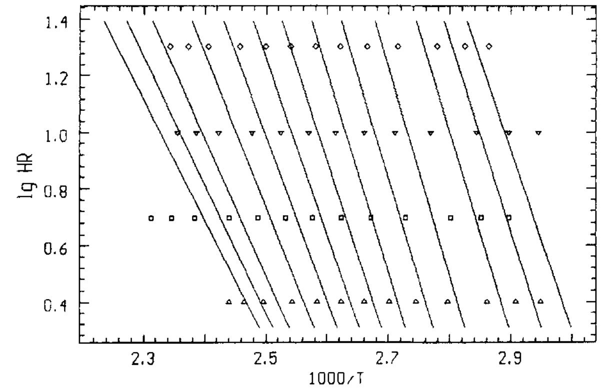

Fig. 2. Ozawa–Flynn–Wall analysis of gelatinization process of potato starch–water system.

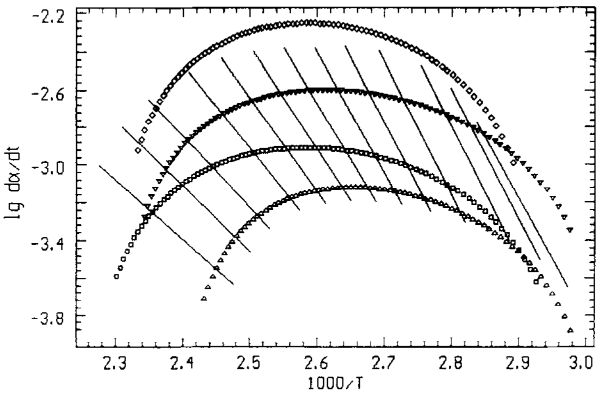

Fig. 3. Friedman analysis of gelatinization process of potato starch–water system.

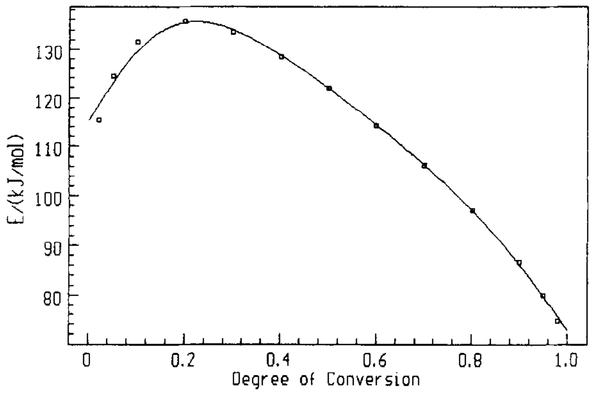

Fig. 4. Energy of activation (E) as a function of degree of conversion (α) for the gelatinization process of potato starch–water system.

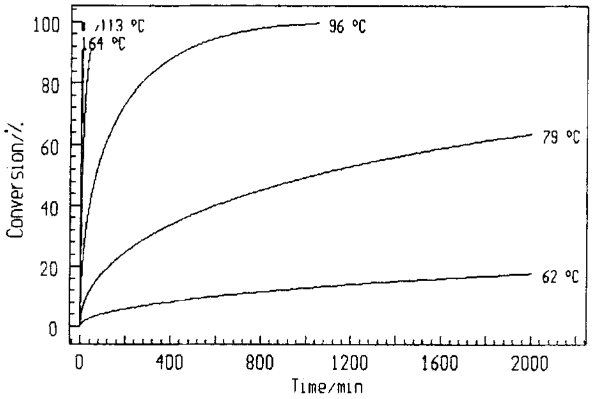

Fig. 5. Degree of conversion vs. time plot for gelatinization of potato starch in the presence of water.

activation energy for $0 < \alpha < 1$. The observed variation of E indicates a complex kinetic scheme for which a simple single-step reaction model is not applicable. During further analysis, using non-linear regression procedures, it was found that a double-step approach is the best approximation; this corresponds well with general observations of the amorphous–crystalline structure and therefrom the resulting double-step gelatinization process of starch, but yields additional, quantitative information about the process.

The calculated kinetic parameters can be of a great practical value for any technological applications since kinetic modelling succesfully replaces time- and material-consuming experiments.

Table 3. Results of F-test to distinguish between the models for potato starch gelatinization

Model	F_{exp}
Fn/D3	1.00
D3	4.36
D4	5.11
D2	5.56
Fn	13.29

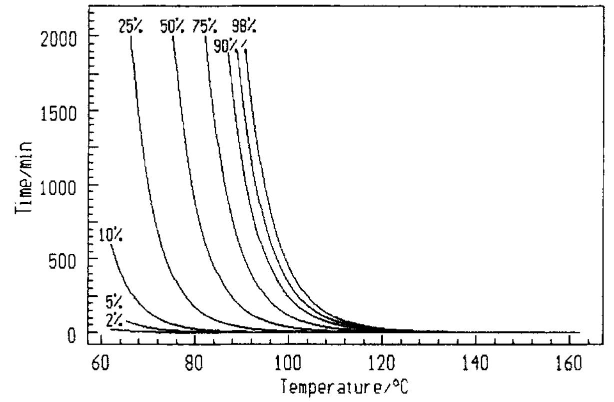

Fig. 6. Time vs. temperature plot for gelatinization of potato starch in the presence of water.

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