Water dispersion kinetics during starch gelatinization

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Abstract

The kinetics of water dispersion during the gelatinization of dilute suspensions of maize starch was studied by analyzing changes in electrical conductance data recorded continuously with time. Several analytical methods were compared for the preliminary study of the activation energy of gelatinization. The probable mechanism of the process was investigated by a number of homogeneous and heterogeneous reaction kinetic models. A modified composite methodology coupled with a reduced-plot method was employed to fit the kinetic data. Two simultaneous elementary reactions, expressed by an autocatalytic kinetic model and a 3D moving phase-boundary rate model, predicted the overall kinetic behavior with appreciable success. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

When a starch suspension is heated in excess water, the term gelatinization usually refers to a number of changes in the starch granule: swelling, loss of birefringence and leaching of granule material. Several theories have been proposed for the mechanism of starch gelatinization but, yet, a universally accepted explanation of the process is not available (Blanshard, 1987). An earlier hypothesis by Donovan (1979) has been reinforced by X-ray scattering measurements (Jenkins & Donald, 1998). According to this hypothesis, the first stage of gelatinization in excess water is the uptake of water by the amorphous background region of the starch granules followed by their subsequent rapid expansion. This swelling exerts a strong destabilizing effect on the crystallites contained within the crystalline lamellae. At the end, these crystallites are disrupted and crystallinity is progressively lost.

Some authors studied the starch gelatinization using a kinetic approach (Slade & Levine, 1991). Kinetic analysis not only allows the estimation of the gelatinization reaction rates but also lead to suitable rate expressions characteristic of possible reaction mechanisms. Gelatinization in excess water represents an interesting situation in terms of kinetic analysis since ideas for both constant volume homogeneous reactions and heterogeneous reactions may approximately apply. This is because under well-mixed conditions, the system is macroscopically homogeneous and of quasi-constant volume whereas, on a microscopic scale, the interaction of water with the solid starch granules constitutes a typical heterogeneous process.

For a range of starches, gelatinization has been widely accepted to follow irreversible pseudo-first-order Arrhenius kinetics (Bakshi & Singh, 1980; Cabrera, Pineda, Duran de Bazua, Segurajauregui, & Vernon, 1984; Kubota, Hosokawa, Suzuki, & Hosaka, 1979; Okechukwu & Rao, 1996a,b; Okechukwu, Rao, Ngoddy, & McWatters, 1991; Pravisani, Califano, & Calvelo, 1985; Suzuki, Kubota, Omichi, & Hosaka, 1976; Zanoni, Smaldone, & Schiraldi, 1991; Zanoni, Schiraldi, & Simonetta, 1995a). However, in order to apply the Arrhenius model, the extent of gelatinization must not be a function of temperature, a condition commonly overlooked by many workers (Lund, 1984).

Changes in apparent viscosity were used by Kubota et al. (1979) and Okechukwu et al. (1991) to quantify gelatinization kinetics in rice and cowpea starches and in cowpea flour. The major shortcoming of rheological methods is the difficulty in determining the initial reference viscosity of low starch concentration suspensions. Suzuki et al. (1976) studied the kinetics of cooked rice by using a parallel

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plate plastometer to measure the compressibility of rice grains. All the earlier studies assumed the gelatinization reaction to follow first-order kinetics.

Lund and Wirakartakusumah (1984), studied the rice starch gelatinization kinetics by isothermal DSC experiments and found that gelatinization followed first-order kinetics only beyond a certain degree of gelatinization. These authors assumed that during the initial phase of heating, gelatinization would only affect the amorphous regions and would not follow the first-order kinetics. During the subsequent phase of the process, the crystalline regions, destabilized by the amorphous component, melt according to first-order kinetics. Pravisani et al. (1985) investigated the kinetics of potato starch gelatinization by dynamic DSC experiments. Once again, pseudo first-order kinetics was assumed but since the activation energy was observed to change with temperature, a two-stage reaction mechanism was speculated. These authors also considered the hydration of the amorphous region of the granules to act as a promoter for further gelatinization of the crystalline regions. Deviations from the first-order kinetic model during the initial heating period were also observed by Okechukwu and Rao (1996a,b) who examined the kinetics of cornstarch and cowpea granule swelling using a laser diffraction technique. Furthermore, some authors have recognized that gelatinization is more correctly modeled as a set of reactions (Kokini, Lai, & Chedid, 1992; Pielichowski, Tomasik, & Sikora, 1998).

Most experimental techniques employed so far to study the gelatinization phenomena involved *batch* samples treated progressively. As a result, fast kinetic data could not be accurately collected over a short time scale. The aim of this study is to investigate the kinetic mechanism of water dispersion during gelatinization utilizing the *continuously sampled* electrical conductance records reported by (Karapantsios, Sakonidou, & Raphaelides, (2000). Electrical conductance footprints of instantaneous water dispersion patterns were considered to be representative indicators of the progress of gelatinization. In this paper, we study the suitability of several proposed analytical methods for the kinetic analysis of gelatinization. In addition to the application of some conventional kinetic models, a few alternative approaches, originally applicable to the degradation of polymeric systems, have also been examined.

2. Experimental

A detailed description of the experiment is given elsewhere (Karapantsios et al., 2000) and only some essential information is provided here. The natural maize starch used had a moisture content of 13.5%. Only starch/water mixtures with concentration 10% w/w were examined. The liquid used was filtered tap water with a specific conductivity between approx. 600 and 700 $\mu S\ cm^{-1}$.

Gelatinization experiments were performed inside a cylindrical Plexiglass test vessel with i.d. = 6.8 cm and height = 23 cm. To assure homogeneity of the liquid mixture, a centrally located stirrer was employed with four impellers mounted along an electrically insulated shaft. Among them, specific reference must be made to a custom-made grid paddle assembly, specially designed to achieve mixing of every part of the gelatinized viscous material. Mixing was performed initially at 260 or 330 rpm until the conductance signal reached a maximum (always around 70 °C) where it was adjusted to a final value of 40, 160 or 260 rpm. Temperature measurements were performed at two positions across the vessel: one at its center axis and another close to the wall.

Contrary to all prior relevant studies that maintained either a constant temperature or a constant heating rate, the present runs were conducted under a constant heat supply provided by a submerged heating coil placed at the top of the vessel. The heating powers were 150 and 300 W ($\Delta T_{liq}/\Delta t_{20-60°} \cong 3$ and 6 °C min^{-1}, respectively). When the final mixing speed was 40 rpm the temperature of the sample rises rapidly to about 70 °C after which no large change in temperature was observed for both 150 and 300 W heating power. These quasi-isothermal conditions for a large part of the gelatinization process permitted isothermal data analysis. On the other hand, when the final mixing speed was 160 and 260 rpm the resulting temperature profiles were increasing almost linearly for at least some part of the gelatinization process. This in turn, allowed dynamic heating data analysis (see below).

Conductance measurements were performed by means of two parallel stainless steel ring electrodes (strips) with a width of 3 mm, located 3 cm apart. The electrodes were flush mounted onto the inner surface of the test section to avoid the disturbance of the cross section of the vessel. An alternating current (ac) carrier voltage of 0.5 V p.p. was applied across the electrodes at a frequency of 25 kHz in order to eliminate the capacitive impedance. Such high frequency electrical measurements are most representative of the free water in the intergranular spaces and in the pores of the material since strongly bound water has a resonance at much lower frequencies, (Hardman, 1985). So, as the granules imbibe rapidly the surrounding free water during gelatinization the electrically accessible free water becomes less and less reflecting the structural changes accompanying starch swelling and solubilization.

The response of the electrodes was fed to a special electronic analyzer. The direct current (dc) voltage output of the analyzer was converted to apparent conductance of the medium between the electrodes, K_{app}, using a calibration curve based on precision resistors. To differentiate between actual structural changes (due to gelatinization) and temperature effects and also to eliminate errors due to liquid conductivity measurement, the apparent conductance signal was reduced with the conductance of the test section filled with water, $K_r = K_{app}/K_{max}$. The degree of gelatinization of samples taken during the course of the experiments was

independently assessed by polarizing microscopy, application of Congo red dye and DSC thermograms (Karapantsios et al., 2000).

3. Kinetic analysis

3.1. Background

In the kinetic analysis, the following symbols are used:

E	apparent activation energy (kJ mol^{-1})
A	pre-exponential factor (min^{-1})
n	apparent reaction order
R	gas constant (8.3136 J mol^{-1} K^{-1})
T	temperature (K)
α	degree of conversion
t	time (min)
β	heating rate (K min^{-1})
k	rate constant

To compare measurements from various experiments for kinetics investigation, it is necessary to introduce a dimensionless degree of conversion. Thus, by normalizing the reduced apparent conductance, K_r, with respect to some reference value, an index of gelatinization is defined. Taking advantage of the virtually constant values of K_r before the onset of gelatinization (a maximum) and for completed gelatinization (a minimum) (Karapantsios et al., 2000), the following degree of conversion is proposed:

$$\alpha = \frac{K_r^0 - K_r^T}{K_r^0 - K_r^{final}} \tag{1}$$

where K_r^0 and K_r^{final} are the pre-gelatinization and post-gelatinization reduced conductance values, respectively. Karapantsios et al. (2000) reported that, $K_r^0 \approx 0.92$ and $K_r^{final} \approx 0.70$ for all experimental conditions.

Kinetic studies customarily utilize the basic conversion rate equation (e.g. Hill, 1977):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where $f(\alpha)$ is a conversion dependent function and $k(T)$, the reaction rate constant. The temperature dependence of the rate constant k may be described by the well-known Arrhenius expression:

$$k(T) = A \exp(-E/RT) \tag{3}$$

An integrated expression of Eq. (2) often appears in the literature as (e.g. Froment & Bischoff, 1979):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T)t \tag{4}$$

Both $f(\alpha)$ and $g(\alpha)$ are functions representative of theoretical models that must be derived with respect to the mechanism of the reaction.

In case of reactions where a single deceleratory rate behavior predominates, it is often possible to assume that the conversion factor, $f(\alpha)$, can be represented as:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

Most simple reactions have integer values of n, between 0 and 3. There are many proposed methods to calculate the kinetic parameters and often the reported values not only depend on experimental conditions but also on mathematical treatment of data (Smith, 1981). That is why, we analyzed the isothermal and non-isothermal conductance measurements of this work by several techniques to increase confidence in the calculation. Non-isothermal data were used to inspect the activation energy of gelatinization and isothermal data to shed some light on the possible mechanism of the reaction. This analysis scheme was dictated by the fact that isothermal conductance experiments were available only at one temperature (70 °C).

3.2. Treatment of non-isothermal data

The non-isothermal data from these experiments were analyzed by five independent methods, all of which are well-known in the dynamic heating analysis of polymeric systems (Jimenez, Berenguer, Lopez, & Sanchez, 1993; Nam & Seferis, 1991). Those were the methods by Flynn and Wall (1966), Friedman (1964), Horowitz and Metzger (1963), Kissinger (1957), and Van Krevelen, Van Heerden, and Huntjens (1951). The first three techniques require measurements at different heating rates but are capable of estimating the activation energy without any assumption about the reaction mechanism. The last two techniques can analyze data from just a single run but an initial guess of an appropriate reaction order is required.

According to the Kissinger's method, the activation energy is obtained from the maximum reaction rate, where $d(d\alpha/dt)/dt$ is equal to zero, under a constant heating rate condition. The resulting equation is:

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = -\frac{E}{R} \tag{6}$$

where T_m is the maximum-rate temperature. Therefore, a plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ gives the activation energy without a specific assumption of the conversion-dependent function. An alternative method is the one reported by Flynn and Wall (1966) with the resulting equation:

$$\frac{d[\ln(\beta)]}{d(1/T)} = -\frac{E}{R} \tag{7}$$

By plotting $d[\ln(\beta)]$ against $d(1/T)$ at several conversion grades, α, the activation energy can be calculated. Both the methods of Kissinger and Flynn–Wall are based on different heating rate measurements.

The method of Friedman (1964) utilizes the conversion rate data which are described by the following logarithmic

Table 1
Ratios of partial reaction times for constant volume systems

Reaction order, n	0	1	2	3
$t_{0.15}/t_{0.35}$	0.429	0.377	0.328	0.281
$t_{0.15}/t_{0.70}$	0.214	0.135	0.076	0.038
$t_{0.35}/t_{0.70}$	0.500	0.358	0.231	0.135

differential equation:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln A + n \ln(1 - \alpha) - \left(\frac{E}{RT}\right) \tag{8}$$

Thus, by plotting $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ versus $1/T$ for several conversion grades, α, it is possible to obtain values for activation energies regardless of the reaction order, n.

Assuming first-order kinetics, Horowitz and Metzger (1963) derived the following expression:

$$\ln\left[\ln\left(\frac{1}{1 - \alpha}\right)\right] = \frac{E\theta}{RT_\mathrm{s}^2} \tag{9}$$

where T_s is the temperature such that $(1 - \alpha) = 1/e$, that is $\alpha = 0.632$, and $\theta = T - T_\mathrm{s}$. By drawing a line of $\ln[\ln(1/(1 - \alpha))]$ versus θ, E can be determined.

According to the method of Van Krevelen et al. (1951), at a fixed temperature T_m, a maximum rate can be measured. Inasmuch as $0.9T_\mathrm{m} < T < 1.1T_\mathrm{m}$ and first-order kinetics are assumed, Eq. (10) is obtained:

$$\ln[-\ln(1 - \alpha)] = \ln\left[\frac{A}{\beta}\left(\frac{0.368}{T^\mathrm{m}}\right)^{E/RT_\mathrm{m}} \frac{1}{\frac{E}{RT_\mathrm{m}} + 1}\right]$$
$$+ \left(\frac{E}{RT_\mathrm{m}} + 1\right)\ln(T) \tag{10}$$

By plotting the LHS term against $\ln(T)$ a straight line is obtained whose slope permits determination of the activation energy.

Table 2
Some common solid-state reaction kinetic equations

Reaction type, $g(\alpha)$	c-value	ate-controlling process
$D_1(\alpha) = \alpha^2$	0.2500	Diffusion, 1D
$D_2(\alpha) = (1 - \alpha)\ln(1 - \alpha) + \alpha$	0.1534	Diffusion, 2D
$D_3(\alpha) = [1 - (1 - \alpha)^{1/2}]^2$	0.0426	Diffusion, 3D (spherical symmetry)
$D_4(\alpha) = (1 - 2\alpha/3) - (1 - \alpha)^{2/3}$	0.0367	Diffusion, 3D (contracting sphere model)
$R_2(\alpha) = [1 - (1 - \alpha)^{1/2}]$	0.2929	Moving phase boundary, 2D
$R_3(\alpha) = [1 - (1 - \alpha)^{1/3}]$	0.2063	Moving phase boundary, 3D
$F_1(\alpha) = \ln(1 - \alpha)$	-0.6931	Random nucleation, first order decay law
$A_2(\alpha) = [-\ln(1 - \alpha)]^{1/2}$	0.8326	Random nucleation, 2D
$A_3(\alpha) = [-\ln(1 - \alpha)]^{1/3}$	0.8850	Random nucleation, 3D

3.3. Treatment of isothermal data

3.3.1. Single homogeneous reactions

Analyses originally developed for isothermal homogeneous reactions were also reported to apply to gelatinization by postulating a constant system volume (Kokini et al., 1992; Lapacin & Pricl, 1995; Zanoni, Peri, & Bruno, 1995b). Under such conditions, the time necessary for a given fraction of a limiting reagent to react will depend on the initial composition of the reactants in a manner that is determined by the rate expression for the reaction. This fact is the basis for the development of the *fractional life* method for the analysis of kinetic data (Hill, 1977). The fractional life approach is most useful as a means of obtaining a preliminary estimate of the reaction order. Moreover, it cannot be used for systems that do not obey nth-order rate expressions.

For constant volume systems, the data of one experimental run or from different runs using the same initial composition, may be utilized to determine the times necessary to achieve different fractional conversions. The ratio of these times is characteristic of the reaction order (Hill, 1977). Table 1 contains a tabulation of some useful ratios of partial reaction times. By using such ratios based on experimental data, one is able to obtain a rapid estimate of the reaction order with minimum effort.

3.3.2. Single heterogeneous reactions

It is generally accepted that solid–liquid reactions can follow a large variety of kinetic equations. In fact, the apparent occurrence of simple order equations is mainly coincidental (Froment & Bischoff, 1979). Many authors have derived expressions that reflect the nature of various reaction types. These may be conveniently recognized from experimental data using the *Reduced Time Plot* method of Sharp, Brindley, and Narahari Achar (1966). In this method, all forms of kinetic expressions are written in the form:

$$g(\alpha) = c\,\frac{t}{t_{0.50}} \tag{11}$$

where c is a constant calculated from the actual form of the kinetic expression, and $t_{0.50}$ is the reaction's half-life (time for 50% conversion).

The selection of the $g(\alpha)$ function is based on the shape of a reduced time plot which describes best the experimental data. By calculating values of α for nine different kinetic equations and plotting them against $t/t_{0.50}$, Sharp et al. (1966) obtained nine corresponding curves, each one having a characteristic shape. These nine reaction types and their corresponding c values are listed in Table 2. Theoretical predicted fractions, α, versus $t/t_{0.50}$, for the various reaction equations, against the experimental data of this study can be seen in Fig. 2 (more about the comparison later). Although the analytical expressions in Table 2 are so different, the respective theoretical curves look quite similar. In fact, data can be classified into three distinct groups. The first group

Table 3
Series first-order reactions. Theoretical partial reaction time ratios for various relative rate constants

$\kappa (= k_2/k_1)$	$\log(t_{0.35}/t_{0.15})$	$\log(t_{0.70}/t_{0.15})$	$\log(t_{0.70}/t_{0.35})$
100	0.415	0.858	0.443
50	0.407	0.847	0.440
20	0.385	0.815	0.430
10	0.366	0.781	0.415
5	0.356	0.748	0.392
2	0.367	0.745	0.378
1.5	0.376	0.757	0.381
1.1	0.388	0.779	0.391
0.9	0.395	0.796	0.401
0.7	0.409	0.826	0.417
0.5	0.425	0.871	0.446
0.2	0.465	1.047	0.582
0.1	0.490	1.249	0.759
0.05	0.506	1.497	0.991
0.02	0.519	1.874	1.355
0.01	0.524	2.166	1.642

includes the four diffusion equations, the second group includes the moving phase boundary and first-order decay equations and the third includes the 2D and 3D random nucleation (Avrami–Erofeev) equations. It is apparent from Fig. 2 that the confusing proximity between some models makes it difficult to identify the correct reaction mechanism. In the words of Sharp et al. (1966) 'considerable accuracy is needed to distinguish experimentally between the various possibilities' whereas 'differentiation within these groups requires very careful and precise experimental data at least up to $\alpha = 0.7$'. Several authors have successfully used the reduced-time plot method to assist the study of the thermal decomposition of a variety of polymers (e.g. Day, Cooney, & Wiles, 1989).

3.3.3. Series homogeneous reactions

The term *series reactions* refers to those reactions in which one or more of the initially formed products undergoes a subsequent reaction to give yet another product. Significant amounts of both the intermediate and the final product species may be present during the normal course of the reaction. The simplest case of series reactions is that in which every reaction in the sequence obeys first-order kinetics. Such a series may be represented in terms of the following sequence of mechanistic equations:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \cdots \tag{12}$$

where k_1 and k_2 are rate constants. In the case of gelatinization, A may represent ungelatinized starch, B, swollen particles and C, solubilized starch (Kokini et al., 1992). For first-order and pseudo first-order reactions of the series type, several methods exist for determining rate constants. The estimation technique originally proposed by Swain (1944) is considered here because of its simplicity. According to this technique, the reaction progress for two

consecutive reactions is given by:

$$50\delta^* = 50\left[2 + \frac{(2\kappa - 1)\mathrm{e}^{-k_1 t}}{1 - \kappa} - \frac{\mathrm{e}^{-\kappa k_1 t}}{1 - \kappa} \right] \tag{13}$$

where $50\delta^*$ is a measure of the percent of the total irreversible reaction that has taken place, i.e. $\delta^* = 2$ corresponds to complete conversion to C and $\kappa = k_2/k_1$.

Let t_1 and t_2 be the times corresponding to reaction progress variables δ_1^* and δ_2^*, respectively, the time ratio t_2/t_1 for fixed values of δ_1^* and δ_2^* will depend only on the ratio of rate constants κ. A typical application of this time-ratio method is presented by Frost and Pearson (1961), who employed calculations of only three time-percentages of the reaction, $50\delta^* = 15$, 35, and 70%, for various relative rate constants κ. These authors constructed a table of κ versus $\log(t_{0.35}/t_{0.15})$, $\log(t_{0.70}/t_{0.35})$, $\log(t_{0.70}/t_{0.15})$, to which one may readily cross-tabulate his data to obtain the corresponding value of κ. Such a table was also employed in the present study (Table 3) for a series of κ values in order to attain the required interpolation accuracy.

3.3.4. Simultaneous complex reactions

For polymeric degradation processes that involve combinations of simultaneous independent reactions, Nam and Seferis (1991, 1992, 1993) have developed a *Composite Methodology* to define an appropriate conversion-dependent function. The first step in this method, is to separate the reaction rate constant, $k(T)$, from the conversion-dependent function, $f(\alpha)$, in an analytical treatment of the basic kinetic equation. Then, $f(\alpha)$ can be determined by construction of a master curve which compares the experimental data with model equations without the effect of temperature.

In order to construct the master curve, a suitable reference time must be chosen. Nam and Seferis (1993) originally suggested the maximum reaction-rate time, t_m for this. However, tests in the present study with the time for 50% conversion, $t_{0.50}$, taken as reference, improved the overall performance of the technique. So, Eq. (4) can be written as:

$$g(\alpha_{0.50}) = k(T)t_{0.50} \tag{14}$$

and combining Eqs. (2) and (14) gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t_r} = g(\alpha_{0.50})f(\alpha) \tag{15}$$

where $t_r = t/t_{0.50}$ is the reduced time. If $\mathrm{d}\alpha/\mathrm{d}t_r$ values plotted against α, fall on the same curve for different isothermal experiments, then $f(\alpha)$ can be obtained from Eq. (15) by fitting this master curve with an appropriate $f(\alpha)$ model equation. However, $g(\alpha_{0.50})$ is still unknown. Manipulation of Eq. (15) using the 50% conversion rate, $\alpha_{0.50}$, of the master curve, yields:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t_r} \right)_{\alpha = \alpha_{0.50}} = g(\alpha_{0.50})f(\alpha_{0.50}) \tag{16}$$
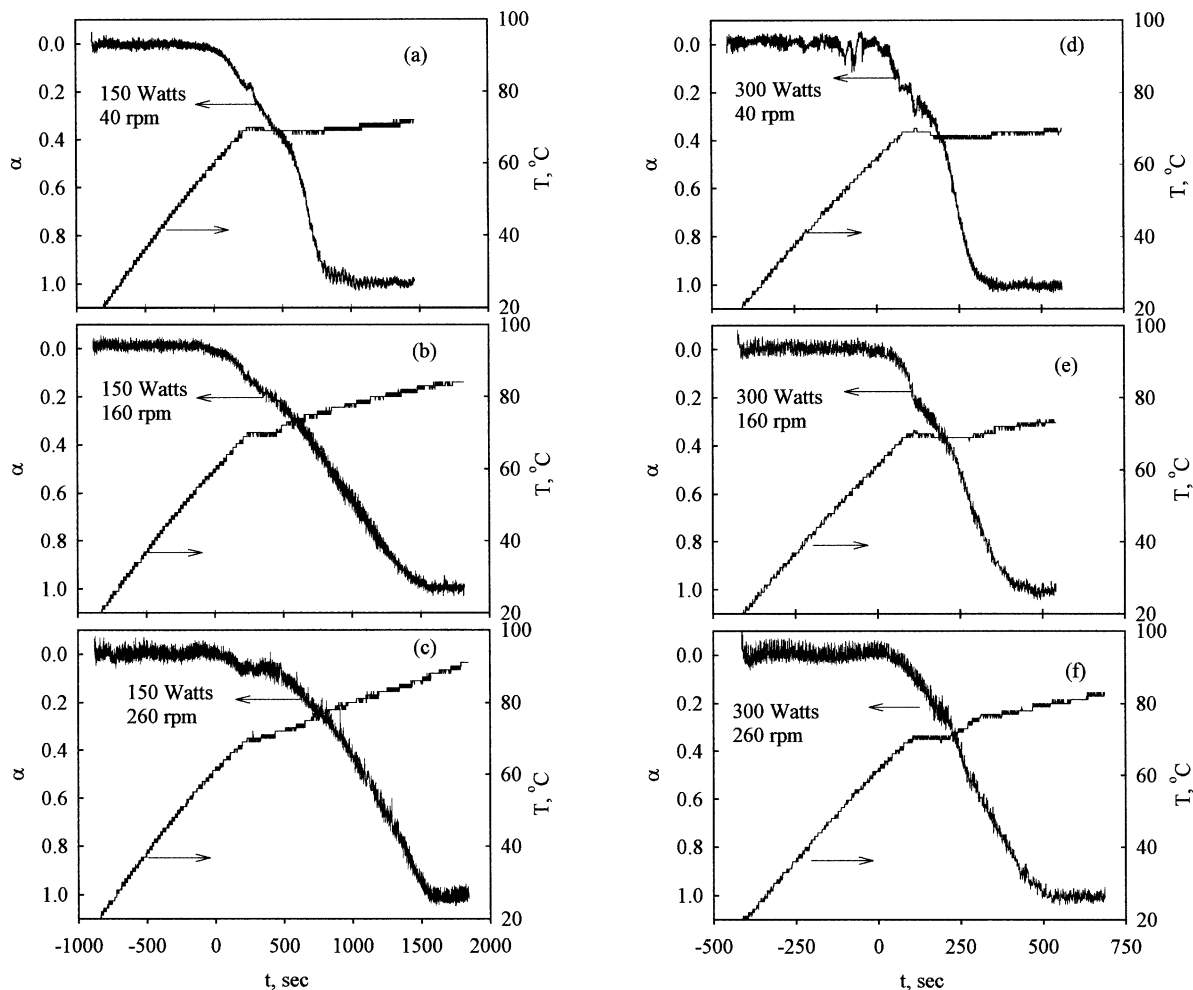
Fig. 1. Degree of conversion, α, versus time taken with 150 W power and mixing speeds of (a) 40 rpm, (b) 160 rpm, (c) 260 rpm and 300 W power and mixing speeds of (d) 40 rpm, (e) 160 rpm, (f) 260 rpm. The respective temperature profiles are also displayed.

Combination of Eqs. (15) and (16) gives:

$$\frac{d\alpha}{dt_r} = \frac{(d\alpha/dt_r)_{\alpha=\alpha_{0.50}}}{f(\alpha_{0.50})} f(\alpha) \quad (17)$$

The value of $(d\alpha/dt)_{\alpha=\alpha_{0.50}}$ can be directly obtained from the master curve for $\alpha_{0.50}$ and then the kinetic parameters of $f(\alpha)$ and $f(\alpha_{0.50})$ are estimated by fitting the master curve.

When several independent competing reactions take place, the whole reaction process can be described by appropriate weighting factors (Nam & Seferis, 1991, 1992, 1993). In that case, the overall conversion-dependent function can be described as:

$$f(\alpha) = \sum_i y_i f_i(\alpha) \quad (18)$$

where the weighting factors, y_i, satisfy the condition:

$$\sum_i y_i = 1.0 \quad (19)$$

A suitable form of $f_i(\alpha)$ may be derived either from fundamental physicochemical aspects of the reaction mechanism

or just by trying combinations of reasonable single conversion rate expressions. Sestak and Berggren (1971) described mathematically a large number of reasonable rate expressions for single heterogeneous reactions and have concluded that the most convenient analytical approximation for the differential Eq. (2) is:

$$\left(\frac{d\alpha}{dt}\right) = k(T)(1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \quad (20)$$

where the values n, m, and p are temperature independent and are chosen so as to represent the model of the reaction path. Eq. (20) was derived on the basis that the most common heterogeneous reactions take place in three stages. An induction or nucleation period, during which reaction centers form within the solid; the interfacial reaction, where these centers expand so that the interfaces between product and reactant increase; and finally decay, when the centers overlap and the interfaces between product and reactant begin to decrease.

Sestak and Berggren (1971) accepted the view that solid-state reactions are activated processes, for which an

activation energy may be calculated from the exponential character of $k(T)$. However, they expressed reservations when describing non-isothermal heterogeneous reactions. Along with this line Draper and Sveum (1970) developed a theory of heterogeneous reactions, which is independent of the Arrhenius equation (have zero activation energy). They recognized that heterogeneous reactions may take place only at a fixed reaction temperature, T_R, dictated by the equilibrium of the process (where the free enthalpy $\Delta G = 0$). The advancement of the reaction is then observed to be controlled by heat transport from the boundaries to the reacting material. This theory was successfully applied to a few decomposition reactions (Draper & Sveum, 1970). These researchers claimed that only samples of macroscopic spherical geometry are satisfactory for conversion-rate analysis which, unfortunately, is not the case with our test samples.

4. Results and discussion

Fig. 1 shows curves of degree of conversion, α, versus time derived from the data of Karapantsios et al. (2000). The corresponding temperature profiles are also shown. Note that $t = 0$ in these curves is the time that the temperature of the mixture attains 62 °C, which is the initiation temperature of gelatinization (Karapantsios et al., 2000). These particular runs are selected for kinetic analysis since it was claimed that they represent best conditions of heat transport and homogeneity in the mixture.

In the curves of Fig. 1, the overall rate of gelatinization, coarsely inferred as the reciprocal of the time period to complete the reaction, appears to depend strongly on heat supply and much less on temperature or mixing speed. This is more pronounced in the curves of 40 rpm, where although gelatinization proceeds for the most part under isothermal conditions (~70 °C), the reaction rate for 300 W is almost twice the rate for 150 W. On the other hand, for a constant heat supply, as the speed of mixing increases the temperature of the sample increases but gelatinization still takes place at a comparable rate. In fact, there even exists a small decrease in the reaction rate as mixing rate increases. This is more easily perceived when comparing the curves of 300 W/40 rpm and 300 W/160 rpm runs where, despite the quite comparable temperature profiles, gelatinization is a little slower with the more intense mixing. This might be attributed to the fairly different textures of the mixture produced by the different mixing speeds, as observed by Karapantsios et al. (2000). Lapasin and Pricl (1995) argued that the gelation process can be accurately depicted theologically only if small deformations are used in the frequency range 0.1–1 Hz. They claimed that under large deformations or/and higher shear rates a competition is induced between gel formation and structure breakdown and differences in texture may be encountered. Thus, the higher of the mixing rates of this work (160 and 260 rpm) might not be so

appropriate for the study of the gelatinization mechanism. Yet, it must be stressed that such high mixing speeds have been repeatedly employed in the past by other workers, e.g. Okenchukwu and Rao (1996a), Wong and Lelievre (1981), and Zamora (1995).

When gelatinization is completed the temperature in the 300 W runs is not as high as in the 150 W. Interestingly, this does not seem to affect the final extent of gelatinization, K_r^{final}, which was found to be essentially the same for all runs (Karapantsios et al., 2000). These observations are a strong indication that heat transport rather than temperature governs the gelatinization progress in our experiments. This is in qualitative agreement with the work of Draper and Sveum (1970) for other heterogeneous systems. Of course, any systematic behavior should be investigated further over a broader range of conditions.

4.1. Treatment of non-isothermal data

It is beyond any doubt that calculation of kinetic parameters from runs at only a few experimental conditions is not advisable. However, it is not the intention of this study to present accurate estimation of kinetic parameters but only a gross range of realistic values. Another concern is to provide preliminary information on whether the activation energy remains the same or varies during gelatinization. Such information will assist the analysis of the isothermal data in a subsequent section. A change in activation energy, above a certain temperature, was reported by Pravisani et al. (1985) who attributed this to a two-stage first-order kinetics for the gelatinization process. However, a variation of activation energy may as well imply a change in selectivity (k_1/k_2) in a series of two elementary reactions, an option that was not examined by Pravisani et al. (1985). A change in E with the degree of conversion was also noticed by Pielichowski et al. (1998) and was ascribed to a complex reaction mechanism.

The experimental evidence form this study suggests that temperature and temperature change with time (heating rate) may not be valid representative parameters of reaction rates unless under constant heat supply conditions. Thus, any meaningful kinetic parameter can be deduced only by analyzing runs with the same heat supply. In order to calculate the activation energy by dynamic heating rate methods, those runs that exhibit constant heating rate periods to some appreciable extent must be selected, (Davis, 1975; Smith, 1981). The runs that satisfy these criteria are those with 150 W heat supply and mixing speeds of 160 and 260 rpm. The 150 W/260 rpm experiment has a considerably constant heating rate of 0.82 °C min^{-1} over the range $\alpha \approx 0.2$–1. Likewise, the 150 W/160 rpm experiment has an almost constant heating rate of 0.62 °C min^{-1} over the more restricted range $\alpha \approx 0.3$–0.9. For the experiments with 300 W such a useful range was not identified perhaps due to problems relating to temperature overshooting or thermal lag in the sample. The non-isothermal data obtained

Table 4
Activation energies of starch gelatinization calculated by different methods

Methods	150 W/160 rpm (kJ mol^{-1})	150 W/260 rpm (kJ mol kJ mol^{-1})
Kissinger (1957)	51 ± 25	51 ± 25
Flynn and Wall (1966)	69.3 ± 3.5 ($\alpha = 0.3$–0.5)	69.3 ± 3.5 ($\alpha = 0.3$–0.5)
Friedman (1964)	10–100 ($\alpha = 0.35$–0.55)	10–100 ($\alpha = 0.35$–0.55)
Horowitz and Metzger (1963)	238.9 ($\alpha = 0.3$–0.8)	212 ($\alpha = 0.2$–0.8)
Van Krevelen et al. (1951)	233.9 ($\alpha = 0.3$–0.8)	204.8 ($\alpha = 0.2$–0.8)

at 160 and 260 rpm may not be so good for studying the gelatinization mechanism because of some possible granule degradation but this will rather not influence the purely thermal effect described by the activation energy.

The activation energy calculated by the method of Kissinger (1957) gives large standard deviation, $E_K = 51 \pm 25$ kJ mol^{-1}. This method proved quite subjective when applied to our data because the region of the maximum degree of conversion is relatively broad and does not have a clear maximum, $\alpha_m \approx 0.5$–0.8. On the contrary, the method of Flynn and Wall (1966) allows calculations at appropriate α values inside the useful range. Thus, for the range $\alpha = 0.3$–0.5 the estimated activation energy is, $E_{F-W} = 69.3 \pm 3.5$ kJ mol^{-1}. Use of a suitable restricted data zone for estimating kinetic parameters is quite common in kinetic analyses (e.g. Day et al., 1989; McNaughton & Mortimer, 1975).

Experimental data for the conversion derivative, dα/dt, are not of the required precision for the Friedman (1964) method. This method is particularly sensitive to fluctuations in dα/dt which result in activation energy values that have a relatively large error associated with them. For the range $\alpha = 0.3$–0.6 the estimated activation energy is in the range, $E_F = 10$–100 kJ mol^{-1}.

To apply the Horowitz and Metzger (1963) and Van Krevelen et al. (1951) methods, first-order kinetics was assumed. The Horowitz and Metzger (1963) method gives $E_{H-M} = 238.9$ kJ mol^{-1} for the 150 W/160 rpm run ($\alpha = 0.3$–0.8; $R^2 = 1.00$) and $E_{H-M} = 212$ kJ mol^{-1} for the 150 W/260 rpm run ($\alpha = 0.2$–0.8; $R^2 = 1.00$). Accordingly, the Van Krevelen et al. (1951) method gives $E_{VK} = 233.9$ kJ mol^{-1} for the 150 W/160 rpm run ($\alpha = 0.3$–0.8; $R^2 = 1.00$) and $E_{VK} = 204.8$ kJ mol^{-1} for the 150 W/260 rpm run ($\alpha = 0.2$–0.8; $R^2 = 1.00$). Table 4

summarizes the activation energies obtained by the five independent methods examined in this work. Since the range of activation energies estimated by the first three methods—which do not make any assumption on the mechanism of the reaction—deviate from the predictions of the last two, it appears, that the reaction is not adequately described by simple first-order kinetics. This is so despite the excellent numerical fit of the data by the methods of Horowitz and Metzger (1963) and Van Krevelen et al. (1951), a fact which might be quite misleading as regards the identification of the order of the reaction. Nevertheless, the excellent fit achieved by these methods for such a broad range of α is an indication that there may exist a *single* activation energy throughout the whole gelatinization process.

Pielichowski et al. (1998) analyzed non-isothermal DSC curves during potato starch gelatinization by the method of Friedman and a modified Flynn–Wall method and found that E varies in the range 75–138 kJ mol^{-1}. Very few studies provide activation energies of maize starch gelatinization, so comparison is indeed limited. Cabrera et al. (1984) reported a value of 76 kJ mol^{-1} based on an alkali solubility method. Okechukwu and Rao (1996a,b) employing a laser diffraction technique to measure granule swelling reported a value of 62 kJ mol^{-1}. Both studies assumed pseudo first-order kinetics to hold beyond a certain degree of initial gelatinization. Seemingly, our activation energy predictions are in the same range of values with these literature values without, however, confirming the first-order reaction approximation.

4.2. Treatment of isothermal data

4.2.1. Single homogeneous reactions

In order to apply the fractional life method to the isothermal

Table 5
Experimental ratios of partial reaction times calculated from the present data

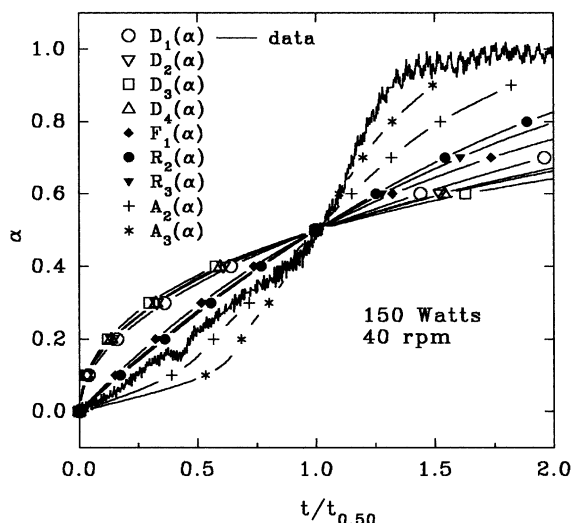|	150 W/40 rpm t_0 at 62 °C	150 W/40 rpm t_0 at 70 °C	300 W/40 rpm t_0 at 62 °C	300 W/40 rpm t_0 at 70 °C
$t_{0.15}/t_{0.35}$	0.474	0.408	0.395	0.658
$t_{0.15}/t_{0.70}$	0.326	0.289	0.290	0.494
$t_{0.35}/t_{0.70}$	0.688	0.710	0.734	0.751
$\log(t_{0.35}/t_{0.15})$	0.324	0.389	0.404	0.182
$\log(t_{0.70}/t_{0.15})$	0.486	0.538	0.538	0.306
$\log(t_{0.70}/t_{0.35})$	0.162	0.149	0.134	0.124

Fig. 2. Reduced-time plot of degree of conversion, α, versus $t/t_{0.5}$ along with theoretical curves calculated for various solid-state reaction equations. The plotted data are quasi-isothermal measurements from the run with a 40 rpm mixing speed and 150 W power.

experiments of the present study, Table 5 is constructed including some characteristic reaction time ratios. The only isothermal runs are, in effect, those with a 40 rpm mixing speed. To avoid the ambiguity of the initial heating-lag period of the sample, a separate set of time ratios is calculated assuming that the reaction begins when the temperature reaches steady conditions ($\sim$70 °C). A similar data reduction was proposed by Lund and Wirakartakusumah (1984), in an earlier gelatinization kinetic study. It must be stressed that such a manipulation is in principal valid only when the same rate expression describes the discarded portion of the data. The compar-
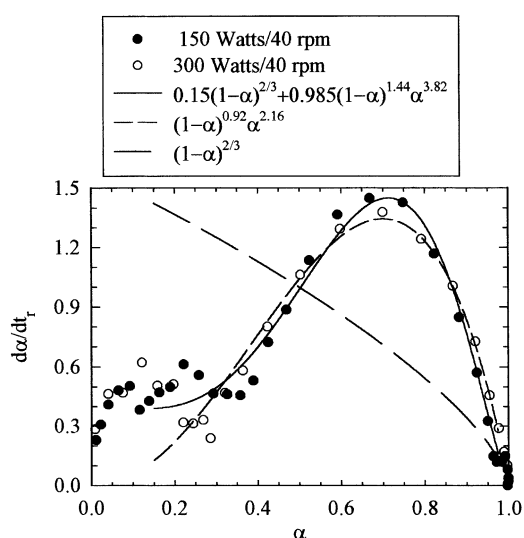

Fig. 3. Reaction rate reduced-time plot (master curve) of the two isothermal runs, 150 W/40 rpm and 300 W/40 rpm, with the reference time for 50% conversion ($\alpha = 0.5$). Comparison is made with the complete model Eq. (22) and separately with its best-fit component terms.

ison of elements from Tables 1 and 5 leaves no doubt that simple order kinetics cannot adequately describe the gelatinization reaction. One could have qualitatively arrived at the same conclusion just by inspecting the shape of the curves in Fig. 1 since it is known that nth-order kinetics exhibit deceleratory-rate and not sigmoidal-rate behavior.

4.2.2. Single heterogeneous reactions

Next, the curves from the two isothermal runs are re-calculated using Sharp's approach. Data only for the 150 W run are plotted in Fig. 2 since the picture is qualitatively similar for the 300 W. The idea is to recognize a reaction mechanism by visually comparing the simulated reaction curves with the data. Up to about $t/t_{0.50} \approx 0.50$ both the experiments appear to fall approximately between the $R_2(\alpha)$–$R_3(\alpha)$–$F_1(\alpha)$ and the $A_2(\alpha)$–$A_3(\alpha)$ group of curves. Beyond that point the reaction shifts towards the $A_2(\alpha)$ and $A_3(\alpha)$ mechanisms but the accord becomes progressively poorer at the final stages of gelatinization. Evidently, the mechanisms employed fail to satisfy altogether the values obtained experimentally.

4.2.3. Series homogeneous reactions

The series reaction type is assessed, next. Table 5 includes the logarithms of three time ratios calculated from the isothermal experiments of this study. According to Swain (1944), each of these experimental ratios should indicate a value of κ by interpolation among the elements of Table 3 and then the results should be averaged. Apparently, there is no single value of κ that satisfies simultaneously the three time ratios. Kokini et al. (1992) claimed that low κ values ($<$0.2) appeared to simulate their viscosity versus time curves. This is nowhere near the case with our data.

4.2.4. Simultaneous complex reactions

Following the procedure by Nam and Seferis (1993), the reduced reaction rates, $d\alpha/dt_r$, of the two isothermal runs are plotted as a function of α, Fig. 3. The data from both runs fall approximately on one characteristic master curve. This master curve depicts the conversion-dependent function $f(\alpha)$ of the reaction rate, which is considered independent of temperature. The data in Fig. 3 shows that $f(\alpha)$ is also independent of heat supply.

For the numerical fitting of the master curve, we have initially tested all single reaction rate expressions presented by Sestak and Berggren (1971), with no success whatsoever. It appears that gelatinization, at least as represented by electrical conductance measurements, is a rather complex phenomenon where more than one reaction steps must be accounted for. Next, a reaction scheme is considered which incorporates two simultaneous elementary reactions—each one described by Eq. (20)—
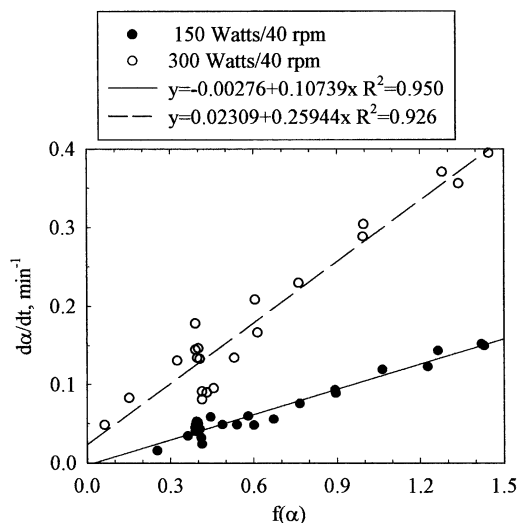
Fig. 4. Reaction rate as a function of conversion-dependent function $f(\alpha)$ for the two isothermal runs, 150 W/40 rpm and 300 W/40 rpm, providing reaction rate constants from the slope of the lines.

and the respective weighting factors:

$$f(\alpha) = y_1\{(1 - \alpha)^{n_1}\alpha^{m_1}[-\ln(1 - \alpha)]^{p_1}\} + y_2\{(1$$

$$- \alpha)^{n_2}\alpha^{m_2}[-\ln(1 - \alpha)]^{p_2}\} \quad (21)$$

Eq. (21) assumes that only one rate constant (i.e. activation energy) is required to describe the whole gelatinization reaction.

For the identification of the composite conversion function $f(\alpha)$, it was decided to use combinations of reasonable rate expressions, such as those proposed by Sestak and Berggren (1971). A non-linear regression method coupled with an optimization numerical technique was employed and it was found that the best fit of the master curve was provided by the following conversion function:

$$f(\alpha) = y_1(1 - \alpha)^{n_1} + y_2[(1 - \alpha)^{n_2}\alpha^{m_2}] \quad (22)$$

with $y_1 = 0.015$, $y_2 = 0.985$, $n_1 = 2/3$, $n_2 = 1.44$ and $m_2 = 3.82$ ($x^2 = 0.26$; $R^2 = 0.95$). Data exclusively for conversions $\alpha > 0.15$ were used in the calculations since they represent the isothermal part of the experiments. The determined conversion-dependent function compares favorably with the master curve in Fig. 3. For comparison, the single term $(1 - \alpha)^{2/3}$ and the best fit solely of the term $(1 - \alpha)^{n_2}\alpha^{m_2}$, are also included in the graph. Although the $(1 - \alpha)^{2/3}$ term, $R_3(\alpha)$, has a small weighting factor, it is apparent from Fig. 3 that it plays a key role in the success of the fitting, especially at the early stages of the process. To increase the accuracy of the parameters' estimation, we repeated the calculations with only the data of the less-noisy 150 W/40 rpm run. No major differences in the parameter values were found, only the statistics of the calculations got better. Looking at the early stages of gelatinization in Fig. 3 it appears that the rate is independent of the degree of conversion, a situation which is customarily described by

zero order kinetics. However, the regression procedure showed a distinctly better overall fit with the $R_3(\alpha)$ than with the zero order model. Pielichowski et al. (1998) working with more concentrated potato starch suspensions (50% w/w) reported a double-step reaction mechanism whereby the first step was a nth-order reaction and the second a 3D-diffusion of Jander's type.

The theoretical basis on which the $R_3(\alpha)$ model is based assumes a reaction mechanism in which nucleation is not a dominant step as it occurs extremely rapidly over the surface of a round particle. Instead, the total process is governed by the movement of a spherical reaction zone (e.g. a water front) towards the center of the granule. The mechanism of water gain from the starch granules during initial swelling is therefore easy to visualize. At higher degrees of conversion, the master curve exhibits a maximum (peak) reaction rate which is a typical feature of the so-called autocatalytic reaction behavior (Prime, 1981). The second term in the RHS of Eq. (21) represents a common form of an autocatalytic-type kinetic model. In this mechanism, the reaction rate is accelerated by the intermediate reaction products. Sestak and Berggren (1971) argue that a value of $m_2 \gg 1$ in this expression is representative of chain growth of nuclei where time has a large power in the progress of the reaction. Lapasin and Pricl (1995) reported a satisfactory data fitting of the storage modulus, G', during amylose (1.37 and 2.75% w/w) gel curing by a similar self-accelerating kinetic model.

Since gelatinization appears to speed up after some initial degree of conversion ($\alpha > \sim 0.3$), it is quite probable that granule solubilization is accelerated by the forming swollen granules. This might be due to an increased surface area for interaction with the bulk or an increased dissociation of the granule components or both. On the basis of the above, the following possible physical picture emerges: as the water molecules penetrate into the closely packed helices of the crystallites, the internal hydrogen bonds that hold the helices in place start to disrupt releasing active hydroxy groups of the glycose units (French, 1984). Gelation occurs as molecular association takes place, presumably through hydrogen bonding, forming a network of junction zones between molecules (Zobel, 1984). These hydroxy groups may form hydrogen bonds with the water molecules and since the water is in excess, the amylose molecules can assume the random coil conformation which enables them to take hold of progressively more water. Measurements from different complementary techniques and over broad conditions are required before definitive statements can be made.

Jenkins and Donald (1998), who measured the degree of crystallinity of starch granules during gelatinization, observed that most of the crystallinity loss occurs fast but only after a significant amount of water has entered the amorphous background region of the granule. Although a direct comparison with that study is not possible, the picture

emerging from the present kinetic analysis is in line with their findings.

According to Eq. (2), if the conversion-dependent function, $f(\alpha)$, is correctly determined, the reaction rate, $d\alpha/dt$, should show a linear relation with $f(\alpha)$. Using the determined $f(\alpha)$ function, the reaction rate constant is obtained from the slope of the $d\alpha/dt$ versus $f(\alpha)$ plots, as shown in Fig. 4. Indeed, a reasonable linear relation is found in both the curves of Fig. 4 from which one obtains $k_{150 \text{ W}} = 0.107 \text{ min}^{-1}$ and $k_{300 \text{ W}} = 0.259 \text{ min}^{-1}$. Thus, the rate constant is dependent on heat supply, as already shown in Fig. 1. For gelatinization at 70 °C, Okechukwu and Rao (1996a,b) reported a rate constant value of $5.36 \times 10^{-3} \text{ min}^{-1}$ whereas Cabrera et al. (1984) a value of 5.47 min^{-1}. This discrepancy lends further support to the notion that experimental parameters other than temperature might be the dominant rate-controlling step. However, information from isothermal runs at several temperatures is necessary to resolve this issue.

5. Conclusions

The kinetic analysis of electrical conductance time records showed that gelatinization is not a simple process and cannot be described by a single reaction rate expression. A very poor fit of the kinetic data was found for both the nth-order kinetic model and a series of first order reactions contrary to what was argued in the past. This was also the case with single reaction models describing diffusion-controlled, phase boundary-controlled and nucleation-controlled mechanisms. On the contrary, a composite reaction scheme of two simultaneous elementary reactions proved successful in describing the gelatinization process. It combines an autocatalytic rate expression with a moving phase-boundary rate expression. The analytical methods of Flynn and Wall (1966), Friedman (1964), and Kissinger (1957), were employed to get a preliminary estimation of the activation energy of water dispersion during gelatinization without assuming a reaction mechanism. The obtained values were found to fluctuate among different methods but in a range comparable to earlier literature data. This might be, at least in part, due to the diverse mathematical treatments of the data. The analytical methods of Horowitz and Metzger (1963) and Van Krevelen et al. (1951), based on the assumption of first-order kinetics, lend support to the concept that a single activation energy value holds throughout the entire gelatinization process.

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