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Characterization of rice cooking: isothermal differential scanning calorimetry investigations

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Abstract

Isothermal calorimetry allows rice cooking to be simulated directly at various temperatures in excess water. The signal can be interpreted as the sum of the thermal effect of the starch gelatinization, which obeys first-order kinetics, and of a further process that can be tentatively related to water diffusion. This effect is greatly reduced in ground rice, as revealed by comparing the behaviour of whole and ground rice samples. Determinations of water uptake seem to confirm this hypothesis. The enthalpy of gelatinization drawn from these data can be matched with that from non-isothermal DSC investigations carried out at low heating rate ($<0.5°C\ min^{-1}$).

Analogous results and conclusions can be drawn from non-isothermal DSC investigations carried out on partially pregelatinized samples.

Keywords: DSC; Heat of gelatinization; Isothermal; Kinetics; Rice; Starch; Water

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1. Introduction

Among the various heat treatments of starchy products, cooking and precooking in excess water are processes of utmost importance in either domestic or industrial practice. In Italy the most popular home cooking of starchy products concerns rice and pasta (about 33 kg per person per year), although, as in other countries, there is an increasing demand for convenience products, such as quick-cooking rice, precooked pasta and frozen cooked cereal-based meals.

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The cooking performance of these starch-based products has been tested for pasta, in relation to the kind of semolina and process conditions used. Much less attention has been addressed to commercial rice and other starchy products.

Cooking significantly modifies the textural and nutritional properties of these foods and therefore should be carefully controlled to avoid any undesired modifications that could reduce the quality of the prepared products and their acceptability by the consumers. Industrial and domestic cooking of pasta and rice may generally be considered as quasi-isothermal processes, being carried out in excess water at the boiling temperature or in pressurized steam. In these conditions, namely considerably above the relevant glass transition temperature T_g (about 60°C), the overall transformation implies water migration from the surface to the core of the product and starch gelatinization, the latter taking place when the local water content is larger than 33–35% (w/w) [1,2].

The process implies a previous etching of the surface with the formation of a first layer of gelatinized product which involves the immediately underlying starch granules. The interface between the gelatinized and the ungelatinized regions would then progress toward the core, being sustained by water diffusion through the gelatinized external layers. It has been proved [3] that water diffusion through the gelatinized zone slows and then reduces the overall process rate. Finally, due to starch gelatinization, the rheological properties are progressively modified and the product becomes edible. However, once the superficial regions of the product are water-embedded and the starch gelatinization is still in progress therein, water is already moving toward the core. Therefore, starch gelatinization and water diffusion are active simultaneously within the sample.

Various attempts have been made to model the physical and chemical phenomena that take place simultaneously in the cooking process. In the case of rice, Bakshi and Singh [4] suggested a cooking model that assumes a moisture distribution within the product along a homogeneous gradient, and simultaneous water diffusion and starch gelatinization. Conversely, Suzuki et al. [5,6] suggested a cooking model where different moisture gradients characterize the external cooked shell and the uncooked core, respectively: the process would then be limited by two water diffusion steps, namely through the cooked and uncooked regions, respectively. Both models require the kinetic constant of starch gelatinization and the water diffusion coefficient to be previously evaluated.

Adequate experimental support for either model can be derived from isothermal calorimetry investigations that allow direct simulation of the cooking process. In previous works devoted to pasta cooking, it was demonstrated that starch gelatinization obeys first-order kinetics [7,8] and water diffusion controls the overall process rate [3].

Calorimetric investigations reveal that the process is endothermic and allow its kinetic parameterization, because the signal obtained is directly proportional to the overall process rate, whether or not this may be diffusion limited. It has been shown [8] that the isothermal calorimetric signal ($\mathrm{d}Q/\mathrm{d}t$) can be described as the product of the process rate and a damping exponential function which accounts for the time lag (τ) due to the heat transfer through the walls of the calorimetric cell

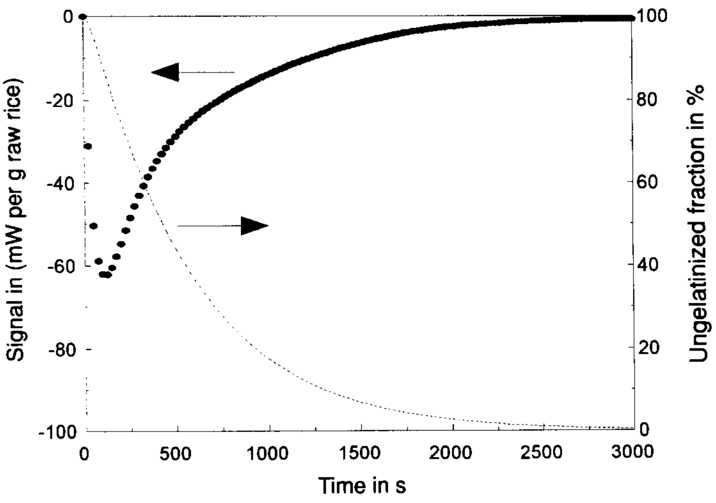

Fig. 1. Typical isothermal trace of whole rice kernels at 95°C. Overlapped curve shows the progress of the gelatinization degree (α) according to Eq. (1)

$$s = \frac{dQ}{dt} = -s_{\max} \exp(-Kt) \exp(-\tau/t) = \exp(-\tau/t)K(1-\alpha) \qquad (1)$$

where the first exponential corresponds to the gelatinization progress, K being the relevant kinetic constant and t the time. It can be shown (Schiraldi and Riva) that

$$s_{\max} = K\, \Delta_{\text{gel}} H$$

where $\Delta_{\text{gel}}H$ is the overall enthalpy change.

Fig. 1 shows a typical isothermal (95°C) trace obtained from rice, when this is poured into excess water, and reports the relevant trend of the gelatinization progress according to Eq. (1).

The present work concerns the study of rice cooking and is an extension of a previous study on pasta cooking [7]. For rice, the effects of water diffusion are much more influential on the overall kinetics and must be considered explicitly. A series of isothermal scans has been carried out at various temperatures on either ground or whole rice of the Padano variety. The investigations include determinations of water uptake and of non-isothermal DSC traces obtained at various heating rates.

2. Materials and methods

2.1. Materials

The rice variety considered here is named Padano and is commonly used for soup-like dishes, because it allows a satisfactory water uptake and, once cooked, is characterized by a soft texture. Commercial samples, which were not polished during refining, were investigated. This rice variety has the following properties (determined on the basis of five replicas): kernel mean weight, 28.126 ± 1.98 mg; kernel mean length, 5.614 ± 0.26 mm; kernel minor diameter, 3.126 ± 0.11 mm; cooking time (according to the producer), 12 min.

The non-starch components of the rice (determined according to the AOAC methods) are: water, 12.20%; proteins, 8.47%; lipids, 1.71%; ashes, 0.51% on dry basis. The samples were used as either whole or milled rice kernels.

Pregelatinized samples were prepared by drying overcooked (20 min at 100°C) rice at low temperature (35°C for 69 h in a thermostatic cell B.E. 85V Bicasa, Milano).

2.2. Calorimetric investigations

The calorimeters used were a differential flux calorimeter Setaram C80 and a Setaram DSC-TG 111. The former was used for isothermal investigations, the latter for runs at given heating rates.

The Setaram C80 contains two high-capacity twin cylindrical inox steel cells whose properties (pressure resistance, mixing facilities, controlled gas perfusion, etc.) were designed to simulate the actual cooking conditions: an aluminium membrane separates the upper from the lower part of both sample and reference cells; below the aluminium membrane, the cell is filled with 5 ml of water, for an adequate rice/water mass ratio; two rice kernels (about 50 mg) were placed in the upper part. The same set-up, except from the presence of starchy material, was repeated for the reference cell. When thermal equilibrium was achieved throughout the calorimeter (about one hour after the introduction of the cells), two stirrers were pushed down simultaneously to pierce the respective membrane: at the same instant, recording of the calorimetric signal was started (for details see Ref. [8]).

Calorimetric scans were carried out at various temperatures within the 80-95°C range: higher temperatures cannot be exploited because when the actual boiling point is approached, vapour convection causes turbulences within the cells and affects the normal thermal balance between them.

The DSC 111 runs were carried out with standard aluminium cells (about 0.5 ml capacity) filled with a mixture of water and rice (a single kernel or 20 mg of ground rice, 3:1 water:rice ratio). The 30-120°C temperature range was investigated at various heating rates (0.5, 2, 5, 10°C min^{-1}).

For both kinds of calorimetric investigations, the signal was analysed through a computational routine [8], namely the TableCurve and Peakfit software (Jandel, USA).

2.3. Cooking tests and physical determinations on rice

Cooking tests were performed with 25 g of rice cooked in 250 ml of tap water for the optimum cooking time (namely that required for the central ungelatinized core to disappear). Some non-isothermal DSC runs concerned rice samples at different gelatinization degrees, attained by periodically stopping the cooking process.

On both rice and pregelatinized rice, the variation in the size and dimensions of the rice kernels were assessed during cooking by means of a caliper (Demm div. 1/20 mm) and the water uptake was evaluated as moisture content by an Ohaus thermobalance, mod. MB 301.

3. Results and discussion

Fig. 2 shows the isothermal calorimetric traces obtained at four different temperatures well above T_g (each trace is indeed the average of three runs): it is easy to recognize that the higher the temperature, the larger the swept area at a given cooking time, i.e. the faster the process. When these traces are worked out according to Eq. (1), the obtained fit is satisfactory only in a first approximation. Fig. 3 (trace obtained at 95°C, here semilog units allow a better inspection of the fit) displays the fit from the product of the two exponential trends, namely the lag time and the gelatinization process, respectively.

When the kinetic constant values from the calorimetric traces are worked out according to the Arrhenius law, the plot reported in Fig. 4 is obtained. The apparent activation energy is about 80 kJ mol^{-1}, i.e. agreement with some literature values [9].

The Arrhenius fit allows the evaluation of the kinetic constant at 100°C and consequently the gelatinization degree (α) attained at the advised (by the producer) cooking time, namely 12 min. The former is $2.2 \times 10^{-3}\ \mathrm{s}^{-1}$, while the latter ranges around 80%: thus optimally cooked rice is not wholly gelatinized, which supports the opinion that the quality of the final product depends on the careful control of the gelatinization, which should never be complete.

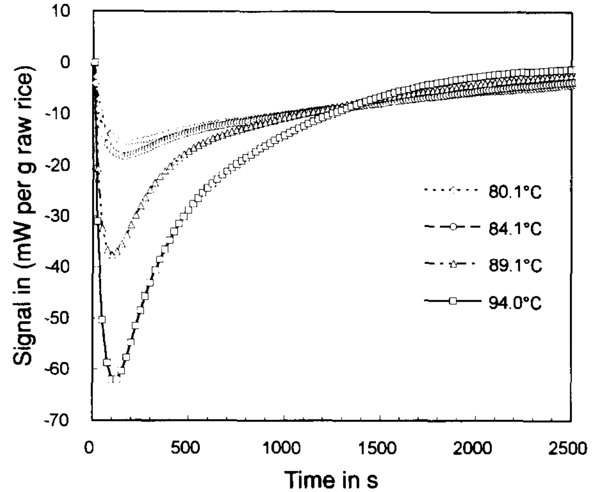

Fig. 2. Isothermal DSC traces at four temperatures obtained from samples of whole kernel rice with excess water.

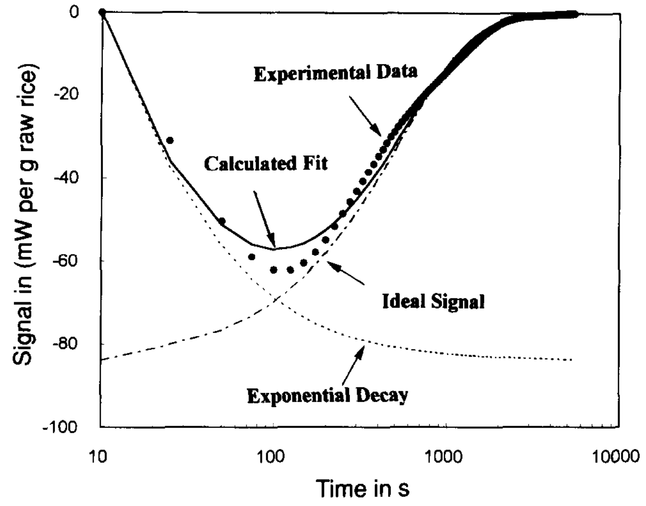

Fig. 3. Isothermal DSC trace of whole rice kernels at 95°C: ●, experimental data; ——, calculated fit according to Eq. (1); – – –, exponential decay of the instrumental lag; ·—·—·—, ideal calorimetric signal due to the reaction progress.

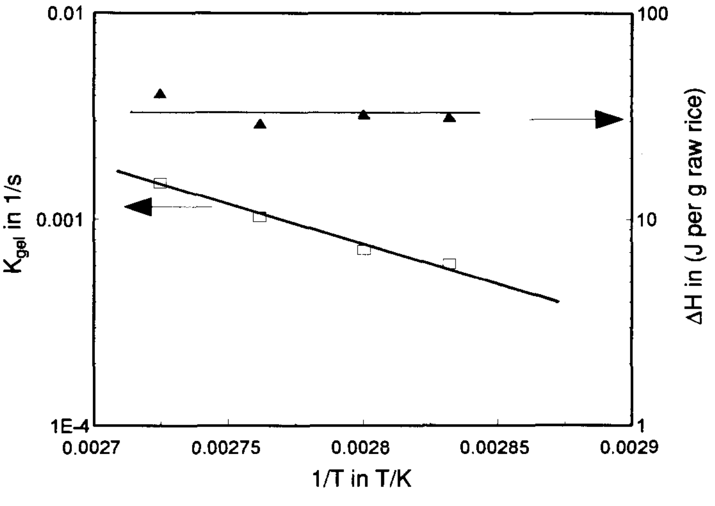

Fig. 4. Arrhenius plot of the gelatinization kinetic constant (——) and enthalpy of gelatinization vs. $1/T$ (· · ·).

The corresponding $\Delta_{\mathrm{gel}}H$ values are practically independent of T, as expected from Eq. (1); however their magnitude, about 30 J per g raw rice, is larger than expected from the literature reports. This discrepancy is discussed below.

A careful inspection of the calculated trend reveals that the above simple model does not fit closely the experimental trend, inasmuch as this looks like the result of two different steps that are better distinguishable at lower temperatures. The actual gelatinization seems delayed, being preceded by another endothermic process.

Eq. (1) does indeed account for a single process, namely starch gelatinization, which is recorded after an instrumental time lag of about 10–20 s (as observed in a blank calibration run concerning the dissolution of NaCl, whose enthalpy is known). However, when directly applied to the experimental data, it gives much larger τ values (≥ 100 s). This discrepancy suggests that some other event actually precedes starch gelatinization.

As simple hypotheses, some protein denaturation or textural changes accompanying water migration were thought to explain this. To test this, it seemed expedient to compare traces obtained at the same temperature from whole and ground rice kernels.

Traces from ground rice were fitted satisfactorily by Eq. (1), which gives $\tau \approx 10$–20 s at every temperature considered in the range 80–95°C: this eliminated any effect due to protein denaturation that would also appear in this kind of specimen. Fig. 5 shows the results obtained at 90°C. The difference between traces of whole and ground rice was again fitted with the product of two exponential functions

$$\text{Diff} = -A \exp(-Dt) \exp(-\tau_D/t)$$

one of which still accounts for a time delay, τ_D, which is about 600 s. The constant D in the first exponential function has the order of magnitude expected from the

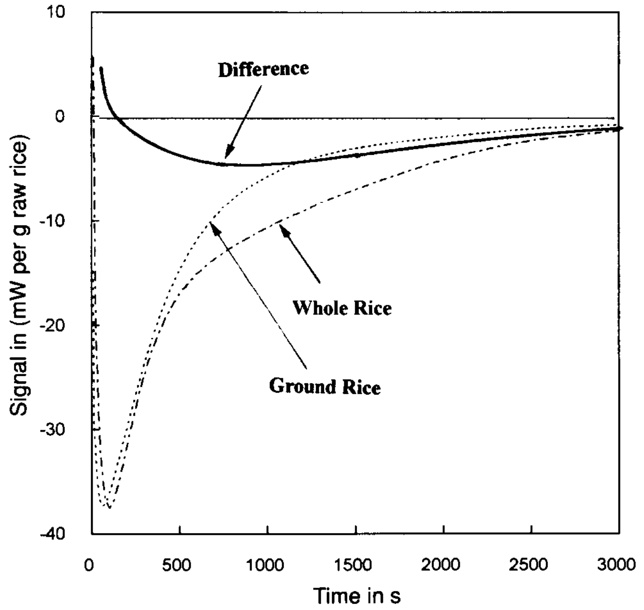

Fig. 5. Comparison between isothermal DSC traces from gelatinization of whole (·——·——), and ground (· · ·) rice at 90°C. The full line represents the difference between the above traces.

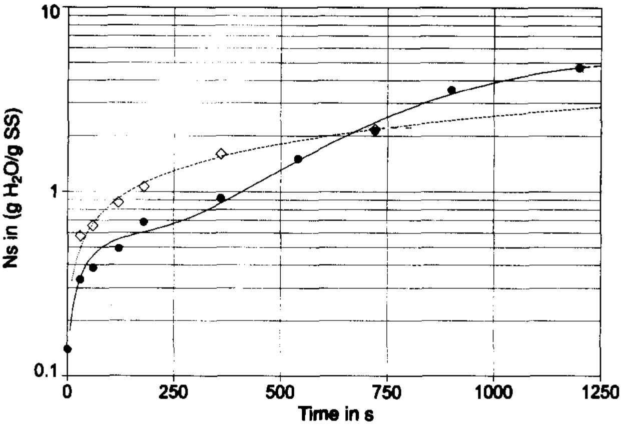

Fig. 6. Water uptake (absolute humidity units) during cooking at 100°C of raw (◇) and pregelatinized (●) rice kernels.

water diffusivity ($D \approx 10^{-5}$ cm^2 s^{-1}, see below) and the length of the diffusion path ($L \approx 10^{-2}$ cm^2), namely 10^{-3} s^{-1}.

Thus, it seems that water migration is responsible for some delay in the progress of the gelatinization towards the kernel core and, due to the accompanying endothermic effect (about 10 J per gram of rice), produces some textural change.

Traditional cooking tests, namely water uptake determinations in the course of the cooking process, give analogous information. When they are carried out on pregelatinized and uncooked rice samples at 100°C, the results of Fig. 6 are obtained. Pregelatinized rice uptakes water according to a simple fickian behaviour: this allows the water diffusivity to be evaluated ($D = 1.7 \times 10^{-5}$ cm^2 s^{-1}), by taking into account both the geometry of the rice kernel and its swelling.

The uncooked rice shows a two-step trend: an early quick uptake of water, which accompanies the starch gelatinization in the external region of the kernel; and a later, slower step where the diffusion of water seems hindered. This behaviour is in accord with the above considerations concerning the isothermal DSC scan from whole rice samples. These results can improve the interpretation of the traditional non-isothermical DSC traces. In the present work these determinations were carried out just after sealing the DSC pans, i.e. without waiting for thorough imbibition of the product. Water diffusion is therefore to be considered for whole kernel samples.

Evaluation of the gelatinization enthalpy is rather uncertain here, because one has to account for a number of events that do not occur in isothermal cooking, namely the glass transition, and the amylose crystallization which follows amylopectin fusion. The latter two partially counterbalance each other, being exo- and endothermic, respectively; the enthalpy evaluation thus requires a reliable deconvolution of the traces into separate simple signals. As shown elsewhere [8], when DSC traces are recorded as ASCII files, it is possible to achieve a reliable deconvolution by means of an adequate computer routine. This procedure, nonetheless, requires the previous choice of the baseline trend across the whole trace. When this includes

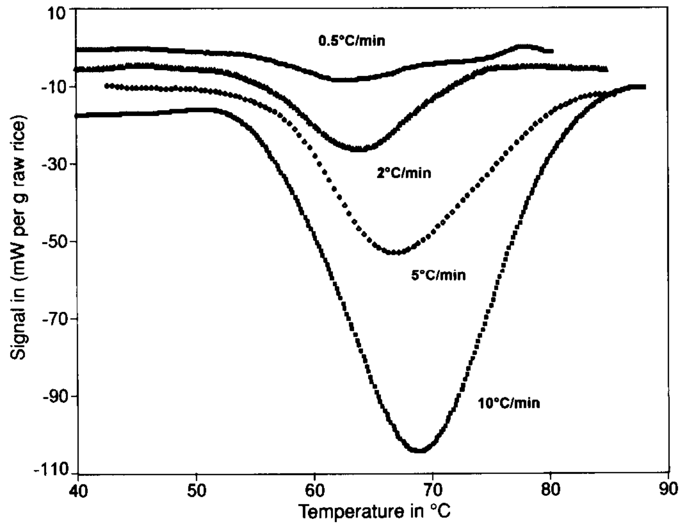

Fig. 7. Non-isothermal DSC traces from ground rice samples. The endothermic signal is shifted toward higher temperatures when larger heating rates are exploited.

a number of partially overlapped signals (as in the present case), the choice of the baseline trend is unavoidably arbitrary, which makes the final deconvolution less reliable than required for quantitative evaluations. With a trial-and-error approach (the overall computing time does not exceed 2–3 min) however, one can eventually attain acceptable results which allow comparison between traces from homologous samples.

The traces that allow an easier interpretation are those from ground rice samples. Fig. 7 shows the effect of heating rate on the calorimetric signal: the higher the heating rate, the higher the temperature of the signal minimum. This result, together with the trend of the relevant enthalpy, is better evidenced in Fig. 8. For the enthalpy change with increasing heating rate, it is apparent that at very low scanning rate it attains the range of values observed in isothermal DSC investigations. Such behaviour can be interpreted as the result of the rate-limiting effect due to water diffusion toward the starch granules: when the heating rate is small, the amount of water supplied is adequate to sustain thorough gelatinization; when heating is too fast, starch granules do not receive enough water to undergo complete gelatinization, and the relevant thermic effect observed decreases.

A comparison between whole and ground rice was also performed for these investigations. Fig. 9 reports the traces obtained at 5°C min^{-1}. The trend of the first derivative allows the glass transition to be identified in both cases: T_g is significantly higher for whole rice. This confirms the hindered water diffusion into this kind of sample.

Another difference between these traces concerns the width of the endothermic signal: ground rice gives a much sharper peak than whole rice, whose gelatinization is delayed and ends at about 95°C. Such a wide signal is in accord with the above

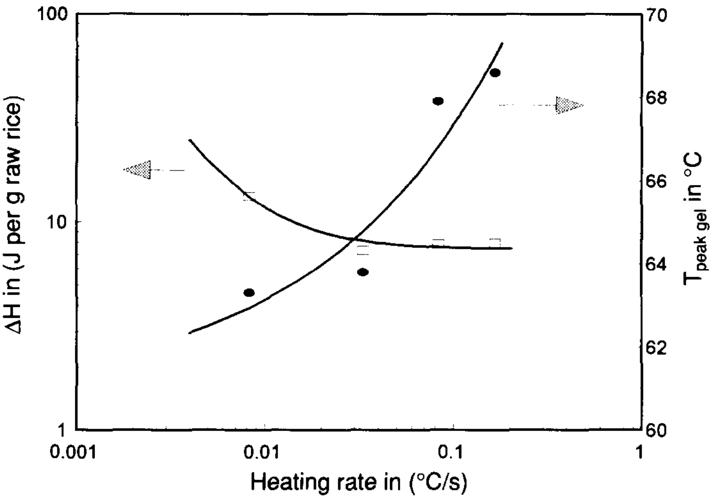

Fig. 8. Temperature of the endothermic peak minimum and relevant enthalpy change observed at various heating rates.

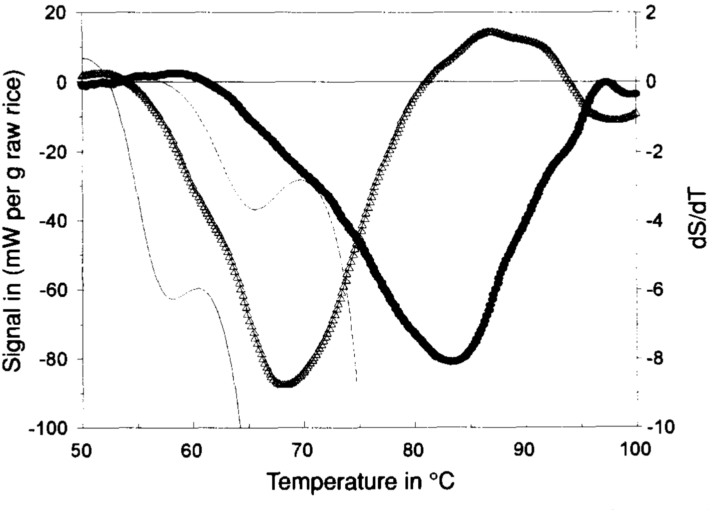

Fig. 9. Comparison between traces obtained from ground (△△△) and whole (●●●) rice kernels. Continuous curves correspond to the trend of the first derivative of each trace and reveal the relevant glass transition temperature, T_g.

interpretation, i.e. it reveals that starch gelatinization in whole rice kernels implies a larger thermal effect, possibly due to the structural change induced by water diffusion. This interpretation agrees with that suggested by Normand and Marshall [10], who reported the results of DSC investigation of whole rice and rice flour samples.

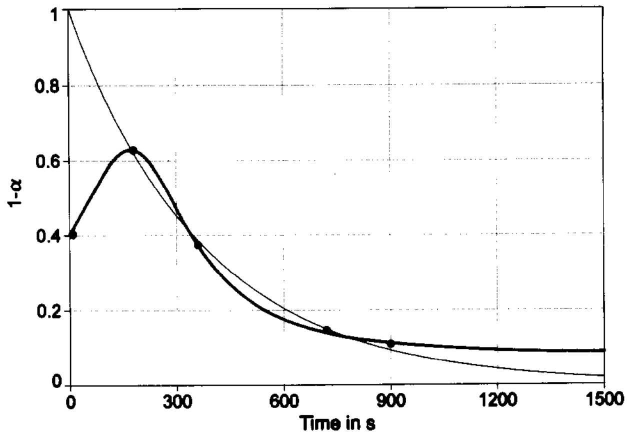

Fig. 10. Ungelatinized fraction of rice after various cooking times at 100°C. The first-order trend (continuous line) has been added for the sake of comparison.

A further evidence comes from the DSC traces of samples previously cooked at 100°C for different times. These traces allow the evaluation of the residual gelatinization enthalpy and the gelatinization degree attained, being

$$1-\alpha=\frac{(\Delta_{\text{gel}}H)_{\text{res}}}{(\Delta_{\text{gel}}H)_{\text{total}}}$$

When these data are plotted as $(1-\alpha)$ versus the cooking time, the trend reported in Fig. 10 is obtained: α remains practically constant for 200 s; it then rises according to first-order behaviour ($K = 2.64 \times 10^{-3}$ s^{-1}), which is rather close to that evaluated from isothermal DSC traces. The extension of the early constant-α phase might be correlated to the time required for water diffusion through the surface of the rice kernels.

4. Conclusions

Calorimetric investigations allow the simulation of rice cooking; they reveal that starch gelatinization is a diffusion-limited process, because water migration through gelatinized starch is slower than through the native structure. The migration of water is accompanied by an endothermic effect that can be tentatively ascribed to some structural change (rice kernels do indeed swell during the cooking process). Because this effect is considerably reduced in ground rice, the comparison between the behaviour of whole and ground rice samples allows a semi-quantitative evaluation of the true enthalpy of gelatinization. When these data are matched with those from non-isothermal DSC traces, the role of the heating rate can be recognized. Analogous results and conclusions can be drawn from non-isothermal DSC investigations carried out on partially pregelatinized samples.

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