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STARCH GELATINIZATION KINETICS IN BREAD DOUGH

DSC investigations on 'simulated' baking processes

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Abstract

Starch gelatinization in wheat flour dough of various moisture contents was quantitatively evaluated by means of DSC. The experimental records were worked out in the form of excess heat capacity *vs.* *T* traces which were deconvoluted to single out the contribution of starch gelatinization from that of the decomposition of amylose-lipid complexes. The quantitative procedure used put into evidence that a third endothermic process would take place in the dough with a poor moisture content.

DSC runs carried out with sealed pans (i.e., at constant moisture level) and open pans (from which some water was free to evaporate) allow simulation of two extreme conditions of a real baking process, namely that relevant to the central core and to superficial layer of a dough loaf, respectively. The extent of starch gelatinization occurred in these conditions was quantitatively assessed. These data were collected at various heating rates and used to define temperature-time-transformation (TTT) diagrams which are useful tools to predict the progress of baking for any given thermal history of the system.

Keywords: bread baking, DSC, starch gelatinization

Introduction

Starch gelatinization is the main transformation of starch in wheat flour dough undergoing baking [1, 2]. For this reason the gelatinization degree is a reliable parameter to describe the progress of baking. This process is very important both for the texture [3–5] and the nutritional properties of the final product: gelatinized starch can be degraded by the gut amylases whereas the ungelatinized fraction undergoes a much slower metabolism and can remain almost totally undigested [6].

In spite of the number of studies reported in the literature about starch gelatinization [7–25] that takes place either in starch water suspensions or in dough, the relevant conclusions cannot be directly used to control starch gelatinization in real baking, as long as this the process implies a number of variables, like actual water content of the dough at the different temperatures experienced during baking: it is indeed well known that extent and rate of starch gelatinization significantly depend on the moisture content of the system considered [7, 8].

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Furthermore, on-line sampling aimed at determining the extent of starch gelatinization is non practical in the course of baking trials for a number of obvious reasons. A much better control can instead be achieved through a reliable lab-scale simulation of the overall process, namely taking into account the technological variables such temperature, heating rate, and real water content of the dough during baking. This approach would provide a 'dynamic' picture of the starch transformation within a wheat flour dough undergoing a real baking. Such a description is allowed by TTT (time, temperature, transformation) diagrams which have been so far used in Polymer Science [9].

In the present work we present an approach to TTT diagrams of starch gelatinization by means of DSC investigations. The results obtained are of general validity and can be used from the bakery industry to control their specific baking processes.

Materials and methods

The wheat flour used was a «0» type commercial product with the following non-starch content: proteins 9.8±0.5, water 14.5±0.3, lipids 1.20±0.05, ash 0.45±0.05 (w/w % of flour mass). The protein content was assessed with the Kjeldahl method (conversion factor=5.7), while moisture was determined as the difference of sample mass after a 24 h heating in a ventilated oven at 105°C.

The flour was manually mixed with distilled water for 10 min: neither salt nor yeast was added. Different moisture contents were considered (see below). As a rule, 20 g dough samples were prepared for each flour/water ratio. 50 mg aliquots of each dough were sampled for the DSC investigations.

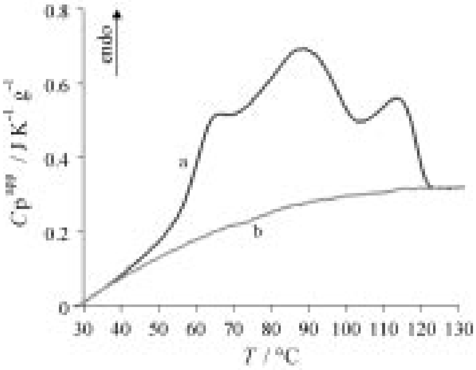

Fig. 1 Experimental DSC records from wheat flour dough with 44.2% (w/w) moisture heated at 2°C min^{-1} (a); DSC record of the immediate re-heating of the same sample to be used as the base line of the former trace (b)

A Perkin Elmer DSC-6 with 60 μL cells was used to investigate starch gelatinization. The reference cell contained a suitable amount of distilled water. Measures were carried out in the 20–150°C range at various (2.0, 5.0°C min^{-1}) scanning rates. Indium was used for calibration. The raw data were worked out with the dedicated software IFESTOS* which was assembled by the authors for handling raw calorimetric data according to the suggestions by Barone *et al.* [26]. The baseline chosen to work out a given DSC trace was the DSC record of the immediate re-heating run (Fig. 1b). It was subtracted from the record of first DSC heating run (Fig. 1a) , which corresponds to the apparent heat capacity $C_p(T)$ of the sample (per g of dry matter), to obtain the trend of the excess heat capacity, $C_p^{ex}(T)$, which allowed evaluation of the enthalpy drop ΔH by a straightforward integration of the corresponding trace. The baseline used did not always reproduce the signal related to the decomposition of amylose-lipid complexes, since, once cooled down, they require a relatively long annealing time when the moisture content of the system is low (this is the case of Fig. 1). At larger moisture levels a slight signal appeared on re-heating which could be easily neglected.

Results and discussion

The record of the excess heat capacity of a dough sample with standard formulation (44.2% w/w moisture), drawn from the experimental DSC trace obtained at 2°C min^{-1} heating rate, is shown on the Fig. 2. The relevant signal shows an on-set temperature, T_0, at about 45°C and three endothermic peaks at about 65, 90 and 120°C, respectively. This signal corresponds to starch conformational and phase transitions, the effects due to the other dough components, like gluten (residual) aggregation and denaturation of soluble proteins giving negligible contributions [9].

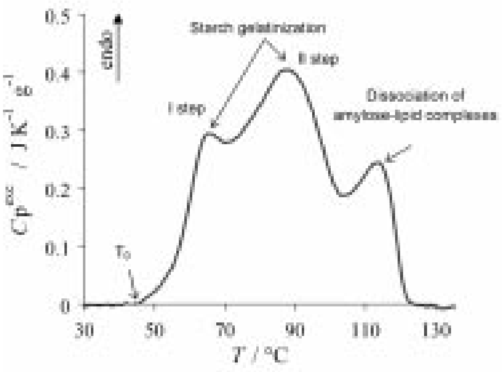

Fig. 2 Excess heat capacity, $C_p^{ex}(T)$, trace obtained from the records reported in Fig. 1

A similar multi peak signal was already found for aqueous suspensions of various starch types [10–15]. Most of the authors suggest that the first two peaks would correspond to the starch gelatinization, although the interpretations proposed for the underlying mechanism do not always coincide. The third peak would be related to the decomposition of amylose-lipid complexes [14, 16–20]. Much fewer examples [21–23] are of-

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* The software can be purchased on request.

fered for cereal flour dough samples, where the available water, which governs starch gelatinization, comes out from the competition between starch, gluten, and other hydrophilic compounds, like soluble proteins, oligosaccharides, pentosans, etc.

Figure 3 shows some DSC records obtained from wheat flour dough samples with different moisture contents, while the whole body of experimental data, namely the enthalpy values, are reported in Table 1. When referred to the actual starch content of the dough samples, these enthalpy values were in line with those reported by other authors [7, 11, 16, 17, 19, 24]. Inspection of Fig. 3 allows one to notice that the onset of the signal, T_0, and the temperature corresponding to the maximum of the first peak are independent on the water content (about 45 and 64°C, respectively, in all cases): this can be easily explained by reminding that the onset of the signal conceals the starch glass transition endothermic shift and therefore depends on the water content within the native starch granules (about 12% in the present case), no matter the overall composition of the sample investigated. The rest of the signal is instead shifted toward high temperatures when the dough moisture decreases. For the lowest water contents, the second peak tends to be overlapped to the third one.

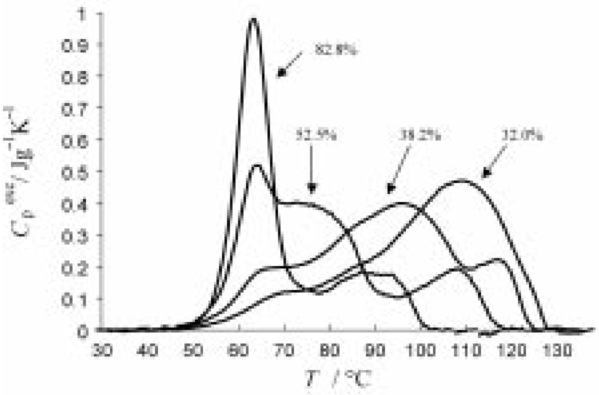

Fig. 3 $C_p^{\mathrm{ex}}(T)$ traces of dough samples with various moisture contents (82.8, 52.5, 38.2, 32.0% w/w)

Runs carried out at different heating rates showed only shifts of the signal without any significant change of the relevant enthalpy (data not shown) [25].

The main scope of these investigations was to single out the contribution of starch gelatinization from the overall signal, in order to assess its extent at any given moisture content. In the presence of excess water all starch granules can undergo gelatinization in a rather narrow temperature range: this allows a better separation of the relevant contribution from that related to the decomposition of amylose-lipid complexes. In the present case, dough samples with 82.8% w/w water showed a DSC record (Figs 3, 4) where the first peak was large and sharp, while the second was reduced to a shoulder of it and the third was apparently split into a couple of components.

Table 1 Overall enthalpy (column II) of the sealed-pan DSC records at various moisture contents (column I). The other columns reports calculated data relevant to starch gelatinization and decomposition of amylose-lipid complexes (see text)

I	II	III	IV	V	VI	VII	VIII
Moisture/ % (w/w)	ΔH/J g^{-1} $\pm$0.1 J g^{-1}	$\Delta_{\mathrm{I\ gel}}H$/ J g^{-1}	$\alpha_{\mathrm{I\ gel}}$	$\Delta_{\mathrm{II\ gel}}H$/ J g^{-1}	$\alpha_{\mathrm{II\ gel}}$	$\alpha_{\mathrm{max\text{-}gel}}$	$\Delta_{\mathrm{am\text{-}lip}}H$/ J g^{-1}
82.8	13.3	8.9	0.85	1.6	0.15	1.00	2.8
75.5	12.8	8.2	0.78	1.8	0.17	0.95	2.8
70.8	12.3	8.2	0.78	1.3	0.12	0.90	2.8
57.9	11.3	7.2	0.69	1.3	0.12	0.81	2.8
52.5	15.9	5.8	0.55	2.1**	0.20*	0.75^	2.8^{+}
44.2	17.7	4.4	0.42	2.5**	0.24*	0.66^	2.8^{+}
38.2	16.9	3.1	0.29	3.2**	0.30*	0.59^	2.8^{+}
32.0	16.9	2.6	0.24	2.8**	0.27*	0.51^	2.8^{+}
30.6	18.2	2.6	0.25	2.5**	0.24*	0.49^	2.8^{+}

$^{+}$assumed value (see text); ^from Fig. 5; *calculated from ^; 120**calculated from $\alpha_{\mathrm{II\ gel}}$

A deconvolution routine was used to single out these contributions: a set of Gaussian functions allowed the attainment of the results reported in Fig. 4; it should be noticed that two gaussian functions were used to reproduce the signal relevant to the decomposition of the amylose-lipid complexes and two peaks were recognized for starch gelatinization.

The relevant enthalpies were evaluated as the integrals of the gaussian functions. The following values were obtained: 10.5 (values of columns III+V in Table 1 at 82.8% moisture) and 2.8 J g^{-1} for starch gelatinization and amylose-lipid decomposition, respectively; both values are referred to the mass of dry matter. The former value, namely $\Delta_{\mathrm{gel}}H$(tot)=10.5 J g^{-1}, corresponds to 100% starch gelatinization, being the sum of the areas of the two relevant deconvolution peaks reported in Fig. 4. This value remained un-

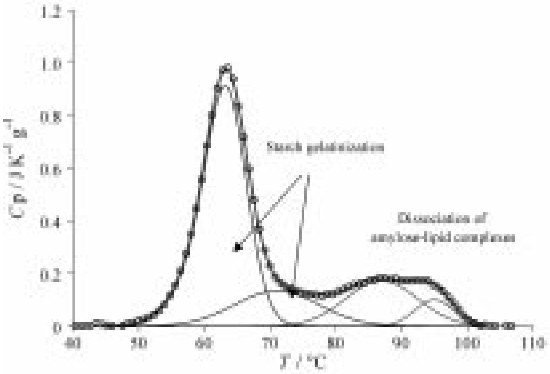

Fig. 4 Deconvolution of the $C_p^{ex}(T)$ trace of 82.8% moisture dough. The PeakFit, AISN Software Inc., program was used to single out the gaussian components

changed for moisture contents above 82% and was used as a reference to evaluate the gelatinization degree in all dough samples (column VII in Table 1) no matter how large was their water content. This last assumption was consistent with the fact that the DSC signal does not allow distinction between wholly and partially hydrated starch granules which undergo gelatinization to different extents, but allows evaluation of the overall enthalpy change which is therefore an average quantity.

The enthalpy of fusion of amylose-lipid complexes as drawn from the trace deconvolution (2.8 J g^{-1}) seemed independent of the dough moisture content.

This approach was found reliable whenever the moisture content of the sample remained above 57.9% w/w: the overall enthalpy indeed decreased as expected with decreasing moisture (Table 1, columns II), while that related to the amylose-lipid decomposition remained constant (Table 1, column VIII). Table 1 reports also the contributions to the starch gelatinization enthalpy corresponding to the areas beneath the two relevant peaks (Table 1, columns III and V), and the corresponding ratio (values are divided by the $\Delta_{gel}H$(tot)=10.5 J g^{-1}) (Table 1, columns IV and VI); the column VII in the table reports the corresponding total gelatinization progress degree that is the maximum for the corresponding moisture content, $\alpha_{max\text{-}gel}$.

For lower water contents the overall enthalpy unexpectedly increased with decreasing dough moisture (Table 1) and a significant overlap appeared between starch gelatinization and amylose-lipid decomposition (Fig. 3). This change of trend seemed rather abrupt, looking like the onset of a new process related to neither starch gelatinization nor amylose-lipid decomposition. For this reason the above deconvolution routine was not used to work out the $C_p^{ex}(T)$ traces of low moisture dough samples. It was instead preferred to evaluate $\alpha_{max\text{-}gel}$ by extrapolating the $\alpha_{max\text{-}gel}$ *vs.* moisture trend determined for higher water contents (Fig. 5) and single out only the first gelatin-

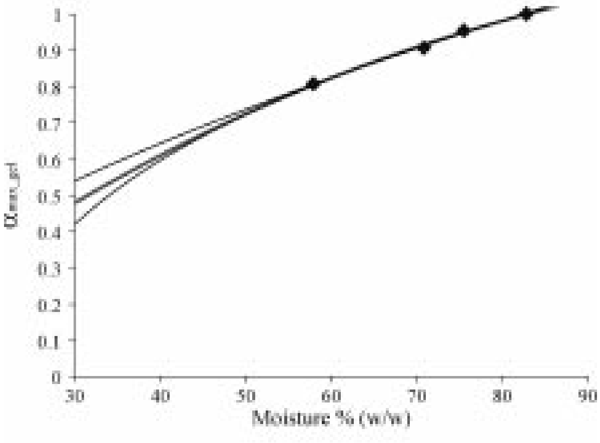

Fig. 5 Maximum starch gelatinization degree, $\alpha_{max\text{-}gel}$, *vs.* moisture content of the dough. The regression curve (heavy curve) fitting the experimental data was used to evaluate $\alpha_{max\text{-}gel}$ at low water contents. Taking into account the small number of available data (full squares), a wide error was assumed for extrapolated values (see thin curves)

ization peak from the $C_p^{ex}(T)$ trace; this allowed evaluation of the enthalpy related to the second gelatinization degree progress (reported as 'calculated' in Table 1). Assuming that the decomposition enthalpy of amylose-lipid complexes would remain constant (namely 2.8 J g^{-1}), the enthalpy of the third unknown process could be estimated (Fig. 6). The assumption seemed reliable since these complexes are mainly formed during the DSC run itself, namely in the course of the starch gelatinization; the formation of the complexes across the relatively short time span of a DSC run is therefore limited, no matter the moisture content of the sample (detailed investigations about the kinetics of the formation and decomposition of these complexes are still in progress and will the matter of a next paper).

Figure 6 reports the trend of the calculated extra effect, $\Delta_{extra}H$, *vs.* the moisture content. Once more, it has to be mentioned that the heating rate of the DSC runs did not affect these evaluations. The relevant enthalpy is naught at large water contents; it suddenly assumes a rather large value at about 52% (w/w) water and then increases according to a straight line trend on decreasing moisture. At present no clear explanation of this effect can be offered: due to its order of magnitude (it is comparable to the overall starch gelatinization enthalpy), it cannot be referred to as some residual of the mathematical fit of the data. Taking into account that dough is a dispersed system where water moves between phases [27] and affects relaxation of the polymer conformation and/or structure, either in starch polysaccharides or in gluten, the extra thermal effect revealed at relatively low moisture levels could be related to this kind of phenomena.

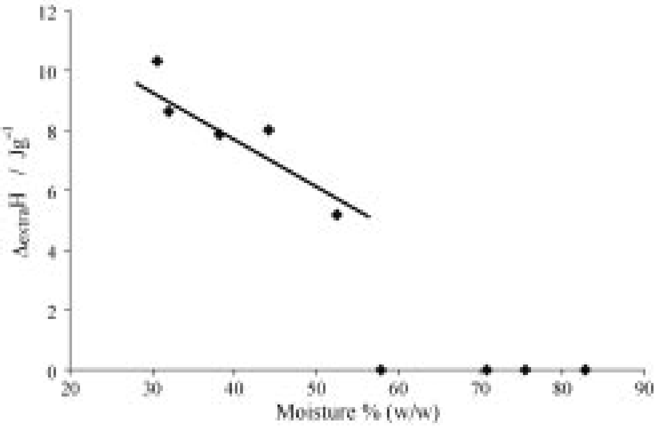

Fig. 6 Calculated enthalpy that could not be attributed either to starch gelatinization or to decomposition of amylose-lipid complexes

In a real baking treatment, the water content of the dough loaves changes because of the concurrent water vaporization. None the less the core of a standard dough loaf does not undergo a substantial moisture decrease: for this reason DSC runs were carried out with sealed pans, *i.e.* in constant moisture conditions, to evaluate the progress of starch gelatinization at various heating rates (0.5, 1, 2, 5°C min^{-1}).

To account for the usual moisture content of a bread dough, the dough samples considered for these investigations had a 44.2% (w/w) humidity. Since the overall enthalpy of starch gelatinization, $\Delta H_{\text{max-gel}}$, was already known (values of columns III+V in Table 1) for this moisture content, the DSC signal could be deconvoluted by imposing the constraint that the first two peaks had to account for $\Delta H_{\text{max-gel}}$. This allowed the interference of the extra contribution (see above) to be overcome. The evaluation of the starch gelatinization degree, $\alpha_{\text{gel}}(T)$ was therefore straightforward:

$$\alpha_{\text{gel}}(T)=\frac{\int_{T_{\text{i}}}^{T} C_{\text{p}}{}_{gel}^{exc}(T)\mathrm{d}T}{\int_{T_{\text{i}}}^{T_{\text{fin}}} C_{\text{p}}{}_{gel}^{exc}(T)\mathrm{d}T}=\frac{\Delta H_{\text{part-gel}}}{\Delta H_{\text{max-gel}}}$$

where T_{i} and T_{fin} stand for initial and final temperature of the range spanned by the first two deconvolution peaks, $C_{\text{p}}{}_{gel}^{exc}(T)$ is the function that is the sum of the two deconvolution peaks related to starch gelatinization, $\Delta H_{\text{max-gel}}$ is the relevant integral, and $\Delta H_{\text{part-gel}}$ is the fraction of the same integral attained at a temperature $T<T_{\text{fin}}$.

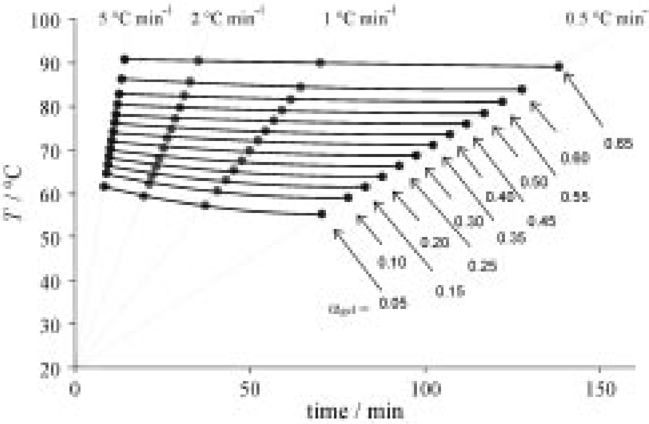

Fig. 7 Temperature-time-transformation (TTT) diagram of starch gelatinization in dough at constant moisture, 44.2% (w/w). Dotted straight lines represent different heating rates during the DSC runs. *Iso*-α_{gel} curves are indicated

Figure 7 reports the results of this evaluation for various heating rates in the classical TTT diagram. In the latter α_{gel} values are reported along the straight lines that represent the heating rates experienced by the samples. *Iso*-α_{gel} lines are also drawn. The use of a TTT diagram for a given dough recipe is rather simple, since it allows any heating treatment to be directly represented in the plot as an ascending curve that crosses the *iso*-α lines. One can accordingly predict the starch gelatinization degree attained at any moment of the treatment.

Water vaporization cannot instead be neglected for the more superficial layers of a dough loaf. This process can be simulated with DSC runs carried out with open pans. None the less determination of the extent of starch gelatinization attained during such a scan is not possible since the enthalpy related to water vaporization is 2–3 orders of magnitude larger than that of starch gelatinization. To overcome this difficulty an indirect approach was followed via evaluation of the residual gelatinization at the end of the open-pan run.

To this aim, dough samples were partially dehydrated by heating them in open DSC pans within the furnace of the instrument at a given heating rate. The run was stopped at an intermediate temperature, T_c and the pans were immediately sealed, cooled to room temperature, and again heated up at the same heating rate in order to evaluate the residual starch gelatinization. The relevant moisture content, W_c, within the sample at T_c (and in the following DSC run with sealed pans) was determined after the DSC run: the cover of the measure pan was pierced and the cell was kept in an oven at 105°C for 24 h; the moisture loss was therefore determined as the cell mass change.

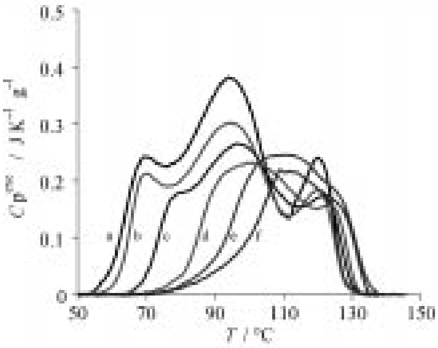

Fig. 8 $C_p^{ex}(T)$ traces relevant to the residual starch gelatinization after previous heating in open DSC pans at the same heating rate (5°C min^{-1}). T_c; a=40, b=60, c=70, d=80, e=90, f=100

Figure 8 reports the $C_p^{ex}(T)$ traces obtained from dough samples pre-heated in open pans up to different T_c at 5°C min^{-1} heating rate. The data relevant to 2 and 5°C min^{-1} heating rate are reported in Tables 2 and 3, respectively.

Table 2 Data relevant to open-pan DSC records. T_c=temperature at which pans were sealed after a previous heating; W_c=residual dough moisture at T_c; $\Delta H(T_c)$=enthalpy drawn from the sealed-pan DSC runs (2°C min^{-1}) carried out according to the procedure reported in the text

T_c/°C	W_c/% (w/w)	$\Delta H(T_c)$/J g^{-1}
20	44.2	17.7
50	36.3	14.1
60	35.7	11.9
70	30.2	10.9
80	31.1	10.0
90	30.7	9.9

Table 3 Data relevant to open-pan DSC records. T_c=temperature at which pans were sealed after a previous heating; W_c=residual dough moisture at T_c; $\Delta H(T_c)$=enthalpy drawn from the sealed-pan DSC runs (5°C min^{-1}) carried out according to the procedure reported in the text

T_c/°C	W_c/% (w/w)	$\Delta H(T_c)$/J g^{-1}
40	38.4	16.8
60	37.8	13.0
70	36.9	10.8
80	34.7	8.6
90	33.0	8.5
100	33.6	6.5

The deconvolution treatment was therefore applied to these traces to evaluate $\alpha_{\text{gel(open-pan)}}$. Since the temperature experienced by the crumb remains below 100°C in any real baking process, only the experimental trace across the 45–110°C range was considered to comprehensively account for starch gelatinization. The calculation routine allowed estimation of the enthalpy of residual starch gelatinization, $\Delta_{\text{res-gel}}H(T_c)$: these data are reported in Tables 3 and 4. The $\alpha_{\text{gel(open-pan)}}$ attained during the previous heat treatment in open pans was accordingly calculated as

$$\alpha_{\text{gel(open-pan)}}=\frac{\Delta H_{\text{max-gel}}(W_c)-\Delta H_{\text{res-gel}}(T_c,W_c)}{\Delta_{\text{gel}}H_{\text{(tot)}}}=$$

$$=\alpha_{\text{max-gel}}(W_c)-\frac{\Delta_{\text{res-gel}}H(T_c,W_c)}{\Delta_{\text{gel}}H_{\text{(tot)}}}$$

where $\alpha_{\text{max-gel}}(W_c)$ is the maximum gelatinization degree attainable at the moisture content W_c remained within the dough when the pan was sealed (its value was drawn from the fit reported in Fig. 5), and $\Delta_{\text{gel}}H_{\text{(tot)}}$=10.5 J g^{-1} is the reference value (100% starch gelatinization) used throughout the present work. Table 4 reports these results.

Table 4 Data relevant to open-pan DSC records. T_c=temperature at which pans were sealed after a previous heating; $\alpha_{\text{gel(open-pan)}}$=total gelatinization degree

Heating rate 2°C min^{-1}		Heating rate 5°C min^{-1}	
T_c	$\alpha_{\text{gel(open-pan)}}$	T_c	$\alpha_{\text{gel(open-pan)}}$
20	0.00	40	0.00
50	0.08	60	0.20
60	0.25	70	0.36
70	0.34	80	0.40
80	0.41	90	0.43
90	0.44	100	0.45

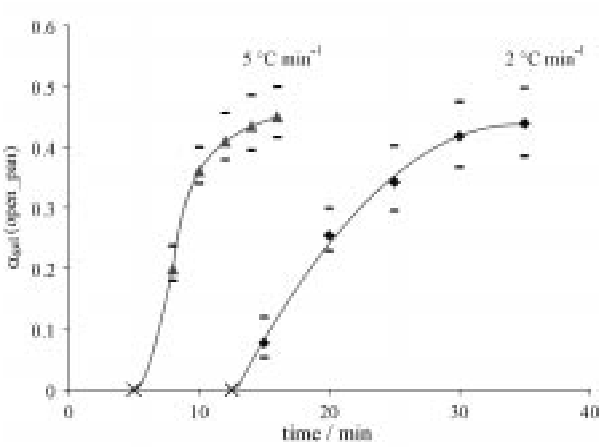

Fig. 9 $\alpha_{gel\ (open\text{-}pan)}$ *vs.* time in a DSC simulated baking process carried out at two heating rates (2 and 5°C min^{-1}). The limits encompassing experimental data are those related to the error margins reported in Fig. 5. The intercepts on the time axis (evidenced with a X symbol) correspond to the onset of the starch gelatinization (namely, 45°C)

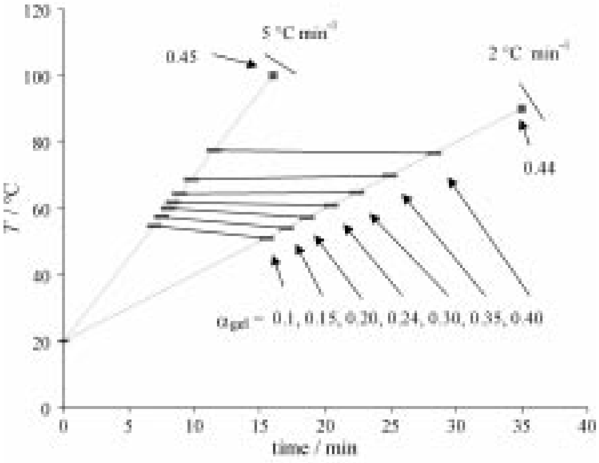

Fig. 10 Temperature-time-transformation (TTT) diagram corresponding to Fig. 9. *Iso*-α_{gel} curves are indicated

The same data can be represented *vs.* the baking time in order to give more evidence to the kinetics of the process at the two heating rates considered. Figure 9 shows the α *vs.* *t* trend, while Fig. 10 is again the classical TTT diagram.

Conclusions

The present work shows that once the dough recipe has been defined, it is possible to define the baking progress through evaluation of the starch gelatinization degree in a ‘simulated’ process with DSC runs. The relevant results should be represented in the form of a TTT diagram where the temperature profile experienced by the dough loaves during the real baking should be also reported. This allows prediction of the extent of starch gelatinization attained at any moment of the process. In the present case one should also account for the different behavior of loaf core and surface, since the moisture changes differ from each other. Therefore the results drawn from sealed and open-pan DSC runs represent two extreme conditions actually met at the central core and the superficial layer of the loaf, respectively. DSC data are indeed relevant to small samples which cannot represent the whole body of a loaf, but only a specific region where the moisture level undergoes well known changes in the course of the baking process. In any real situation the actual progress of starch gelatinization would be at an intermediate position between the two extremes described above.

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