Bread Staling: A Calorimetric Approach[1]

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ABSTRACT

Simple recipe breads with different water contents were allowed to stale in well-defined conditions. Bread crumb was investigated using differential scanning calorimetry, thermogravimetry analysis (TGA), and stress-strain determinations. Calorimetric investigations extended to subambient temperature allowed an exothermic signal to be recognized just about room temperature that appeared partially reversible on repeated heating-cooling cycles across the –10 to 35°C range. The corresponding thermal effect was maximum after aging 8–10 hr. According to the TGA investigations, the release of water on heating revealed two main binding states: water-1 and water-2. The relevant fractions were bread-age dependent; water-1 reached a minimum after aging 8–10 hr at room temperature, while the overall water content remained practically unchanged. These findings suggested a model for the extension of a crosslink network throughout the bread crumb. Water molecules would be displaced along polymer chains acting as sliders of an interchain zipper. The consequent direct interchain crosslinks would allow formation of a network that would justify the increasing firmness of the crumb. The same mechanism would also sustain the growth of amylopectin crystals. Accordingly, the observed correlation between starch retrogradation (evaluated from the endothermic effect of amylopectin fusion) and increased crumb firmness should be reconsidered in the frame of a more general picture where water molecules play a key role in the definition of the product structure.

A number of works (Lindet 1902, Schoch and French 1947, Bechtel and Meisner 1954, Bechtel and Meisner 1959, Zobel and Senti 1959, Senti and Dimler 1960, Cornford et al 1964, Herz 1965, Schoch 1965, Zobel 1973, Maga 1975, D'Appolonia and Morad 1981, Kulp and Ponte 1981, Pyler 1988, Stear 1990, Kulp 1991) have been devoted to the study of bread staling to explain the different processes that take place in the course of the shelf life and significantly modify the sensorial properties of the product. At present, no interpretation is available that encompasses the whole body of changes observed, although some tentative models have been proposed. Most of these recognize a key role of water and its mobility (Zeleznak and Hoseney 1987, Czuchajowska and Pomeranz 1989, He and Hoseney 1990, Piazza and Masi 1994). Great attention was paid to ingredients that interact with water, such as nonstarch compounds, proteins (gluten and nongluten), dextrins, sugars, emulsifiers, and hydrocolloids, etc., as well as endogenous and exogenous enzymes like amylases that can partially degrade the starch components to produce smaller polysaccharides (Whilloft 1973, Dragsdorf and Varriano-Marston 1980, He and Hoseney 1990, Rogers et al 1988, Martin et al 1991, Martin and Hoseney 1991).

Some works have been devoted to the kinetic parameterization of bread crumb staling. The reported studies mainly deal with the change of mechanical properties of the crumb and with DSC investigations. Either approach is adequate to characterize the shelf life of baked cereal products (Hollo et al 1959a,b; Kim and D'Appolonia 1977; Biliaderis et al 1980; Eliasson 1985; Zeleznak and Hoseney 1987; Kou and Chinachoti 1991; Swyngedau et al 1991; Biliaderis 1993; Riva and Schiraldi 1993). Some authors have assumed starch retrogradation is a parameter of bread staling (Eliasson 1985), a qualitative correlation was suggested between extent of starch retrogradation and the increased firmness of the bread crumb. Although true for a given kind of bread, the correlation significantly changes when other bread recipes are considered. This confirms the expectation that other nonstarch components can significantly affect either the extent of starch retrogradation or that coexistent phenomena contribute to the overall increase of firmness of the crumb.

Most of these findings were reproduced in this work. Among the changes that contribute to the overall picture of the bread crumb staling, we focused our attention on starch retrogradation (assessed form endotherms of differential scanning calorimetry [DSC] traces); increase of firmness (measured as increase of elastic modulus); and water binding (evaluated from thermogravimetry analysis [TGA]). This article reports the results of calorimetric investigations extended to subambient temperatures: aside from the well-known endothermic peak due to starch retrogradation, an exothermic effect was recognized just above room temperature that seemed directly correlated with the change of the elastic modulus of the bread crumb. A mathematical treatment of DSC and TGA traces allowed: 1) overcoming the poor reproducibility of the traces obtained from food samples compared with those from pure compounds or physically homogeneous systems (solutions, polymers, rocks, metal alloys, etc.); 2) scaling meaningful DSC and TGA profiles from the relevant baselines to recognize the number and type of distinguishable components of a given signal that can be related to separate events underlying the overall record.

MATERIALS AND METHODS

Breadmaking

Different kinds of bread were prepared on laboratory scale with conventional baker's yeast fermentation and simultaneous mixing of all ingredients.

The raw material used was soft wheat patent flour (water content 14.45% (w/w) wb; total protein: 11.01% (w/w) wb) obtained from a commercial source (Molini di Vigevano, Vigevano, Italy); and stored at 4°C. The control bread (CB) was prepared from a dough of 100 g of soft wheat flour, 60 g of water and 3.75 g (4.2% [w/w] db) of compressed baker's yeast (*S. cerevisiae*, Vinal Gist-Brocades, Casteggio, Italy), and 1 g of NaCl. No fat was added.

Breads prepared according to different recipes were also considered. These breads contained the same yeast content as the CB (4.2% [w/w] db) and different water or protein proportions. Samples included water-enriched bread (WEB) and water-poor bread (WPB) with 100:65 and 100:55 flour-to-water weight

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ratios, respectively; and gluten-enriched bread (GEB), where 2 g of freeze-dried gluten (obtained by hand-washing the CB dough with tap water) were added to the CB recipe.

Ingredients were mixed with a spiral arm mixer (Sottoriva, Marano Vicentino, Italy) for 12 min and let to rest for 10 min at room temperature. Loaves (200 g) were then formed in baking pans and proofed at 30°C and 70% rh for 60 min in a climatic cell (Heraeus Votsch HC0020, Balingen, Germany).

Baking was performed for 25 min at 225°C in a forced convection oven (Moretti, MIKRO, Marotta, Italy). Baked loaves were then naturally cooled to room temperature (≈120 min). The moisture content determined for CB, WEB, WPB, and GEB, respectively, just after cooling was: 46.56, 47.79, 45.36, and 45.53% (w/w) wb. Cooled loaves were finally wrapped in a polyethylene envelope and frozen in a home-style freezer at –20°C, where bread loaves reached an –18°C core temperature in 24 hr. To work with comparable samples, the loaves were thawed before each investigation, which significantly reduced the variability of the analytical results and allowed use of thawed CB as reference. Loaves to be thawed were transferred into a thermostatic cell at 20°C. Annealing for 4 hr in these conditions were necessary to complete the process. The bread aging (at 20°C) was assumed to start at that point. Some CB samples were used for additional aging trials at 15 and 25°C.

DSC and TGA Investigations

In classic DSC investigations, the pans used are mechanically closed in a mold. This sealing can support the 2–3 atm overpressure caused by the increase of vapor pressure when dough or bread crumb samples are heated. Water evaporation is therefore suppressed by sealing the cells. The resultant baseline shows a slight bending trend from which endo- and exothermic peaks can be easily scaled. If open pans were used to study the same kind of samples, water would be released on heating (as in real baking), with a consequent decrease of the overall heat capacity of the sample and large upward bending of the baseline of the DSC trace. This is described by the relationship:

$$s_{base} = v \times (m_{ref}Cp_{ref} - m_{sample}Cp_{sample})$$

where v is the heating rate and the subscripts refer to reference and sample cell, respectively. However, this baseline trend is overbalanced by the endothermic process of water vaporization. The overall record obtained with open pans is therefore a descending trace that goes through a broad minimum at 100°C and does not show any definite signal onset. As the vaporization enthalpy of water (≈42 kJ/mol) is very large, the signals related to starch gelatinization and retrogradation become almost undetectable.

Accordingly, a Mettler DSC20 calorimeter (Greifensee, Switzerland) operating with sealed pans was used to detect signals relevant to the starch retrogradation and other transitions, whereas a SETARAM TG-DSC111 (Lyon, France) operating with open pans was used for thermogravimetric determination of water losses. The latter instrument does indeed allow mass loss and heat flux to be simultaneously determined: two open ampules suspended to the arms of a balance are hanging into the parallel cylindrical cavities of a twin Calvet calorimeter (a schematic view is given in Fig. 1). In the course of a heating run (at a given heating rate), heat flux and balance shift are simultaneously recorded. However, this instrument was employed only to study water loss in the course of a temperature scan at given heating rate.

Both DSC and TGA investigations were performed at 2°C/min heating rate; such a low heating rate allows the signal onset temperature to be more accurately determined. The typical sample mass was ≈40 mg. The DSC reference pan contained aluminum slices to counterbalance, as much as possible, the sample heat

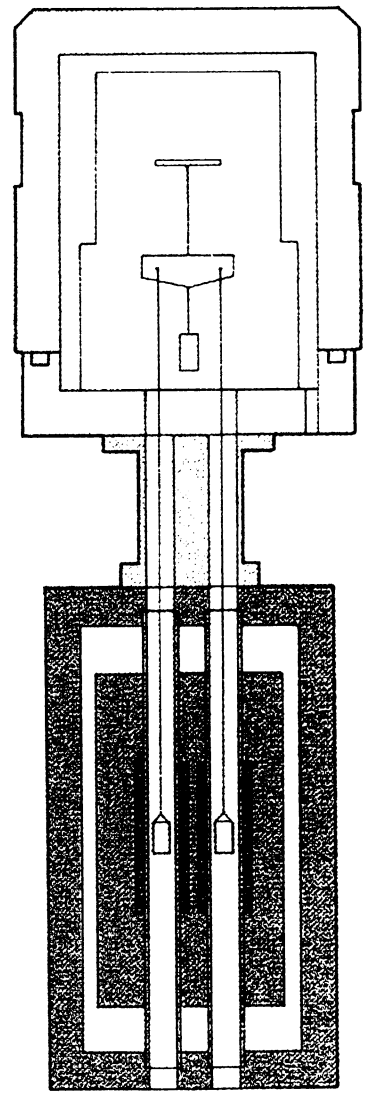

Fig. 1. Schematic view of thermogravimetry apparatus (Setaram TG-DSC 111) used for determination of water losses.

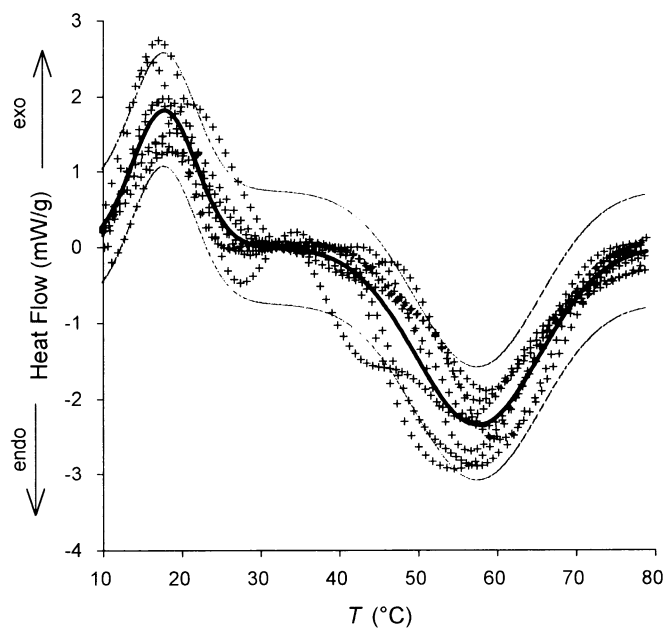

Fig. 2. Average of differential scanning calorimetry traces (2°C/min heating rate) from eight control bread samples stored at 20°C for 5 hr. – – – = Relevant 95% prediction limits. ——— = Relevant average fit.

capacity. An empty reference cell was used for TGA determinations.

DSC runs covered the temperature range −10 to 80°C. The lower end of this range was attained by use of a liquid nitrogen top-freezer-settled over the furnace. The traces recorded were switched into ASCII format to be conveyed to a personal computer and worked using suitable software (Table Curve and Peakfit, Jandel Sci., Erkrath, Germany).

The data analysis (baseline assessment, trace smoothing, and trace deconvolution) was performed according to previous work (Riva and Schiraldi 1993). Data collected in the −10 to 10°C range were discarded because of the starting drift of the record.

At least three replicates of the DSC trace were obtained from loaf core crumb samples of every bread at every aging interval.

The reliability of the results was assessed, mindful of the usual serious problems of reproducibility of food specimens. In the case of bread crumb samples, there is unavoidable variability in dough preparation and baking conditions. Furthermore, some peculiar details of the DSC traces correspond to minor thermal effects and must be singled out from the normal trace noise. For these reasons, confidence and prediction limits of our results were preliminarily assessed through a statistical analysis of several replicates obtained from CB crumb. Figure 2 reports the traces obtained from eight samples of the same bread lot.

Each trace shows two major features: an exothermic peak in the early region 10–30°C and an endothermic peak in the region 40–80°C. The differences between various traces revealed the intrinsic uncertainty of this investigation and were treated as random errors to be smoothed with an average procedure to attain a statistically reliable trace. The thick solid line in Figure 2 represents the relevant average fit based on a sum of two gaussian functions to directly account for the observed exo- and endothermic peaks. The r^2 regression parameter was 0.900 with a fit standard error of 0.38 for 95% confidence limits. Figure 2 also shows the 95% prediction limits of the fit throughout the investigated temperature range. These statistical parameters confirm the reliability of the exo- and endothermic signals as the major features of the DSC traces.

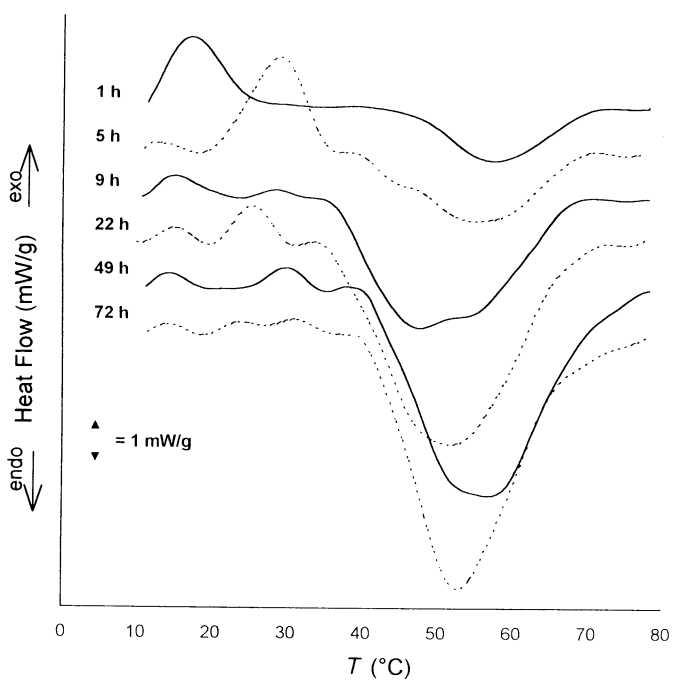

Fig. 3. Differential scanning calorimetry traces of control bread samples (2°C/min heating rate) at different storage times. Traces are shifted to one another for the sake of clarity.

The underlying areas were determined as the integrals of the gaussian functions and showed a relative standard deviation of 15–18%, which is in line with the expectations from this kind of investigation and can be indeed associated to all the calorimetric data of the present work.

Water loss was determined in the course of a temperature scan from 10 to 140°C at 2°C/min heating rate. The data analysis was performed along the same lines as that for the DSC results. The relevant reproducibility was analogous. The experimental data were fit with a couple of sigmoidal functions to attain a closer description of the actual trace, which showed a trend shift at some intermediate temperature within the range considered. The asymptotic value of the fit directly gave the total amount of water released (that was practically equal to the total crumb moisture). The derivative TG (DTG) profile therefore reproduces the sum of the single derivative functions (each per sigmoidal function).

Mechanical Characterization

Deformation tests were performed on bread crumb by uniaxial compression with a universal testing machine (Instron UTM 4301, Instron Ltd., High Wycombe, UK). Cylindrical crumb samples (30-mm high, 25-mm dia.) were compressed with 80-mm dia. plane surface plunger, 100 N loading cell at 20 mm/min crossbar speed. Six replicates were obtained, each corresponding to a separate sample of the crumb core. From each half of a bread loaf, a slice was carefully cut by means of a guided knife to obtain parallel faces and definite size. Then a cylindrical crumb sample was drawn by boring the central part of the slice.

The compression test was performed after a 2-min rest to allow a full relaxation of the sample and stopped at 80% deformation.

Force-deformation curves (recorded as ASCII files by the built-in routine of the instrument) were worked out with the Table Curve software. Data were expressed as strain vs. Henky deformation. Because the dead shift of the plunger was previously removed from the overall displacement, the elastic modulus (g/mm^2) was evaluated from the linear region of the trace. An 8–10% relative standard deviation was found for these results.

Water Activity (a_w)

A Rotronic Hygroscope DT (Rotronc AG, Zurich, Switzerland) operating at constant temperature (20°C) was used to evaluate water activity of bread crumb samples. Crumb cylinders (10-mm thick, 45-mm dia.) taken from just-thawed samples were placed in the measuring chamber up to 72 hr and a_w data were collected at constant intervals. The kinetic of the a_w change was finally worked out with the Table Curve software.

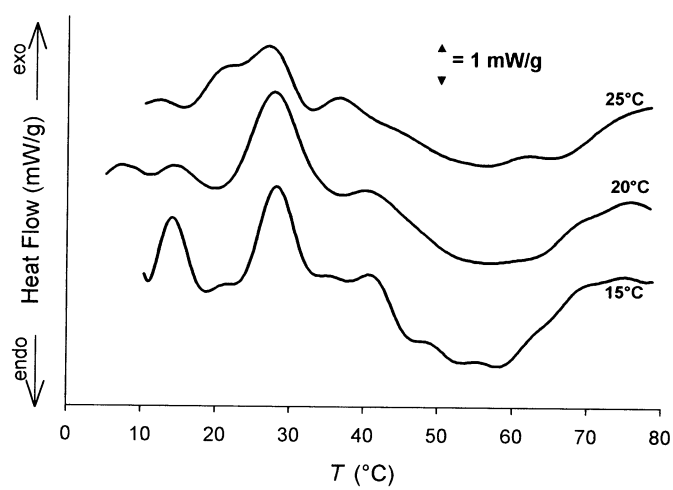

Fig. 4. Differential scanning calorimetry traces of control bread samples (2°C/min heating rate) stored for 8 hr at different temperatures. Traces are shifted to one another for the sake of clarity.

RESULTS AND DISCUSSION

Control Bread

It is well known that DSC traces obtained from aged bread crumb show an endothermic signal with an underlying area that increases with the bread age; the signal is attributable to the fusion of amylopectin crystals (Eliasson 1985) and is a reliable measure of the starch retrogradation. This was observed in the present work for every bread type studied.

At lower temperatures, an exothermic signal was always present (Fig. 2). To our knowledge, such an effect was never reported in literature, perhaps because the reported DSC records from staled bread usually start just above room temperature and (because of the heating rate chosen of 5 or 10 deg/min) present a starting drift that does not allow a clear definition of the baseline but just before the endotherm onset of the amylopectin fusion; another reason could be that the exothermic signal can be small and show a poorly reproducible onset temperature. Both limitations were overcome in the present work by selecting a more adequate heating rate of 2°C/min and using a statistical analysis to work out the data.

Figure 3 shows DSC averaged (Fig. 2) traces obtained from CB crumb samples of different age.

Figure 4 shows the traces obtained from samples of the same bread crumb stored for 8 hr at different temperatures. Note that the intensity of the endothermic peak decreases with increasing storage temperature, whereas the exothermic effect is much more erratic either for the shape (at low storage temperature is split into a couple of peaks) or for the overall underlying area. The maximum effect was observed for storage at 20°C.

TGA data were worked out by fitting the corresponding DTG profile as a sum of two peak-shaped functions with well-separated maximum temperatures at ≈70 and 90°C, respectively.

Figure 5 shows a typical TGA trace together with the corresponding DTG (1st derivative of the TGA trace) The corresponding DSC traces were not considered here, because their overall bending did not allow any reliable treatment to single out two components related to the sigmoidal TGA fitting functions. These would indeed give the relevant vaporization enthalpies.

Hence, it was argued that the crumb water could be grossly shared in two distinguishable conditions (water-1 and water-2) related to the low and high temperature DTG maximum, respectively. The relevant water amounts, simply evaluated as the integrals of the corresponding DTG peaks, went through a broad minimum and maximum, respectively, just after aging 8–10 hr, while the total water content (the asymptotic value of the TGA fit) remained practically unaffected (Table I).

It seemed reasonable to search for some connection between these findings and the DSC data from aged bread crumb to find some interpretation of the exothermic signals observed. The starting point of our speculation was the well-established role of water in starch retrogradation (Zeleznak and Hoseney 1986), at up to 40% water content, both the rate and the extent of starch retrogradation increase with increasing moisture. This suggested matching the maximum of water-2 with the maximum rate of formation of amylopectin crystals, because both were observed at the same aging time.

The plasticizing action of water has been reported as a qualitative explanation of the water-sustained starch retrogradation (Biliaderis 1990). Accepting this, water molecules can be reasonably supposed to form weak links, like hydrogen bonds, with polymer chains. To act as plasticizers, these molecules must remain mobile, i.e., able to move from one binding site to another along a polymer chain. Once a water molecule is displaced from a binding site, it becomes available to form a bond with another water molecule. This simple diffusion mechanism cannot, however, account for the formation of a crystal phase which implies direct linking between polymer chains and insertion of water molecules. It is therefore necessary to guess that water molecules can somehow affect the mutual orientation of next-neighbor chains so as to allow formation of direct bonds (allegedly hydrogen bonds) between them. This can occur when a water molecule forms a bridge between chains. Its displacement leaves two binding sites facing each other and capable of forming a direct link.

Interpretation of the Exothermic Peak

Formation of bonds is an exothermic process (the energy is released to the ambient), while bond rupture is endothermic.

TABLE I
Amount of Two Distinguishable Water Fractions in Bread Crumb as a Function of Storage Time

Time (hr)	Water-1 (g/100 g)	Water-2 (g/100 g)	Total Water (g/100 g)
1	29.78	16.22	46.00
5	28.83	17.04	45.86
8	27.67	18.52	46.18
21	28.80	16.59	45.39
48	30.40	13.89	44.29
72	29.74	13.39	43.13

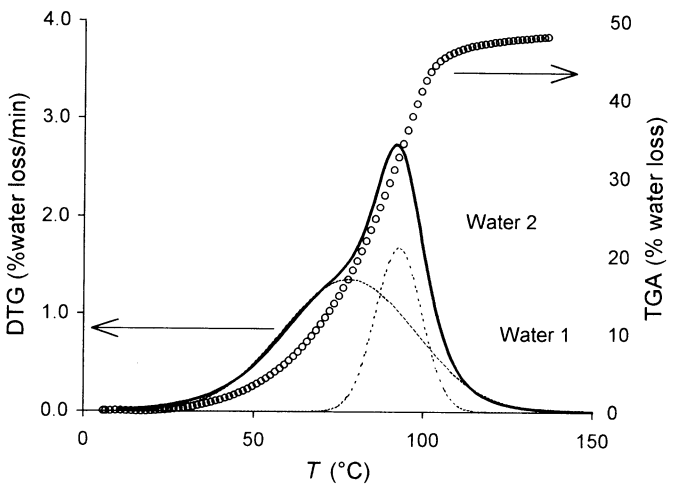

Fig. 5. Thermogravimetry (TGA) and derivative TG (DTG) traces recorded with 2°C/min scanning rate on 5-hr aged control bread samples. Dotted and dashed lines represent deconvolved components of the DTG curve.

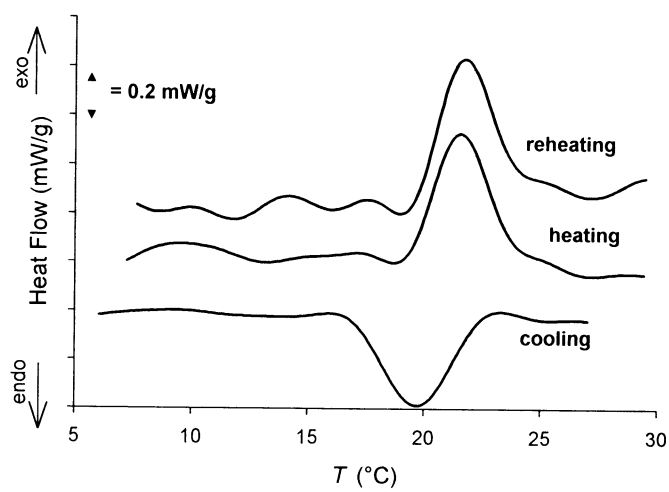

Fig. 6. Differential scanning calorimetry traces of a control bread sample (2°C/min heating or cooling rate) in a three-run cycle over a 5–30°C temperature range.

Accordingly, when an overall exothermic effect is recorded, it must account for the formation of bonds. An exothermic process is usually enhanced by a decrease of temperature. However, there are cases where an exothermic signal appears on heating the system. When the system is thermodynamically unstable (glasses, amorphous polymers, etc.), it releases the excess energy trapped in the course of a previous cooling. Or, thermoset polymers release the heat of reticulation when undergoing thermal cure. In any case, a temperature threshold must be attained (glass transition temperature, T_g) to activate interchain adjustments. The exothermic DSC signal observed in these cases is irreversible (no endothermic effect appears on recooling the sample) (Angell et al 1994).

These points had to be coupled with the assumed role of water to propose an interpretation of the experimental findings of the present work which can be summarized as follows.

Figure 4 shows that samples of CB crumb aged at 15°C gave an exothermic effect clearly split in two peaks: the maximum of peak 1 occurred practically at the storage temperature of the crumb, whereas peak 2 showed its maximum at 27–30°C. For crumbs aged at higher temperatures (25°C), peak 1 appeared as a shoulder of peak 2, whose maximum still occurred at 27–30°C.

To check the hypothesis that the double signal could correspond to the release of excess energy trapped during the previous cooling to subambient storage temperature, the same sealed pan was subjected to a heating-cooling-heating cycle (in the 5–30°C range) and the relevant trace was recorded (Fig. 6). A neat endothermic peak appeared on cooling (with a little hysteresis). The associated enthalpy change was slightly smaller than that for the exothermic signal recorded on heating.

The exotherm was not present when the sample had been previously heated above the temperature range where the amylopectin melts.

The reversibility, however, apparently concerned only peak 2, because no endotherm appeared as the reverse of peak 1. Moreover, peak 1 did not appear upon reheating, while peak 2 was always well reproduced. It was therefore concluded that peak 1 could be attributed to the release of excess energy trapped in the crumb on cooling the bread from the oven temperature to the shelf life conditions, while peak 2 should be attributed to some reversible event. The maximum of enthalpy change related to peak 2 was attained after aging 8–10 hr (Fig. 7a), that is, concomitant with the maximum rate of starch retrogradation and the maximum of water-2 (Fig. 7b). The increase of the elastic modulus of the crumb (which can be related to an increase of firmness) attained a maximum rate aging ≈10 hr, while its progress is poorer for longer aging (Fig. 7c). A tentative interpretation of the underlying mechanism was thus envisaged.

It is widely accepted that interchain links within a bunch of long-chain polymers produce a random network with a rigidity that increases with their number. The overall process is exothermic and irreversible, being sustained by thermally activated sliding movements of the polymer chains.

In a similar way, the structure of a baked product would depend on the number and kind of links between nearest neighboring biopolymer chains in the starting dough. Interchain links can be hydrogen bridges (Hoseney, 1984) and, when proteins are involved, disulfide bonds too (Zeleznak and Hoseney 1986, Zeleznak and Hoseney 1987, Martin et al 1991, Martin and Hoseney 1991, Zhang and Morita 1993). A network of hydrogen bonds between polysaccharide polymers, like amylose and amylopectin, is supposed to be formed when starch undergoes gelatinization (Jay-Lin 1993).

The dough structure is rubbery and the product is plastic because much water is available to act as a plasticizer. During baking, part of the water is lost and part is structured, i.e., directly engaged to form links with biopolymers (starch polysaccharides, proteins, nonstarch-polysaccharides, etc.) (Roos and Karel 1991, Slade and Levine 1991, Noel and Ring 1992, Slade and Levine 1993). Its mobility progressively decreases, and the crumb struc-

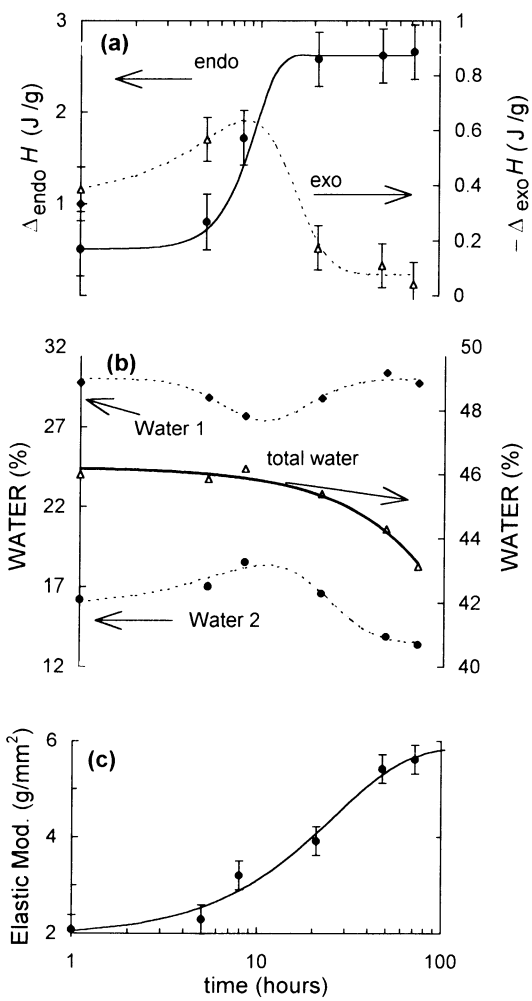

Fig. 7. Control bread crumb changes observed in the course of aging. **a,** Endo- and exothermic effect; **b,** water-1, water-2, and total water reported from thermogravimetry data; **c,** elastic modulus.

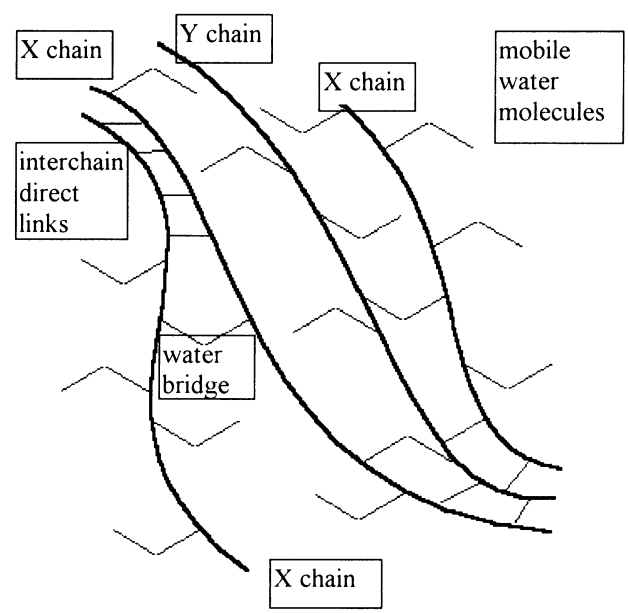

Fig. 8. Schematic representation of the zipper mechanism of water mobility in bread crumb.

ture becomes increasingly firmer. This does not mean that water is definitely bound (Franks 1993); it can still diffuse, although much more slowly than in a dough. Water diffusion is to be seen as a series of displacements of the molecule toward next-neighboring binding sites, like –OH groups of the glucose units of polysaccharide molecules able to form hydrogen bonds (Hoseney 1984). The process is thermally activated and should mainly support the redistribution of water within the staling crumb. When a water molecule forms a bridge between each-other-facing binding sites, a direct bond between chains can be easily formed by displacement of the intermediate water molecule, which can diffuse toward next neighboring sites and promote the formation of a new direct interchain link. A schematic view of this mechanism is shown in Figure 8.

In the Figure 8, X and Y are the residues of biopolymer chains with some hydrogen affinity; X and Y can belong either to the same chemical species, e.g., both being amylose or amylopectin residues, or to different compounds, e.g., being a polysaccharide and a protein, respectively. Once the number of so-formed direct bonds is large, the structure becomes a tight network where the water diffusion is eventually no longer active. The process is therefore exhausted.

The water molecule would then act as the slider of an interchain zipper that can be shifted unless entanglements stop its course. Because the water displacement would be driven along polymer chains, no long-range order could be directly born. The network formed should be irregular, like that of thermoset polymers and glasses. As for the related enthalpy changes, the mechanism can split in the following steps:

$$X + W \leftrightarrow (X - W) \qquad \Delta_1 H < 0$$

$$(X - W) + Y \leftrightarrow (X - W - Y) \qquad \Delta_2 H < 0$$

$$(X - W - Y) \rightarrow (X - Y) + W \qquad \Delta_3 H \geq 0$$

The overall thermal effect could, therefore, be figured as the sum of three different contributions and would correspond to the formation an interchain link, with an overall exothermic response that can be matched with peak 2.

According to this model, the driving force of the mechanism is the formation of links between chains that shifts the equilibria toward the right-hand side, in the opposite direction they would follow in the absence of the third irreversible step. When the system is cooled down, this force decreases and the equilibria can be shifted to the left-hand side accompanied by an endothermic effect that would correspond to the reverse of peak 2 observed on cooling.

If K_1 and K_2 are the equilibrium constants of step 1 and 2, respectively, while k_3 is the kinetic constant of the third step, the rate of the third process can be phenomenogically described as:

$$v = (k_3 K_1 K_2) \times [X] \times [Y] \times a_w$$

K_1 and K_2 decrease with temperature, both being related to exothermic processes, while k_3 should obey the Williams-Landel-Ferry equation (Williams et al 1955, Slade and Levine 1991) and rise with temperature. Because the peak 2 maximum occurs at 27–30°C, the rate of interchain linking should be maximum at this temperature. It can be argued that such a behavior may depend on the overall trend of the product ($k_3 K_1 K_2$) that would go through a maximum just in this temperature range, as a result of an internal balance among its three terms. As for the a_w that appears in the equation, no large effect can be expected because its value does not significantly change, although a regular variation was observed (Fig. 9) up to a plateau level at aging ≈10 hr.

The commonly observed effect of water binding compounds, like simple sugars, alcohols, pentosans, hydrocolloids, etc., on the rate of staling (Kulp and Ponte 1981) can be accordingly justified. They would indeed compete with large biopolymers for water and reduce a_w, thus hindering water redistribution and starch retrogradation, producing a more plastic structure, and slowing the overall crumb staling.

According to this model, when a sample of bread crumb aged for some hours at room temperature is cooled down, all these events should be quenched, ready to rise again and produce the exothermic DSC signal when temperature reapproaches the room temperature. However, the longer the room temperature aging, the tighter the network formed and the smaller the signal observed (Fig. 7).

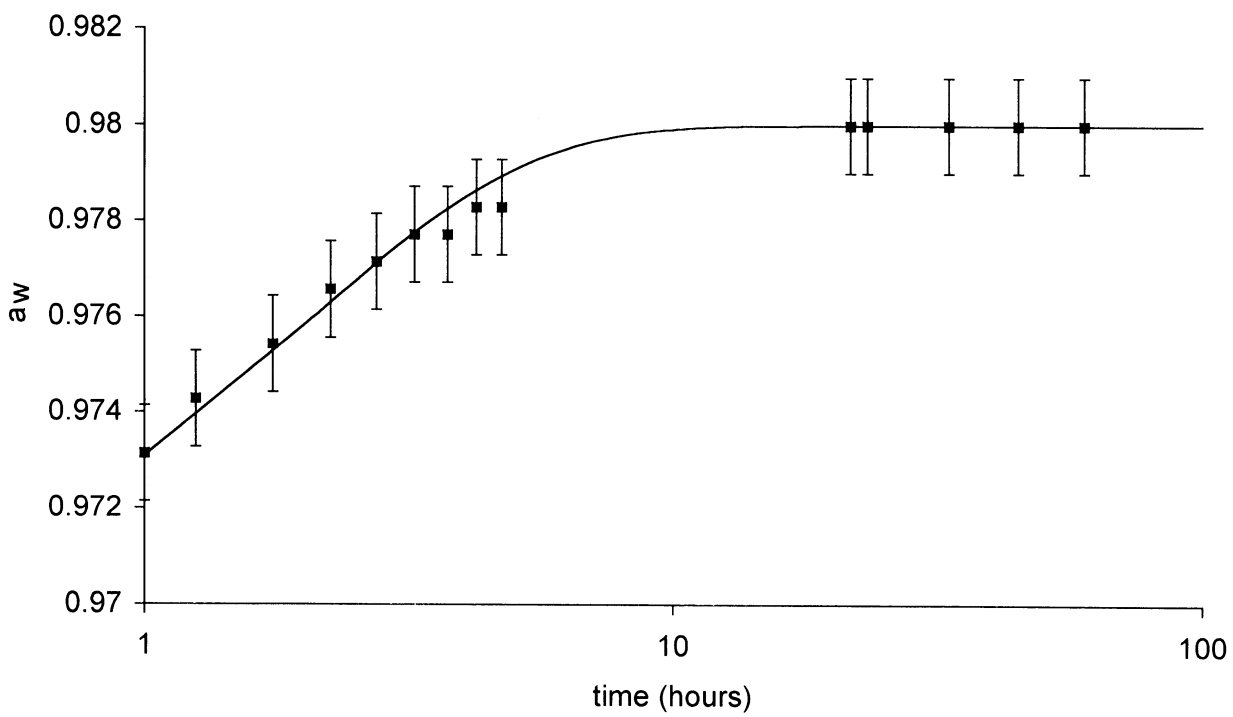

Fig. 9. Trend of the water activity (a_w) vs. aging for control bread samples.

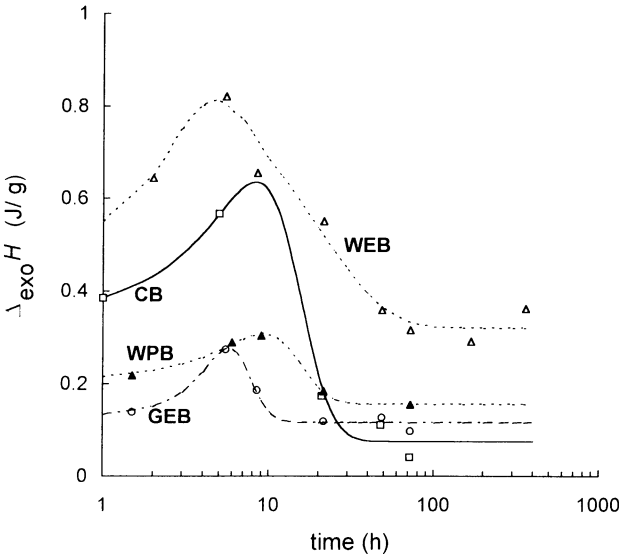

Fig. 10. Comparison between the exothermic effects ($\Delta_{exo}H$) observed for crumb samples from different breads at various aging times. CB = control bread; WEB = water-enriched bread; GEB = gluten-enriched bread; WPB = water-poor bread.

TABLE II
Endothermic ($\Delta_{endo}H$) Values for Various Bread Types[a] with Aging

Time (hr)	CB	WPB	WEB	GEB
1	0.52	0.40	1.00	0.44
5	0.80	1.72	0.74	0.71
8	1.72	···	1.39	1.17
21	2.58	2.00	1.47	1.72
48	2.62	1.80	1.69	1.86
72	2.66	1.72	2.12	1.81
120	···	···	2.28	···
168	···	···	2.82	···
360	···	···	2.81	···

[a] CB = control bread; WPB = water-poor bread; WEB = water-enriched bread; GEB = gluten-enriched bread.

Modified Breads

To attain some preliminary confirmation, breads with modified formulation were investigated. In WPB and GEB, the above mechanism is expected to have a limited effect because of less available water. The intensity of peak 2 was weaker. The opposite occurred for WEB. Figure 10 shows these experimental findings. Note that the intensity of peak 2 goes through a maximum at aging ≈8–10 hr in these breads also. The largest intensity of the exotherm concerns, as expected, the WEB samples that precede CB, WPB, and GEB.

The extent of starch retrogradation appeared in line with the water availability, the relevant endotherm of amylopectin fusion was in the order WEB > CB > GEB > WPB (Table II).

According to determinations of the elastic modulus (g/mm^2), the firmness attained after aging 72 hr was in the order WEB (7.2) > GEB (7.1) > CB (6.6) > WPB (6.3). This result seems to indicate that crumb firmness is enhanced in the presence of gluten, although it decreases with decreasing water content for WEB, CB, and WPB, as in the case of starch retrogradation.

To check a possible correlation between starch retrogradation and bread firmness, the elastic modulus observed for each bread type at various aging was plotted against the fusion enthalpy of amylopectin (Fig. 11). Each bread showed a specific correlation, although all the experimental results remained between the trends observed for WEB and CB. It can nonetheless be noted that, for a given fusion enthalpy, the crumb firmness, i.e., the underlying network tightness, is higher for WEB where more water is available. Therefore, it seems that bread firmness would depend on the formation of a crosslinked network rather than amylopectin crystals.

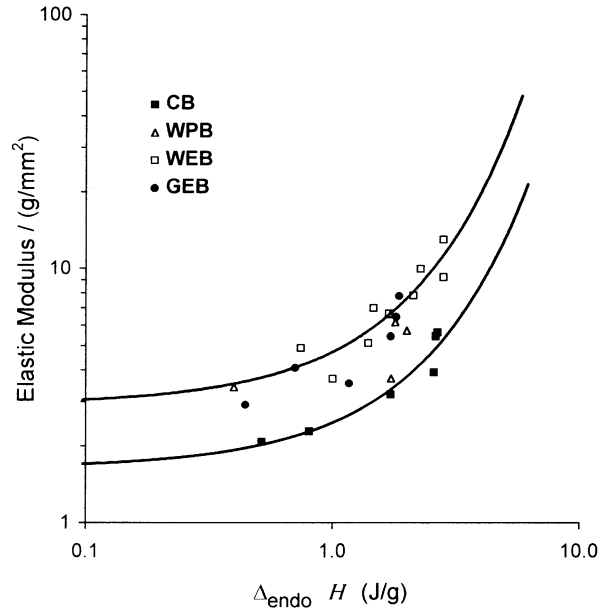

Fig. 11. Plot of the elastic modulus vs. $\Delta_{endo}H$ of amylopectin fusion. CB = control bread; WEB = water-enriched bread; GEB = gluten-enriched bread; WPB = water-poor bread. Trends observed for WEB and CB are evidenced.

CONCLUSIONS

The results of this work add some evidence to the role of water mobility on the structure of the bread crumb and allow tentative expectation of the possible effects of water binding compounds included in the dough recipe. The zipper mechanism proposed is still rather naive and cannot convincingly account for some experimental findings mentioned above: 1) the exothermic peak is not observed when the sample is heated above the temperature range where fusion of the amylopectin crystals occurs; 2) the intensity of the exothermic effect should monotonically decrease with aging with no intermediate maximum.

To hazard some reconciling hypotheses to be experimentally checked in future works, the extension of crosslink network could be supposed to start from previous embryos (possibly crystal nuclei). Once these are destroyed by the melting process, the zipper mechanism would be inactive. This would also justify why the maximum of the exothermic peak is observed only after some previous aging (8–10 hr). On the other end, once triggered, the zipper mechanism might underlay and sustain the crystal growth; the irreversible fraction of the DSC exotherm could be indeed related to this.

Further work is necessary to define the way to control the actual state of water molecules after the dough preparation to the shelf life conditioning of the baked product. In this respect, gluten and soluble proteins and nonstarch polysaccharides that could affect the process should be explicitly included in a more detailed model.

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