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Water properties in wheat flour dough II: classical and knudsen thermogravimetry approach

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Abstract

Thermo-Gravimetric Analysis (TGA) investigations suggest that water in a wheat flour dough is partitioned in various states related to the different disperse phases of the system. Classical TGA results indicate the gross water partition at the macroscopic level, while Knudsen TGA investigations, that allow evaluation of the relative humidity of the dough at room temperature, suggest the involvement of water in the structure of the dough at a supra-molecular level. The overall moisture content, the mechanical stresses and the presence of extra non-starch polysaccharides and/or soluble proteins, can affect this partition, either promoting water displacements across the inter-phases, or modifying the supra-molecular structure of the system. The investigations, extended to bread crumb during ageing, indicate that water undergoes displacements and forms stronger links with the components of the aged crumb with a kinetic law that can be influenced by the presence of extra non-starch polysaccharides.

Keywords: Water; Bread dough; Thermogravimetry; Knudsen TGA

1. Introduction

Water is ubiquitous in food products, where, because of its small molecular mass, is the major mobile component. As it easily forms hydrogen bonds with a number of substrates, water can either solvate ions and/or polar molecules (or functional groups) keeping them apart from one another, or become a structure component of supra-molecular clusters. Water that occupies intermediate sites between solvated molecules, thanks to its high mobility, acts as a plasticizer of the whole system (Slade & Levine, 1995). For these reasons, water is responsible for many physical properties of food systems, as well as for the microbial growth, which can produce degradation processes and texture changes. Studies on the role of water may therefore be referred to as a major sector of the literature on food science.

A number of papers (Bell & Labuza, 2000 and therein quoted literature) are devoted to the thermodynamic activity of water, a_W, which seems phenomenally related to the effects produced by this component. a_W is usually determined at room temperature as a function of the water content, the results of these investigations being typically reported in the form of adsorption/desorption isotherms. Usually, when a true equilibrium is attainable, three regions can be recognized (monolayer water, multilayer and capillary linear region, and solvent or "free" water region) along a given adsorption/desorption isotherm. Unfortunately this description does not match many food systems (were it so, food science and in particular food chemistry would be much simpler). In practice since in most food products water is partitioned among different phases, either as a result of the preparation process or as a consequence of the thermodynamic incompatibility between the polymer components of the system, a single a_W value may have a reliable physical meaning only if a true equilibrium has been attained, i.e., when the system is thermodynamically stable. However almost every food can be referred to as a system far from the true thermodynamic equilibrium

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(Slade & Levine, 1991; Roos, 1995), especially when it is kept below its lowest glass transition threshold (a heterogeneous system has several glass transitions). This means that water in a food system can be found in various states, each with its own water activity. As a consequence, the experimental adsorption and desorption isotherms actually describe a phenomenological property that is time dependent and may not be representative of the whole water content of the system.

A wheat flour dough is an example of such a system. The major components of wheat flour (starch and non-starch polysaccharides, gluten proteins, etc.) are polymers incompatible with one another (Tolstoguzov, 1997; Grinberg & Tolstoguzov, 1997; Fessas & Schiraldi, 2004) and therefore compete for the available water forming separate aqueous phases, each with a peculiar composition. The effects of the whole moisture content on the overall properties of the dough (and the resulting bread) must therefore be explained assessing the behaviour of water in each single phase of the system.

In a previous paper appeared in this Journal (Fessas & Schiraldi, 2001), a description of the properties of the water in a wheat flour dough was drawn from Thermogravimetry (TGA) investigations. The experimental results supported the picture of water partitioned in at least two main states, namely, free to evaporate (with a fickian diffusion law from the core to the surface of the dough), and trapped within a gluten rich phase, from which water can escape only above a high temperature threshold. It was also found that the dough overall moisture and the mechanical stresses and/or relaxations experienced by the sample at room temperature could affect the water partition. These conclusions find some confirmation in recent works (Kim & Cornillon, 2001) where displacements of water in a hard wheat flour dough were determined with NMR relaxometry.

The present paper aims at perfecting the interpretations of the role of water in a wheat flour dough correlating the TGA data with determinations of the relative humidity, RH, of dough samples in isothermal conditions and extending the investigations to the bread crumb at various aging times. The role of other dough ingredients which can be added in small amounts to modify the dough recipe and have proved influence in breadmaking (Fessas & Schiraldi, 1998), like globular proteins and non-starch polysaccharides (water-extracted pentosans), are also described.

2. Materials and methods

2.1. Flour and extracts

Wheat flour was a commercial product with the following non-starch content (w/w with respect to the flour mass): proteins 9.85 ± 0.47 (Kjedahl nitrogen, conversion factor = 5.7), water 14.5 ± 0.2, lipids 1.19 ± 0.01, ash 0.45 ± 0.01. Moisture was determined gravimetrically by heating samples in a ventilated oven at 105 °C for 24 h. This moisture value is only indicative and used for the formulation in the dough preparation. The true dough moisture was attained by thermogravimetry (see below). Soluble (globular) proteins (albumins and globulins in the sense of Osborne) and water extractable pentosans were extracted from centrifuged water suspensions of flour according to a previous work (Fessas & Schiraldi, 1998).

2.2. Dough samples

The wheat flour dough was prepared with wheat flour and distilled water, without adding any salt and yeast for the sake of reducing the number of variables that could affect water partition within the dough. The recipe was modified by changing the water content and/or by adding globular proteins or water-extracted pentosans.

Mixing. Previous observations shows that the mechanical stresses influence the water partition in the dough. In order to compare the results with previously published data (Fessas & Schiraldi, 2001) mixing was performed according to the two procedures described below.

- *Manual mixing dough*. For each type of dough, 30 g of water–flour mixture were manually mixed for 10 min (2 min in a beaker, and 8 min with manual kneading). Two types of dough were prepared in this way: (a) with an overall 42% moisture and no extra ingredients; (b) with an overall 42% moisture added with 0.48% (w/w with respect to the flour mass) liophylized soluble proteins.
- *Mechanical mixing dough*. Dough was prepared mixing 300 g flour + desired amount of water with mechanical mixer (Hobart mixer, USA) for 30 min. The dough was let at rest for 2 h before any measurement. The following types of dough were prepared in this way, namely, (a) with a 40%, 42%, 43.5%, 47% (w/w) overall moisture and no extra ingredients; (b) enriched with 1% (w/w with respect to the flour mass) water-extracted pentosans and an overall 40% (w/w) moisture (aqueous solutions of water-extracted pentosans were used to prepare this type of dough, carefully planning the water content of the solution in order to achieve the desired overall dough moisture).

2.3. Crumb samples

Bread crumb samples were directly produced in the thermobalance pans loaded with 50 mg of a given starting dough [dough was prepared mixing 500 g flour and 52.7% water (w/w with respect to the flour mass) with a mechanical mixer (Hobart mixer, USA) for 10 min. No rest time was allowed. The thermal treatment

experienced included a heating run (2 °C/min) up to 95 °C, followed by cooling down to 25 °C and a 1-h rest at this temperature (in order to simulate the baking process). This treatment transformed the starting dough into a not leavened crumb-like product (no crust was observed on the sample surface at the end of the runs). At the end of the thermal treatment the samples were sealed in plastic bags and stored at room temperature for 0, 0.5, 3, 5, 24, 48, 72, 96 h. This procedure allowed a direct detection and control of the moisture content of the crumb-like samples.

2.4. Classic TGA

The TGA instrument was a SETARAM TG-DSC111 (Lyon, France) with the simultaneous output of the thermal effect (heat flow-vs-T), TG trace, namely, mass loss-vs-T, and its time derivative DTG. The typical sample mass was 30 mg. Each run was repeated at least twice. The ratio between the heat flux and the related mass loss rate was found equal to the enthalpy of water evaporation in whole temperature range. This check confirmed that the mass loss was substantially related to water evaporation only. Possible losses of volatiles therefore were meaningless in our case. This finding is indeed rather common in food systems and, as reported in the literature (Park, 1996), the water content determined trough a TGA run extended well above 100 °C faithfully reproduces the results of a Karl Fisher determination.

All the TG traces were normalized to 100 mg water: accordingly, the DTG traces were expressed as mg of lost water per degree K (with reference to the scanning rate used), and the related heat flow as apparent specific heat, Cp/J K^{-1} g^{-1}.

2.5. Knudsen TGA

Knudsen TGA investigations required substantial innovations of the TGA cell and the operating conditions. The standard pans were replaced with Knudsen cells of similar size, the cover of which (tightly screwed around the external cell surface) had a 20 μm orifice, pierced with an accurately focused laser beam. Details of this technique are reported elsewhere (Schiraldi & Fessas, 2003). The measure cell was loaded with a 30 mg ball-shaped dough sample, while the reference cell was empty and sealed. Once attained the thermal equilibrium at a fixed temperature (25 °C in the present work), a pre-vacuum treatment was performed with a standard pump in order to reduce the pressure within the calorimeter chambers as gently as possible and suck away air bubbles from the sample. When the pressure was reduced below 10^{-2} Pa, the turbomolecular pump was switched on to reduce the pressure in the calorimeter down to 10^{-4} Pa and allow the dehydration process to start.

In Knudsen regimen, the driving force that sucks water molecules out of the cell is the drop of the water partial pressure, p_W, across the orifice. It can be shown (Schiraldi & Fessas, 2003) that the ratio between DTG (dm/dt) traces obtained, at the same temperature and with the same Knudsen cell, from the sample of a given material and a sample of pure water corresponds to the relative humidity, RH, of the material considered:

$$RH = \frac{(dm/dt)}{(dm/dt)^*} = \frac{p_w}{p_w^*},$$

where the apex "*" stands for pure water.

The TG trace (Fig. 1) is a record of the mass decrease that corresponds to the water released, m_W, vs. time, that allows evaluation of the mass of the dry matter, $m_{d.m.}$, as the sample mass at the end of the run. One can therefore plot the $m_W/m_{d.m.}$ ratio versus RH to define the corresponding desorption isotherm.

However, in the operating conditions considered for the present work only about 90% of the overall dough moisture is sucked away (as proved from classical termogravimetry tests on the same sample after the Knudsen TGA measurement), while the remaining 10% does not undergo desorption, in spite of the high dynamic vacuum applied. Accordingly, the sample mass at

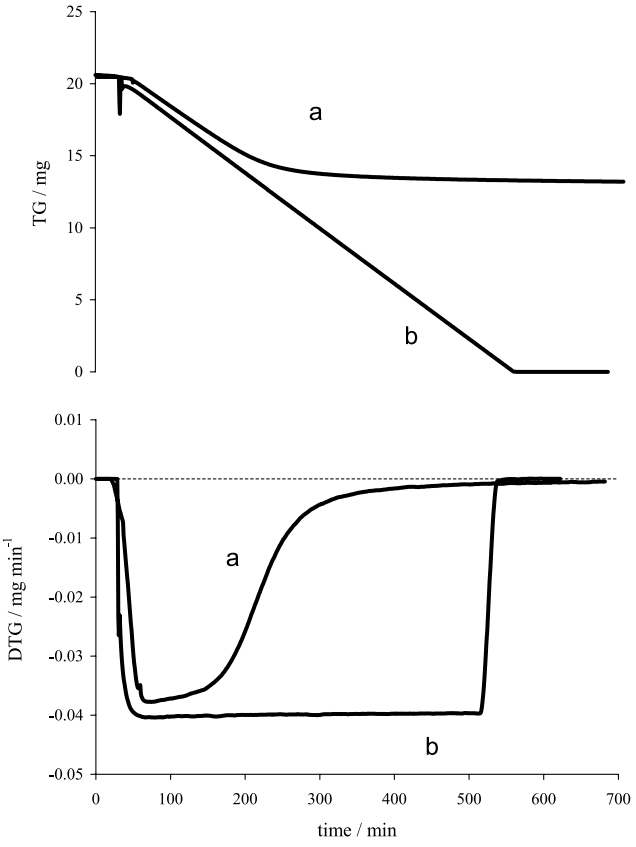

Fig. 1. Knudsen TGA: TG (upper) and DTG (lower) traces of a manually mixed dough sample with an initial 42% overall moisture (curve a) and of pure water (curve b).

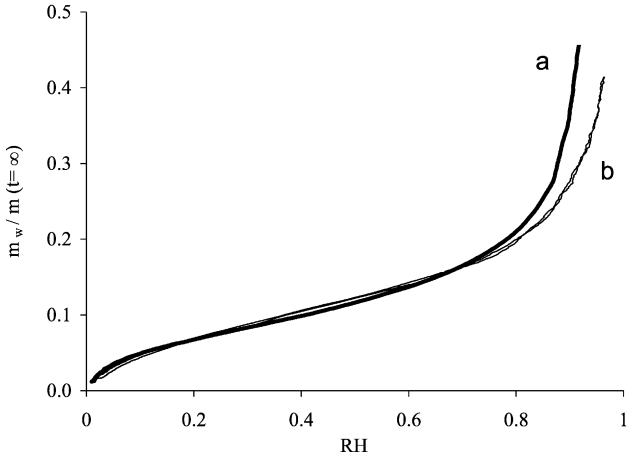

Fig. 2. Desorption isotherms of dough samples with an initial 42% overall moisture: manually mixed dough (curve a); two replicas of mechanically mixed dough (curves b).

the end of the run, $m_{(t=\infty)}$, which does not correspond to the mass of the true dry matter, was used to evaluate the mass ratio, $m_W/m_{(t=\infty)}$, to be plot versus the relative humidity, RH, to obtain the desorption trends (Fig. 2).

3. Results and discussion

Fig. 3 shows the DTG records of standard-recipe dough samples (mechanical mixing and 2 h rest) at different moisture content 47%, 43.5% and 40% w/w. Each record shows two main peaks, the detailed interpretation of which is reported in a previous paper (Fessas et al., 2001). Suffice it to say that these peaks correspond

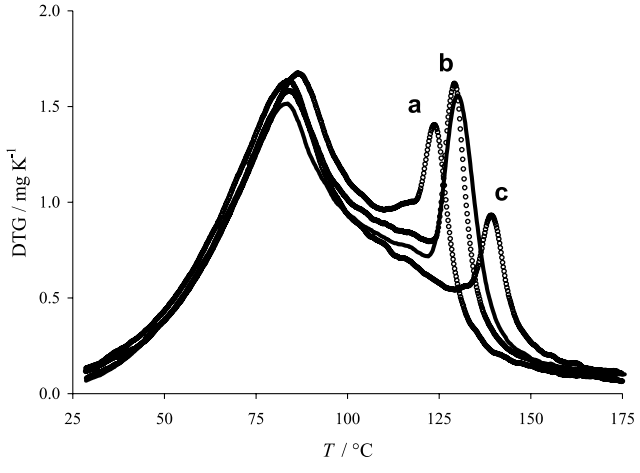

Fig. 3. Classical TGA: DTG traces obtained from dough samples with different initial moisture content, 47%, 43.5% and 40% w/w, (dotted curves a, b and c, respectively) and from a dough sample enriched with 1% (w/w with respect to the flour mass) water-extracted pentosans and an overall 40% (w/w) moisture (thick line). All samples come from mechanically mixed doughs let at rest for 2 h before the TGA run.

to the vaporization of the dough water that therefore would be present in at least two states, namely,

I. Free to diffuse through the medium, whose viscosity increases with increasing T because of the drying and the transformations related to starch and gluten (low temperature peak).
II. Tightly bound to the gluten network and able to flash off only at rather higher temperatures (high temperature peak).

The comparison of the DTG records reported above can be perfected with a mathematical deconvolution of the traces into gaussian contributions. The deconvolution of the DTG traces gives the best fit of the experimental record when three gaussian functions are used (Fessas et al., 2001), i.e., when an intermediate contribution is inserted between the two main peaks described above. This would account for the shoulder of the descending branch of the low-T peak and correspond to a water fraction less tightly bound to the gluten rich phase of the dough. This fraction is strongly affected by the mechanical stresses experienced by the dough in the course of the preparation: it decreases and tends to vanish when the dough is let at rest for a couple of hours (Fessas et al., 2001). The results of this treatment in different replicas of the measurements show that, although most of the dough samples considered in the present work had be let at rest, some minor differences could still exist between them, resulting in a 10% error in the evaluated (by integration of the corresponding gaussian peaks) amounts of the water fractions. None the less the split of the trace is rather accurate and reproducible as for the temperatures of the peak maximums, T_{vap}.

Fig. 3 shows that an increase of the overall dough moisture makes the high-T DTG peak to occur at a lower temperature, while the position of the low-T peak, remains practically unaffected. This implies that the overall moisture of the dough influences the gluten network structure and, in turn, the strength of water binding within this structure. The higher the overall moisture, the lower the binding strength.

Fig. 3 also reports the DTG trace of 40% moisture dough added with 1% (w/w with respect to the flour mass) water-extracted pentosans. In this case too the low-T peak seems unaffected by the change of the dough composition. The high-T peak instead occurs at lower temperature with respect to the reference dough with the same moisture content. It is well demonstrated (Fessas et al., 1988) that in the presence of these polysaccharides a weaker gluten network is formed. Their presence within the gluten phase would therefore affect the gluten structure so as to reduce also its trapping strength for water.

These findings show that classical TGA can provide useful information about the gross partition of water between the dough phases, especially for what concerns

the water trapped within the gluten phase, by monitoring the DTG high-T peak maximum. This approach, however, cannot provide any detailed suggestions about the actual state of water at the molecular and supramolecular level, like those based on the spin–spin and spin–lattice relaxation times determined with NMR investigations (Ruan & Chen, 1998; Hills, 1998; Kim & Cornillon, 2001), which also allow detection of various states of dough water.

Knudsen TGA that was used in the present work to complete the information on the states of water in a wheat flour dough allows a complementary and substantially improved view that may be compared with the conclusions drawn from spectroscopic investigations. This technique, that is described in details elsewhere (Schiraldi & Fessas, 2003), promotes water release at room temperature thanks to the sucking action of a turbo-molecular pump. As already mentioned (see Section 2), in the operating conditions considered for the present work, only about 90% of the overall dough moisture is sucked away. Combined measurements of classic and Knudsen TGA on samples from the same dough matrix show a good correlation (see Fig. 4) between the water content in the gluten phase (high-T DTG peak in classic TGA) and the amount of water remaining in the dough after a Knudsen TGA run. This evidence proves that, at room temperature, the driving force applied in a Knudsen TGA run is unable to sustain the desorption of the water fraction bound to the gluten phase, while it is adequate to draw the water fraction related to the low-T DTG peak.

As a further peculiarity of the desorption that occurs during a Knudsen TGA run, it must be noticed that the softer driving force indeed allows detection of differences that cannot appear in the much harder conditions of a classical TGA run.

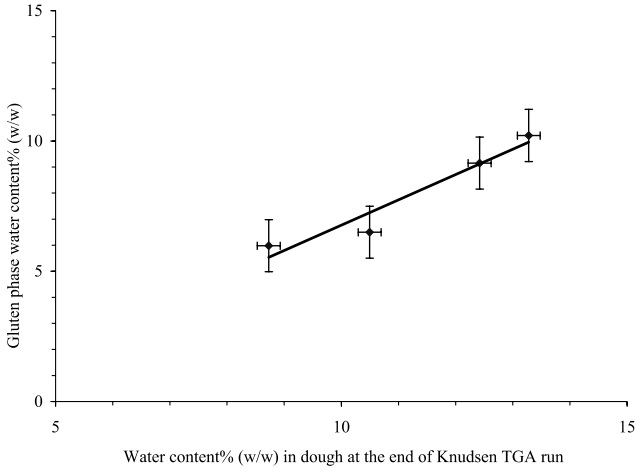

Fig. 4. Correlation between the water content in the gluten phase (evaluated by integration of the high-T DTG peak in classic TGA) and the amount of water remaining in the dough at the end of a Knudsen TGA run. The data come from separate measurements, namely classic and Knudsen TGA, performed with samples of the same dough.

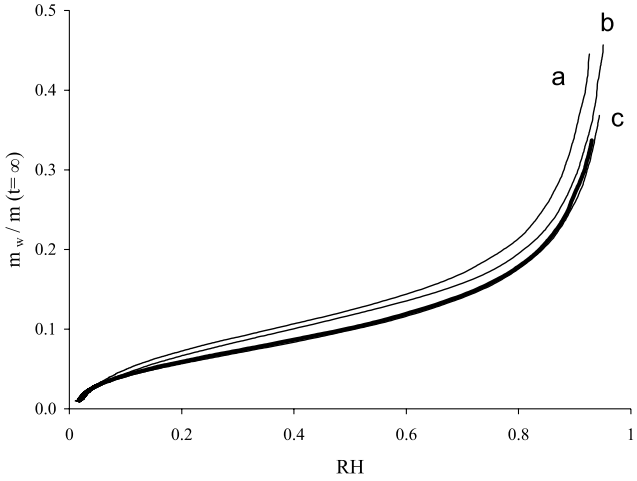

Fig. 5. Knudsen TGA: Desorption isotherms obtained from dough samples with different initial moisture content, 47%, 43.5% and 40% w/w, (thin curves a, b and c, respectively) and from a dough sample enriched with 1% (w/w with respect to the flour mass) water-extracted pentosans and an overall 40% (w/w) moisture (thick curve). All samples were from mechanically mixed doughs let at rest for 2 h before the Knudsen TGA run.

Fig. 5 shows the desorption isotherms of dough samples of a standard-recipe dough (mechanical mixing and 2 h rest) at different moisture content 47%, 43.5% and 40% w/w. and the desorption isotherm of 40% moisture dough added with 1% (w/w with respect to the flour mass) water-extracted pentosans (this is the same type of samples described in Fig. 3).

Examining the curves in the descending way, namely from high to low relative humidity (RH) range, we observe that all the samples at the starting moisture level showed RH$\sim$1 (although the actual RH values could not be precisely detected because of the noise related to the switch on of the turbomolecular pump). This early desorbed water would likely correspond to the most mobile fraction which mainly plays a plasticizing role.

Once the dough moisture attained a lower level, i.e., $m_W/m_{(t=\infty)} \sim 0.5$, (that corresponds to a dough moisture of about 30% w/w), substantial differences could be observed. Surprisingly enough, for a given ratio of lost water, the larger the starting moisture, the lower the RH level attained. Taking into account that a smaller RH value stands for a lower fugacity, i.e., a stronger involvement of water molecules with the adsorbing substrate, one can argue that a larger starting dough moisture would sustain a better structural organization of water within the dough in the non gluten phase.

That water can be a main component of the structure of supra-molecular clusters is a matter of fact assessed on the basis of several experimental evidences, like X-ray diffraction on starches (Zobel, 1988) and NMR investigations on a number of cereal products (Leung,

Magnuson, & Bruinsma, 1983; Richardson, Baianu, & Steinberg, 1986; Hills, 1998), and described with structural and dynamical models (Schiraldi, Piazza, & Riva, 1996; Belton, 1999). Water molecules can occupy intermediate sites between polymer chains, being bound to them through hydrogen bonds. Such bridging molecules still have a relative mobility and can be drawn away from their sites by relatively weak driving forces, like mechanical stresses (see Fig. 2), such as those experienced in mixing, kneading and extruding treatments, or gentle dehydration of the sample. A large moisture content allows an easier re-alignment of the polymer chains and an easier insertion of bridging water molecules within the structure of supra-molecular clusters.

The Knudsen TGA analysis was applied also to dough samples enriched with water-extracted pentosans. Fig. 5 shows that the relevant desorption isotherm is practically overlapped to that of the plain dough with the same starting moisture content. This means that, at this level of concentration (1%, w/w with respect to the flour mass), these polysaccharides do not affect the water properties in the non gluten phase. The shift of the high-T DTG peak toward lower temperatures (see Fig. 3) indeed indicates that these polymers are almost completely involved within the gluten rich phase of the dough, the moisture of which is not released during the Knudsen TGA runs at room temperature. A similar evidence was collected investigating dough samples enriched with extra globular proteins, albumins and globulins (in the sense of Osborne), extracted from the same wheat flour used to prepare the dough. Addition of albumins and/or globulins to the dough recipe did not imply significant changes in the relevant desorption patterns (Fig. 6) which were practically overlapped to that of the reference dough. Once again this lack of effects in the desorption pattern has to be matched with the significant shift of the high-T peak of the DTG record (Fessas et al., 2001) toward higher temperatures. The thermodynamic incompatibility between biopolymers is the basis for this selective action of either extra ingredients (pentosans and globular proteins) in a specific water phase in the dough.

The same experimental approach was used to study water states and displacement in bread crumb samples. In a previous work it was found that the DTG of a freshly baked bread crumb has a trace where two peaks can be recognized (Schiraldi et al., 1996). This finding was confirmed in the present investigation which was extended to the analysis of crumb samples aged up to 24 h. Fig. 7 reports the DTG records obtained. The maximum of the high-T peak (evidenced by the arrows in Fig. 7) was shifted toward higher temperatures in the course of ageing, attaining the rather surprising value of 175 °C for a 24-h ageing.

Since the first peak instead occurred at practically the same temperature, the gap between the signals was

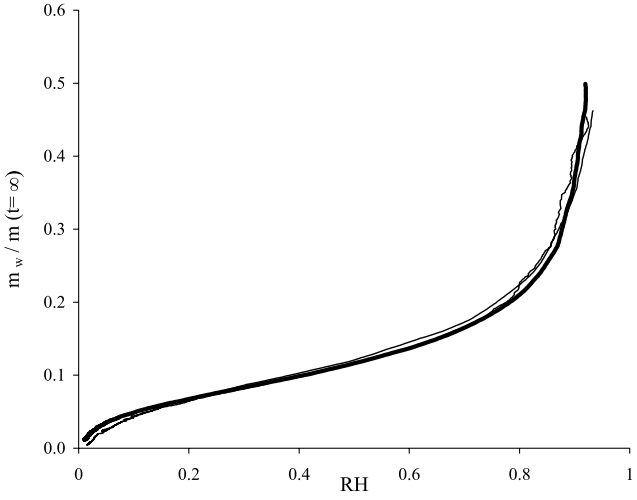

Fig. 6. Knudsen TGA: comparison of the desorption isotherms obtained from dough samples with an overall 42% moisture: no extra ingredients (thick curve); added with 0.48% (w/w with respect to the flour mass) soluble proteins, namely, wheat albumins and globulins in the sense of Osborne (thin curves).

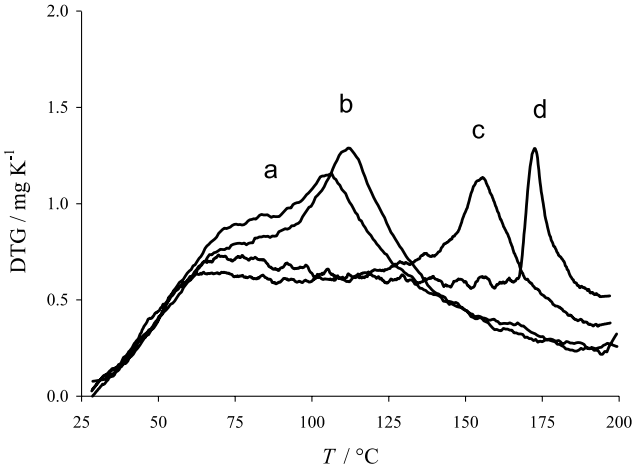

Fig. 7. Classical TGA: DTG traces, obtained from 0, 0.5, 5, and 24 h aged crumb samples.

widened with increasing storage time. It was also apparent that the width of the high-T peak decreased with ageing. This behaviour suggests that the less mobile water fraction could undergo some progressive involvement within the structure of the adsorbing substrate. It has to be noticed that the overall moisture content of the crumb samples considered remained practically unchanged during the storage. This evidence supports the assumption that the "structuring" process of a water fraction was accompanied by some displacement of the remaining water (Piazza & Masi, 1995). Aside from the early vaporized moisture, that reasonably corresponds to the most mobile molecules, there must be a water fraction with intermediate mobility that vaporizes at higher temperature and is re-

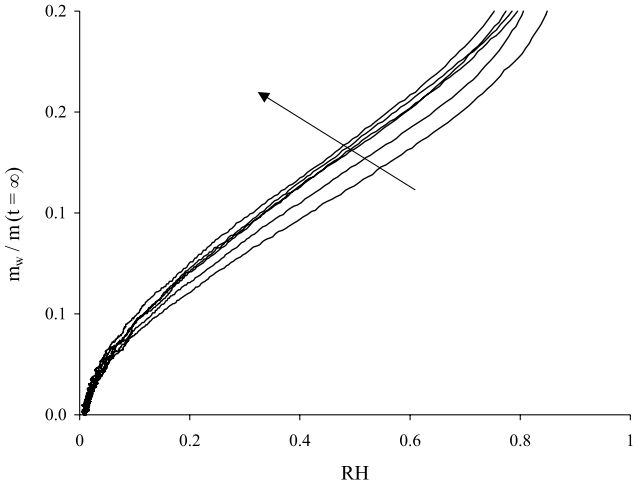

Fig. 8. Knudsen TGA: Desorption isotherms, obtained from 0, 3, 5, 24, 48, 72, 96 h aged crumb samples (the arrow indicates the direction of ageing).

sponsible for the part of the DTG trace that precedes the high-T peak. Taking into account that the area beneath each part of the DTG records corresponds to the relevant amount of vaporized water, the shape of records from the more aged samples suggests that the fraction of this "intermediate" water increases with ageing mainly at the expenses of the fraction responsible for the high-T peak that shrinks.

The relevant desorption isotherms, obtained with Knudsen-TGA investigations on crumb samples, are reported in Fig. 8. Ageing (0, 3, 5, 24, 48, 72, 96 h) was accompanied by a shift of the desorption trend toward lower RH. Once more such a shift was interpreted as a result of the enhanced organization of the adsorbed water, in line with the conclusions supported by the evidence of classical TGA investigations.

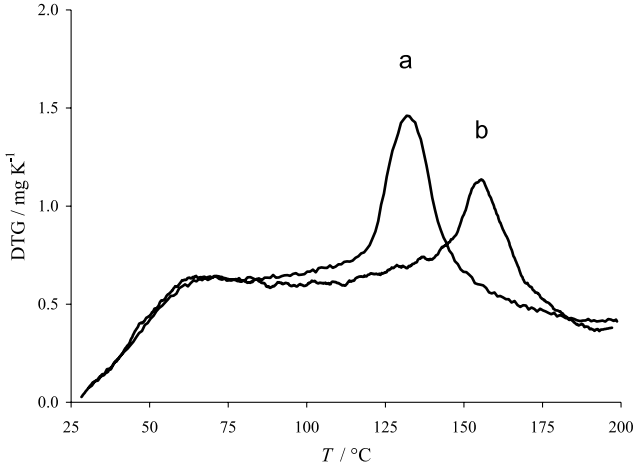

Fig. 9. DTG traces of crumb enriched with 1% (w/w with respect to the flour mass) water-extracted pentosans after 24-h ageing (curve a) compared with a reference sample of the same age (curve b).

When the crumb was prepared from a water-extracted pentosans enriched dough, the DTG trace showed a shift of the high-T peak toward lower temperatures with respect to the reference. Fig. 9 reports the case of crumb enriched with water-extracted pentosans after 24-h ageing compared with a reference sample of same age. This evidence suggests that addition of water-extracted pentosans delays the displacement of water during the bread ageing which is in line with some anti-staling effect as often reported in the literature.

In conclusion we remark that since thermodynamic properties (i.e., incompatibility) is the basis of the action of non starch polysaccharides and globular proteins (Fessas & Schiraldi, 2004) they must be added to the dough after a thorough solubilization in water. Whenever this preparation procedure is not followed, (for example if these extra ingredients are added as liophylized powders to the flour), they can have no reliable and reproducible effects neither in TGA findings nor in the bread-making practice.

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