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Texture and staling of wheat bread crumb: effects of water extractable proteins and 'pentosans'

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Abstract

The increase of crumb firmness prepared from doughs enriched with water-soluble proteins and/or water-extractable pentosans was investigated at various aging times with DSC, to assess starch retrogradation, and with an Instron dynamometer, to determine the elastic modulus. The crumb enriched in soluble proteins became firmer, and that with extra pentosans remained softer than the standard recipe crumb. It was soon evident that neither starch retrogradation nor water loss (due to the crumb-to-crust migration) were affected by the presence of extra proteins and/or pentosans: thus, neither process could explain the observed differences in the trends of the elastic modulus. According to image analysis investigations, the protein-rich crumb had narrow and regular alveoli, which were well separated from one another, whereas a coarser structure was obtained by adding extra pentosans to the dough recipe. It was, therefore, concluded that differences of crumb firmness might be mainly due to the structure formed in the course of leavening and baking, rather than to starch retrogradation and moisture loss. These processes indeed contribute to significantly increase the rigidity of the alveolar walls, but the overall elastic modulus of a sponge-like system, like a bread crumb, largely depends on the manner in which imposed strains are spread through the alveolar structure. Accordingly, for a given rigidity of the alveolar walls, the elastic modulus of the crumb will depend on the size, shape and distribution of the alveoli. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Bread is a biochemically inactive colloidal system (if kept in sterile conditions), where many concurrent changes, such as increase of crumb firmness and harshness, loss of crust crispness, replacement of the 'fresh bread' by the 'stale bread' flavor, contribute to the overall modification toward a sensorially stale product [1]. Because of its economic relevance (significantly reduced market range of bread industrial production), bread staling has been thoroughly studied to recognize the underlying physico-chemical processes [2–7]: however, although some of them have been definitely assessed, the overall mechanism still remains obscure, inasmuch as it is not yet possible to state whether, and to what extent, these processes are related to one another and, therefore, which of them can be referred to as the most responsible [8–10].

It is well known that gelatinized starch undergoes a partial crystallization, usually named retrogradation, when cooled down to ambient or subambient temperatures [11–13]. This transition implies hardening of the starch gel and, therefore, is supposed to be responsible for the increased firmness of the stale bread crumb [14]. Bread starch, however, is not exhaustively gelatinized since the water content of

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doughs is not sufficient to sustain the process thoroughly [15–17]: a great deal of the dough water is indeed intimately associated with other hydrophilic components, like proteins, sugars, pentosans, etc. and becomes only partially available to enhance starch gelatinization in the course of baking. The amount of retrograded starch in stale bread is, therefore, only a minor fraction of the starch content and it is not clear how it could so remarkably affect the overall mechanical properties of the crumb texture. On the other hand, a comparable crumb firmness can be observed in microwave treated bread, where no starch retrogradation can be detected [3] and references therein.

The role of water is another important element of the puzzle. Staling rate is supposed to depend on the moisture content, since a slower staling was observed in breads richer in water [19]; starch retrogradation would, nonetheless, be enhanced on increasing the water content up to 50% w/w in starch gels, being reduced at larger moisture levels which, however, are largely above those of bread crumb [19,20]. In the course of staling of bread, the moisture migrates from the crumb toward the crust [21–24]: the former, therefore, becomes drier and accordingly tougher, since its glass-transition temperature, T_g, rises when the moisture fraction decreases, while the latter loses its crispness mainly for the same reason, i.e. its T_g decreases because of the local rise of moisture [25–27].

The dough ingredients that can affect water activity and mobility, and, therefore, play an outstanding role in the dough behavior on baking [28] when the crumb texture is assessed, as well as in bread staling when water moves from crumb to crust [24]. Although strong correlations are supposed to exist between gluten proteins of the flour and bread crumb texture and staling, many discrepancies are found in literature, most of which can depend on the presence of other components, such as globular proteins (grossly shared into albumins and globulins, according to Osborne [29]), oligo-saccharides, 'pentosans', lipids, glycolipids, glycoproteins, ferulic acid, etc. which can significantly modify the overall dough environment, its behavior on baking, and the staling rate of bread [18,30–37]. It should be stressed that these ingredients do not act in the same way and do not simply compete with one another for the available water. As an example, Delcour et al. [38] found that water-extractable proteins of wheat flour would counterbalance the effect of water-extractable pentosans on the loaf volume of wheat bread, whereas those extracted from rye did not produce the same effect. In the same work, the authors suggested that a main role of water-extractable pentosan would be the increase of dough viscosity, just as observed for addition of other hydrocolloids, such as xanthans, to a standard dough recipe.

Water-extractable pentosans (arabinoxylans and arabinogalactans) are heterogeneous non-starch polysaccharides which, in spite of their small concentration in cereal flours (0.4–0.8% w/w), are believed to have a significant impact on bread properties, like loaf volume, crumb texture and staling rate [39–43]. Many discrepancies, however, remain about the mechanism of their action, possibly because of different separation procedures, actual purity and composition of related extracts (protein and starch residues, arabinoxylan/arabinogalactans ratio), and starch/water ratio of the starting doughs [44–52].

In the present work, water extractable proteins and 'pentosans' were added to a standard bread dough recipe to check the modifications produced in the crumb texture and on its staling rate. In order to reduce the number of variables, both proteins and pentosans were extracted from the same flour used to prepare bread doughs. Since some water-extractable pentosans are bound to protein moieties which could play a major role in the interaction with gluten and non-gluten proteins, the separation procedures followed were aimed at the preparation of solutions containing both globular proteins (viz. albumins and globulins in the sense of Osborne [29]) and pentosans, and solutions containing globular proteins alone. The bread crumb texture was investigated with image analysis and dynamometry, while the extent of starch retrogradation was determined with DSC.

2. Materials and methods

2.1. Flour and extracts

Wheat flour was a "0" type commercial product with the following non-starch content (w/w % of flour mass.): proteins 9.85 ± 0.47, water 14.5 ± 0.2, lipids 1.19 ± 0.01, and ash 0.45 ± 0.01. The protein content was assessed with the Kjeldahl method [53] (conver-

sion factor=5.7), while moisture was determined gravimetrically by heating samples in a ventilated oven at 105°C for 20 min.

Proteins were extracted from centrifuged water suspensions of flour according to the flow sheet reported in Fig. 1. Non-gluten proteins were obtained from the supernatant, where ions, peptides, aminoacids, water extractable pentosans were also present. The pentosan content, determined according to Bubois [54], was 1.5% w/w of the supernatant solution. Because of the salt content of the flour, the ionic strength of the supernatant solution was sufficient for salting in albumins and globulins (in the sense of Osborne). These were separated by elution through a couple of ion-exchange columns with opposite polarity. Two main protein fractions were collected, namely, a 'white' and a 'red' fraction including albumins and globulins, respectively.

2.2. Bread-making

Compositions are given as % w/w with respect to the flour mass:

- *Reference bread* (RB): water 58%; commercial yeast 3.75%, no salt.
- *Bread added with soluble proteins and pentosans* (PAB): water 58% (560 mg of the supernatant solution+17 mg of pure water for 1 kg flour); soluble proteins (in solution) 0.48%; arabinoxylans (in solution) 0.85%; commercial yeast 3.75%; no salt.
- *Bread added with soluble proteins* (PB): water 58%; soluble proteins (lyophilized) 0.48%; commercial yeast 3.75%; no salt.

After a 1 min mixing, water and other ingredients were added to the flour. The dough was then mixed for 10 min and allowed to rest for 10 min. Dough loaves of ca. 150 g were leavened at 30°C for 1 h and baked in a ventilated oven at 225°C for 30 min. Bread loaves were cooled at ambient temperature in cabinets kept at 75% relative humidity. Finally, they were sealed in plastic bags and stored at 25°C.

2.3. Differential scanning calorimetry (DSC)

Calorimetric measurements were carried out with a Mettler DSC 20 apparatus, operating across the 0–100°C range at 2.0°C min^{-1} scanning rate. The raw data were processed with the THESEUS software, according to the procedure of Barone et al. [55], to obtain a smoothened profile and define the base-line, which corresponds to the true heat capacity of the system throughout the temperature range investigated; this was finally subtracted from the smoothened trace to obtain the trend of the excess heat capacity per gram of dry matter, $C_p^{ex}(T)$, which allowed evaluation of the enthalpy drop by direct integration (Fig. 2(A)).

2.4. Dynamometry

Stress-strain, σ vs ϵ, curves (Fig. 2(B)), were obtained from compression tests at a 30 mm min^{-1} compression rate carried out with an Instrom UTM dynamometer (Instron 4301, Instron, High Wycombe, UK). Cylindrical crumb samples (28 mm high, 25 mm diameter) were obtained by boring the core of the loaf. The slope of the straight line trend observed just after the onset of the σ vs ϵ curve was evaluated by regression analysis of the experimental data and referred to as the Young modulus, E, of the crumb, which was assumed as a measure of the crumb firmness [56].

2.5. Image analysis

Crumb images of the central region of bread slices (3 mm depth) were obtained by means of a Hewlett–Packard Scanjet II CX scanner, and then mathematically treated with the Image Pro Plus (Media cybernetics, MD) software to evaluate the distribution of alveoli and determine the ratio between alveolar cross section and slice areas.

2.6. Loaf volume and density

The loaf volume and density were determined with the Archimedes approach using tiny glass spheres of known density. The results reported are the average of five replicas.

2.7. Colorimetry

A Chroma Meter II (Minolta) colorimeter was used (reflecting mode) with a xenon arc-lamp as a light source to determine the chromatic parameters L, a and

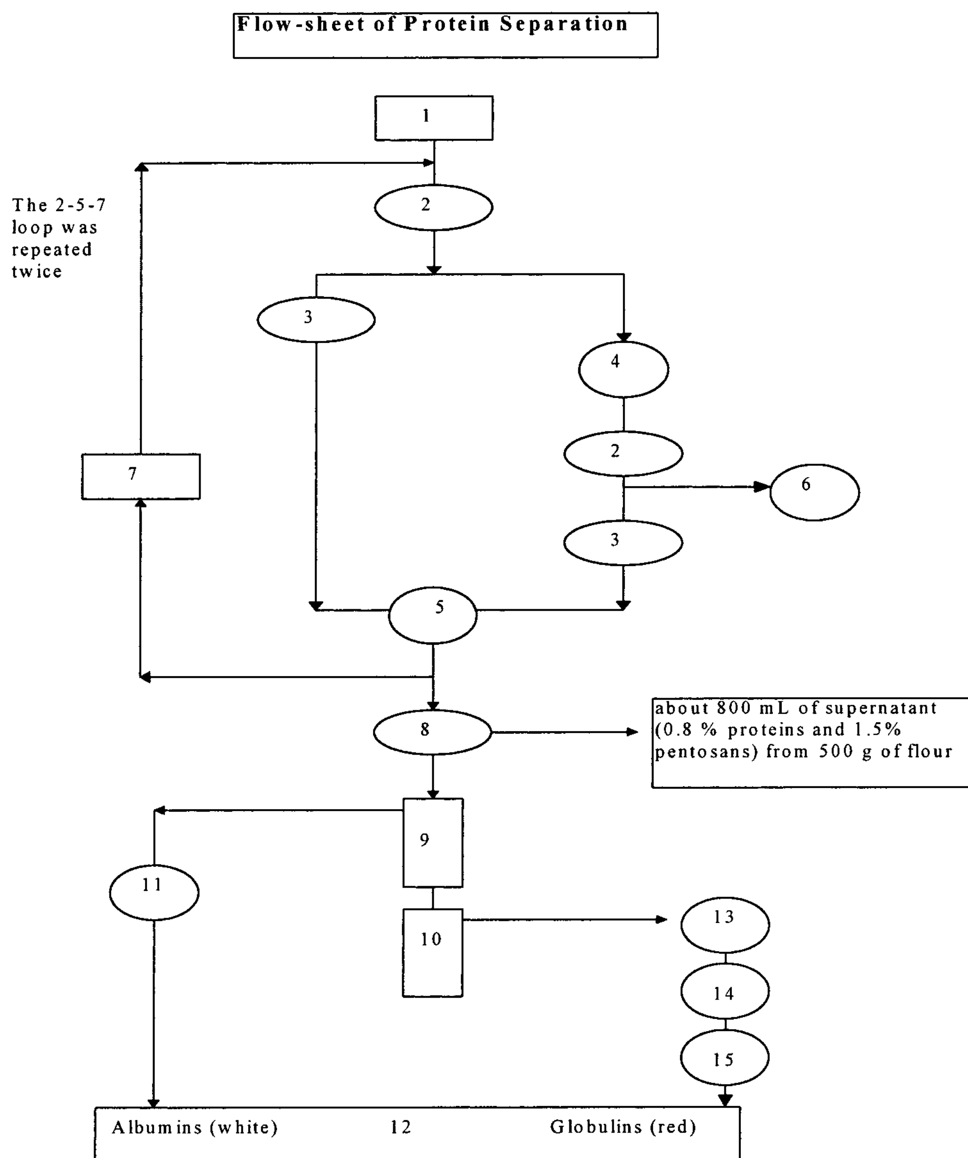


Fig. 1. (1) A flour–distilled water mixture (100 g in 300 ml) is gently stirred for 10 min; (2) the mixture is centrifuged at 10^4 rpm for 20 min; (3) the supernatant is recovered; (4) the precipitate is resuspended in 200 ml of distilled water; (5) all the supernatant recovered is put in a single batch; (6) the precipitate is discarded; (7) fresh flour is mixed with the supernatant (point 5) in a 1 : 3 weight ratio and stirred for 10 min; (8) the final supernatant is recovered and used in bread making; (9) elution with an IEC column packed with DE52 (Whatman) and buffered with phosphate at pH 8.5; (10) the proteins trapped in the column are eluted with 10 mM phosphate buffer (pH 8.5) added with 1 M NaCl; (11) the eluate is centrifuged at 10^4 rpm for 1 h at 10°C to eliminate residual starch in suspension. The supernatant is diluted (1 : 1) with distilled water and reconditioned at pH 8.5 with concentrate NaOH; (12) proteins are precipitated by adding $(NH_4)_2SO_4$ (80% w/v) at 4°C under gentle stirring; the suspension is allowed to rest for 24 h at 4°C; the precipitated is separated by centrifugation at 10^4 rpm for 1 h at 10°C and again suspended in distilled water and dialyzed against water (20-fold volume with 5 bath changes) for 24 h at 4°C. The final solution is lyophilized; (13) the eluated is passed through an S-Sepharose (Pharmacia) packed column (4.5×15 cm) equilibrated with 25 mM acetate buffer at pH 5.5; (14) basic proteins trapped in the column are eluted with 50 mM tetraborate buffer at pH 9.2 containing 0.5 M NaCl; and (15) the eluate is centrifuged at 10^4 rpm for 1 h at 10°C to eliminate residual starch in suspension. The supernatant is diluted (1 : 1) with distilled water and reconditioned at pH 5.5 with concentrate HCl.

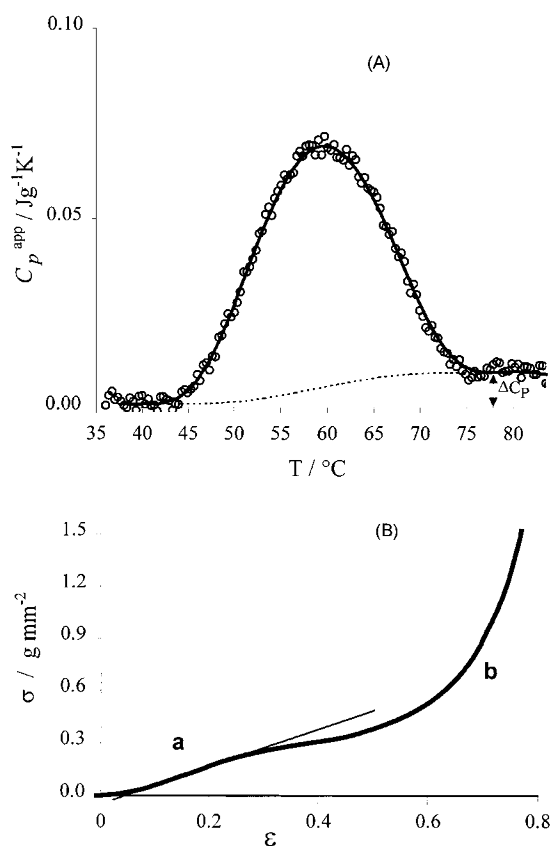


Fig. 2. (A) Smoothing and base line definition of a typical endothermic DSC signal related to the fusion of amylopectin crystals. (B) Typical σ vs. ε trace obtained in a compression test carried out with a Instron UTM: (a) early trend the slope of which was referred to as the elastic modulus, E'; and (b) trend observed when the alveolar walls undergo full compression.

b. Each evaluation was the mean of five determinations in different points of the bread crust: the results reported are the average of three replicas per type of bread.

3. Results and discussion

Volume, density, and moisture loss after baking observed for the tree types of bread are reported in Table 1. With respect to the reference (RB), PAB samples showed larger volume and smaller density, whereas opposite effects were observed for PB samples. The three types of bread underwent comparable moisture losses during baking.

Color parameters (Table 2) indicated that PAB crust was less reflecting and more brown, whereas PB crust was more reflecting and less brown than RB.

The DSC traces of the RB crumb obtained at different aging time (5, 15, 24, 96 h) are reported in Fig. 3. An endothermic peak (absent in fresh bread) was observed at ca. 60°C for aged crumb samples and attributed to the fusion of the amylopectin crystals formed on aging. The corresponding enthalpy change was referred as to the progress of starch retrogradation.

Fig. 4 allows a comparison of the signal obtained after 24 h aging for the three types of crumb (RB, PAB, PB). Fig. 5 reports the enthalpy of fusion of amylopectin crystals determined at the various aging times.

E' (Young modulus) data obtained from the three types of bread crumb at different storage times (Fig. 6) showed a strongly increasing trend. In this case differences were observed: addition of soluble proteins would enhance this behavior, whereas that of pentosans would produce the opposite effect.

Table 2

	L	*a*	*b*
RB	56.2±2	9±1	31±1
PAP	49.7±2	12±1	31±1
PB	58.2±2	9±1	33±1

Table 1

	RB	PAP	PB
Volume/ml	347±5	364±5	320±5
Density/g ml^{-1}	0.355±0.005	0.337±0.005	0.385±0.005
Moisture loss (% of the loaf weight)	18.3±0.5	18.6±0.5	18.2±0.5

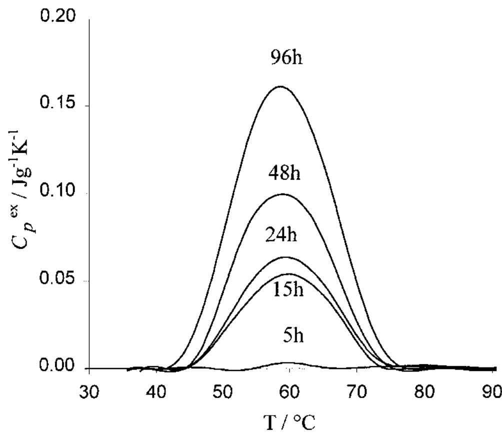


Fig. 3. Increase of the endothermic peak related to the fusion of amylopectin crystals at various aging times.

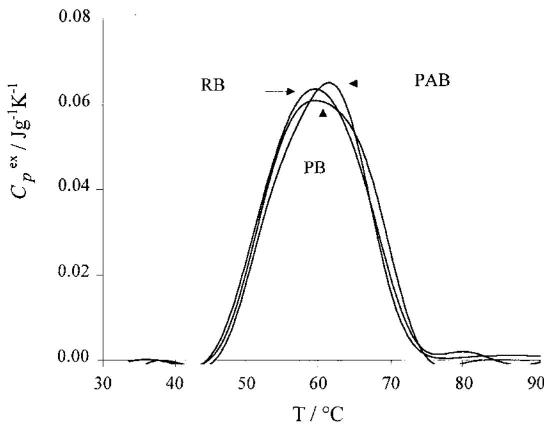


Fig. 4. Comparison of the endothermic peak related to the fusion of amylopectin crystals in 24 h aged crumb samples of different composition: RB, PB, and PAB stand for reference bread, extra protein-enriched bread, and extra protein- and pentosan-enriched bread, respectively.

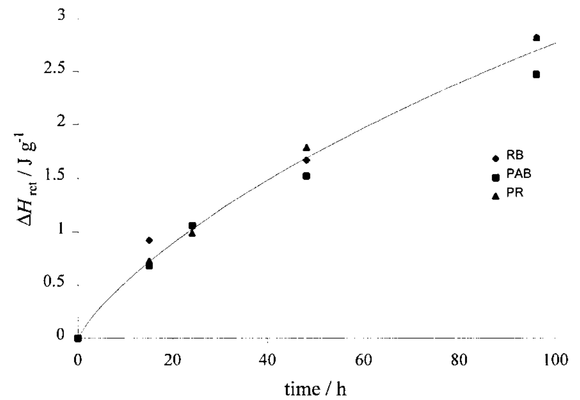


Fig. 5. Enthalpy of fusion of amylopectin crystals vs. aging time in crumb samples of different composition (lettering as in Fig. 4).

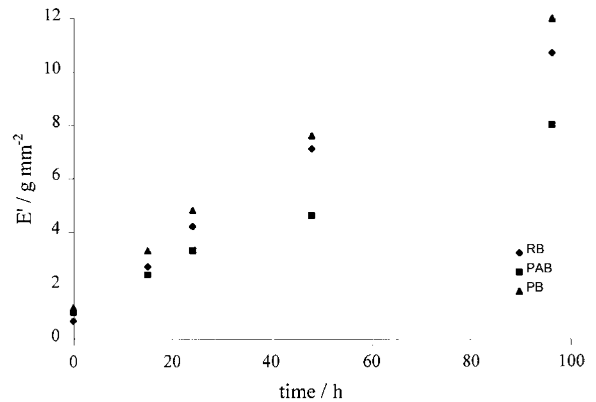


Fig. 6. Elastic modulus vs. aging time for crumb samples of different composition (lettering as in Fig. 4).

It could, therefore, be concluded that, according to the DSC results, starch retrogradation was not affected (neither in the extent nor for the kinetic law) by the addition of soluble proteins and/or pentosans, whereas, according to E' data, these ingredients should play a direct role on crumb firmness, since soluble proteins seemed to accelerate the increase of crumb firmness, whereas addition of pentosans (in the presence of the same protein content) produced the opposite effect. Similar findings had been already reported in a previous work [60].

A main reason for the increase of the elastic modulus could be the moisture loss that occurs within the crumb because of the water migration toward the crust [24] (the total humidity did not change since the samples were kept in sealed pouches). In the present case, however, all the three types of crumb showed the same moisture loss (Fig. 7). This was rather in line with the above conclusions about starch retrogradation which is supposed [19] to significantly depend on the moisture content.

Other processes have been so far proposed to justify the increase of firmness of stale crumb: mobile water molecules could sustain the formation of new cross-link between polymer (starch and/or gluten) chains [3]: because of the involvement of water molecules, such processes could be affected by highly hydrophilic

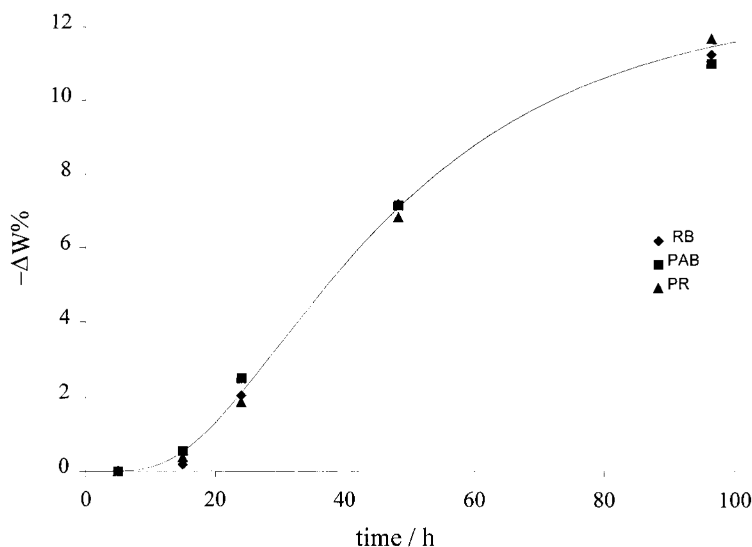


Fig. 7. Water loss (% of initial moisture of crumb in fresh loaves) of crumb samples of different compositions observed at various aging time (lettering as in Fig. 4).

compounds, like water-soluble proteins and pentosans. However, the available data of the present work did not allow to support or reject this hypothesis.

One could only guess that water soluble proteins would sustain the cross-linking within the gluten network, whereas pentosans would be of some hindrance to its extension.

A more tenable interpretation was therefore proposed on the basis of image analysis investigations.

Images of crumb slices and alveolar cross-sectional area (reported as histograms) were obtained through the image analysis of the three types of bread crumb (Fig. 8). With reference to RB, PB showed more regular (spherical) and smaller alveoli, which apparently did not communicate with one another, and a sharper distribution of the alveolar cross-sectional area; the opposite was observed for PAB. The ratios between alveolar cross section and total slice area were 20±2%, 39±2%, and 29±2%, for RB, PAB, and PB, respectively.

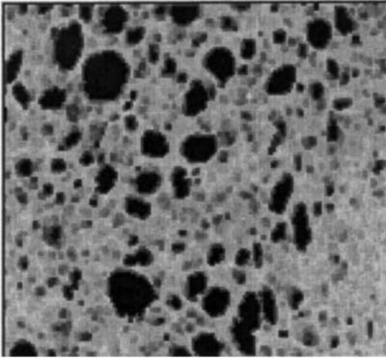
Extra proteins and pentosans can indeed affect water properties and, therefore, produce modification of the alveolar structure. A possible interpretation could come from the finding [57,58] that soluble proteins act as surfactant compounds within an aqueous film that covers the alveolar walls in the course of leavening. Extra proteins would, therefore, sustain an overall development of such interface by producing a larger number of smaller alveoli.

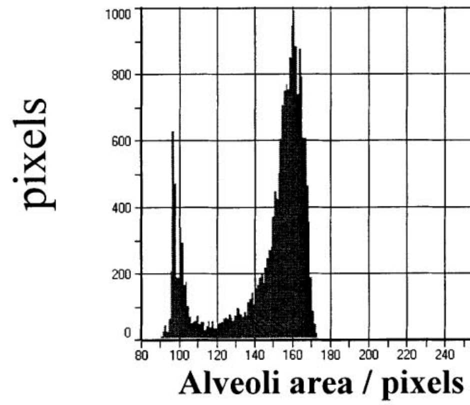
Excess pentosans would instead trap large amounts of water which would be less available to the main components of the dough [59]: as a consequence, gluten mobility and cross-linking would be reduced, together with the extent of the interfacial liquid phase. This would overwhelm the role of the proteins, and broader and irregular alveoli would be formed.

Differences in the E' increasing trends observed for the three types of crumb could, therefore, be related to the alveolar structure formed in the course of leavening and baking; all the other contributions to the crumb firmness (which are practically the same for all of them) would affect the rigidity of the alveolar walls. In other words, the alveolar walls would harden to the same extent in all the types of crumb considered, but the overall sponge-like structure would show different mechanical properties (namely E' trends) because of the shape and distribution of the alveoli.

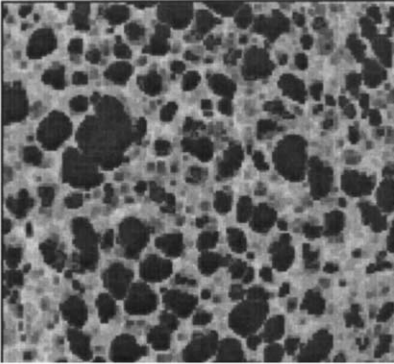
The ($E'-E'_{RB}$) vs t plot (Fig. 9) shows that PB, where alveoli were small and regularly packed, was more rigid, and PAB, where alveoli were broad and irregularly distributed, was less rigid than RB. These differences increased with aging, i.e. with the increase of the intrinsic rigidity of the alveolar walls. This means that when alveolar walls harden, the fraction of

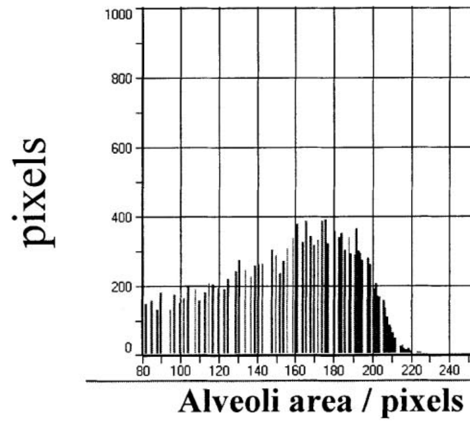
RB



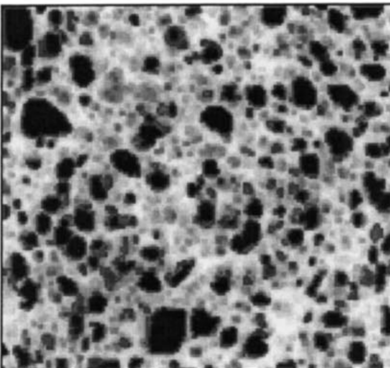


PAB





PB



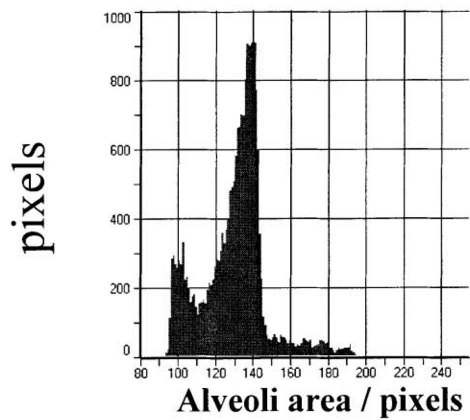


Fig. 8. Images and image analysis of slices of crumb samples (lettering as in Fig. 4). Histograms are the output of the software used and describe size and distribution of alveoli.

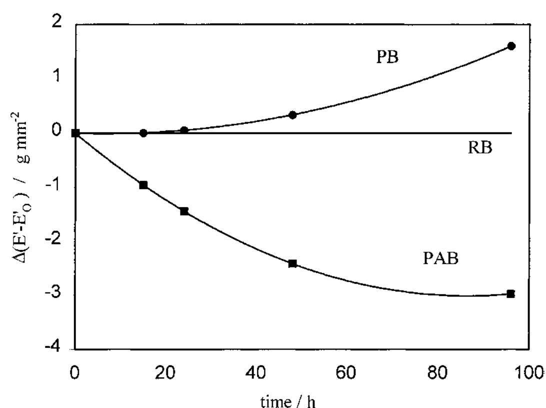


Fig. 9. Comparison of the increase of elastic modulus, E', of crumb samples of different composition observed at various aging times (lettering as in Fig. 4). The E' determined for the crumb of the reference bread (RB) was subtracted from that observed for the other crumb types.

the imposed stress which is spread toward the neighboring cavities increases: small and densely packed alveoli would enhance this effect more than structures with broader and irregularly distributed alveoli.

4. Conclusions

Stale bread crumb are firmer because of a number of reasons: water loss and starch retrogradation run together with crumb aging, but the overall rigidity of a staling bread crumb largely depends on its sponge-like structure, where applied stresses and strains can be spread. The former two processes are practically unaffected by the addition of extra proteins and/or pentosans to the dough recipe, and mainly concern the bulk properties of the alveolar walls. Shape and distribution of the alveoli throughout the crumb are related to the compliance of the gluten network to the expansion of fermentation gases on leavening and baking (either process occurring above the crumb T_g), i.e. when the actual water mobility and availability should play a major role [15].

A tight gluten network, where a large number of cross-links have been formed, underlies a fine and regular alveolar structure. This can occur when the polymer mobility is enhanced by plasticizing water. A further effect could arise because of the surfactant action of proteins that would sustain the development of a larger number of smaller alveoli. If the dough water is bound to hydrophilic non-gluten compounds, like arabinoxylans, it can neither allow adjustments of the polymer chains necessary to the extension of cross-linking, nor form an extended liquid film over the alveolar walls: the gluten network is loose and fermentation gases can expand more easily yielding a coarse alveolar structure.

All these findings and considerations suggest that differences of the increase of firmness in a stale bread crumb containing extra proteins and pentosans may largely depend on its structure formed on dough leavening and baking.

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