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GUIDELINES FOR BUCKWHEAT ENRICHED BREAD
Thermal analysis approach

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Thermal analysis was used to check the role of the main components of buckwheat flour (polysaccharides and proteins) to assess guidelines for novel recipes for bread from wheat and buckwheat flour blends with improved nutritional properties.

The structure-related poor protein quality, namely, the lack of network-forming links, severely limits the use of buckwheat flours in bread-making.

Data from TG and DSC analysis indicate that the introduction of a de-hulling step in the buckwheat milling diagram and the addition of some buckwheat polysaccharide fractions, isolated from the buckwheat husk, that contribute to the formation of the crumb structure thanks to their effect on the phase separation driven by the thermodynamic incompatibility with wheat gluten proteins, allows one to tune opposite effects and obtain bread from de-hulled buckweat/wheat flour blends with alveolar distribution much close that of the wheat bread.

Keywords: *bread making, buckwheat, DSC, food polymers, TG*

Introduction

The increasing demand of improved nutritional quality of food is largely related to the lack of peculiar functionalities of most food products prepared from raw materials and ingredients coming from large scale crops and animal sources that are more easily available for the industrial practice. This trend has severely reduced the diversity of food sources and the diet-related micronutrients that are nowadays recognized crucial for the human health. This is the reason why it can be of interest to recover or extend the use of some products (amaranth, quinoa, oat, etc.) of the traditional agriculture which were, in a not far past, basic food sources selected by human communities because of their peculiar nutritional properties and easy cultivation. One of these products is buckwheat that can grow in harsh environments with a very short growing span. Its flour is widely used to prepare noodles in Asian and European countries, but can also be blended with wheat to produce bread [1–4].

Unlike most cereals, buckwheat is a highly nutritious pseudocereal whose seeds contain starch (65–75%), proteins (10–12.5%) and many anti-oxidants, minerals (K, P, Zn, Mg) and dietary fibers [5, 6]. Among others, rutin (quercetin-3-rutinosid), a flavonol glycoside, is a component of buckwheat flour that antagonizes the increase of capillary fragility associated with hemorrhagic disease and reduces high blood pressure and blood cholesterol [7]. It was found [1, 3, 4] that a buckwheat rich diet selectively stimulates the growth and activity of bifidobacteria and Lactobacilli in the colon.

Buckwheat (BW) is a gluten-free pseudocereal [7, 8] and therefore is a candidate to enter the diet for celiac patients, unless they show a specific intolerance to buckwheat seed proteins (celiac disease is indeed sometimes accompanied by other adverse reactions). These proteins have a high biological value because of the well balanced amino acid composition (rich in lysine and arginine) which is rather close to that of soybean proteins [9, 10].

All these properties make buckwheat a pre-biotic ingredient of the diet. It should be noticed that most of the healthy components of buckwheat prevail in the seed hull, but nonetheless are still present in the flour coming from a standard milling [2, 11, 12].

The salt-soluble fraction of buckwheat proteins (buckwheat globulin, BWG) is a legumine-like protein, with a typical quaternary structure, composed of six acidic and six basic polypeptides that are linked by disulfide bonds, the six monomers being non-covalently bound to one another [5]. Like soybean proteins, BWG shows emulsion-forming and water holding capacity [9, 10] and a peculiar thermal aggregation and gelation behaviour: upon heating, hydrophobic and

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free SH groups become accessible and favour intermolecular interactions and formation of soluble aggregates. Other changes produced by the heat treatment imply the formation of specific unsoluble regular strand aggregates [5, 13]. The buckwheat proteins show a high affinity with the lipids, which can therefore affect their thermal properties [14–16]. These peculiarities make buckwheat flour a good ingredient in many food preparations.

Although most of the chemistry and biochemistry of buckwheat (and related nutritional and health advantages) have been thoroughly investigated and understood, much of the physics underlying the technological properties and potentialities of this pseudocereal has not yet been described. One way to approach this issue is based on the evidence that the behaviour of a flour dough is directly related to the role played by the macromolecules which induce phase separation and govern the water partition [17]. Globular and fibrous proteins, starch and non-starch carbohydrates are responsible for the mesoscopic structure of the dough and determine the texture of the final product, namely dough, bread, pasta, etc. [18]. This is because of the thermodynamic incompatibility between carbohydrate polymers and proteins that makes their aqueous solutions to form disperse systems for concentrations larger than 5% in either polymer [17]. Protein-rich droplets are dispersed in a continuous carbohydrate-rich aqueous phase, the viscosity of which governs the droplet size and the water partition between phases. The molecular peculiarities of the carbohydrates, namely, their molecular size and branching degree, directly affect the water solubility of these compounds and their effect on the viscosity of the continuous phase [19].

A gluten-free dough cannot be satisfactorily leavened, since the dough structure collapses. For this reason no real crumb can be obtained from the dough of a gluten-free cereal flour, unless the collapse of the structure is avoided with a careful adjustment of the viscosity of the continuous carbohydrate-rich phase and a selection of surfactants that stabilize the liquid/air interface.

In the presence of gluten, the phase separation directly affects the tightness of the dough and the alveolar structure of the crumb formed on baking. Every component that can keep the gluten particles apart form one another upon mixing produces a loose dough structure and large and irregular crumb alveoli. This is the case of water soluble arabinoxylans [18]. Conversely, every component that acts as a good surfactant at the liquid/air interface favours the formation of densely packed small alveoli. This is the typical role of globular proteins [18, 20].

These effects are accompanied by a peculiar partition of the available moisture which can be assessed by means of thermal analysis, namely, thermogravimetry (TG) and differential scanning calorimetry (DSC) [18, 19, 21–23].

In this work thermal analysis was used to check the role of the main components of buckwheat flour (polysaccharides and proteins) to assess guidelines for novel recipes for breads with improved nutritional properties.

Experimental

Materials

Flour samples

The flours used in this work were: 1) a commercial wheat flour (WF) produced in Italy (humidity 13.91%; protein 15.18%; starch 77.18%); 2) a commercial integral buckwheat flour (BWI) produced by milling whole commercial grains from China; 3) a commercial buckwheat flour obtained by milling dehulled grains from China (BWD). Composition data for the two buckwheat flours are reported in Table 1.

Preparation of husk extracts and of doughs

The husk coming from the de-hulling/sieving treatment was boiled in excess water for 2 h in order to extract the water soluble compounds. The drained water suspension was concentrated and used to prepare bread dough samples enriched in the extracted substances.

Five types of yeast free and salt-free dough samples for DSC and TG investigations were prepared, namely, with WF (reference), BWI, BWD, a 50 mass/mass% WF/BWI and WF/BWD flour blends (mixI and mixD, respectively), all with 41 mass/mass% moisture content attained by adding de-ionized water.

Table 1 Composition data for the buckwheat flours used in this study

Type of flour	Humidity/%	Proteins/% d.m.	Starch/% d.m.			Fiber/% d.m.	
			total	damaged	amylose	soluble	insoluble
BWI	13.6	12.7	63.0	6.0	13.9	1.2	20.4
BWD	13.9	14.0	72.7	3.8	2.8	0.01	4.5

(d.m. is dry mass)

A simplified (yeast and salt free) recipe was chosen for the sake of reducing the number of variables that could affect water partition within the dough.

The dough preparation requires a suitable mixing treatment. The results of previous works [21] showed that mechanical stresses influence the water partition in the dough. In order to compare the results of this work with previously published data, the dough samples for DSC and TG experiments were manually mixed for 10 min (2 min in a beaker, and 8 min by hand kneading).

The leavened (but not salted) dough used for breadmaking (see table below) instead contained 46% moisture. In some dough recipe the de-ionized water was replaced with the aqueous suspension drawn from 100 g husk (see above) that had been previously concentrated so as to achieve the desired overall dough moisture (typically, 355 mL water or aqueous suspension for 600 g of flour). Five main formulations were studied: WF+de-ionized water, mixI+de-ionized water, mixD+de-ionized water, WF+aqueous suspension, mixD+aqueous suspension. The yeast (Lievitalia S.p.A., Italy) content was 3.75% (with reference to the of the flour mass) for all the recipes considered. A Hobart-N50G mixing machine was used to knead the dough. The dough loaves were set in a metallic mould and baked in an oven equipped with a proofing cell.

Methods

Analytical methods

Moisture was determined as the mass loss after 24 h in a ventilated oven at 105°C. This moisture value was used for the dough recipe, while the true dough humidity for each sample was measured by thermogravimetric analysis (TG, see below). The protein content was assessed with the Kjedahl method (with N×6.25 as conversion factor for nitrogen).

Protein solubility was assessed by extraction into buffer systems of different composition. Buckwheat flour (500 mg) was suspended of in 10 mL of 50 mM phosphate buffer, 0.1 M NaCl, pH 7.0, at 25°C for 30 min. When indicated, 8 M urea and 10 mM dithiothreitol (DTT) were added to the buffer. The amount of soluble protein was determined according to Bradford [24].

Accessible –SH groups were measured directly on suspensions of flour in 50 mM phosphate buffer, pH 7.0, containing 0.2 mM 5,5'-dithiobis-(2-nitrobenzoate) (DTNB, Ellman 1959), and 8 M urea when indicated, following procedures detailed elsewhere [25].

ICC Standard Methods were used to assess the content of total (ICC N. 168) and damaged starch (ICC N. 164), whereas the method of Gibson *et al*. [26] was used to determine amylose. The content in various fiber fractions was measured according to the AOAC Official Method 991.43 (1995).

DSC

A PerkinElmer DSC-6 with 60 μL sealed cells was used. The reference cell contained a suitable amount of distilled water. Measures were carried out in the 20–150°C range with 2.0°C min^{-1} scanning rate. Indium was used for calibration. The typical sample mass was 30 mg. The raw data were worked out with the dedicated software IFESTOS which was assembled by the authors for handling raw calorimetric data according to the suggestions by Barone *et al*. [27]. The base-line chosen to work out a given DSC trace was the DSC record of the immediate re-heating run. It was subtracted from the record of first DSC heating run, which corresponds to the apparent heat capacity $C_p(T)$ of the sample (per gram of dry matter), to obtain the trend of the excess heat capacity, $C_p^{ex}(T)$, which allowed evaluation of the enthalpy drop ΔH by a straightforward integration of the corresponding trace.

Classic TG

The TG instrument was a Setaram TG-DSC111 (Lyon, France) with the simultaneous output of the thermal effect (heat flow *vs*. T), TG trace (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 flow and the related mass loss rate was found equal to the enthalpy of water evaporation throughout the investigated temperature range. This check confirmed that the mass loss was substantially related to water evaporation only, losses of other volatiles being poorly relevant. In such conditions, the water content determined with TG is in good agreement with that obtained with the Karl Fisher method [28].

All the TGA records were normalized to 100 mg water. The DTG and heat flow traces were accordingly given in mg K^{-1} and J K^{-1} g^{-1} units (with reference to the scanning rate used), respectively, the heat flow being converted into apparent specific heat, C_p, dividing the instrument output (in mW units) by the product [sample mass·scanning rate] (in mg K s^{-1} units).

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, Maryland USA) software to evaluate the distribution of alveoli and determine the ratio between alveolar cross section and slice areas.

Table 2 Solubility and accessible thiol content of buckwheat proteins

Flour sample	Soluble proteins/mg (g flour)$^{-1}$		Accessible thiols			
			nmol/mg flour		nmol/mg protein	
	buffer	+8 M urea	buffer	+8 M urea	buffer	+8 M urea
BWI	51.6	85.5	2.30	3.30	44.57	38.59
BWD	55.0	88.3	3.32	4.02	60.36	45.52

Results and discussion

Properties of proteins in buckwheat flours

The solubility of the proteins of buckwheat flour was evaluated by extraction in buffers with different dissociating ability. Previous studies indicated a coarse correlation between the physico-chemical properties of proteins – including their aggregation state – and their behavior during food processing in cereals [29] and in pseudo-cereals [25, 30].

Solubility in phosphate buffer of buckwheat proteins from the two flours – in the presence and in the absence of denaturants – is reported in Table 2. The high content of buffer-soluble proteins confirms that a large fraction of buckwheat proteins (about 50% of the total proteins) belong to the albumin family. Addition of urea increased the amount of extracted protein to about 70% of the total protein (as nitrogen). These figures did not increase significantly when the disulfide reducing reagent dithiothreitol was present together with the denaturant (not shown). This suggests the absence of significant reticulation of buckwheat proteins by inter-protein disulfide bridges. The solubility data collected make it evident that non-covalently bound protein aggregates are present in buckwheat flours, and that the amount of soluble proteins and their aggregation state are quite independent of the de-hulling treatment.

Sulfhydryls (–SH) and disulfides (–S–S–) groups play an important role in the structure and reactivity of food proteins, and, consequently, in the technological properties of flours [31, 32]. The arrangement of thiols in the two buckwheat flours was studied by assessing the amount of –SH groups reactive towards the bulky thiol reagent, DTNB, under the different conditions reported in Table 2. The number of exposed –SH groups was similar either in the presence or in the absence of urea, suggesting that protein denaturation of individual polypeptides and dissociation of non-covalent aggregates did not lead to an increase in the number of accessible thiols. Thus, it appears that acquisition of a compact structure and formation of a protein network depending on the presence and/or formation of intra- and intermolecular –S–S– bonds may be difficult to achieve with buckwheat proteins. However, in the de-hulled flour the content of accessible protein thiols is higher than in the integral flour, both in the presence and in the absence of denaturants. This suggests that some protein components, characterized by a low content in accessible thiols, may be preferentially removed from the grains during the de-hulling step. However, in view of the absence of intermolecular disulfides in all these protein fractions, as proved by our DTT/urea solubility data, these minor changes in composition are not likely to alter the network-forming ability of proteins in either flour.

In conclusion, the overall proteins properties of buckwheat proteins show rather modest variations as a consequence of the de-hulling process, suggesting that the different physico-chemical properties of buckwheat-derived dough, as detected by the thermal investigations reported below, may be mainly ascribed to the polysaccharide components.

DSC analysis of dough samples

Figure 1 reports the DSC traces of dough samples obtained from WF, BWI, BWD, mixI and mixD. Each trace shows the trend expected for the starch gelatinization process (from 45 up to 95°C) followed by the fusion of the amylose-lipid complexes (between 105

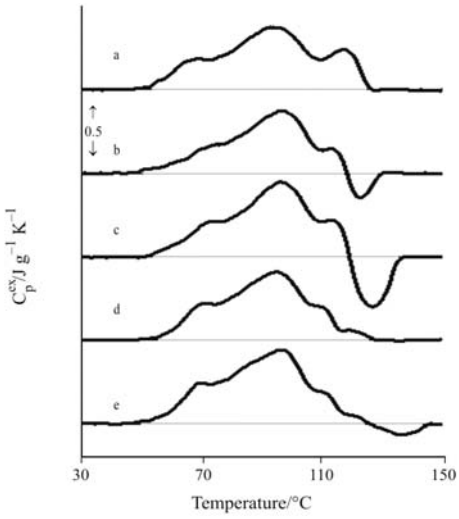

Fig. 1 DSC traces of dough samples prepared with a – wheat b – integral buckwheat, c – de-hulled buckwheat flours and 50 mass/mass% mixed flour, namely, d – wheat + integral buckwheat and e – wheat+de-hulled buckwheat. Every dough had a 41% moisture content

and 115°C) [33, 34]. Major differences instead appear at higher temperature, where BWI and BWD traces show a large exothermic effect that can be mainly related to the aggregation of proteins that are much more abundant in buckwheat than in wheat flour. The protein content in BWD flour is higher than in BWI, as shown above, because the de-hulling treatment eliminates many other non-starch and non-protein ingredients. Accordingly, the relevant aggregation exotherm is larger in the BWD than in the BWI trace.

Literature reports [17] and our previous work [18, 35] support the expectation that starch carbohydrates and flour proteins are thermodynamically incompatible and therefore may not be involved in specific direct interactions with each other. The phase separation driven by the thermodynamic incompatibility implies that conformational and structure transitions experienced by carbohydrates and proteins of a given dough are not chemically correlated, the only allowed interactions being those related to physical properties of the relevant phases and interfaces, namely, steric hindrance, surfactant effects, water displacements, phase viscosity, etc. The same can be said for the interaction between starch carbohydrates and gluten proteins, as proven by isothermal titration calorimetry investigations [35]. These inter-phase interactions govern the formation of the macroscopic structure and the texture of the final baked product [18].

The DSC data of the present work allow a further support of this view. The first evidence comes from the comparison of the DSC records obtained from BWI dough samples with different moisture contents (Fig. 2): the endothermic components related to starch gelatinization and fusion of amylose-lipid complexes (mainly, the peak maxima) move toward lower temperature on increasing the overall dough water content [33], while the exothermic effect related to the protein aggregation moves in the opposite direction [35]. This is just the behaviour expected from each single component of the flour: gelatinization of starch granules in an aqueous suspension and the fusion of amylose-lipid complexes in a given dough are actually shifted to lower temperature (although the onset of the former remains unchanged), while proteins in aqueous solutions undergo unfolding and aggregation at higher temperature, when the water content of the system is increased.

Were there any direct interaction between different dough biopolymers (namely, carbohydrates and proteins), the change of moisture content would produce some 'intermediate and balanced' effect on the temperatures of the DSC peaks.

The second strong evidence comes from the fact that it is possible to 'reproduce' the mixI DSC trace as the weighed sum of the WF and BWI records. This

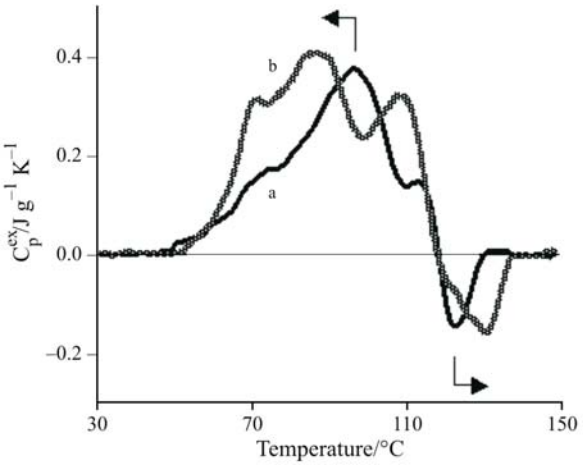

Fig. 2 DSC traces of buckwheat flour dough a – with 41% and b – 46% moisture content. arrows point toward the relevant drift on increasing moisture (see text)

approach requires some preliminary considerations about the mixed flour dough: a) gluten is largely replaced by buckwheat proteins that are the major protein components of BW flour; b) gluten can hold water much more tightly than buckwheat proteins (see below); c) because of these facts, the starch rich phase can trap more water than in the presence of larger amounts of gluten. Accordingly, for a given overall dough moisture, the starch-rich phase of the mixI dough has a larger water content, while the protein-rich phase is more concentrated than in either WF or BWI flour dough. As a result, the mixI DSC trace should have both starch-gelatinization (including fusion of amylose-lipid complexes) and protein-aggregation component shifted toward lower temperature with respect to the corresponding signals of the WF trace.

The weighed sum (50% of each trace) has therefore to be performed after a rigid shift of the whole BWI trace toward lower temperature: it was found that a 4-degree shift is enough to meet the expectation (Fig. 3).

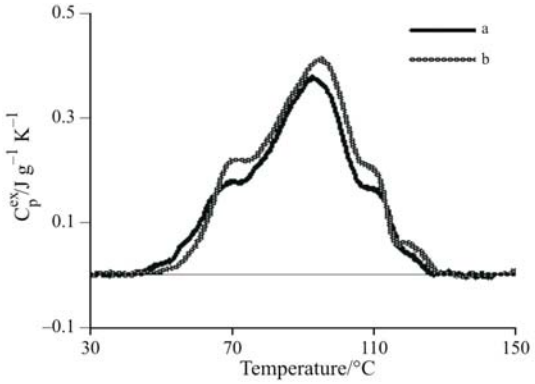

Fig. 3 Match of the a – weighed algebraic sum of the DSC traces obtained from WF and BWI flour dough and the b – experimental DSC trace obtained from a mixI flour dough sample. The water content is 41% for either trace

TG analysis of dough samples

Previous work was devoted to study the water partition and displacements in wheat dough and bread by means of classical and Knudsen TG [21–23]. In this kind of dough gluten tightly traps a fraction (about 15%) of the moisture that is released well above 100°C, while the rest of the moisture undergoes a diffusion limited evaporation throughout a wide temperature range. The overall DTG record of this kind of dough (Fig. 4, WF dough curve) therefore shows a couple of major signals, namely, a broad signal which accounts for the easy-to-remove water and a narrow peak that mainly deals with the moisture fraction trapped by gluten. The temperature gap between the two maxima is related to the looseness of the gluten network: the smaller the gap, the looser the network [18, 21]). The sample of a dough enriched with few (0.5–1 mass/mass%) soluble polysaccharides of large molecular mass, like arabinoxylans, shows a DTG record where the two peaks are closer to each other [14]: the gluten network is therefore loosened by the arabinoxylans and, as accordingly expected, a larger fraction of free SH groups is accessible. The results of several previous works concur to support the conclusion that the overall moisture content, the mechanical stresses and the presence of extra non-starch polysaccharides and/or soluble proteins can affect water partition, either promoting water displacements across the inter-phases, or modifying the supra-molecular structure of a wheat dough [21].

The DTG records obtained in the present work from BWI and BWD flour dough samples show a single broad peak (Fig. 4). Similar DTG traces were obtained from dough samples prepared with other cereals, pseudo-cereals and legumes which do not contain gluten, but have a comparable or larger overall protein content with respect to wheat. This finding has to be interpreted as follows: the aqueous phases that are separated because of the thermodynamic incompatibility of their solutes (carbohydrates and proteins) can easily exchange the solvent between one another. The water that evaporates from one aqueous phase is quickly replaced by the water migrating from any neighbouring aqueous phase. As a result, the dehydration of the samples looks like a single process governed by the core-to-surface diffusion of moisture. This means that there is no real competition between starch polymers and non-gluten proteins for fixing water. A minor shoulder on the DTG peak relevant to the BWD dough may indeed be related to the soluble protein rich phase which, for this kind of dough, is more concentrated than for either WF or BWI. Nonetheless the effect is much less striking when compared to that of gluten.

Figure 5 shows the DTG records obtained from mixI and mixD flour doughs. In either of them the 'gluten peak' is present, although in the case of the mixI sample it is much closer to the first broad evaporation signal. This finding is in line with the expected effect of the soluble non-starch carbohydrates of the buckwheat husk which should indeed play the same role as the arabinoxylans on the tightness of the gluten network (see above). It must be said that such differences are more striking for low moisture contents and tend to vanish in the presence of excess moisture, because the competition for the available water becomes much weaker.

This information was of help in some tentative bread making trials aimed at confirming the expectations about the alveolar structure of bread loaves produced from these types of dough.

Image analysis of bread crumbs

Thin slices of bread loaves were used check the extension and the homogeneity of the alveolar structure of the crumb. Figure 6 shows the pictures of four different breads obtained from WF (Fig. 6a), mixI

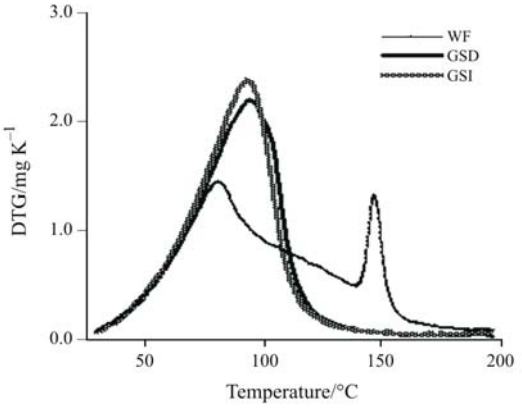

Fig. 4 DTG traces from dough samples of wheat WF, BWI and BWD flour with 41% misture content

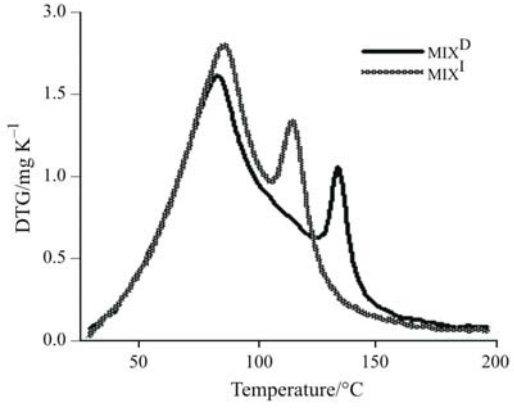

Fig. 5 DTG traces from dough samples of mixI and mixD flour with 41% misture content

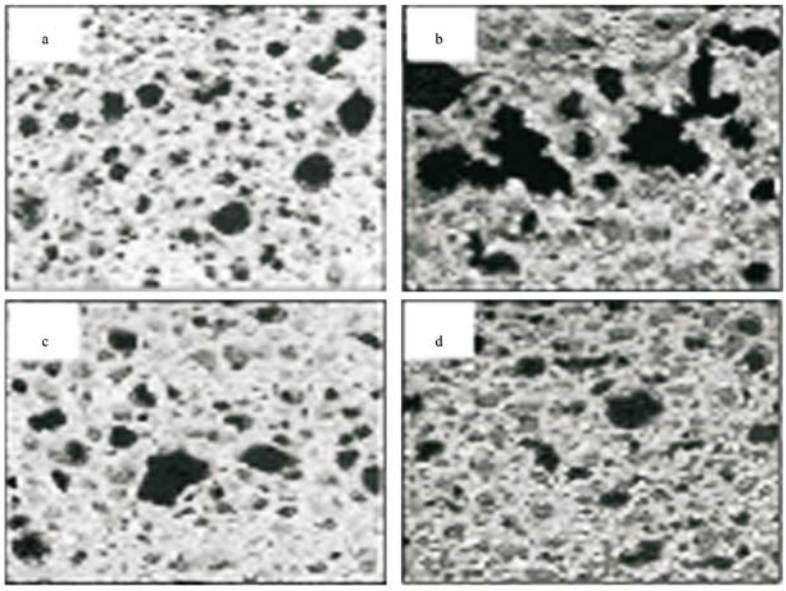

Fig. 6 Pictures of the alveolar crumb structure of bread from a – wheat, b – mixI, c – mixD and d – mixD added with soluble polysaccharides. Image scanning zoom was set 1:1. The original dimension of each picture is 5.5×4.0 cm

(Fig. 6b), and mixD (Fig. 6c) dough. Figure 6 is related to mixD enriched with soluble non-starch polysaccharides.

Figure 6b relevant to the mixI bread shows a 'broken' crumb, with large and irregular alveoli, which can be seen as a consequence of the lower gluten content and the effect of soluble non-starch polysaccharides that weaken the gluten network. A different picture is that of the mixD bread (Fig. 6c), where the alveoli are still irregular but smaller and distributed in a more tight matrix. In this mixD dough the effects of soluble non-starch polysaccharides is reduced and counterbalanced by that of the globular proteins which act as surfactants that stabilize the dough matrix/air interface. Addition of water soluble polysaccharides, extracted from the buckwheat husk ('Materials and methods'), allows one to tune these effects and obtain an alveolar distribution much closer than of the wheat bread.

Table 3 reports the % values of loaf volume and alveolar area (that is assumed as representative of the alveolar volume in a selected crumb region).

Although the alveolar distribution and mean size of the wheat bread has been attained by enriching the mixD dough with soluble polysaccharides, the overall loaf volume is smaller. This finding is in line with the above reported results relevant to the chemical properties of the BW proteins, which cannot replace gluten as they do not form disulphide cross-links, but play a simple surfactant role.

Table 3 Percent of loaf volume with respect to the reference bread from WF and percent of alveoli area for a given crumb surface

System	Loaf volume/%	Alveoli area/%
WF	100	23
MixI	73	60
MixD	66	16
MixD1	69	27

Conclusions

This study shows how the physico-chemical and structural properties of proteins and polysaccharides in buckwheat are differently affected by the introduction of a de-hulling step in the milling diagram. Molecular evidence indicates that the protein fraction is relatively unaffected by de-hulling (safe for the removal of thiol-poor proteins that apparently are more abundant in the outer layer of the grains).

Conversely, data from TG and DSC analysis indicate that de-hulling removed some polysaccharide fractions that are relevant to the formation of the crumb structure, thanks to their effect on the phase separation driven by the thermodynamic incompatibility with gluten proteins.

The structure-related poor protein quality, namely, the lack of network-forming links, severely limits the use of buckwheat flours in bread-making. However, water soluble polysaccharides isolated from the BW husk allow the preparation of acceptable breads from de-hulled BW/WF blends.

This role is highlighted by DSC and TG investigations which therefore seem promising tools for further studies on products from other cereals and pseudocereals.

Acknowledgements

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