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Bread staling: Effect of gluten on physico-chemical properties and molecular mobility

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ABSTRACT

Three gluten enriched breads were produced (5% and 15% gluten samples where water was adjusted with farinograph determination, and a 15% sample with the same water amount of the control). The effect of gluten on bread staling (7 days) was evaluated, focussing on texture, amylopectin retrogradation, water status and ^{1}H molecular mobility.

The addition of gluten at higher levels (15%) resulted in breads, that retained higher softness, springiness and cohesiveness upon storage. Crumb moisture content was not affected by gluten but at a macromolecular level (DSC) 15% samples showed higher frozen water content. NMR measurements showed a significant effect of gluten on proton T_2 relaxation time distributions, revealing a larger presence of protons strongly interacting with water and a more pronounced proton exchange with increasing storage time. The results suggested that, in the presence of gluten, a larger amount of water might be available to plasticize the crumb structure, resulting in a softer product.

1. Introduction

Bread staling is a process that originates from different physico-chemical events occurring in different space-time domains, and resulting in crumb hardening, crust softening and loss of the characteristic fresh flavour of the product (Gray & Bemiller, 2003).

Starch, gluten and water, the major components of bread crumb, undergo major modifications during storage that lead to the development of a staled product. The role of starch has been extensively investigated and in particular starch retrogradation is known to contribute to crumb hardening during storage, but significant evidence is available to indicate that other factors contribute to bread staling, including water and gluten network changes (Hallberg & Chinachoti, 2002; Vodovotz, Vittadini, & Sachleben, 2002).

Water is recognized to play a fundamental role in bread staling, in terms of both macroscopic and molecular redistribution during storage. A macroscopic migration of water occurs from crumb to crust (Baik & Chinachoti, 2001; Lin & Lineback, 1990; Schiraldi & Fessas, 2001), but also at molecular level water changes its location and status: it becomes partially incorporated in retrograded amylopectin crystals (Imberty & Perez, 1988), looses phase separating capability (decreased "DSC freezable water" content) (Slade & Levine, 1991; Vittadini & Vodovotz, 2003; Vodovotz, Hallberg, & Chinachoti, 1996), and is redistributed among bread domains (Callejo, Gill, Rodriguez, & Ruiz, 1999; Leung, 1981; Slade & Levine, 1991). Water molecular mobility (probed by nuclear magnetic resonance) has been found to decrease during storage (Chen, Long, Ruan, & Labuza, 1997; Sereno, Hill, Mitchell, Scharf, & Farhat, 2007; Vodovotz et al., 2002).

The gluten network represents, with leached amylose, the continuous phase of bread, and its proper formation and hydration contributes to the perceived characteristics of a fresh bread. During storage of bread the gluten network is expected to undergo physico-chemical changes (i.e. dehydration and, consequently, loss of plasticity/flexibility; modified interaction with starch), contributing, possibly, to bread staling. However, a positive effect of gluten has also been reported, in starch-gluten model systems, where gluten reduced starch recrystallization (Eliasson, 1983a, 1983b; Ottenhof & Farhat, 2004) and interacted via hydrogen bonds with starch partially preventing its recrystallization (Every, Gerrard, Gilpin, Ross, & Newberry, 1998; Kim & D'Appolonia, 1977; Martin, Zeleznak, & Hoseney, 1991). The addition of gluten to bread has been reported to reduce bread firmness (Callejo et al., 1999) and to

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improve bread loaf aspect and flavour sensory analysis (Codina, Bordei, & Paslaru, 2008). A role of gluten in modifying water molecular redistribution during storage has also been suggested (Schiraldi, Piazza, & Riva, 1996; Vodovotz et al., 2002). However, more research is needed to better understand the role of gluten in bread staling, also in relation to its effect on starch and water.

Low resolution ^{1}H NMR spectroscopy has been previously applied to investigate molecular mobility in model systems and bread, in an attempt to relate how water, starch and gluten are interacting at a molecular level and their relation to product properties (Bosmans, Lagrain, Deleu, Fierens, Hills, & Delcour, 2012; Bosmans, Lagrain, Ooms, Fierens, & Delcour, 2013; Chen et al., 1997; Curti, Bubici, Carini, Baroni, & Vittadini, 2011; Curti, Carini, Bonacini, Tribuzio, & Vittadini, 2013; Engelsen, Jensen, Pedersen, Norgaard, & Munck, 2001; Sereno et al., 2007; Wang, Choi, & Kerr, 2004).

The aim of this work was, therefore, to study the effect of different gluten levels on bread staling, by focussing on physico-chemical properties and proton molecular dynamics.

2. Materials and methods

2.1. Bread formulation and storage

Four bread types were produced according to the formulations reported in Table 1. A control bread (STD) and two bread formulations where flour (moisture 14%, proteins 12.5% dry basis, ash 0.65% dry basis, fibre 2.5% dry basis, starch 84.35% dry basis, Molino Seragni s.p.a., Rivolta D'adda, Italy) was partially substituted with 5 g gluten/100 g flour (GLU5) and 15 g gluten/100 g flour (GLU15) of vital wheat gluten (moisture 10%, gluten 81% dry basis, ash 1% dry basis, Roquette Freres, Lestrem, France) were produced. The amount of water added to the formulations was adjusted by measuring water absorption at 500 BU (Brabender Units) (AACC Method 54-21.02). In an attempt to better discuss the effect of gluten and water in the formulation on water status and physico-chemical properties of bread, a 15 g gluten/100 g flour enriched bread ($GLU_{std}15$) was produced adding the same amount of water used for STD.

Bread loaves were produced with a home bread-maker (BM3986, Severin, Sundern, Germany; first kneading, 43 min; second kneading 56 min; first fermentation, 45 min; smoothing 1 min; second fermentation, 18 min; smoothing 1 min; third fermentation, 35 min; baking, 55 min). Bread loaves were cooled to room temperature, placed in polyethylene bags sprinkled with about 4 ml of ethanol and stored at room temperature. Samples were analysed fresh (day 0) and after 1, 3, 5 and 7 days. Two bread productions were carried out on different days.

2.2. Volume and crumb grain

Volume of bread loaves was measured following the American Association Cereal Chemistry 10-05 method (Guidelines for Measurement of Volume by Rapeseed Displacement). Three bread loaves were used to measure loaf volume of each formulation.

Crumb grain was studied by means of a Image Pro Plus digital image analysis software (Media Cybernetics, Bethesda, USA) as previously described (Curti et al., 2013). Three bread loaves were analysed for each formulation. Images (600 dpi resolution) of the three central slices (20 mm thickness) from each loaf were captured with a scanner Scanjet 8200 HP (Hewlett–Packard, Cupertino, CA, USA). The total number of pores (expressed as percentage) was measured in six preselected areal dimensional classes: class 1: 0.01–0.025 mm^2; class 2: 0.025–0.05 mm^2; class 3: 0.05–0.1 mm^2; class 4: 0.1–1 mm^2; class 5: 1–10 mm^2; class 6: 10–50 mm^2.

Table 1
Breads formulations (water and ingredients are expressed as percentage on a 100 flour basis).

Ingredients	STD	GLU5	GLU15	$GLU_{std}15$
White flour	100	95	85	85
Gluten	–	5	15	15
Water	59	61	64	59
Sugar	4	4	4	4
Yeast	3	3	3	3
Seeds oil	3	3	3	3
Salt	2	2	2	2

2.3. Moisture content

Moisture content (MC) (%, g water/100 g sample) of crumb (from loaf centre) and crust (outermost layer, 1.5 mm thick) was determined by weight loss by drying in a forced-air oven ISCO NSV 9035 (ISCO, Milan, Italy) at 105 °C to constant weight. At least triplicate samples of crumb and crust were analysed for each bread loaf.

2.4. Texture

Bread crumb texture was measured using a TA.XT2 Texture Analyzer (Stable Micro Systems, Goldalming, UK). At least six cubic portions (8 cm^3) of crumb were extracted from the central slices of bread loaves and compressed with double compression TPA test (force = 0.05 N) to 40% deformation using a cylindrical probe (P/35 Dia Cylinder Aluminium). Crumb texture was described in terms of Hardness (maximum height of the first compression peak), Cohesiveness (ratio of the areas of the second to the first compression peak) and Springiness (ratio of the length of the second to the first compression peak).

2.5. Thermal analysis

2.5.1. Frozen water content

Frozen water content was measured using a Q100 Differential Scanning Calorimeter (TA Instruments, New Castle, DE, USA), calibrated with indium (melting point: 156.6 °C, melting enthalpy: 28.71 J/g) and mercury (melting point: −38.8 °C, melting enthalpy: 11.4 J/g). Crumb (4 g, from loaf centre) was compressed with a 2.5 kg weight to obtain a flat and compact sample to maximize heat transfer during the experiment. Compressed crumb samples (5–10 mg) were taken and placed in stainless steal pans (Perkin Elmer, Waltham, MA, USA) that were then hermetically sealed, quench cooled to −80 °C and then heated to 130 °C at 5 °C/min. DSC thermograms were analysed using an Universal Analysis Software, Version 3.9A (TA Instruments, New Castle, DE, USA).

"Frozen" water content (at the given experimental conditions; FW) was calculated from the endothermic peak around 0 °C (Baik & Chinachoti, 2001; Vodovotz et al., 1996) using the following equation:

$$FW = \text{Enthalpy Ice Fusion} \times \left(\frac{1}{\text{latent heat ice fusion}}\right) \times \left(\frac{1}{MC}\right) \times 100$$

where FW is Frozen water [%, g frozen water/100 g water], Enthalpy Ice Fusion [J/g product], Latent heat of ice fusion is 334 J/g ice and MC is Moisture Content [% g water/g product].

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