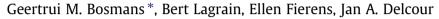
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The impact of baking time and bread storage temperature on bread crumb properties



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ABSTRACT

Two baking times (9 and 24 min) and storage temperatures (4 and 25 °C) were used to explore the impact of heat exposure during bread baking and subsequent storage on amylopectin retrogradation, water mobility, and bread crumb firming. Shorter baking resulted in less retrogradation, a less extended starch network and smaller changes in crumb firmness and elasticity. A lower storage temperature resulted in faster retrogradation, a more rigid starch network with more water inclusion and larger changes in crumb firmness and elasticity. Crumb to crust moisture migration was lower for breads baked shorter and stored at lower temperature, resulting in better plasticised biopolymer networks in crumb. Network stiffening, therefore, contributed less to crumb firmness. A negative relation was found between proton mobilities of water and biopolymers in the crumb gel network and crumb firmness. The slope of this linear function was indicative for the strength of the starch network.

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1. Introduction

Wheat bread is an important staple food in the western world. During storage, fresh bread loses part of its desired texture and aroma associated with freshness. The crumb firms, crust loses its crispiness and the flavour of fresh bread disappears. Firming during the first days of storage (*ca*. 5 days) is mainly related to *amylopectin recrystallisation* (also referred to as retrogradation) and the formation of a continuous, rigid, partially crystalline starch network (Bosmans, Lagrain, Ooms, Fierens, & Delcour, 2013). Inclusion of water in this starch network withdraws water from the amorphous networks in bread crumb and reduces the amount of freezable water (FW) (Bosmans et al., 2013; Slade & Levine, 1991).

Also, when proteins and polysaccharides are mixed in water at sufficiently high concentrations such as in dough, they phase sep-

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arate and the polysaccharide phase is enriched in water (Tolstoguzov, 1997). In the case of bread, it had already been reported that starch has a higher affinity for water than gluten (Willhoft, 1971). The thermodynamic immiscibility of protein and starch forms the basis for diffusion of water from gluten to starch during storage of bread (Bosmans et al., 2013). In contrast to amylopectin retrogradation, this diffusion process occurs faster at higher temperatures (Willhoft, 1971). When bread is stored, water migrates from crumb to crust, leading to an additional reduction of the crumb moisture content. As such, the local moisture content of the gluten network can drop below the critical point for gluten to be fully plasticised. The resulting increased *stiffness of the gluten network* also contributes to the increase in crumb firmness during storage (Bosmans et al., 2013).

The formation of crystals and changes in water distribution can be monitored with low resolution proton nuclear magnetic resonance (LR ¹H NMR). Bosmans et al. (2013) demonstrated a clear relation between the amount of amylopectin crystals formed during bread storage and the area of the most rigid proton population (fastest relaxation with relaxation time T_2 between 10 and 15 µs). A negative relation was also found between the mobility (T_2) of the large mobile proton population (slow relaxation with T_2 between 5 and 10 ms) and the firmness of bread crumb. These results show that ¹H NMR provides information related and complementary to





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Abbreviations: FW, freezable water; LR ¹H NMR, low resolution proton nuclear magnetic resonance; T₂, spin–spin relaxation time; DSC, differential scanning calorimetry; MC, moisture content; DM, dry matter; $\Delta H_{melting}$, melting enthalpy of ice in the sample; ΔH_{ice} , melting enthalpy of ice; FID, free induction decay; CPMG, Carr–Purcell–Meiboom–Gill; au, arbitrary units; ΔH_{AP} , melting enthalpy of retrograded amylopectin.

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differential scanning calorimetry (DSC) and texture analyses about amylopectin retrogradation and crumb firming, respectively.

The extent of bread crumb firming depends on the processing history of dough/bread. The heating rate and time at the maximum temperature reached in bread crumb during baking are related to the internal structure of the crumb cellular matrix and therefore also to the crumb mechanical properties (Le-Bail, Agrane, & Queveau, 2012; Patel, Waniska, & Seetharaman, 2005). Lowering the baking temperature or time decreases the level of protein polymerisation (Giovanelli, Peri, & Borri, 1997; Lagrain, Brijs, & Delcour, 2008) and results in less amylose leaching from the granules (Giovanelli et al., 1997; Patel et al., 2005). This, in turn, can affect *initial crumb firmness*, which is largely determined by the amylose network formed during cooling and the thermoset gluten network (Goesaert, Slade, Levine, & Delcour, 2009; Patel et al., 2005). In addition, less starch granule disruption due to reduced baking temperatures or times results in breads with less amylopectin retrogradation and a slower firming rate during storage (Giovanelli et al., 1997; He & Hoseney, 1990; Le-Bail et al., 2012). Besides the baking process, storage conditions also affect changes in bread crumb texture. Amylopectin recrystallisation is a nucleation-limited process (Cornford, Axford, & Elton, 1964; Eerlingen, Crombez, & Delcour, 1993; Gray & Bemiller, 2003), with a maximal rate of recrystallisation in the 4-14 °C temperature range (Slade & Levine, 1991). Amylopectin retrogradation and crumb firming occur faster at lower storage temperatures (Cornford et al., 1964; Gray & Bemiller, 2003; Zobel & Kulp, 1996). Upon heating to at least 50-60 °C, stale bread can be refreshened by melting the amylopectin crystals formed during storage (Delcour & Hoseney, 2010). The more stable amylose crystals do not melt during reheating up to 100 °C (Zobel & Kulp, 1996).

To further explore the importance of the degree of heat exposure during baking and the storage temperature on the extent of amylopectin retrogradation, diffusion related phenomena and bread crumb firming, we here compared the impact of different baking times and storage temperatures on crumb texture and proton mobilities.

2. Materials and methods

2.1. Materials and compositional analysis

Wheat flour (Crousti) [(69.7% starch, 11.6% protein, 13.8% moisture content (MC)] was provided by Dossche Mills (Deinze, Belgium). Starch content was determined by gas–liquid chromatography as in Courtin and Delcour (1998). Protein content was determined using an adaptation of the AOAC Official Method (AOAC, 1995) to an automated Dumas protein analysis system (EAS vario Max C/N, Elt, Gouda, The Netherlands), with 5.7 as nitrogen to protein conversion factor. MC of flour and bread crumb and crust was determined according to AACC Method 44-15.02 (AACC, 1999). All reagents, solvents and chemicals were of analytical grade and obtained from Sigma–Aldrich (Bornem, Belgium) unless indicated otherwise.

2.2. Bread making

Bread was made according to a straight-dough method (Finney, 1984) for 100 g of flour. Dough ingredients [100.0 g wheat flour (14.0% moisture), 5.3 g compressed yeast (AB Mauri, Merelbeke, Belgium), 6.0 g sucrose, 1.5 g NaCl, 59.0 ml water, 0.25 g calcium propionate] were mixed for 240 s in a 100 g pin mixer (National Manufacturing, Lincoln, NE, USA) at 25 °C and fermented in a fermentation cabinet (National Manufacturing) for 90 min (30 °C, 90% relative humidity) with intermediate punching at 52 and 77 min and final punching at 90 min using a dough sheeter (Na-

tional Manufacturing). Subsequent to moulding and proofing (36 min at 30 °C, 90% relative humidity) in a baking tin [internal dimension (width × length × height), 8.0 cm × 14.5 cm × 5.5 cm], dough was baked at 215 °C for 9 or 24 min in a National Manufacturing rotary hearth oven. The resultant breads are further referred to as 9 or 24 min breads. Prior to further analyses, breads were cooled for 1–2 h. The cooled breads had a mass of 155.6(±0.3) g (9 min bread) or 136.7(±0.5) g (24 min bread).

2.3. Storage of bread and crumb sampling

After cooling, three samples, each from the centre of the crumb of different breads (9 min breads or 24 min breads) were placed in separate NMR tubes and sealed. These tubes were stored at 25 $^\circ C$ (9 min breads or 24 min breads) or at 4 °C (24 min breads) and analysed with ¹H NMR after storage for 2, 48, 120 and 168 h. In this way, the effect of the extent of amylopectin retrogradation on the proton distributions in bread crumb during storage could be studied without interference by water migration from crumb to crust. At the same time, fresh whole breads were wrapped in plastic foil and stored at 25 °C (9 min breads and 24 min breads) or at 4 °C (24 min breads) for 168 h in sealed plastic bags to prevent moisture loss. Centre crumb samples were then also withdrawn and transferred into NMR tubes which were then sealed. In this way, the additional effect of water migration from crumb to crust on the proton distributions during storage could be studied. Breads (three for each storage time) were analysed with DSC, crumb compression experiments and ¹H NMR after storage for 2, 48, 120 and 168 h (see Sections 2.4-2.6). After storage for 168 h, part of the NMR tubes containing crumbs from 24 min breads stored at 25 °C was heated in an oil bath at 110 °C for 10 min. The samples were cooled for 60 min and stored again at 25 °C for another 168 h in the tubes. In this way, the impact of reheating on proton distributions and amylopectin retrogradation in bread crumb could be studied.

2.4. Differential scanning calorimetry

DSC was performed with a Q1000 DSC (TA Instruments, New Castle, DE, USA). Bread crumb was freeze-dried after different storage times for analysis of the extent of amylopectin retrogradation. The freeze-dried samples were accurately weighed (2.5–4.0 mg) in quadruplicate in aluminium pans (Perkin Elmer, Waltham, MA, USA). Deionized water was added in a ratio of 1:3 [w/w, sample dry matter (DM):water]. The pans were hermetically sealed and equilibrated at 0 °C before heating to 120 °C at 4 °C/min (together with an empty reference pan). Before analysis, the system was calibrated with indium. The temperatures and enthalpies corresponding to melting of amylopectin crystals (retrogradation) were evaluated from the thermograms using TA Instruments Universal Analysis software. Enthalpies were expressed in J/g sample (on DM basis).

Next to the extent of amylopectin retrogradation, the amount of FW (i.e. water that transforms into ice upon cooling below 0 °C) in bread crumb was determined. Hereto, bread crumb (10–15 mg) was accurately weighed in aluminium pans. The samples were equilibrated at 15 °C and cooled to -40 °C at 4 °C/min, held for 5 min at -40 °C, and reheated to 30 °C at 4 °C/min. From the melting enthalpy, measured between -6 and 0 °C, and the MC of the sample, the amount of FW was calculated as

$$\% \text{ FW} = \frac{\Delta H_{\text{melting}}}{\Delta H_{\text{ice}} \times \text{MC}} \times 100 \tag{1}$$

where $\Delta H_{\text{melting}}$ is the melting enthalpy of ice in the sample (J/g sample, on as is basis); ΔH_{ice} is the melting enthalpy of ice (334 J/

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