Biopolymer interactions, water dynamics and bread crumb firming

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Introduction and Objective

Bread crumb firming is a complex process. It is generally accepted that amylopectin retrogradation is an important contributor to crumb firming during storage, but there is no direct cause and effect relationship between both processes¹. Besides formation of amylopectin crystals¹, water diffusion also affects crumb firmness during storage. Literature is scarce about the impact of such diffusion. It occurs on a macroscopic scale, i.e. from crumb to crust², as well as on a molecular scale, i.e. from gluten to starch³. However, the relative importance of water redistribution and amylopectin retrogradation for bread firming is still under debate. Since water related phenomena are involved in crumb firming, the use of low resolution (LR) proton Nuclear Magnetic Resonance (¹H NMR) to examine bread crumb holds promise.

the objective of this study was to investigate changes during bread storage, thereby distinguishing between the effect of crumb to crust migration and evaporation of water and the effect of amylopectin recrystallization with water incorporation into the resulting starch network.

Experimental

Bread making process

Bread was made using a straight-dough method [100.0 g wheat flour (14.0% moisture), 5.3 g compressed yeast, 6.0 g sucrose, 1.5 g NaCl, 57.0 mL water] as described in Bosmans *et al.* (2012)⁴.

Differential scanning calorimetry (DSC) measurements

The melting enthalpy of retrograded amylopectin (ΔH_{AP}) and the relative amount of freezable water (FW) were determined with DSC⁵.

Firmness measurements

Crumb firmness was detected with an Instron 3342 (Instron, Norwood, MA, USA) on fresh, stored (for 168 h) and dried bread crumb⁵.

¹H NMR measurements

Proton relaxation measurements were performed on a Bruker Minispec mq20 spectrometer (Bruker, Rheinstetten, Germany) operating at 20 MHz and at 25 ° C⁴.

Results and Discussion

During storage of bread for 168 h, ΔH_{AP} increased while the relative amount of FW decreased (Table 1). Water becomes unfreezable due to inclusion into the amylopectin crystals but also due to inclusion into the continuous, rigid amylopectin network. No amylopectin retrogradation was observed during drying. Crumb firmness increased during storage and drying (Figure 1).

Table 1: Relative amount of freezable water (FW) and melting enthalpy of retrograded amylopectin (ΔH_{AP}) of bread crumb stored at 23 ° C.

Storage time after cooling (h)	FW (%)	ΔH_{AP} [J/g crumb (DM)]
0	47.0 (4.1)	0.25 (0.02)
48	48.0 (1.3)	2.03 (0.06)
120	39.9 (4.5)	3.26 (0.18)
168	38.5 (1.7)	3.34 (0.22)

Standard deviations are shown between brackets
DM: dry matter.

Figure 1: Firmness in function of moisture content obtained by drying and storage of bread.

The decreased crumb moisture content during storage did not result in an increased crumb firmness (Figure 1), showing that amylopectin retrogradation was largely responsible for crumb firming during storage. However, the increase in melting enthalpy levelled off after a couple of days of storage (Table 1), while crumb firmness increased further. This points to an additional phenomenon which contributes to crumb firmness.

With ¹H NMR, changes in the distribution of protons from water and biopolymers can be observed. During storage of bread, the area of population A (rigid protons) increased due to formation of amylopectin crystals (Figure 2a). In addition, the mobility (T_2 relaxation time) and area of population E (mobile exchanging protons in the formed gel network) decreased during bread storage due to formation of a continuous, rigid amylopectin network and crumb to crust moisture migration (Figure 2a).

During drying of fresh bread crumb, similar changes in proton distributions occurred, except for the merging of populations C (mobile CH protons) and D (hydrated protons of gluten) (Figure 2b). The moisture content (36%) was still high enough to hydrate the gluten network. Dehydration of this network in stored bread crumb contributed to the increase in crumb firmness after a couple of days of storage (Figure 1).

Figure 2: Free Induction Decay (FID) and Carr-Purcell-Meiboom-Gill (CPMG) proton distributions of bread crumb (a) before and after storage (for 168 h) and (b) before (44% moisture) and after (36% moisture) drying.

Conclusions

The combined results from ¹H NMR, DSC and texture analyses allowed proposing a more profound interpretation of the bread crumb firming mechanism. Amylopectin retrogradation and the formation of a continuous, rigid, semi-crystalline starch network which includes water in its structure were strongly related to the increase in crumb firmness, especially during the first days of storage. This water inclusion, together with moisture diffusion from gluten to starch and from crumb to crust, reduce the moisture content of the gluten network. After a couple of days of storage, the moisture content had dropped below the critical point for gluten to be fully plasticized, resulting in increased stiffness that contributed to crumb firmness.

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