



Staling of fresh and frozen gluten-free bread

Felicidad Ronda^{a,*}, Yrjö H. Roos^{b,1}

^a Department of Agriculture and Forestry Engineering - Food Technology, College of Agricultural and Forestry Engineering, University of Valladolid, Av. Madrid, 44, 34004 Palencia, Spain

^b School of Food and Nutritional Sciences, College of Science, Engineering and Food Sciences, University College Cork, Ireland

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ABSTRACT

The difficulty in finding gluten-free bread and its high price make it necessary to prolong its shelf life to facilitate its availability. Freezing is an interesting alternative. The storage of bread at over zero temperatures, 20 °C and 4 °C, showed faster staling at refrigerator temperatures. A good relationship between crumb firmness and the extent of starch recrystallization was obtained, although the effect of water loss was also detected. The study of freezing and frozen storage at −14 °C and −28 °C for 7 days showed a substantial effect of the storage temperature on gluten-free bread quality and shelf life. Breads stored at −28 °C retained a quality similar to that of fresh breads while a marked deterioration of the breads stored at −14 °C was observed. This effect, the strongest on bread texture, was a result of starch recrystallization. The glass transition, T_g' and onset of ice melting, T_m' of the maximally freeze-concentrated bread crumb were -37.1 ± 0.6 °C and -19.3 ± 0.2 °C respectively. The higher amount of unfrozen water at −14 °C could explain the acceleration of reactions responsible for bread staling during frozen storage. The use of storage temperatures below T_m' is recommended to retain high quality of the gluten-free bread during frozen storage.

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1. Introduction

People allergic to proteins in wheat (e.g., those with celiac disease) are increasingly diagnosed. Nowadays, an incidence of one of each 130–200 people is recognized in the industrialized countries (Sollid, 2002). A strict gluten-free (GF) diet for life is the only treatment for celiac disease. The high cost of GF specialty foods, significantly higher than gluten-containing foods, and the problems in their availability in the common market are some of the biggest concerns for celiac patients. Bread is a widely consumed food, also for celiac patients, and its quality is rapidly lost due to staling. An approach for increasing GF bread availability and reducing costs for celiac people is the use of home freezing and frozen storage. However, previous studies with wheat breads have shown that frozen storage cannot always reduce bread staling (Carr et al., 2006; Ronda et al., 2011).

Abbreviations: DSC, differential scanning calorimetry; GF, gluten-free; T_g' , temperature of glass transition of the maximally freeze-concentrated state; T_m' , ice melting temperature of the maximally freeze-concentrated state.

* Corresponding author. Tel.: +34 979108339/34 979108359; fax: +34 979108302.

E-mail address: fronda@iaf.uva.es (F. Ronda).

¹ Tel.: +35 3 (0)214902386; fax: +35 3 (0)214270001.

Staling involves hardening of the crumb that is a complex phenomenon in which multiple mechanisms operate. Factors affecting wheat bread crumb staling have been extensively investigated (Chinachoti and Vodovotz, 2001; Zobel and Kulp, 1996). All of them involve starch retrogradation. However, many studies have shown that starch retrogradation is not the only factor responsible for crumb staling (Baik and Chinachoti, 2000). Water plays a critical role in bread staling. When the retrogradation of amylopectin occurs, water molecules are incorporated into the crystallites and the distribution of water is shifted from gluten to starch/amylopectin, thereby changing the nature of the gluten network (Gray and BeMiller, 2003). Besides the molecular order of starch, water also plays an important role in crumb firmness due to its plasticizing effect on the crumb network (Hug-Iten et al., 2003).

GF breads based on rice flour require polymeric substances that mimic the viscoelastic properties of gluten to provide structure and retain gas (Toufeili et al., 1994). Gums and hydrocolloids such as hydroxypropylmethylcellulose (HPMC) appear to improve gas retention and water absorbing characteristics usually supplied by wheat gluten (Kadan et al., 2001; McCarthy et al., 2005). Very little is available in the literature about the starch retrogradation within this HPMC network in a gluten-free system. HPMC has shown a good anti-staling action in wheat bread by retarding crumb hardening and amylopectin retrogradation (Barcenas and Rosell, 2005, 2007).

Starch retrogradation involves reassociation of starch component molecules into a partially crystalline, ordered structure. Amylopectin recrystallization requires several days. Because firming of bread also develops over several days, most staling models view the changes in amylopectin as the primary cause for crumb firming (Zobel and Kulp, 1996). The slow crystallization of amylopectin was referred to as a nucleation-limited growth process, which occurred above the glass transition in a mobile, viscoelastic, fringed-micelle network (Roos, 1995). Our previous studies (Ronda and Roos, 2008) have shown that starch recrystallization during storage was enhanced by a prefreezing treatment at temperatures above T_g' . This temperature, that determines the glass transition of a maximally freeze-concentrated state, is used to characterize frozen materials (Roos, 1995). Above T_g' , molecular mobility is enhanced and consequently molecular rearrangements for nucleation can take place. Further storage at a higher temperature enhances the growth and the maturation of crystals leading to more rapid recrystallization in comparison with unfrozen systems (Ronda and Roos, 2008). This could explain deterioration of frozen breads when stored at temperatures around -18°C and the more rapid aging after thawing than is found for fresh, unfrozen bread (Ronda et al., 2011).

The effect of freezing on the quality and shelf life of wheat breads, fully baked or partially baked, has been widely studied (Barceñas et al., 2003; Fik and Surowka, 2002; Ronda et al., 2011), including studies using starch gel model systems (Ronda and Roos, 2008). However, to our knowledge, there are few studies on the effect of freezing, and specifically on the effect of the temperature of frozen storage on gluten-free bread quality. The aim of the present study was to investigate the effects of freezing and frozen storage on GF bread quality and shelf life, depending on the frozen storage temperature. Two freezing temperatures, -28°C and -14°C , were selected for the study. These values represented the typical minimum and the maximum temperature limits of operation of a home chest freezer. These two conditions allowed us to predict the likely quality extremes of the frozen bread stored in a domestic freezer. On the other hand, this range of temperatures covered T_m' of the bread ($-28^\circ\text{C} < T_m' < -14^\circ\text{C}$) which indicates the onset of ice melting and relates to the quantity of unfrozen water during frozen storage. The present study also compared the fresh bread staling kinetics at room temperature and at refrigeration temperature, allowing an assessment of whether frozen storage could provide superior quality in comparison to fresh gluten-free bread.

2. Material and methods

2.1. Bread processing

Rice flour (15.1% moisture, 0.32% dry basis (db) ash, 7.25% db protein and 81% db starch) was supplied by Harinera Castellana S.A., Medina del Campo (Spain); salt, sugar, and sunflower oil were purchased from a local market; Hydroxy Propyl Methyl Cellulose (HPMC) (E464) was supplied by Shin-Etsu Chemical Co Ltd. (Japan); Commercial dry yeast (Saf-instant, Lesaffre, France) was used.

A straight dough process was performed using the formula on a flour basis: 110% water, 6% oil, 5% sucrose, 2% salt, 2% HPMC and 3% yeast. Firstly, solid ingredients were blended in a kitchen-aid professional mixer (KPM5) during 10 s at speed 2. Then the liquid ingredients (water and oil) were added and mixed for 5 min at speed 6. The dough, 400 g, was placed into a stainless steel oil coated pan and was proofed at 30°C and 80% relative moisture for 45 min. Subsequently, baking was carried out in a Salva convection oven (Lezo, Spain) at 200°C for 45 min. After baking, the breads were removed from the pan and left 1 h at room temperature. After the cooling phase, the breads were packaged in polyethylene bags and

kept under the specified conditions. To study the effect of freezing and frozen storage on bread quality and shelf life, breads were kept at $(-14 \pm 2)^\circ\text{C}$ and $(-28 \pm 1)^\circ\text{C}$ for 7 days and then stored for 0, 1, 2, 6 and 8 days at $(20 \pm 2)^\circ\text{C}$ after thawing. The frozen breads, once taken out of the freezer, were kept 3 h at $(20 \pm 2)^\circ\text{C}$ before analysis. To compare crumb hardening kinetics of fresh breads at room and refrigeration temperatures, breads were stored at $(20 \pm 2)^\circ\text{C}$ and $(4 \pm 2)^\circ\text{C}$ for 0, 1, 2, 3, 4, 7, 11, 14 and 18 days. The initial crumb hardness (0 storage days) of the fresh bread and the initial retrogradation enthalpy were measured at 3 h after baking.

2.2. Physical measurements

A Mettler Toledo-DSC 822e (Schwerzenbach, Switzerland) was used. DSC was performed on 25–30 mg of bread crumb taken from the centre of the bread loaf. The glass transition (T_g') and the ice melting (T_m') temperatures of the maximally freeze-concentrated systems were obtained as reported by Roos and Karel (1991) and Ronda and Roos (2008). The water (FW) fraction that was frozen was derived from the relationship between the enthalpy of ice melting in the maximally freeze-concentrated system and the latent heat of ice melting (334 J/g). Starch retrogradation was evaluated from DSC endotherms obtained during the temperature scanning from 0°C to 105°C at a heating rate of 5°C/min . The samples (bread crumb) for the measurements of the melting enthalpy of the recrystallized amylopectin were stored, during the specified temperature and time, directly in the DSC pans ($40\text{ }\mu\text{L}$). For the study of starch retrogradation kinetics of unfrozen crumbs, pans with samples were stored for 0, 1, 2, 4, 7, 11 and 18 days at 4°C and 20°C . For the study of the effect of freezing and frozen storage on starch retrogradation, pans with samples were stored 7 days at -14°C and -28°C and after thawing, were stored at 4°C for 0, 1, 2, and 8 days. Each measurement was performed in duplicate. The melting enthalpy was expressed in J/g of solids.

Water content was determined in bread crumb and crust in duplicate following the standard method 44-15A (AACC, 2000).

Bread volume was determined in duplicate using a volume analyzer BVM-L370 TexVol Instruments (Viken, Sweden).

Crumb texture was determined in triplicate with a TA-XT2 texture analyser (Stable Microsystems, Surrey, UK) provided with the software "Texture Expert". An aluminium 25 mm diameter cylindrical probe was used in a "Texture Profile Analysis" double compression test (TPA) to penetrate to 50% depth at 1 mm/s test speed with a 30 s delay between the first and second compression. Hardness (N), chewiness (N), cohesiveness, elasticity and resilience were calculated from the TPA results (Gomez et al., 2007). The analysis was carried out at $(20 \pm 2)^\circ\text{C}$ for bread slices of 20 mm thickness taken from the centre of the loaf.

2.3. Modelling of crystallisation and firming kinetics

Modelling of crystallization data was carried out using the Avrami equation (Eq. (1)) (Avrami, 1940) which was written in the form of Eq. (2) for fitting the equation to melting enthalpies with time of crystallization (Jouppila et al., 1998):

$$\theta = 1 - e^{-k \cdot t^n} \quad (1)$$

Where θ is crystallinity, t is time, k is a rate constant, and n is the Avrami exponent.

$$1 - \theta = \frac{H_\infty - H_t}{H_\infty - H_0} = e^{-kt^n} \quad (2)$$

Where H_∞ is the levelling-off value of melting enthalpy at which the extent of crystallization in starch ceased. This depends on the

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