Bread Staling: Updating the View

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Word count: 21517

Running title: Bread staling review

ABSTRACT: Staling of bread is cause of significant product waste in the world. We reviewed the literature of last 10 years with the aim to give an up-to-date overview on processing/storage parameters, antistaling ingredients, sourdough technology, and measurement methods of the staling phenomenon. Many researchers have been focusing their interest on the selection of ingredients able to retard staling, mainly hydrocolloids, waxy wheat flours (WWF), and enzymes, but different efforts have been made to understand the molecular basis of bread-staling with the help of various measurement methods. Results obtained confirm the central role of amylopectin retrogradation and water redistribution within the different polymers in determining bread-staling, but highlighted also the importance of other flour constituents, such as proteins and non-starch polysaccharides. Data obtained with thermal, spectroscopy, nuclear magnetic resonance, X-ray crystallography, and colorimetry analysis have pointed out the need to encourage the use of one or more of these techniques in order to better understand the mechanisms of staling. Results so far obtained have provided new insight on bread staling, but the phenomenon has not been fully elucidated so far.

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List of abbreviations

ALG, sodium alginate; β-CD, β-cyclodextrin; BGF, β-glucan-rich fraction; BM, barley flours; BR, ungerminated brown rice; CMC, carboxymethylcellulose; DATEM, mono or diacylglycerols alone or esterified; DB, dough bread; D_{eff}, effective moisture diffusivity; DE, dextrose equivalent; DF, dietary fiber; ΔH, enthalpy of melting; DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; DTMA, dynamic thermomechanical analysis; EPS, exopolysaccharides; FB, fully baked bread; FD, frozen dough; FFC, fast field cycling; FPBFB, frozen part-baked French bread; FRF, fiber-rich fractions; FTIR, Fourier transform infrared spectroscopy; FW, freezable water; GG, guar gum; GHP, gluten hydrolysate; GO, glucose oxidase; ^{1}H NMR, hydrogen-1 nuclear magnetic resonance; HPMC, hydroxypropyl methylcellulose; HPP, high-hydrostatic-pressure processing; K, k-carragenan; KGM, konjac glucomannan; LAB, lactic acid bacteria; λC, λ-carrageenan; MGL, fat-monoglycerides; MIR, middle-infrared spectroscopy; MRI, magnetic resonance imaging; MTS, chemically modified tapioca starches; NIRS, near-infrared reflectance spectroscopy; PB, par-baked bread; PBGR, pre-germinated brown rice; PCA, principal component analysis; PGA, γ-polyglutamic acid; RVA, rapid visco-analysis; SAD, sponge-and-dough baking method; SAXS, small-angle X-ray scattering; SEM, scanning electron microscopy; SOM, self-organized map; SSL, sodium stearoyl lactylate; TA, texture analysis; T_g, glass-transition temperature; T_g', T_g of the maximally freeze-concentrated state; Tgm, transglutaminase; TPA, Texture Profile Analysis; UFW, unfreezable water; WISP, water-insoluble pentosans; WSP, water-soluble pentosans; WVP,water vapor permeability; WWF, waxy wheat flours; WWS, waxy wheat starch; XG, xanthan gum; XRD, X-ray diffraction; Xyns, Xylanases.

1. Introduction

Bread stales and unfortunately it is a certainty and causes significant product waste all over the world (Collar and Rosell 2013). Staling results in loss of important sensory parameters of bread, like flavor and texture, and it is a consequence of a group of several physical-chemical changes occurring during bread storage that lead mainly to an increase of crumb firmness and loss of freshness (Kulp and Ponte 1981; Gray and Bemiller 2003). Although the staling mechanism has not been well established, the most important causes responsible for this alteration are starch transformation, starch–gluten interactions, and moisture redistribution (Schiraldi and Fessas 2001).

Bread staling is being continuously studied and researchers have been focusing their interest on mechanisms, factors and measurement, thus a huge body of literature is available, including a number of reviews and book chapters dealing with the different causes of bread staling and/or specific topics (Table 1). Most of the reviews and book chapters do not cover all aspects dealing with bread staling. A rather complete state of the art of molecular basis and most of the factors influencing the quality of bread, as well as of the main antistaling agents, has been, however, covered by Gray and Bemiller (2003), while reviews published later focused again only on specific aspects of bread staling, such as the influence of water, enzymes, frozen dough, and partially baked bread, waxy and high-amylose wheat starches and flours, sourdough, and analytical methodology (Table 1). More than 300 papers have been published in international peer-reviewed journals since 2003 on this topic, thus we attempted to collect the most important literature to give a new and up-to-date picture on bread staling. In particular, this review will focus on new information regarding the following aspects of bread staling: processing/storage parameters, surface-active lipids, enzymes, carbohydrate ingredients, flours and other major ingredients, as well as new measurement methods and sourdough technology. The review will take into consideration only papers dealing with wheat bread and not with models such as diluted and concentrated starch pastes as well as gluten-free bread. In the case of papers dealing with the effect of different factors (such as storage temperature, ingredients, or ingredients of different origin), we use hierarchic considerations to select the proper section of discussion. Moreover, the reader has to refer to the literature previously reported and in particular to the paper of Gray and Bemiller (2003) and others that will be cited for more general information, molecular basis, and mechanisms of bread staling. As a general rule, only papers not cited by specific or general reviews, which will be reported in the proper sections, are discussed in this review. However, papers already cited in reviews, but not properly discussed with regard to bread staling will be reviewed again.

2. Main ingredients affecting bread staling

2.1. Flours

Flours other than wheat or deriving from amylose-free wheat flours (waxy) have been extensively studied during this last decade. The particular composition of some flours or the absence of amylose (with its role on staling) have been proposed in the production of mixed flour breads in order both to improve nutritional aspects and bread aging.

Non-wheat flours

It raises a great deal of recent interest that minor cereals, ancient crops and pseudocereals, besides wheat, constitute highly nutrient-dense grains with feasible breadmaking applications despite the poor viscoelasticity they exhibit when mixed with water.

Salehifar and Shahedi (2007) have confirmed earlier the beneficial effects found by Zhang and others (1998) using oat flour in reducing firmness of breads stored at room and chill temperature for up to 3 days, provided a maximum 20% oat flour substitution is accomplished, in order not to impart a strong bitter taste.

The ability of high β-glucan barley (HBGB) flour versus regular commercial barley (CB) to make highly nutritious wheat (WT) blended breads has been recently discussed (Collar and Angioloni, 2014a). Mixed breads obtained by 40 % replacement of WT flour by HBGB flours are more nutritious than those replaced by CB flours and much more than regular WT flour breads preserving the sensory acceptance and improving bread keepability during storage. The high content of β-glucan of barley flour has been described help in reducing the starch crystallization thus delaying significantly the staling rate of bread when used at the 20% level, even if it increased the firmness of fresh product (Gujral and others 2003). Moreover, when barley flour was used together with wet gluten and ascorbic acid they reduced both initial firmness and staling rate, especially when the higher level of the 3 additives was used. Purhagen and others (2008) proposed that water had a greater effect on bread staling as assessed by TA, with respect to amylopectin retrogradation measured with DSC, when normal or heat-treated barley flours (BM) were supplemented at 2 or 4% levels. In fact, although the retrogradation enthalpy of supplemented breads was higher than control breads, the firmness values of barley loaves were significantly lower during 7 days of storage at room temperature. However, the authors suggested that this effect could not be simply explained by the higher amounts of water in barley formulations, but by differences in the water-binding ability of flour formulations with BM or soluble fibers. Staling rate was retarded in laboratory-produced breads by using pressure-treated barley flour, as well as waxy and pre-gelatinized waxy barley starch at the 3% level (Purhagen and others 2011b). The best results in retarding crumb firmness were found for pre-treated and pre-gelatinized additives, with respect to the other formulations, including control bread, regardless of the storage time, even if a higher amylopectin retrogradation was revealed. The authors explained this result with the increased water retention during storage of substituted formulations. Unfortunately, they did not manage to retard staling when the pre-gelatinized additives were used in an industrial baking trial.

Vittadini and Vodovotz (2003) used thermal analysis to assess that soy flour may have a role in modulating bread staling. Results indicated that replacing up to 40% of soy flour in the bread formulation caused a significant decrease in amylopectin recrystallization as well as promoted moisture retention during storage, with respect to control bread, thus leading to decreased staling. Lodi and Vodovotz (2008) studied the effect of the partial substitution of wheat flour with soy flour and the addition of raw ground almonds (5%). The incorporation of almond increased the loaf specific volume of bread and reduced the crumb firmness changes over a 10-day storage period, if compared to bread obtained with only soy, even if no differences in amylopectin recrystallization rate or formation of amylose-lipid complexes were detected between the 2 formulations. The authors postulated that the addition of almond to soy flour probably resulted in a stronger interaction between proteins of wheat and soy, favored by the high lipid content of almonds. On the other hand, the bread produced with only soy staled at a lower rate than control bread, due to a better homogeneous water distribution, as revealed by different thermal determinations and by MRI (Lodi and others 2007a,b).

Watanabe and others (2004) reported that substitution of wheat flour with powdered pre-germinated brown rice (PBGR) was able to reduce the staling rate of bread stored for 3 days at room temperature, with respect to both control formula and bread supplemented with ungerminated brown rice (BR). The replacement of 10% to 20% PBGR resulted in delayed staling with respect to BR sample, while 10% PGBR slowed starch retrogradation, compared to control loaves, but supplementation of 30% PGBR accelerated bread hardening. According to the authors, 10% PGBR addition enhanced softness of bread due to a certain amount of starch granules being gelatinized during PGBR production, while 30% supplementation led to accelerated staling owing to the high water content needed to obtain dough.

Mentes and others (2008) reported that substitution of wheat flour with ground flaxseed flour resulted in delayed staling of bread after 24 hours in storage, with respect to control all-wheat bread, as assessed by a mechanical penetration test, but the authors did not give any explanation of the probable causes. The best result was obtained by using 15% flaxseed flour.

Wu and others (2009) studied the effect of potato paste substitution at 5 to 30% on hardness evolution of bread during a 3-day storage period and found that staling decreased in 1-day stored samples obtained with 5% to 20% potato paste, with respect to control breads, and they associated this with the differences in water-binding capacities of potato paste and with interaction with starch, thus affecting starch retrogradation.

Begum and others (2010) evidenced that bread obtained with the use of 10% fermented cassava flour or 10% soy-fortified cassava flour was softer after 3 days at room temperature, with respect to wheat bread [Note: the authors did not make an explanation for this result and did not report the amount of soy used to fortify cassava flour].

In a recent paper (Angioloni and Collar 2011), the suitability of associated mixtures of minor/ancient cereals (rye, oat, Kamut® wheat, spelt wheat) and pseudocereals (buckwheat) was assessed in multigrain wheat flour highly replaced matrices. A quaternary blend of oat, rye, buckwheat and common wheat flours (20:20:20:40 w/w/w/w) without any additive and/or technological aid in the formulation was proposed to make highly nutritious baked goods meeting sensory standards and exhibiting a low staling rate during ageing.

The quality profile of binary mixtures of oat–wheat (60:40 w/w), millet–wheat (40:60 w/w) and sorghum–wheat (40:60 w/w) was significantly improved in presence of some additives in terms of keepability during storage, mainly for oat–wheat blends which stale at a similar rate or even at lower rate than 100% wheat breads (Angioloni and Collar, 2013). Dilution up to 20% of the basic rye/wheat flour blend by accumulative addition of amaranth, buckwheat, quinoa and teff flours (5% single flour) did positively impact both bread keeping behavior during aging, and nutritional characteristics of mixed bread matrices (Collar and Angioloni, 2014b).

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Waxy wheat flours

Most of the research work on flour has been focused, however, on the use of waxy wheat flours (WWF), because, due to its lack of amylose, WWF can reduce the initial phase of retrogradation (Graybosch 1998). A comprehensive review on the production and characteristics of WWF and waxy wheat starch (WWS) and their application for food processing is that of Hung and others (2006).

Baik and others (2003) suggested that the increased starch retrogradation of bread crumb, as assessed by DSC, may not be the cause of retarded staling during a period of 7 days in storage at 4 °C in bread obtained with double-null partial WWF, with respect to bread produced with hard red spring wheat flours. They proposed that the low amylose and high protein contents of the waxy lines were beneficial in retarding the increase in hardness. Peng and others (2009) reported that the use of 15% WWF combined with 2 other wheat flours was the optimal solution for retarding staling up to 6 days without impairing bread quality, as revealed by sensory analysis, if compared with the control. Data from Hung and others

(2007a) gave evidence of the relationship between the use of whole WWF and delayed staling. Breads made with 30 and 50% whole WWF substitution were softer up to 1 day in storage due to the higher amount of water absorbed by the dough as well as the high moisture content in breadcrumbs. In a further paper, the same authors (Hung and others 2007b) by using 100% whole WWF managed to delay staling of whole waxy bread up to 3 days by adding 40,000 U g^{-1} of cellulase, due to the particular pentosans present in the enzyme hydrolysate. Moreover, they obtained white WWF by removing the bran and germ, and the resulting breadcrumbs kept softer for 5 days, with respect to breadcrumbs from both the whole regular and whole waxy wheat, probably as a result of the enrichment of the amylopectin fraction of the white WWF. Park and Baik (2007) made a comparative test with wheat genotypes of wild type, partial waxy, and waxy starch, in order to study the influence of starch amylose content on French bread performance of wheat flour. Their study evidenced that wheat flours with reduced starch amylose content allowed the production of breads with better retained crumb moisture and delayed staling up to 48 hours of storage, probably because the greater crumb moisture resulted in a delay in amylopectin retrogradation, even if DSC analysis did not evidence significant differences in enthalpy values of the various wheat genotypes with different amylose content. Slowing the migration of water from the gluten phase to the starch phase by WWF (5-30%) has been hypothesized as the cause of diminution of firmness evolution, as determined with compression analysis (Mouliney and others 2011).

The low amylose content of flours obtained from 2 new Japanese wheat varieties was related to reduced staling of bread, especially in the first 48 h of storage at 20 °C, with respect to samples obtained with 2 representative bread wheat classes that are N. 1 Canada western red spring and hard red winter (Ito and others 2007). DSC data of enthalpy and X-ray patterns evidenced a slow retrogradation of starch gel in the bread obtained with the new varieties, thus accounting for their softer texture that resulted in softness and high cohesiveness of the loaves. Apparently different results were found when replacing hard wheat flours with 15 to 45% with two hard WWF (Garimella Purna and others 2011). In fact, substitution led to softer bread, but only at day 1 after baking, while staling was not retarded during storage. The combination of less amylose and more soluble starch from amylopectin characterizing WWF could have resulted in a soft crumb structure on day 1 after baking, while after 7 days the bread was as firm as the control, due to a similar content of soluble starch, thus confirming a previous study (Ghiasi and others 1984).

Yi and others (2009) studied the effect of partial WWF substitution on staling of bread made from FD. They found that when modulating WWF and water amounts it was possible to reduce the staling rate, with respect to control formulations. The best combination was 45% WWF replacement and 65% water. By using pulsed hydrogen-1 nuclear magnetic resonance (^{1}H NMR) they concluded that bread with higher WWF content held more water and limited the movement of water from one domain to another.

Very recently, Lafaye and others (2013) obtained bread using waxy durum flour and concluded that this flour acted as a unique bread softener. The authors did not make any additional analysis in order to suggest a satisfactory explanation of the antistaling effect of this flour, however provided a well-described picture of the possible causes leading to the beneficial effect of waxy flour supplementation by summarizing literature results.

2.2. Carbohydrates

A consistent research activity has been carried out during the last decade on the role of carbohydrate ingredients in reducing bread staling. Hydrocolloids, modified starches, dextrins, and maltooligosaccharides and other fibers will be covered in this section.

Hydrocolloids. The antistaling effect of hydrocolloids (Table 2) has been extensively studied and attributed to controlling and maintaining the moisture content, stabilizing the dough, and influencing the crust structure (Davidou and others 1996; Collar and others 1999; Rojas and others 1999; Mandala and Sotirakoglou 2005; Mandala and others 2007; Rosell and Gomez, 2007). Some interesting reviews focused on molecular structure, physicochemical properties, and uses in food products of the whole class of hydrocolloids as bread improvers (Kohajdová and Karovičová 2009) and more specifically of barley β-glucans and arabinoxylans (Izydorczyk and Dexter 2008). A book chapter by Milani and Maleki (2012) gives a classification of hydrocolloids and of their functions, according to Hollingworth (2010).

The use of DSC allowed to establish that hydroxypropyl methylcellulose (HPMC) and k-carragenan (K) decreased the retrogradation enthalpy of amylopectin, thus retarding staling of part-baked breads produced with an interrupted baking process and frozen storage (Barcenas and others 2003). The latter results were in part in contrast to what was reported previously by Sharadanant and Khan (2003) who found a detrimental effect on bread firmness evolution during storage of K-supplemented breads. In a later paper, Barcenas and Rosell (2005) gave a more detailed explanation of the possible cause of the antistaling effect of HPMC. The authors, in fact, determined the microstructure of bread crumb by cryo-SEM and found that HPMC use resulted in gas cells with a more continuous surface and a thicker appearance, with respect to the control. Thus, the presence of HPMC enfolded the other bread constituents, with a consequent hindering of their interactions and avoided some of the processes involved in bread staling. The HPMC was suggested as the best antistaling ingredient also for Lavash flat bread made with 2 different wheat flours and stored for 48 hours (Tavakolipour and Kalbasi-Ashtari, 2007). Similar results on another flat bread, the Barbari, have recently been reported by Maleki and others (2012) who found that hydrocolloids other than HPMC, namely GG, XG, and CMC, reduced staling of bread up to 5 days, due to the limitation of water mobility that influenced the gelatinization process by decreasing the ΔH, that was also reported by Ghanbari and Farmani (2013) who revealed a significant antistaling effect of K, especially when supplemented at 0.5%. Mandala and Sotirakoglou (2005) suggested that the use of XG and GG in fresh or microwave-heated bread after frozen storage was able to retain water in the crumb and, consequently, moisture migration to the crust, thus resulting in the crust to fail at greater deformation, that is, the samples were less stiff. XG used at low concentrations, on the other hand, improved the crumb viscoelastic properties on defrosted and microwave-heated samples, probably by hindering the deteriorating effects and avoiding the development of a spongy structure during frozen storage, as suggested by Ferrero and others (1993). Moreover, XG has been addressed to retard amylose retrogradation, due to reduced amylose–amylose interactions. In 2 separate papers the effect of 4 different hydrocolloids was studied, namely XG, GG, locust bean gum (LBG), and HPMC on staling retardation of dough bread (DB), PB and full-baked (FB) breads stored at chilling (Mandala and others 2007) or frozen temperature (Mandala and others 2008) and finally re-baked (DB and PB). The crust puncture test and relaxation test of the crumb revealed that XG addition resulted in a significantly less firm crust on PB and FB breads after chilling storage, with respect to the other samples. X had also the more evident effects on crumb viscoelastic properties, as revealed by relaxation tests, as it gave PB breads with an elastic crumb, DB with a more viscous crumb, and FB breads with an even more viscous crumb (Mandala and others 2007). In the case of frozen samples (Mandala and others 2008), XG supplementation was able to give a softer plastic crust, but only in PB breads, with respect to control and other supplemented samples, probably due to the thickening effect on the crumb walls associated with the air spaces that resulted in a less rigid structure. Finally, the addition of XG to formulations allowed PB and FB breads to have a more elastic crumb when compared to the other samples, thus revealing that this hydrocolloid is more efficient against crumb deterioration in a FB product than in the DB, and highlighting a very different behavior from that found during chilling storage (Mandala and others 2007), in which FB breads presented a complete viscous and deteriorated crumb when hydrocolloids were used. Shittu and others (2009) reported that increasing the dosage of XG up to 2% resulted in a major hindrance of gluten-starch interaction in the presence of hydrocolloid molecules, thus conferring a significantly higher softness to fresh composite cassava-wheat bread. They also reported that crumb hardening and moisture loss followed a linear sequence up to the 1% XG level, which, thus, was proposed as the optimum concentration to reduce both phenomena, even if the 2% XG level best estimated the crumb firming rate. Shalini and Laxmi (2007) investigated the effect of 4 different hydrocolloids, HPMC, GG, K, and CMC on textural characteristics of Indian chapatti bread stored at ambient or chilling temperature and evidenced that 0.75% w/w supplementation of GG gave the softest bread and decreased the loss of extensibility up to 2 days in storage at both temperatures, with respect to the control. The authors suggested that GG has a softening effect, probably by an inhibition of the amylopectin retrogradation, prevention of water release, and polymer aggregation during refrigeration, as well as interference during interchain-amylose association. In a further paper, Shalini (2009) gave more explanations on the effects of GG on staling parameters and found that moisture, water-soluble starch and in vitro digestibility enzyme contents in GG incorporated chapatti were higher than in the control chapatti at both storage temperatures. Smitha and others (2008), on the other hand, working with another flat bread, the unleavened Indian parotta, found that supplementation of hydrocolloids (gum arabic, GG, XG, CMC, and HPMC) resulted in delayed staling 8 hours after baking, with respect to non supplemented breads. HPMC gave the best results in terms of reduction of hardness, while XG was judged by panelists as the best for preserving sensory attributes like softness and chewiness. Angioloni and Collar (2009a) proposed the viability of LBG and CMC blended with oligosaccharides, at a medium-high substitution level, as very valuable sources of dietary fiber (DF) for the baked goods with both “healthy” characteristics and extended shelf-life, due to reduced staling. These conclusions were drawn after modeling the crumb firming kinetics parameters obtained during storage with the Avrami equation. Moreover, good relationships between the main parameters obtained with the different physical analyses (small dynamic and large static deformation methods, viscometric pattern, and image analyses) performed on raw materials and intermediate and final products were found. The effect of ALG and konjac glucomannan (KGM) supplementation at 0.2 and 0.8% w/w flour basis was studied in terms of staling behavior of Chinese steamed bread by Sim and others (2011) who reported that the higher supplementation dose of both hydrocolloids resulted in a significantly lower staling rate up to 4 days, with respect to the control bread, probably because of the hindering effect of gums on macromolecular entanglements thus causing starch recrystallization delay. Wang and others (2006) studied the effect of gluten hydrolysate (GHP)/λ-carrageenan (λC) ratio on the increase in the bread crumb firmness during storage and proposed that the changes occurring in the amorphous part of the starch, when a concentration of 0.5% GHP/γC was used in the product formulation, thus significantly delaying bread staling.

The use of hemicelluloses has been the topic of different studies during the last 10 years. A penetrometric test revealed that supplementation of 0.3, 0.5, or 0.7% hemicelluloses (extracted from buckwheat) increased the penetration depth of the crumb after 72 h of storage at 30 °C, thus delaying crumb hardening, and resulted in bread with an higher specific volume than the control during a 3-days storage period. The best results were in the order 0.5>0.3>0.7% both for hardness and volume (P=0.01) (Hromádková and others 2007). Symons and Brennan (2004) reported that a β-glucan-rich fraction (BGF) extracted from barley and incorporated at 2.5% into a bread formulation reduced crumb staling after one day in storage, as detected by TA, but they did not formulate any explanation of the causes [Note: the discussion of data on firming is not exhaustive, as the authors did not explain neither the rate of staling, nor highlighted that there were no significant differences in firmness between control and BGF-supplemented bread]. The BGF gave, moreover, breads with lower volume, confirming previous results (Gill and others 2002). Jacobs and others (2008) gave interesting new knowledge about the influence of bread production on bread quality when fiber-rich fractions (FRF), enriched β-glucans, and arabinoxylans from hull-less barley were used. They, while confirming the results of Symons and Brenan (2004), found that supplementation of FRF (12% on flour basis, corresponding to 2.5 g of arabinoxylans and β-glucans per 100 g of flour**)** and Xyn within the sponge-and-dough (SAD) baking method, improved the loaf volume, appearance, and crumb structure and resulted in crumb hardness and staling rate similar to that of the control bread, while other baking methods (Canadian short process, remix-to-peak) gave negative results [Note: the main part of the paper deals with a comparison of the 3 baking methods by using a 20% on flour basis supplementation and the authors concluded that the quality of the 20% FRF-enriched SAD bread was equal to or better than the remix-to-peak bread, but they neither presented a statistical comparison between data of the 2 baking methods, nor did they explain why they evaluated the impact of lower FRF addition only with the SAD method]. Skendi and others (2010) studied the supplementation of 2 wheat flours differing in bread making quality (poor and good) with two different-molecular-weight barley β-glucan isolates (at 0%, 0.2%, 0.6%, 1.0%, and 1.4% w/w on a flour dry weight basis) and found that the crumb hardness of β-glucan supplemented breads, measured after 24 h of storage, decreased with its increasing level up to reaching a minimum, and then with a reverse trend, however the values were always lower than the control bread, if we ignore one sample. Moreover, the antistaling effect was more pronounced up to 8 days in storage when the higher-molecular-weight β-glucan isolate was used in both flour types. The authors proposed that the beneficial effects found could be ascribed either to the higher water retention capacity and a possible inhibition of the amylopectin retrogradation of β-glucan, as already suggested (Biliaderis and others 1995), or to the increase of the total area of gas cells. An increase in bread firmness with respect to control wheat formulation was, on the other hand, found by Hager and others (2011) after addition of oat β-glucan, suggesting that this increase in hardness might be ascribed to the increased water-binding capacity of the polysaccharide, thus hindering the development of the gluten network. They also evidenced a consistent increase in staling after the addition of the fat replacer inulin, thus confirming previous results (Wang and others 2002; O'Brien and others 2003; Poinot and others 2010) and in part in agreement with the study of Peressini and Sensidoni (2009) who used 2 commercial inulin products, with lower (ST) and higher (HP) degrees of polymerization, to supplement 3 different wheat flours, moderately strong (MS) and weak (W), and found that the ST inulin addition to MS flour significantly increased the volume and lowered bread firmness, with respect to the control. The authors hypothesized that a delayed starch gelatinization during baking, due to the presence of 12% solutes, and the significant reduction of dough water absorption of ST inulin, may explain this result. The beneficial effect of inulin gel at 2.5% flour basis on increasing the loaf volume and maintaining the hardness value, with respect to a control bread, was also reported by O'Brien and others (2003). In a very recent paper the antistaling effect of substitution of wheat flour with barley flour (28%, 56%, and 84%) or β-glucan (1.5%, 3.0%, and 4.5%) on chapatti bread was assessed by DSC (Sharma and Gujral 2014). Storage at 4 °C for 24 h induced retrogradation in baked chapatties, as revealed by the increase in ΔH, but it was concomitantly reduced up to 44 or 64% when β-glucan or barley flour was used, respectively. The authors proposed that barley flour supplementation increased the levels of soluble as well as insoluble DF, with an increased water absorption and change of the nature of the starch and protein, thus preventing better the staling of chapatties, with respect to loaves obtained with only β-glucan alone, as suggested by Purhagen and others (2012).

The use of pectin slowed crumb hardening in bread that was part-baked and stored at chilling (PB) or sub-zero (PBF) temperatures for variable times (Rosell and Santos 2010). The authors also revealed that PBF pectin-supplemented breads showed a similar hardening trend, with respect to their conventionally baked counterparts, as also demonstrated by using the Avrami equation. Correa and others (2012) reported that the incorporation of high-methoxyl pectin at 1 or 2% resulted in protection with respect to staling, especially when salt was used in the formulation, as it reduced the hardness values with respect to the control sample, as well as maintaining the chewiness. They proposed that the improved specific volume of high-methoxyl pectin-supplemented bread, which gave both a more cohesive and more resilient crumb with a different alveolus structure, which was the main reason for retarded staling.

A certain interest during the last years has been focused also on an animal hydrocolloid, chitosan, a nonbranched linear homopolymer obtained from shrimp and other crustacean shells. Chitosan is a water-soluble cationic polyelectrolyte, while most of the other polysaccharides are neutral or negatively charged at acid pH. In a first paper of Kerch and others (2008), addition of 2% chitosan resulted in increased staling rate of bread, and the author, through DSC analysis and SEM, suggested an increase in water migration rate from crumb to crust and in dehydration rate both for starch and gluten and a prevention of amylose-lipid complexation in breads supplemented with chitosan.

In a following paper, Kerch and others (2010) proposed and analyzed, with the aid of mechanical and DSC measurements, the main possible mechanisms leading to staling in breads obtained with supplementation of different chitosan and chitosan oligosaccharides. They confirmed that staling was the result of 2 independent processes, the first during the first two days of storage depended on changes in the organization of starch polymer chains, later on it was caused by loss of water by gluten. They suggested also that chitosan increased the firming rate during the first stage due to its ability to bind lipids and prevent amylose-lipid complexation, while in the second stage it was enhanced dehydration of gluten due to its water-binding ability. In their work, however, they found that both chitosan oligosaccharides and low-molecular-weight chitosan decreased significantly the staling rate, if compared to middle-molecular-weight chitosan, and they hypothesized that low-molecular-weight substances inhibited crosslink formations between starch granules and protein fibrils which, in turn, are responsible for staling. Later on, Kerch and others (2012a) demonstrated with DSC that when chitosan was used in bread production by the straight-dough or the sponge-and-dough method it accelerated or slowed down the decrease of bound water content during the first stage of staling, respectively, thus delaying or accelerating staling during the first 2–3 days of storage (first stage of staling). In a further paper they showed that supplementation of ascorbic acid to chitosan-enriched bread resulted in a more pronounced decrease of water content during baking in fresh bread compared to the control bread (Kerch and others 2012b).

Modified and damaged starches. The use of modified starches for retarding staling has been suggested since the 1990's, for their ability to influence amylopectin crystallization (Inagaki and Seib 1992; Yook and others 1993; Toufeili and others 1999). Due to the fact, however, that other linear fractions of starch may affect retrogradation, an increased interest has been registered on cross-linked starches, due to their ability to increase the gelatinization temperature, setback viscosity, and decrease the transition enthalpy of gelatinization (Zheng and others 1999; Woo and Seib 2002). A well-focused review on this topic has been published by Myiazaki and others (2006).

According to Leon and others (2006), the content of damaged starch directly influences bread staling through the increase of amylopectin recrystallization, as detected by DSC analysis. The authors concluded that the limited use of damaged starch is a key factor to control the quality of fresh bread and of its shelf-life, in contrast to what was reported earlier by Tipples (1969). In a paper of Miyazaki and others (2008) chemically modified tapioca starches (MTS), but with different degrees of modification, have been used to retard staling in breads obtained from FD, which was subjected to one freeze-thaw cycle and one-week frozen storage. Highly MTS retarded significantly the increase in firmness during 3 days of storage, thus confirming the results of previous papers, due to the slow retrograding rate of amylopectin.

Dextrins and maltooligosaccharides. Dextrins are the product of starch hydrolysis and, since bread staling has been attributed partly to its retrogradation, shortening the starch chain length, as obtained with particular α-amylases, results in reducing the rate of staling.

Miyazaki and others (2004), using DSC, found that among 6 different dextrins (dextrose equivalent 3-40) used at 20%, those with low molecular weight (DE 19, 25, and 40) at 2.5% of substitution retarded retrogradation, as revealed by the ΔH of retrograded amylopectin, but did not delay staling during 3 days of storage. They postulated that the antistaling mechanism following addition of dextrin differed from the retarding effect of dextrin produced by Am, as already reported (Akers and Hoseney 1994; Morgan and others 1997). They also highlighted that retrogradation is not related to water mobility in crumbs, as assessed by the determination of water activity. An interesting study involving the use of TPA, XRD, and DSC reported that the use of β-cyclodextrin (β-CD) resulted in retardation of bread staling during 35 days of storage at 4°C, as changes of some TPA indexes (hardness, cohesiveness, and springiness) were reduced (Tian and others 2009). Data on hardness were fitted with the Avrami equation that evidenced a significant reduction of the rate constant (k), while increasing the Avrami exponent, thus suggesting a retarded crumb-firming kinetic for β-CD-supplemented bread. Moreover, data of XRD showed a delay in changes of crystalline patterns occurring in crust and crumb and this retardation was attributed to a complex amylose–lipid β-CD, as observed by DSC, that resulted in transformation of nucleation type and lowered rate of bread staling.

Jakob and others (2012), studied for the first time, the beneficial effects of different fructans produced by acetic acid bacteria on the texture of bread. Out of 21 strains tested, 4 of them were able to produce high amounts of exopolysaccharides (EPS), as detected by HPLC analysis, which elicited, when supplemented at 1-2% of flour basis, significantly the increase in bread volume and retarded the hardness increase of crumb up to 1 week of storage, the highest differences being observed after addition of 2% sugar polymer from *Neoasaia chiangmaiensis*. The authors proposed that the functional properties of the tested EPS were due to their hydrocolloid character, allowing a high water retention, and due to interactions between polysaccharides and other dough components like gluten and starch, thus influencing the final structure of the baked product. They, moreover, compared effects of EPS to HPMC.

Other fibers. In this section the effect of dietary fiber (DF) other than previously defined hydrocolloids and dextrins on bread staling will be reviewed. According to the Codex Alimentarius Commission, DF are “Carbohydrate polymers with more than 10 monomeric units, which are not hydrolyzed by the endogenous enzymes in the small intestine of humans” (ALINORM 09/32/26 2009). Recently dough properties of bread enriched with DF have been reviewed and the reader is redirected to this paper for the aspects dealing with the interaction of this component in dough development and bread baking (Sivam and others 2010). Fibers investigated during this last decade are of cereal or noncereal origin.

Maeda and Morita (2003) proposed the polishing of soft wheat grain from the outer layer in increments of 10% of total weight to obtain flours with a high content of pentosans and damaged starch. In particular, both water-soluble (WSP) and water-insoluble pentosans (WISP) from the inner part of the wheat grain were added to the conventional flour and their effects on loaf volume and bread staling were assessed. The results indicate that both pentosans gave an increase in loaf volume and a significant decrease in staling up to 3 days in storage, with respect to the control bread. The authors presumed that the high viscous and gelling properties of WSP may improve the strength of gluten and the retention of gas generated in the dough.

Mandala and others (2009) studied the effect of different ingredients (hydrocolloids, polydextrose, oat flour, inulin, and commercial shortening) on crust firmness and crumb elasticity of breads obtained after thawing and baking of FD (at sub-zero temperatures for 1 week) and PB breads, and found that inulin was the best of them in reducing bread crust firmness, probably due to a better moisture redistribution, even if fresh sample had the firmer crust.

Gomez and others (2003) found that the use of fibers of different origin (cellulose, cocoa, coffee, pea, orange, and wheat), while increasing the crumb firmness of fresh bread with respect to the control, reduced its evolution during 3 days of storage, and they postulated that this effect may be attributed to the already demonstrated water-binding capacity of fiber, which in turn reduced water loss during storage, as well as the probable interaction between fiber and starch, resulting in the delay of starch retrogradation. The best effect in delaying the bread staling was noticed after 2 days by using a short-length wheat fiber.

Collar and others (2009) found a positive effect on reducing staling rate during 16 days of storage of breads enriched with 2 kinds of cocoa fiber, as assessed by hardness and chewiness fitted with the Avrami equation, when increasing the dose of addition up to 6%, especially when the formulation was supplemented with alkalinized cocoa-soluble fiber, while over-dosage resulted in a staling rate similar to that of the control breads.

Zhou and others (2009) correlated the reduction of starch retrogradation after X-ray measurements and application of the Avrami model with increasing levels, from 1 to 5%, of tea polysaccharide, which was able to reduce the slope of the staling rate up to 9 times, with respect to the control. The authors also found that the magnitude of bread staling retardation strongly depended on the type of wheat flour used.

Addition of butternut fiber at 10g/kg of flour decreased the staling rate of bread after 7 days of storage, as measured by compressibility, DSC, and digital image analysis (Pla and others 2013). The authors clearly showed that fiber extracted from the peel resulted in a drastic reduction of the firmness value, suggesting a retardation of amylopectin retrogradation, more air occluded (cell area 100/total area), same number of particles (alveolus or gas cells) per square centimeter, and higher mean size of particles, with respect to the control bread. The authors concluded that the particular composition of fiber extracted from peel, that is presence of lignin, less-branched pectin chains, and significant higher protein content than the other butternut fiber used, may have accounted for the results obtained.

2.3. Lipids and shortenings

The role of surface-active lipids and shortenings has been well described by Gray and Bemiller (2003), and later on by Kohajdova and others (2009), thus we will report briefly the new knowledge not or only partially covered by these 2 reviews focused mainly on the use of mono or diacylglycerols alone or esterified (DATEM).

Collar (2003) suggested that individual and/or binary supplementation of fat-monoglycerides (MGL) and sodium stearoyl lactylate (SSL) to bread dough positively influenced the level of the pasting parameters assessed by RVA (peak viscosity, pasting temperature, and setback during cooling) that are associated with a significant delay in bread firming. Moreover, she does not recommend binary use of MGL/carboxymethylcellulose (CMC) and SSL/CMC, as the antagonistic effects of the pair gum/surfactant resulted in a nullification of the benefits exerted by the individual emulsifiers.

Ribotta and others (2004a) evidenced the beneficial effect of DATEM on retarding crumb firming at 4 and 20 °C aging temperature of bread from both non frozen and FD, and they supposed that the formation of complexes with amylose and amylopectin inhibited the staling phenomenon. Sawa and others (2009) studied the effects of a wide range of purified saturated and unsaturated MGL at different concentrations on the crumb firmness evolution during bread storage and reported that the use of C16:0 and C18:0 and cis- and trans- C18:1 resulted both in a lower crumb firmness, even if depending on the baking process used, and in delayed bread staling, when compared to control bread. They suggested the interaction of MGL with amylose and amylopectin as the main cause of the obtained results. Manzocco and others (2012) proposed that a particular system morphology, as assessed by proton density/mobility using magnetic resonance imaging (MRI), was generated in bread in which palm oil was replaced with a MGL-sunflower oil-water gel. The morphology change resulted in a 81% reduction in bread fat content as well as in a delay in bread staling during storage. The incorporation of the gel resulted, in fact, in a reduced proton density/mobility in comparison with standard formulation, thus it was concluded that the physical architecture of the lipids used in the formulation could contribute to modulate the retrogradation rate. Smith and Johansson (2004) reported that the increase of solid fat of a shortening containing fully hydrogenated soybean oil was able to delay bread staling and they suggested that saturated triacylglycerols acted in a similar way as saturated monoacylglycerols, that was an interaction with amylopectin. Mnif and others (2012) proposed a new biosurfactant obtained by *Bacillus* *subtilis* as antistaling agent and compared it to soy lecithin. The bioemulsifier supplementation significantly reduced the bread staling over an 8-day period, depending on its amount, and the maximum decrease of staling rate was obtained with a 0.05% biosurfactant addition, which was also the dose that resulted in the highest bread specific volume. The authors suggested that the slower firming may be ascribed to the capacity of the emulsifiers to form a complex starch-emulsifier, which in turn delayed wheat starch crystallization. Additionally, the biosurfactant reduced the susceptibility to microbial growth during bread storage.

2.4. Minor ingredients affecting bread staling

The functional effects on fermentation and bread baking of whey protein and casein have been reported by Erdoghu-Arnozcki and others (1996). Casein and whey, together with sodium alginate (ALG) and k-carragenan (K) were used in an attempt to improve the quality of FD, specifically to retard its quality loss during freezing time and after 3 freeze-thaw cycles (Yun and Eun 2006). Bread made with milk proteins and hydrocolloids were softer after 4 days in storage, with respect to control bread, probably because of better moisture retention and improved emulsification of these ingredients. Similar results were obtained in a later paper of Shon and others (2009).

Addition of juices to wheat bread formulations have been proposed to ameliorate its nutritional profile (Batu 2005), as sweeteners and color enhancers, and to increase volume and extend shelf-life (Matz 1989). Lasekan and others (2011) postulated that the high concentration of monosaccharide of the pineapple juice concentrate used at a 1.5% level in the formulation of white bread interfered with protein-starch interaction and delayed staling, but only after one day of storage. Sabanis and others (2009) studied the effect of supplementation (at 50% level sucrose substitution) of 2 types of raisin juices, concentrated and dried on evolution of crumb firmness of bread obtained with both bread wheat and durum wheat. The dried juice decreased the wheat starch gel rigidity and retrogradation for the presence of glucose and fructose, thus resulting in reduced staling after 2 days of storage, with respect to control loaves, especially when durum wheat flour was used.

Tomato pomace has been suggested as a good source of hydrocolloids and was thus proposed (0, 1, 3, 5, and 7%) for flat bread production by Majzoobi and others (2011b), who detected delayed bread staling up to 4 days of storage at 25 °C in tomato-pomace supplemented bread, with respect to control sample, due to the concomitant increase in volume and moisture content and decreased starch retrogradation.

Surface coating treatments have been patented for improving the quality of bakery products (Lang and others 1987; Lonergan 1999; Hahn and others 2001; Jacobson 2003; Casper and others 2006, 2007). The main advantages proposed for glazing were the improvement of flavor and appearance. The moisture barrier exerted at the surface of baked products allows retaining and aiding dough expansion during baking, thus resulting in a reduction of surface defects, improvement of color, and higher baked volume. Recently, however, other beneficial effects of glazing have been described. Jahromi and others (2012) studied the effect of different glazing treatments, including natural substances, polyol, sugar, and hydrocolloids on the staling rate of breads stored up to 12 days. Increased moisture and reduction of water movement have been addressed as the main causes of delayed staling by different glazing ingredients, mainly, water, egg yolk, propylene glycol and starch, while at intermediate storage periods (2, 5, and 8 days) also other glazing substances significantly retarded the increase in crumb firmness, with respect to control bread.

Chin and others (2012) focused their work also on crust behavior following different glazing applications. Glazing with cornstarch, skim milk, and egg white were able to reduce the rate of moisture loss in bread crumb during 6 days of storage, thus reducing the staling rate of glazed bread, with respect to the control. Moreover, glazing resulted in an increase in crust firmness, although the moisture content of the crust increased, probably because the rate of moisture migration from crust to the surrounding atmosphere could be lower with respect to that from the crumb to the crust region.

Sodium chloride impact on bread staling has recently been well reviewed and ascribed mainly to the increased gas retention effect of dough with NaCl that allows an increase in crumb porosity and a consequent decrease in crumb firmness (Beck and others 2012a). The retrogradation effect ascribed to Na+ inclusion in starch molecules during storage of bread has been suggested as delaying staling (Beck and others 2012b). In particular, a decrease in bread staling following the decrease in NaCl levels was shown. Furthermore, a linear relationship between rheofermentometer data, bread volume, and crumb firmness was demonstrated, thus suggesting that the quality of bread could be predicted by gas release measurement.

3. Enzymes

The role of enzymes on bread staling has been one of the preferred topics during this last decade and along with quite recent reviews (Haros and others 2002; Butt and others 2008; Goesaert and others 2009), an important number of papers have appeared, which will be discussed. Apart from the effects of amylases, an increasing interest in transglutaminase, a protein modifier enzyme and other non-starch polysaccharide-modifying enzymes has been recorded.

α-amylases and transferases. The action of α-amylases in reducing bread staling has been the topic of numerous studies (Gray and Bemiller 2003), and different ways of action have been proposed. The paper of Goesaert and others (2009) provided new knowledge on the α-amylase mode of action and its antistaling activity. In particular, they found that the maltogenic α-amylase from *B. stearothermophilus* degraded significantly the outer amylopectin branches, thus producing amylopectin chains that are too short to crystallize. The result was the prevention of a "permanent" (based on amylopectin crystallites junction zones) amylopectin network, thus staling was delayed. Maeda and others (2003) proposed that a particular thermostable mutant, α-amylase (M77), purified from *Bacillus amyloliquefaciens* F increased the specific volume of the bread and improved the softness of bread crumb, when compared to the commercial exo-type α-amylase Novamyl (NM). They also showed that softness evolution of breadcrumb during storage was not correlated with thermostability. Rao and Satyanarayana (2007) found that the addition of α-amylases produced by *Geobacillus thermoleovorans* to wheat flour improved the fermentation rate and decreased the viscosity of dough, while increasing the volume and texture of bread, moreover, it also increased its shelf-life by retarding staling, with respect to control sample, but they did not give any explanation of this beneficial effect. Jones and others (2008) managed to develop a new maltogenic α-amylase from *Bacillus sp.* TS-25, formerly *B. stearothermophilus*, which increased thermal stability and the possibility to work at acidic pH values that are typical of sourdough and rye breads. Kim and others (2006) reported that the addition of a fungal α-amylase to polished flour resulted in an improvement of gas cell distribution and softness of breadcrumbs and delayed staling, without lowering the loaf volume with regard to control bread made with hard wheat flour.

Blaszczack and others (2004) studied the effect of 2 α-amylases, one of fungal and the other of bacterial origin, on the texture and microstructure of bread. The two α-amylases resulted in different microstructure of bread, with respect to control bread, as revealed by light SEM, thus staling was delayed. The authors proposed distinct antistaling mechanisms for the two α-amylases.

Xylanases. Xylanases (Xyns) are enzymes able to retard bread staling, as reviewed by Butt and others (2008), to which the reader is redirected.

A recombinantly produced Xyn B (XynB) from *Thermotoga maritima* MSB8 retarded the staling of frozen PB bread (Jiang and others 2008). When added to the formulation the resulting bread had a 40% reduction in crumb firmness and retarded staling, as bread supplemented with XynB after 4 days of storage at 4 °C had the same firmness as control bread after 1 day of storage. Data obtained with DSC analysis showed that XynB was able to retard amylopectin crystallization. Recently, Zheng and others (2011) found the right dosage to be used for two GH 10 Xyns, a psychrophilic (XynA from *Glaciecola mesophila*) and mesophilic one (EX1 from *Trichoderma pseudokoningii*), with the aim to retard bread staling. Both Xyns exhibited similar anti-staling effects on the bread, but while XynA proved to be more effective in reducing the firming rate, the EX1 performed better in reduction of the initial bread firmness. The optimal dosage of the psychrophilic Xyn was much lower than that of the mesophilic counterpart, probably because the temperatures used for dough preparation and proofing were in the range of optimum activity of psychrophilic XynA, as otherwise reported (Collins and others 2006).

Recent results of the application of a thermostable enzyme cocktail from *Thermoascus aurantiacus* showed an antistaling effect (Oliveira and others 2014). The main enzyme found on the cocktail was Xyn, xylose being the main product released through enzyme activity after prolonged incubation, and its application at 35 Units of Xyn/100 g significantly delayed staling of bread up to 10 days at 4 °C if compared to control loaves. On the basis of DSC results (lower enthalpy) it was suggested that products deriving from Xyn activity interfered with the reorganization of the amylopectin and/or with the redistribution of water in the system, with a consequent retrogradation reduction. Recently Ghoshal and others (2013) suggested that the reduction of crystallization and reduction of crystal growth in bread, as assessed by using n and k parameters of the Avrami equation, was caused by Xyn addition in whole-wheat bread stored at 4 and 25 °C for 10 days, thus resulting in delayed staling. Measurement of thermal properties confirmed the beneficial effects of Xyn, as it lowered the endothermic peak for staling and the change of enthalpy during storage, with respect to control bread.

Enzyme mix. The difference in mode of action of the various enzymes has been used recently by several authors, which depended on additive or synergistic effects in order to retard staling.

Leon and others (2002) studied the effects of 2 commercial enzyme mixtures containing α−amylase and lipase activity on staling rate. Both mixtures helped in slowing down the staling rate, especially the blend with the higher α−amylase activity. The beneficial effect was attributed to a delay in amylopectin retrogradation and to the formation of amylose-lipid complexes, both revealed by DSC analysis.

The use of a microbial transglutaminase (protein-glutamine γ-glutamyl transferase, Tgm), which catalyzes the formation of ε-(γ glutamyl-)-lysine crosslinks in proteins via an acyl transfer reaction (Motoki and Seguro 1998; Larre and others 2000), has received a great deal of interest. Tgm with or without added amylolytic (maltogenic bacterial α−amylase in granulate form (NMYL)) or non amylolytic (PTP) had beneficial effects on hardness evolution of bread obtained with white (Collar and Bollain 2005) and whole-meal flour (Collar and others 2005). Bread softness was reduced up to 16%, with respect to control bread, when interactive effects were tried, and the best combination was the addition of NMYL to Tgm breads, ascribing this effect to the relevant softening effect of NYML.

Gambaro and others (2006) proposed that the addition of a mixture of α−amylase and Xyn was able to extend the shelf-life of brown pan bread by retarding staling, as assessed by sensory and instrumental analyses. They suggested that the mixture produces low-molecular-weight dextrins with high water retention capacity, and that could be partly responsible for the lower staling rate. Moreover, they found a high correlation between both sensory and instrumental parameters and staling rate.

Caballero and others (2007) studied the single and synergistic effects of some gluten-crosslinking enzymes (Tgm, glucose oxidase, and laccase), and gluten-degrading enzymes (α−amylase, Xyn, and protease) on bread staling. They found that α−amylase, Xyn, and protease were able to lower significantly the staling effect promoted by Tgm and proposed different mechanisms of action for each enzyme. In particular, they suggested that α−amylase and Xyn could have an effect on the dough polysaccharide fraction, while the protease may counteract Tgm-action, by a simultaneous action on the dough protein fraction.

Waters and others (2010) proposed that the highest Xyn and α−amylase activities of 5 thermozyme cocktails with different hydrolytic enzyme profiles produced by *Talaromyces emersonii* resulted in delayed staling. The enzyme cocktail B was the best in reducing crumb hardness evolution after 5 days of storage, with respect to control bread.

Others. The oxidizing effect of glucose oxidase (GO) was exploited for retarding staling of bread (Bonet and others 2006). When used at a concentration of 0.001%, GO delayed significantly the bread staling up to 12 days at 25 °C. The antistaling effect suggested was due to the large amount of total pentosans produced by GO that can associate with the glutenin macropolymer, thus leading to retain of high amounts of water.

4.Associated mixtures of ingredients and/or enzymes

In this section we will summarize the results of the main studies dealing with ingredients and/or technological aids not included in the previous classes or combinations of different ingredients. An interesting review on shelf-life improvement of polyols, to which the reader is redirected, has recently been published (Bhise and Kaur 2013).

Wang and others (2007) reported that, when 1% of wheat gluten hydrolysate was used, the hardness value of 3-days-old bread was equivalent to that of 1-day-old control bread, probably for the higher, even if not significantly, specific volume and moisture content of wheat gluten hydrolysate -supplemented sample.

Abu-Goush and others (2008) found a beneficial effect of sodium-propionate in delaying staling of Arabic flat bread and correlated this result to moisture loss, starch retrogradation, and protein interaction effects, as revealed by near-infrared spectroscopy data.

Shaikh and others (2008) tested 8 different antistaling agents on unleavened chapatti bread and measured various staling parameters such as moisture content, texture, water-soluble starch, in vitro enzyme digestibility, enthalpy change and sensory quality during 10 days of storage, at 4 and 29 °C. When comparing the effect of the added ingredients the authors found that maltodextrin had the highest rank at both temperatures, while the worst result was exerted by glycerol monostearate, following the order maltodextrin> GG> α–amylase>sorbitol> XG> SSL> propylene glycol> glycerol monostearate. Moreover, when trying 6 combinations, SSL + Am gave the best texture values, suggesting that α-amylase first breaks starch molecules, and then SSL forms the complex with fragments derived from starch rupture.

The lowest amylopectin retrogradation of soy milk powder was addressed as the cause of delayed staling rate in wheat-soy bread (Nilufer-Erdil and others 2012). This result was attributed to the synergistic effect of soluble fiber and partly denatured soy proteins and higher lipid content of the soy milk powder. The delay of staling was confirmed by Instron firmness measurements, although loss moduli revealed by dynamic mechanical analysis (DMA) did not give significant differences of stiffness among formulations, contrary to what had been reported previously by Vittadini and Volovodtz (2003).

Jekle and Becker (2012) studied the effects of pH adjustment, water, and sodium chloride addition in order to model bread texture and staling kinetics of bread crumb. By using the Avrami equation and the firming rate, which gave a better square correlation coefficient, the authors managed to predict the staling rate as a function of pH, NaCl, and water addition. In particular, they found an increase in the firming rate with increased NaCl concentration and pH reduction and a decrease when water was added to the dough, probably as the change in the volume of bread had a better influence on the staling rate, with respect to the effect of the chemicals, since the literature well correlated the specific volume of breads with the firming rate (Axford and others 1968; Russel 1983).

The addition of γ-polyglutamic acid (PGA) at 3 concentrations (0.5, 1.0, and 5.0 g kg^{-1}, w/w) was suggested by Shyu and others (2008) to evaluate its effect on staling of wheat bread. The hardness value of the 6-day 1.0 kg^{-1} PGA stored bread was less than the value of control bread after 1 day, thus PGA significantly reduced staling rate, as also demonstrated by the decrease in cohesiveness, which was significantly delayed by the PGA addition.

Response surfaces and mathematical models were used by Gomes-Ruffi and others (2012) to show the beneficial effect of the contemporary addition of SSL and of the enzyme maltogenic α-amylase (MALTO) on both the increase of bread volume and the reduction of firmness, especially after 10 days of storage, when the combination of 0.50 g SSL/100 g flour and 0.02 g MALTO/100 g flour resulted in the same firmness value as the control at day 1 of aging. The authors suggested that SSL formed complexes with starch molecules, while MALTO reduced the molecular weight of the starch molecules, thus reducing retrogradation.

Pourfarzad and Habibi-Naiaf (2012) used the positive results in changing the hardening rate of Barbari bread obtained with an antistaling liquid improver, made up of glycerol, SSL, and enzyme-active soy flour, at different amounts, to test the consistency of 11 new mathematical staling models. They found that all models presented high values, the best being the rational and the quadratic, thus concluding that these models are suitable to simulate staling kinetics. The best improver formulation contained 1.27% glycerol, 0.41% SSL, and 1.59% enzyme-active soy flour.

The plasticizing effect of the sorbitol on starch/gluten biopolymers has been described by Pourfarzad and others (2011) as the main reason of anti-staling effect of soy-fortified bread for storage times longer than 2 days and up to 5 days. The same effect was found also for propylene glycol when used at 5 g/100 g flour.

5. Processing factors affecting staling rate

Researchers have focused their attention during the last 10 years mainly on baking technology, process parameters, and storage temperature, but other factors will also be reported.

5.1. Storage temperature

The effect of storage temperature on staling has been reported by different authors, and the main characteristic is a negative dependence between staling rate and temperature (Colwell and others 1969).

The consumer request to have ‘‘fresh’’ bread available at any time of the day (Matuda and others 2005) has stimulated the bakery industry to exploit freezing technology and this has driven researchers to focus their attention mainly on effects of freezing and frozen storage on bread staling, especially on dough and par-baked (PB) samples.

A comprehensive picture up to 2008 on the effect of raw material requirements, processing conditions, and baked bread quality from frozen dough (FD) and PB bread are reviewed by Rosell and Gomez (2007), Selomulyo and Zhou (2007), and Yi (2008), to which the reader is redirected.

Carr and others (2006) carried out a sensory comparison between frozen part-baked French bread (FPBFB) and fresh bread during a week of frozen storage with daily inspections. The FPBFB had a lower weight and specific volume, with respect to fresh bread, but was rated better after 4 days of frozen storage by a consumer acceptance test (difference from control test) with respect to commercial brand bread. Moreover, data on texture and sensory analysis of FPBFB stored for a week were similar to that of fresh bread. Frozen storage of PB chappati, a Indian unleavened flat bread, was beneficial for maintaining its quality (Gujral and others 2008). In particular, the extensibility of par-baked chapatti after rebaking was very similar to that of the fresh conventionally baked sample. The main feature was that sample of PB bread stored at ambient temperature or frozen (after thawing and rebaking), showed a significant higher extensibility when compared to the same sample of conventionally baked chapatti breads, thus giving loaves with better sensory quality than frozen conventionally baked chapatties. Yi and Kerr (2009) highlighted the influence of freezing rate (rate 1:15 °C/h, rate 2:33°C/h, rate 3:44 °C/h and rate 4:59 °C/h), dough storage temperature (-10, -20, -30, and -35 °C) and storage duration on bread quality. They found that sample frozen at the lower freezing rates and stored at the higher temperatures had higher specific volume, were softer, and were lighter in color, but staled more easily, due probably to the higher damage to the starch-gluten network at slower freezing rates (Yi 2008). They noted that response of gluten structure and yeast activity to freezing rate and temperature should be balanced in order to find the optimal freezing conditions. Aguirre and others (2011) confirmed the existence of moisture equilibration between crumb and crust during bread storage, and demonstrated that storage at -18 °C resulted in very limited water movement when compared to bread stored at 4 and 25 °C. As a consequence, water activity values were almost constant in bread stored for 23 days at -18 °C. They showed that the starch molecules re-associate during storage to give a new crystalline structure with a typical X-ray diffraction (XRD) B-type structure and that storage at -18 °C, that is a temperature below the glass-transition temperature (T_g), slowed down but did not stop the recrystallization speed, and only crystal growth occurred. The effect of vacuum-cooling on the staling rate of sourdough whole meal flour bread was assessed by Le-Bail and others (2011). Vacuum-chilled bread showed higher moisture loss, crumb hardness, and enthalpy of melting (ΔH) of amylopectin crystals than conventionally cooled bread. The authors concluded that the negative effects of the quick vacuum-cooling is the result of the increased number formation of amylopectin crystallites and, thus, of recrystallized amylopectin. Ronda and others (2011) studied the effect of prolonged storage time on staling of PB and fully baked (FB) breads. Three parameters, namely moisture content, firmness, and starch retrogradation as well as the T_g of the maximally freeze-concentrated state (T_g'), were considered to evaluate bread aging. The thawed and rebaked PB bread showed significantly lower amylopectin ΔH values than that of FB bread, and this may partially explain the similarity of PB bread with fresh bread. The authors evidenced the need to select a proper frozen storage temperature, sufficiently lower than T_g'. Frozen storage time, moreover, resulted in a significant decrease in firmness of PB bread crumb. Based on the obtained results, the authors proposed that hardening of bread during storage may not be related only to starch crystallization or water loss and developed a regression study describing how the combined effect of both variables could better explain the firming evolution. Majzoobi and others (2011a) hypothesized that the higher moisture content of Barbari PB flat breads after full baking was the cause of delayed staling up to 72 hours, with respect to control sample, and proposed that bread crumb structure is formed completely during the part-baking stage, while staling occurs in PB bread during storage at ambient temperature, even if full-baking leads to the disappearance of many signs of staling, thus the resulting bread has softer texture. Finally, they suggest storing the part-baked bread at frozen temperature for no more than 2 months to reduce deterioration of bread caused by the growth of ice crystals. In a subsequent paper Majzoobi and others (2012) recommend the addition of 15% wheat germ for the general sensory improvement of Barbari bread, although that did not manage to retard staling.

In 2 separate papers Karaoglu (2006) and Karaoglu and Kotancilar (2006) evidenced the influence of par-baking on quality of wheat bran and white breads, respectively, supplemented or not with calcium propionate, during chilling storage (4 °C) up to 21 days. Both papers gave similar results, which were a softer bread crumb, with respect to a control group, in breads PB for 10 min, rebaked, and stored for 7 and 14 days.

5.2. Sourdough fermentation

Sourdough fermentation has been known since ancient times and, among the beneficial effects, reduction in staling has been reported and recently discussed in 2 reviews (Arendt and others 2007; Chavan and Chavan, 2011), to which the reader is redirected. The different metabolites produced by lactic acid bacteria (LAB) have proved to have a beneficial effect on texture and staling. EPS, for example, are a valid and economic alternative to hydrocolloids, while organic acids affect the protein and starch fractions and reduce the pH that results in an increase in protease and amylase activities of the flour, thus reducing staling.

Katina and others (2006a) managed to delay bread staling at 3 and 6 days of storage, with respect to white wheat bread, by combining wheat bran sourdough and an enzyme mix (α-amylase, Xyn, and lipase). The crumb hardness of the supplemented bread after 6 days of storage was the same as that of white bread at day 1. The authors used NMR, DSC, and microscopy to explain this result and found fewer changes in amylopectin crystallinity and rigidity of polymers in bran sourdough bread with enzymes, which also showed starch granules much more swollen, with respect to white bread, as a result of the higher water content and degradation of cell wall components. In another paper, Katina and others (2006b) proposed the use of surface-response methodology to optimize sourdough process conditions aimed at improving flavor and texture of wheat bread. They found that combining flour with low ash content, and optimizing sourdough fermentation time, staling was reduced up to 4 days. The best result was, in particular, obtained using *Saccharomyces cerevisiae* sourdough fermented bread for 12 h at 32 °C and with flour ash content of 0.6 g/100 g. It was also found that the fermentation time had an important linear effect on softness of bread crumb. Finally, it was confirmed that higher ash content of flour increased firmness in sourdough breads fermented with *Lactobacillus brevis, S. cerevisiae* or a combination starter (Collar and others 1994). Plessas and others (2007) proposed the use of sourdough with immobilized cells, as it resulted in a threefold delay in staling, compared to the traditional compressed baker's yeast bread. The authors hypothesized that the retention of higher moisture levels after baking and reduced moisture loss rates are due to the more compact texture in breads obtained with the suggested technique. In particular, they showed that sourdough breads presented lower loaf volumes for the same loaf weights, and fewer holes of higher size, with respect to conventional baker's yeast bread. Dal Bello and others (2007) confirmed that the higher volume of bread produced by the sourdough fermentation activity of the antifungal strain *Lactobacillus plantarum* FST 1.7 and of *Lactobacillus sanfranciscensis* LTH 2581, with respect to chemically or nonchemically acidified bread, delayed crumb staling up to 3 days. Additionally, the *L. plantarum* FST 1.7 revealed inhibitory activity against *Fusaria*.

Fadda and others (2010) found that durum wheat bread produced with sourdough at a dose higher than 10% significantly lowered and slowed crumb-firming kinetics, as assessed by TA and DSC results, the latter used with the Avrami equation, provided gluten and yeast were added.

Recently, Tamani and others (2013) associated the increased EPS production during dough formation following the inoculation of ropy LAB starter cultures (*Lactobacillus delbrueckii* subsp. *bulgaricus* LB18; *Lactobacillus delbrueckii* subsp. *bulgaricus CNRZ* 737, and *Lactobacillus delbrueckii* subsp. *bulgaricus* 2483) with increased bread volume and reduced staling over 5 days of storage, with respect to the control bread, while one nonropy LAB (*Lactobacillus helveticus* LH30) did not result in beneficial effects. The authors suggested that the higher levels of EPS obtained with LAB may have resulted in greater water retention, leading to the softer crumb structure of these breads, even if they evidenced that the EPS production did not correlate with the extension of shelf-life, thus their effect was more qualitative than quantitative.

5.3. Baking and fermentation

It has been reported that both baking time and temperature affect the quality and staling rate of bread (Seetharaman and others 2002). Patel and others (2005) studied the effects of the use of different ovens and dough size, when baking at constant temperature for varying times, on texture, thermal properties, and pasting characteristics of products. Breads baked at the lower heating rates had lower amylopectin recrystallization, rate of bread firmness, and amount of soluble amylose. Similar results were obtained by Mouneim and others (2012). Baking temperature and time affected some physical properties of bread from composite flour made by mixing cassava and wheat flour at a ratio of 10:90 (w/w) as revealed by central composite rotatable experimental design (Shittu and others 2007). Both the baking temperature-and-time, among others, influenced the dried crumb hardness, due to the complex effect of temperature and time combination, but the developed second-order response surface regression equations could not predict satisfactorily most of the measured properties, thus the authors proposed further studies to optimize the cassava and wheat flour bread baking process. Three different heating temperatures corresponding to 3 heating rates were also tested by Le-Bail and others (2009) with an innovative protocol in which a degassed piece of dough was baked in a miniaturized oven, in order to compare it with traditional dough. Hardening of the crumb occurred after retrogradation of amylopectin, as revealed by calorimetric tests, and higher baking kinetics resulted in faster staling rates. Additionally, the relative Young modulus, expressed as the ratio of the modulus of the cellular crumb vs. the modulus of the degassed crumb, was proportional to the square of the relative density of the crumb. In a further paper Le-Bail and others (2012), working with a degassed sourdough, confirmed the previously obtained results and gave more explanation on the effect of prolonged baking on staling rate, that was an increase of the amount of amylose leaching from the starch granule, leading to a higher Young's modulus of the crumb at the end of staling.

Different heating rates were recently associated with water vapor permeability (WVP), effective moisture diffusivity (D_{eff}), and sorption of bread crust and crumb (Besbes and others 2013). The authors showed that baking at 240 °C gave both crust and crumb with higher moisture diffusivity coefficient and that the crust had a higher WVP than that of sample baked at 220 °C. They proposed a more pronounced porosity of crumb and crusts of breads baked at the higher temperature, as revealed by porosity values and scanning electron microscopy (SEM) determinations, as the cause of the obtained result. Purhagen and others (2012) concluded that breads obtained with different fibers (fine durum, oat bran, rye bran, and wheat bran) baked in pan remained softer after 7 days of storage, with respect to free-standing baked sample, and attributed this to the lower specific volume of pan-baked breads due to their high water content. Moreover, pan-baked loaves lost less water during storage, with respect to free-standing sample, probably because of the smaller crust area of these loaves. The difference in staling behavior between the 2 baking methods was not attributed, however, to starch retrogradation, while the influence of fibers was small, if compared to the baking method, thus confirming data obtained in another paper in which other antistaling agents, namely α-amilase, distilled monoglyceride, and lipase, were compared to the baking method (Purhagen and others 2011a).

The effect of fermentation on the firming kinetics could not be explained only by its effect on volume, but also with the presence of different enzymes, such as amylases, proteases, or lipases that, alone or in combination with other enzymes, may help in reducing the firming rate in white or wholemeal bread, thus longer fermentation times enhanced the action of the enzymes, with a resulting reduction of the staling rate (Gomez and others 2008). The higher the yeast dose, the higher the quantity of dough enzymes previously cited. Temperature of fermentation, on the other hand, had a minor impact on bread staling. Moreover, the authors managed to adjust the firmness parameters to simple curvilinear equations and obtained high correlation coefficients (>90%). Ozkoc and others (2009) compared different baking methods, namely conventional, microwave, and infrared-microwave combination, in order to assess staling kinetics of hydrocolloid-supplemented breads during 120 h of storage, by using several methods, namely texture analysis (TA), differential scanning calorimetry (DSC) rapid visco-analysis (RVA), and X-ray and Fourier transform infrared spectroscopy (FTIR). The starch retrogradation of breads obtained with a combination oven was similar to that of conventionally baked ones, as revealed by ΔH values and FTIR outputs, thus leading the authors to postulate that it was possible to produce breads by combination heating with a staling rate similar to that of conventionally baked ones. Moreover, data from RVA and X-ray showed that the rapid staling rate typical of microwave baking can be mitigated by infrared-microwave combination heating. As expected, the addition of a xanthan gum (XG)-guar gum (GG) blend to the formulation retarded staling.

5.4. High-hydrostatic-pressure processing (HPP)

This unit operation may change structural and functional properties of proteins and cereal starches and is being investigated to improve quality of breads made with flours alternative to wheat.

In a fundamental study on the use of HPP to improve the bread making performance of oat flour Huttner and others (2010) subjected oat batters to 3 levels of HPP (220, 350, and 500 MPa) and the treated samples replaced untreated oat flour in an oat bread recipe, by 10, 20, or 40%. Staling rate, as assessed by a Texture Profile Analysis (TPA) crumb hardness test, was reduced when 10 to 40% oat batter treated at 200 MPa was used, if compared to the control. The HPP-treatment at 200 MPa weakened the proteins, affected the moisture distribution, and also influenced the interactions between proteins and starch, which caused a decrease in the staling rate of the oat-bread. Opposite results were presented in another paper published some months later (Vallons and others 2010). The authors replaced 2 or 10% of a sorghum bread recipe with sorghum batters HPP-treated at 200 and 600 MP and found that breads containing 2% sorghum treated at 600 MPa had slower staling rates than control. More recently Angioloni and Collar (2012) worked with fixed amounts of oat, millet, and sorghum HPP-treated flours (350 MPa), which replaced (60% for oat, 40% for the other 2) wheat flour. Half of the control bread was prepared by applying HPP to 50% of wheat flour. Results indicated that HPP-treated wheat and oat breads lowered final values of crumb hardness and Avrami exponent, thus giving softer breads with slower staling kinetics, with respect to control bread.

6. Measurement methods

The results reviewed above refer to one or more measurement methods to assess bread staling, but there has not been up to now a methodology that allows a complete measurement of the staling phenomenon to the same extent as that described by a consumer (Sidhu and others 1996). Different specific reviews before that of Gray and Bemiller (2003) have dealt with the methods used to assess the rate and/or degree of staling such as those mentioned by Maga (1975), Kulp and Ponte (1981), and Ponte and Ovadia (1996). In most cases bread staling, apart from the more simple and direct texture analysis (TA), is indirectly measured as the extent of starch retrogradation, as also reviewed by Karim and others (2000). An interesting review, moreover, revisited crumb texture evaluation methods (Liu and Scanlon 2004), while another one summarized the more frequently used analytical methodologies for assessing bread staling (Choi and others 2010). In the following pages the major reports dealing with new methodologies and/or new applications used to measure bread staling during the last ten years will be reviewed.

6.1. Thermal analysis

Bollain and others (2005) proposed small dynamic deformation and large static deformation methods to evaluate the thermodynamic and physical-mechanical changes of enzyme-supplemented white or whole bread during staling. They successfully detected rheological changes of bread, as influenced by recipe and storage time, with dynamic thermomechanical analysis (DTMA) in the compression mode. They detected that the onset frequency (f_0) and the rubbery or plateau moduli (E') rose as the bread aged in a similar way to the hardening and firming curves. Moreover, relationships between the dynamic (DTMA) and static (TA) methods were found.

Ribotta and Le Bail (2007) used DSC and DMA to study bread staling. DSC evidenced water migration from the crumb to the crust and changes of water properties as initial and onset temperature of ice melting decreased significantly after 1 day and freezable water (FW) and unfreezable water (UFW) decreased and increased, respectively, as a consequence of aging. DSC results suggested the existence of a possible second transition, due to ice-melting transition being diverted to lower temperatures. The authors proposed that a concomitant water migration from the crumb to the crust and an incorporation of water molecules into the starch crystalline structure, developing after bread staling, may account for the decrease in FW after 4 days of storage at 4 °C. Moreover, they suggested that some water molecules were incorporated in the crystalline lattice when starch crystallized. DMA analysis showed significant changes in the thermo-mechanical profile of the crumb during staling, as aged breads contracted at a lower rate during cooling, but they evidenced a greater deformation during freezing and higher retraction within the complete cooling–freezing cycle, thus suggesting that the higher matrix rigidity, a consequence of the higher amount of retrogradated starch, affected contraction capacity. The authors postulated that interactions during the hydration of the gluten network might explain the latter phenomenon.

6.2. Infrared spectroscopy

Near-infrared reflectance spectroscopy (NIRS) was used to obtain spectra during staling of bread and the results were compared with those obtained by TA (Xie and others 2003). Results showed that NIRS spectra were highly correlated with firmness values assessed with the more common TA. Moreover, the authors evidenced that NIRS measurements had a better correlation with storage time and also lower batch variability, with respect to TA-derived data, thus NIRS was suggested as a better tool than TA to study bread aging, probably because NIRS may follow both physical and chemical changes occurring during the staling process, while TA was limited to the only aspect of firmness evolution. In a further paper, Xie and others (2004) proposed the use of NIRS as a fundamental tool to study bread staling with the help of DSC, as well as the effects of starch, protein, and temperature (storage at 12.5 or 31.5 °C) on bread staling. DSC data showed that temperature strongly affected the staling rate, while the protein contribution was limited, if compared to temperature during 4 days of storage. Using the enthalpy ratio between bread supplemented with starch and sample produced with starch-protein it was possible to conclude that protein might retard bread staling not only by diluting starch (Kim and D'Appolonia 1977; Every and others 1998), but also by interfering with amylopectin retrogradation. NIRS was found to be very useful in studying bread staling, as it was able to study accurately amylopectin retrogradation and to obtain a very good correlation with DSC data when looking for protein and temperature effects on amylopectin retrogradation development, even if it showed difficulty in measuring the changes of the amylose-lipid complex during storage. The authors proposed 550, 970, 1155, 1395, and 1465 nm as important wavelengths of NIRS and concluded that amylopectin retrogradation was probably the main factor in bread staling and that the amylose-lipid complex contributed little to bread staling after one day of storage.

Cocchi and others (2005) coupled middle-infrared spectroscopy (MIR) with principal component analysis (PCA) to follow bread shelf-life in a rapid and affordable way. Spectra of breads stored up to 7 days at ambient temperature were acquired in attenuated total reflection mode with a FT-IR spectrometer, normalized and then subjected to PCA. The authors revealed that the first PC increased with aging of samples and that the more influential variables on PC1 corresponded to spectral regions attributed to typical starch bond vibrations. Pikus and others (2006) proposed for the first time the small-angle X-ray scattering (SAXS) method to study bread staling. The authors, by using fresh dry and fresh water suspension samples, found that bread staling is accompanied by significant electron density changes, indicating that there were significant changes at the nanoscale level during the staling process. They suggested, by analyzing results obtained with the dynamics of the scattering intensity changes in the bread samples, along with those of SAXS investigations on native starch, that SAXS scattering changes for the dry samples originated mainly from the gluten phase, while for water suspension samples they were mainly from the starch matrix. The authors concluded that a comparison of results of SAXS with data obtained with other methods, on the same bread sample, would be interesting.

Piccinini and others (2012) proposed, for the first time the use of NIR Fourier-transform-Raman spectroscopy to monitor starch retrogradation in stored hard-wheat bread and, with the help of TA data, to follow bread staling for 20 days. The authors found, by applying the 2D correlation analysis applied to the Raman spectra of bread crumb during storage, that both the peak shift and narrowing of the band at 480 cm^{-1} during retrogradation correlated well with the crumb-firming data obtained using the stress relaxation tests and that during starch retrogradation a new band peaking at 765 cm^{-1} appeared.

6.3. Nuclear magnetic resonance spectroscopy

Curti and others (2011) used ^1H NMR relaxometry and, for the first time in bread, the ^1H NMR fast field cycling (FFC) technique to follow the changes in ^1H T_1 relaxation in the 0.01-20 MHz frequency range, in order to check for the interactions of water molecules with paramagnetic and large-sized macromolecular system during bread staling. ^1H T_1 relaxation data at 20 MHz confirmed previous results, while studies conducted at a lower frequency (0.52 MHz) evidenced, for the first time, the presence of two T_1 proton populations, which were tentatively attributed to protons of the gluten domain at early storage times. The authors suggested that the use of the ^1H NMR FFC technique at different frequencies may be an additional way for monitoring molecular dynamics in bread and therefore a new valuable instrument to help understand the bread staling phenomenon.

Bosmans and others (2013) used H NMR relaxometry, along with DSC and wide-angle X-ray diffraction, to better elucidate the relationship between biopolymer interactions, water dynamics, and crumb texture evolution during 168 h of storage of bread. The NMR analysis allowed finding 6 proton populations in bread crumb and from the NMR profiles of bread crumb they were able to deduce the extent of formation of both amylopectin crystals and of crumb firmness. On the basis of data obtained they concluded that the increase in crumb firmness of stored bread was caused by a combination of different events that were amylopectin retrogradation and the formation of a continuous, rigid, crystalline starch network that included water in its structure. They also noticed moisture migration from gluten to starch and from crumb to crust, resulting in additional reduction of moisture in the gluten network, with the consequence that the subsequent increase in stiffness contributed to the increase in crumb firmness.

6.4. X-ray crystallography

Del Nobile and others (2003) developed a mathematical model able to predict the starch retrogradation kinetics of durum wheat bread in order to link it to the crumb staling. Two equations were proposed dealing with data obtained with wide-angle X-ray diffraction (starch retrogradation) and compression tests (crumb firming process), and related to samples held at 5 °C and 2 water activity values, in order to accelerate the test. The proposed model fitted well the obtained results; moreover, the authors evidenced that lowering the water activity value resulted in a higher overall starch crystal growth rate, due to the increase of the starch nucleation rate.

X-ray patterns were studied with different methods, namely relative crystallinity, total mass crystallinity grade (TC), B-type mass crystallinity grade, and V-type mass crystallinity grade, in order to increase knowledge of the relationship between starch crystallinity and bread staling during 7 days of storage at 4 °C (Ribotta and others 2004). The authors pointed out that: a) fresh baked bread contained only a V-type structure, while the B-type structure appeared after 24 h and increased during bread staling; b) TC and relative crystallinity significantly increased during the first 24 h, then slightly decreased, thus indicating the appearance of the B-type structure; c) TC and relative crystallinity decreased at the end of aging, which is associated with an increased degree of ordering of the amorphous phase caused by staling. They suggested that staled bread showed reformation of the double helical structures of amylopectin and a reorganization, during aging, into crystalline regions that imparted rigidity. With this in mind, they concluded that amylopectin retrogradation is an essential step to consider to better understand bread staling.

6.5. Colorimetry

Popov-Raljić and others (2009) used, for the first time, a MOM-color 100 tristimulus photo colorimeter, in CIE, CIELab, ANLAB, and Hunter systems to correlate crust color changes and staling of bread of different compositions packed in polyethylene film during 3 days at 20 °C. The color of 3-day-stored bread samples was always lighter, as the stored breads showed higher average reflectance, with respect to just baked loaves. The authors hypothesized the moisture loss as the cause of this color change and, by fitting the values of average reflectance with a curve describing the dependence of average reflectance with storage time, they found a correlation coefficient of 0.99, thus they concluded that the change in color is the direct consequence of staling [Note: it would be more useful to correlate crust color changes with objective bread staling measurements, such as hardness, more than with time].

6.6. Rheological methods

Textural assessment of staling has been reviewed by Chung and others (2003). Fiszman and others (2005) investigated the relationships between mechanical behavior of pan bread, supplemented or not with an amylolytic enzyme, a nonamylolytic enzyme and a combination of the 2, and loss of sensory quality during 20 days in storage. TPA at 40% and 80% was proposed for the first time as well as a new penetration test. The authors positively correlated hardness with sensory “difficulty in swallowing”, “crumbliness”, “hardness”, and “oral dryness”, and negatively correlated it with sensory “cohesiveness”, “softness”, and “size of soft zone”, while these parameters correlated well also for springiness and cohesiveness detected at 80% TPA, thus evidencing that TPA values obtained at the compressions resulted in greater sample distortion and gave information that was better correlated to sensory perception. Finally, the analysis of the penetration profiles gave data that were very useful to complement the TPA results, in order to assess bread staling.

Angioloni and Collar (2009b) suggested the complementarities of instrumental static (TPA, firmness, and relaxation test) and dynamic (innovative oscillatory test) analyses with empirical sensory characteristics in assessing commercial whole and white bread quality during a 10-day storage period, although the 2 different approaches investigated the bread characteristics at molecular or macroscopic level. In particular, the authors found that static relaxation parameters initial force (F_0), momentary force at time (t) F(t), constants related to stress decay k1(s) rate and residual stress at the end of the experiment (k2t) and dynamic (stress) bread crumb rheological attributes were correlated well, thus both techniques were useful in evaluating crumb textural characteristics of fresh and staled breads. Moreover, the sensory attributes (softness) and the overall acceptability were negatively correlated with either dynamic stress or static F_0. The authors concluded that the obtained results were quite promising for a proper bread crumb quality assessment, as the novel proposed approaches gave data with better accordance with consumer awareness.

6.7. Electrical impedance

Bhatt and Nagaraju (2009) developed an instrument working with electrical impedance to assess the electrical properties of wheat bread crumb and crust, and they investigated changes in electrical impedance behavior during 120 h of storage with the use of multichannel ring electrodes. Variations in crust capacitance showed that there was a sharp increase in value after 96 h of storage at 17.6% moisture content, so after that period a glass transition occurred with a content of more than 17.6% of moisture at room temperature. On the other hand, the resistance measurements of crumb showed a decrease during staling, thus revealing that the starch crumb recovered its crystallinity during the storage time of 120 h. Data on crust capacitance and crumb resistance were validated by results obtained with DSC analysis (variation in glass transition temperature and enthalpy). The authors concluded that the proposed instrument was suitable for rapid and nondestructive measurement of electrical properties of bread at different zones with minimum error, thus enabling to study staling at crust and crumb simultaneously.

6.8. Mixed instrumentation

Primo-Martín and others (2007) gave new insight on staling of bread crust by using a wide range of measurement techniques, namely, confocal scanning laser microscopy, wide-angle X-ray powder diffraction, polarized light microscopy, solid-state 13C cross-polarization-magic-angle spinning nuclear magnetic resonance, and DSC. The authors found that baking resulted in gelatinization of only 60% of the crust starch, and this fraction retook its cristallinity after a long time, compared to crumb. The authors, thus, concluded that staling of the crust cannot be ascribed to amylopectin retrogradation that was measurable only after 2 days of storage, while loss of bread crust freshness happened before 1 day of storage, as already reported by Primo-Martín and others (2006).

A very interesting application was that proposed by Botre and Garphure (2006) who used a tin oxide sensor array and self-organized map (SOM)-based E-nose for analysis of volatile bread aroma, in order to correlate the obtained data with bread freshness and, thus, predict staling. Data obtained on bread stored for 5 days at 25 °C over 3 weeks and purchased by 3 producers showed that the E-nose was able to predict freshness or staleness of bread with an accuracy of up to 97%, when using data sets and the SOM network of the same week, while this value dropped to 75–85% when considering the 3 weeks. Moreover, when different bread producers were considered, the accuracy value was again high and ranged from 76 to 83%. The authors, thus, suggested that the SnO_2 gas sensor and SOM neural network based electronic nose was an attractive, low-price alternative for assessing bread freshness.

Lagrain and others (2012) considered bread crumb as a linear-elastic, cellular solid with open cells in order to better understand its mechanical properties at the fresh state and during storage, when applying low stresses in the evaluation. They used static compression of bread crumb and developed a new instrument probe to determine the shear storage modulus by applying a sinusoidal shear force to the sample. Cellular structure evolution during storage was assessed by digital image analysis, while a noncontact ultrasound technique was used to measure crumb open porosity and mean size of the intersections in the crumb cell walls. Results of image and acoustic analyses showed that the original crumb structure was not affected by staling and crumb physical measurement confirmed this behavior, as the Poisson coefficient ν obtained from texture data yielded a time-independent value. Moreover, by changing gluten functionality with redox agents (potassium bromate and glutathione) the authors found that the increase in evolution of the normalized modulus, which was the ratio between the Young’s modulus E and the crumb density ρ (E/ρ), was independent from ρ, thus molecular changes in the gluten protein network induced by the redox agents had effect on crumb cell wall stiffening. Finally, changing starch properties with a maltogenic exo-α-amylase, while reducing crumb stiffening during 168 h of storage, as expected and as revealed by amylopectin recrystallization (DSC), did not result in changes in the cellular structure.

7. Conclusion

Bread staling continues to be responsible for huge food wastes all over the world. The phenomenon is still far from being fully elucidated, but this literature review of the last 10 years confirmed existing theories and gave new insights. The text points out the central role of starch and starch-gluten interactions at the basis of the staling mechanism and highlights the effect of different ingredients (hydrocolloids, enzymes, or WWS), as well as the increased interest in dough or frozen PB bread for extending bread shelf life. Despite new measurement techniques, such as NIRS, NMR, and X-ray, which give novel and interesting details on bread firming and also evidence of their importance as complementary tools to traditional measurement techniques, the real challenge still remains the knowledge of the precise mechanism(s) of staling. Further efforts must be exerted to explore and exploit the power of novel technologies in bread processing, particularly the non-thermal technologies (high hydrostatic pressure, ultrasound processing, pulse-light technology, and other), and their effects on the retardation of bread staling.

Acknowledgments

The authors acknowledge the financial support of following European Institutions: Regione Autonoma della Sardegna, Legge 7, project title “Ottimizzazione della formulazione e della tecnologia di processo per la produzione di prodotti da forno gluten-free fermentati e non fermentati,” and Consejo Superior de Investigaciones Cient´ı-ficas (CSIC), and Ministerio de Econom´ı-a y Competitividad (Project AGL 2011-22669) of Spain.

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Table 1 – Topics regarding bread staling covered by reviews or book chapters.

Topic	Review	Book or book chapter
Enzymes	Amos 1955; Haros and others 2002; van der Mareel and others 2002; Butt and others 2008; Goesaert and others 2009.	Bowles 1996.
Fibers	Sivam and others 2010.	
Freezing and partial baking	Rosell and Gomez 2007; Selomulyo and Zhou 2007; Yi 2008.	
Fundamental causes	Kulp and Ponte 1981; Le Meste and others 1992.	
Hydrocolloids	Izydorczyk and Dexter 2008; Kohajdová and Karovičová 2009; Kohajdova and others 2009.	Milani and Maleki 2012.
Methodologies	Choi and others 2010; Karim and others 2000; Chung and others 2003; Liu and Scanlon 2004.	Ponte and Faubion 1985; Ponte and Ovadia 1996; Vodovotz and others 2001.
Pentosans	Hoseney 1984.	
Polyols	Bhise and Kaur 2013.	
Proteins		Davies 1986.
Sodium chloride	Beck and others 2012a.	
Sourdough	Arendt and others 2007; Chavan and Chavan 2011.	
Starch	Myiazaki and others 2006.	Alsberg 1928; Slade and Levine 1987; Slade and Levine 1989; Hung and others 2006.
Staling	Hertz 1965; Zobel 1973; Maga 1975; Knightly 1977; D'Appolonia and Morad 1981; Hoseney and Miller 1998; Schiraldi and Fessas 2001; Gray and Bemiller 2003.	Alsberg 1936; Chinachoti and Vodovotz 2000; Pateras 2007; Cauvain and Young 2008.
Surface-active lipids and shortenings	Knightly 1973; Stampfli and Nersten 1995; Kohajdova and others (2009a).	

Water	Choi and others 2008.	Cauvain and Young 2008.

Table 2 – Main hydrocolloids proposed during the last decade for staling reduction.

Hydrocolloid class	**Hydrocolloid name**	**Effect**	**Suggested references**
Cellulose	HPMC[a]	Interaction with other bread constituents and in particular with water (retention capacity and starch-gluten interactions)	Bell 1990; Collar and others 1999; Barcenas and Rosell 2005; Tavakolipour and Kalbasi-Ashtari 2007.
Hemicellulose	GG	Inhibition of amylopectin retrogradation	Ribotta and others 2004; Shalini and Laxi 2007.
	LBG	Increased loaf volume and improved texture	Sharadanant and Khan 2003; Selomulyo and Zhou 2007; Angioloni and Collar 2009a.
	KGM	Hindering effect on macromolecular entanglements	Sim and others 2011.
	Arabinoxylans and β-glucan	Competition for water, limitation of starch swelling and gelatinization	Izydorczyk and Dexter 2008; Jacobs and others 2008; Hager and others 2011.
Microbial	XG	Increased water absorption, retardation of amylose retrogradation, gluten-starch interactions	Collar and others 1999; Mandala and Sotirakoglou 2005; Mandala and others 2007; Shittu and others 2009
Pectins	Pectin, HMP	Competition for water, reduction of amylopectin recrystallization	Rosell and Santos 2010; Correa and others 2012
Animal	Chitosan	Inhibition of crosslink formation between	Kerch and others 2010, 2012a,

starch granules and protein fibrils	2012b.

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[a] For abbreviations see the list of abbreviations at the start of this review.