

## **REVIEW OF LITERATURE DIFFERENT HYDROCOLLOIDS AS BREAD IMPROVERS AND ANTI STALING AGENTS .**

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### **ABSTRACT**

#### **Some definition of staling:**

Broadly speaking, bread staling refers to all changes that occur in bread after baking. Changes occur in both the crumb and the crust of the bread. The increase in crumb firmness has probably been used to the largest extent by investigators following bread staling. Other changes, however. Such as loss of flavor, decrease in water absorption capacity, amount of soluble starch and enzyme susceptibility of starch, increase in starch crystalline and opacity.

Firmness is an important sensory attribute of bread. Bice and Greddes (1949) concluded that firmness and crumbliness are related closely to organoleptic assessment of staleness . Literature on the staling of bread and on the methods for the measurements of the extent of the staling are scarce.

#### **Type of anti-staling :**

Today, several anti-staling agents are used in the bread making industry. These anti-staling agents have different mechanisms, which provides the opportunity to influence the properties of the product:

#### **1-Water content of dough and bread :**

Water content of dough and bread affects the properties of different chemical components of dough and bread. In the oven, heating rate of the dough piece and baking temperature affect the swelling and gelatinization of starch and, as a consequence the crumb structure .Water is assumed to have a significant role in the staling process. Water is more abundant in the swollen amorphous regions of starch, facilitating local polymer chain mobility (plasticization) and sub- sequent crystallization and retrogradation (Chinachoti and Vodovotz,2001).Water distribution within regions in gluten, amorphous and crystalline starch is assumed to play an important role in starch and gluten rigidity.

#### **2-Sourdough fermentation :**

Sourdough fermentation is used to improve the texture, volume and shelf-life of breads (Brummer and Unbehend, 1997; Corsetti *et al.*, 1998 ). Combined use of exogenous enzymes and sourdough in the same baking process has been reported to enhance rate of acidification, improve bread volume and retard white wheat bread staling (Martinez-Anaya *et al.*, 1998; Corsetti *et al.*, 2000 ).

#### **3-Hydrocolloids and its role:**

Hydrocolloids are widely used as additives in the food industry, because they are useful for modifying the rheology and texture of aqueous suspensions (Dziezak, 1991). Hydrocolloids due to their high water retention capacity confer stability to the products that undergo successive freezethaw cycles (Lee,*et al.* 2002; Sanderson, 1996). Today, several antistaling agents are used in the bread making industry. These antistaling agents have different mechanisms, which provides the opportunity to influence the properties of the product. Locust bean gum (LBG), methyl cellulose and

hydroxy propyl methyl cellulose (MC/HPMC), microcrystalline cellulose (MCC), pectin, starch, and xanthan. Our early studies promising that sweet potatoes could be potential new member of this team in bakery products and may be mouth feel enhancers in rice bread (Abdeen, *et al.* (2006).

Supplementation of several hydrocolloids with different chemical structure and from diverse origin to the bread making process is presented. The effect of hydrocolloids (sodium alginate, xanthan, k-carrageenan and hydroxypropylmethylcellulose) on fresh bread quality and its influence on bread staling were studied. Physical properties (moisture, hardness, volume) and sensory properties of fresh bread and after storage of 24 h were analyzed. Hydrocolloids affected in different extent to the fresh bread quality, and concentrations of 0.1% (w/w, flour basis) were sufficient for obtaining the observed effects. Although different improvements were observed associated to specific hydrocolloid, HPMC was the hydrocolloid with an improvement effect on all the parameters tested, specific volume index, width/height ratio, and crumb hardness; in addition good sensory properties for visual appearance, aroma, flavor, crunchiness and overall acceptability was obtained. All hydrocolloids were also able to reduce the loss of moisture content during bread storage, reducing the dehydration rate of crumb. In addition, during storage, alginate and HPMC showed an anti-staling effect, retarding the crumb hardening. Hydrocolloids are widely used as additives in the food industry, because they are useful for modifying the rheology and texture of aqueous suspensions (Dziejake, 1991).

Methylcellulose and gum Arabic have been used as gluten substitutes in the formulation of gluten-free breads (Toufeili *et al.*, 1994). Carboxy methylcellulose (CMC) and guar gum have been added in rye bread recipes to improve the quality of that bread (Mettler and Seibel, 1995).

In addition, an improvement in wheat dough stability during proofing can be obtained by the addition of hydrocolloids, namely sodium alginate, k-carrageenan, xanthan gum and hydroxypropyl methyl cellulose (HPMC) (Rosell *et al.*, 2001). Later, Collar, *et al.*, (2007) studied the effect of CMC and HPMC addition on dough and bread performance of formulated wheat breads, and their interaction with  $\alpha$ -amylase and emulsifiers. It has also been proposed the use of xanthan in frozen dough to increase its stability during freeze – thaw cycles (Dziejak, 1991).

A different approach is the use of hydrocolloids as antistaling agents, Schiraldi, *et al.*, (1996) reported the use of guar gum and locus bean for improving the fresh bread quality, although did not find an evident antistaling role. A similar study with locus bean, xanthan gum and alginate revealed a softening effect of those hydro- colloids, due to the high water retention capacity in the case of locus bean, or for hindering the gluten – starch interactions in the case of xanthan gum and alginate (Davidou, *et al.*, 1996). From above, it is evident the wide use of hydrocolloids in bread making, nevertheless the properties of the hydrocolloids vary in a great extent depending on their origin and chemical structure (Rojas, *et al.*, 1999). For instance CMC has a preferred interaction to gluten while HPMC shows preferential binding to starch (Collar *et al.*, 2007). In addition, pasting properties of wheat starch are largely modified by hydrocolloids addition,

although the extent of their effect depends upon the chemical structure; xanthan and pectin increase the cooking stability while k- carrageenan mainly affect the bump area related to the formation of amylose – lipid complex (Rojas *et al.*, 1999). The economic loss resulting from bread staling encourages research to control or retard staling process. Antistaling agents may have a direct or an indirect influence on starch retrogradation, one of the key factors contributing to staling. Examples of direct influences are degradation of the amylose and/or amylopectin molecules, the formation of inclusion complexes with amylose or the outer branches of the amylopectin molecule, and a delay in the swelling and rupture of the starch granules. These effects can be caused by enzymes and emulsifiers. Starch-diluting anti-staling agents, for example, gluten, have an indirect influence on starch retrogradation.

#### **4-Enzymes and its role:**

Amylases, which have a direct influence on starch retrogradation, are divided into a- and b-amylases. They both act on the a-(1,4) Glycosidic bonds. a-Amylase acts randomly, giving low-molecular- weight dextrin's and other oligosaccharides, while b-amylase cleaves every second bond producing maltose and b-limiting dextrin (Goesaert, *et al.*, 2009). The hydrolysis hinders the formation of amylopectin double helices, thereby preventing the cross linking of the amylopectin molecules, and weakening the three-dimensional network (Goesaert *et al.*, 2009). It has been shown that the retrogradation of amylopectin is dependent on the exterior chain length; less retrogradation being seen for shorter chains (Lundqvist,*etal.*,2002). Furthermore, the addition of a-amylases effectively reduces the firmness of the bread (Goesaert *et al.*, 2009; Hug-Iten, *et al.*, 2003; Martin and Hosene, 1991), improves the crust color and flavor due to Maillard reactions (Goesaert *et al.*,2009),enlarges the gas cells,and retards amylopectin retrogradation.

The effects of sourdough and enzyme mixture (a-amylase, xylanase and lipase) on the specific volume, staling and microstructure of wheat pan bread supplemented with wheat bran were studied. Staling of bread was followed for 6 days by measuring the crumb firmness, changes in crystallization of amylopectin . increase in signal from the solid phase and by light microscopy. The most effective treatment in improvement of quality was the combination of bran sourdough and enzyme mixture. During storage the rate of changes in crumb firmness, amylopectin crystallinity and rigidity of polymers were greatest for the white wheat bread. The most pronounced microstructural changes were swelling of starch granules and separation of amylose and amylopectin in the starch granules. Least changes in crumb firmness, amylopectin crystallinity and rigidity of polymers were observed in bran sourdough bread with enzymes. In contrast to white wheat bread, the starch granules were very much swollen in bran sourdough bread with enzyme mixture. This was hypothesized to be due to the higher water content of bran bread, and degradation of cell wall components leading to altered distribution of water among starch, gluten and bran, Katina,*et al.*,(2005).

Lipases also have a direct influence on starch retrogradation, by hydrolyzing the di- and triglycerides into mono- or diglycerides and lysolipids (Castello, *et al.*, 1998). The addition of lipases enhances the gluten strengthening effect in dough, affording increased stability and improved bread qua (Si, 1997). Furthermore, lipases affect the amylase-lipid complex, resulting in an increase in the energy required to melt the complex, i.e. increased complex formation (Andreu, *et al.*, 1999; Siswoyo, *et al.*, 1999). Amylose-lipid complexes may have an inhibiting effect on starch retrogradation when storage times are long (Davidou, *et al.*, 1996), but not for short periods (<15 days) (Andreu *et al.*, 1999). The addition of lipases to dough improves the bread volume, air-hole regularity, crumb structure, and texture, and retards staling. (Si, 1997; Siswoyo *et al.*, 1999).

The effects of the water content and its distribution between the crust and the crumb during storage on anti-staling parameters were also studied. used in the study were  $\alpha$ -amylase (Novamyl 10000 BG, granulated maltogene amylase from *Bacillus subtilis*, 10,000 manu/g, provided by Novozymes A/S, Bagsvaerd, Denmark), lipase (Lipopan Xtra BG, granulated lipase from *Aspergillus oryzae*, 7.2 KLU/g, also provided by Novozymes A/S), mono- glyceride (Dimodan HP 75/B Kosher, distilled monoglyceride made from palm-based oil, Lipases also have a direct influence on starch retrogradation, by hydrolyzing the di- and triglycerides into mono- or diglycerides and lysolipids (Castello, *et al.*, 1998). The addition of lipases enhances the gluten strengthening effect in dough, affording increased stability and improved bread quality (Si, 1997). Furthermore, lipases affect the amylase-lipid complex, resulting in an increase in the energy required to melt the complex, i.e. increased complex formation (Andreu, *et al.*, 1999; Siswoyo, *et al.*, 1999). Amylose-lipid complexes may have an inhibiting effect on starch retrogradation when storage times are long (Davidou, *et al.*, 1996), but not for short periods (<15 days) (Andreu *et al.*, 1999). The addition of lipases to dough improves the bread volume, air-hole regularity, crumb structure, and texture, and retards staling. (Si, 1997; Siswoyo *et al.*, 1999).

#### **5-Modified flour :**

Other ways of influencing the staling of bread are to change the ratio of starch to protein (Erlander and Erlander, 1969; Kim and D'Appoloni, 1977), or change the composition of the starch (Bhattacharya, *et al.*, 2002; Park and Baik, 2007), which can be regarded as indirect ways of influencing starch retrogradation. This can be achieved by adding more gluten protein or waxy flour/starches to the dough. With higher gluten protein content in the flour, the strength and water absorption of the dough increase, as well as the specific volume, leading to improved crumb texture with decreased firmness (Callejo, *et al.*, 1999; Cornell, 2003; Maleki, *et al.*, 1980). In starch gels, amylopectin retrogradation has been found to increase with increasing proportion of amylopectin in the gel (Gudmundsson and Eliasson, 1990; Russell, 1987). However, when adding waxy flours, the water absorption of dough increases and a decrease in both the firmness and the amylopectin retrogradation enthalpy during storage can be achieved, although small or no changes in volume have been

found (Bhattacharya *et al.*, 2002; Hayakawa, *et al.*, 2004; Park and Baik, 2007; Qin, *et al.*, 2009). It is thus not clear how manipulation of the amylose/amylopectin ratio will affect staling. Furthermore, the origin and the chain length of the amylopectin must also be considered when adding waxy starches/flours to a dough, since these influence the extent of starch retrogradation (Fredriksson, *et al.*, 1998). The retrogradation of amylopectin is considered to be the major factor causing staling of bread. However, other factors have also been suggested to play important roles, such as water distribution water-related factors (i.e. the water content and the distribution of water between the crumb and the crust). Staling was measured in terms of firmness and springiness. Moreover, two new methods of assessing staling, crumbliness and cutability, were introduced for additional evaluation of staling. In order to investigate the retro-gradation of amylopectin, several common anti-staling agents known to affect amylopectin retrogradation by different mechanisms were used.  $\alpha$ -Amylase was used to hydrolyze the starch molecules, whereas lipase hydrolyzes the lipids.

Soy products with their high content of soy protein, isoflavones, omega-3-fatty acid and dietary fibre are potential functional food ingredients (Potter, 1998; Riaz, 2001). Epidemiological and experimental evidence suggests that consumption of soybean products may have a significant impact upon health (Birt, *et al.*, 2001; Messina and Loprinzi, 2001; Messina, *et al.*, 1994; Scheiber, *et al.*, 2001; Setchell, 1998). Soy products are being recognised as reducing menopausal symptoms, as well as having potential roles in the prevention, treatment and reduction of risk of diseases such as cancer, osteoporosis, kidney disease and heart disease (FDA, 1999; Garcia, *et al.*, 1997). For the functional and significant health effects they are providing, there is an increasing trend in product development to incorporate soy in conventional foods, either as a complete or partial replacement (Messina, *et al.*, 1994). The challenge of formulating with soy hinges on incorporation at levels sufficient to induce health benefits, while maintaining organoleptic quality; Hasler, 2002).

Traditionally, soy ingredients have been added to white bread in low amounts (1–3%) for whitening the crumb colour and lowering the staling rate (Hoseney, *et al.*, 1980; Maga, 1975). Soy based ingredients are used for a variety of functional and nutritional reasons in bakery products. Defatted soy flour is the primary soy product used as a partial replacement (up to 3%) for non-fat dry milk (NFDM) since it provides improved water absorption, dough handling properties and a tenderizing effect (Lusas and Riaz, 1995). Bread freshness was maintained due to the hygroscopic nature of soy protein that retains moisture during the baking cycle, extending the shelf life (decreasing staling rate) of the product (Vittadini and Vodovotz, 2003). Soy protein products are also known to improve crust colour, crumb body, resilience and toasting characteristics in bread (Boyacioglu, 2006; Endres, 2001; Nilufer, *et al.*, 2008; Stauffer, 2002) while extending shelf-life (Vittadini and Vodovotz, 2003).

Addition of fibre to bakery products can enhance softness of the crumb by binding and retaining water during baking, thereby affecting staling rate and crumb firming of breads (Gomez, *et al.*, 2003; Nelson, 2001).

The effect on loaf volume depends on the type of fibre added. Insoluble fibres decrease the loaf volume by the reduction of dough's gas retention ability, which is attributed to the interaction between fibre and gluten (Gomez *et al.*, 2003; Nelson, 2001), while use of low levels of soluble fibres (about 2%) increases loaf volume (Czuchajowska, And Poneranz, Y. (1989); Nelson, 2001).

Soy milk powder (SMP) contains no less than 38.0% soy protein, 13.0% soy fat and 90% total solids (SAA., 1996; Zhang, *et al.*, 2005). Commercial soy milk powders generally contain approximately 15.5–16.0% total dietary fibre (TDF) which can originate from either the soybean hull or the cotyledon and include different ratios of soluble and insoluble fibres.

#### **5-Emulsifier agents ;**

The emulsifier added (distilled monoglycerides) and products resulting from the action of lipase affect amylose and amylopectin by complex formation. Waxy wheat flour was added to change the ratio between amylose and amylopectin, and gluten was added to dilute the starch concentration in the dough. Monoglycerides have a direct influence on starch retrogradation, and are commonly used to improve the softness of the crumb and the volume of the loaf (Forssell, *et al.*, 1998; Gómez *et al.*, 2004; Heflich, 1996). Their physical state when added to the dough is of importance for their anti-staling effect; the lamellar liquid-crystalline phase being the most effective for the formation of inclusion complexes with amylose and amylopectin (Krog and Nybo Jensen, 1970). A correlation has been found between the amylose complex formation index and the anti-staling effect (Krog and Nybo Jensen, 1970; Krog, *et al.*, 1989). However, monoglycerides are process sensitive to the processing conditions, and too short proofing time may result in a decrease in dough stability, bread volume and in the softening effect (Gómez *et al.*, 2004). Emulsifiers also have good film-forming properties, resulting in reduced starch granule swelling and rupture during the baking process, due to coating of the granules (Eliasson, 1985). When adding monoglycerides, brighter crumb color, less gumminess, improved slicing and a tighter and more uniform crumb structure can be expected (Heflich, 1996).

Moreover, two new methods of assessing staling, crumbliness and cutability, were introduced for additional evaluation of staling. In order to investigate the retrogradation of amylopectin, several common anti-staling agents known to affect amylopectin retrogradation by different mechanisms were used.  $\alpha$ -Amylase was used to hydrolyze the starch molecules, whereas lipase hydrolyzes the lipids. The emulsifier added (distilled monoglycerides) and products resulting from the action of lipase affect amylose and amylopectin by complex formation.

#### **6-Flour replacement:**

But flour replacement by functional health promoting ingredients changes the quality of the final product. Adverse effects of flour replacement by dietary fibers in bread making include weakened gluten network and disruption of the starch-gluten matrix in dough, reduction in starch availability for gelatinization, reduction of the initial starch granule swelling, decreased

loaf volume, lowered gas retention and unsuitable taste (Collar, et al., 2007). In addition to Chitosan increases the rate of bread staling, increases water migration rate from crumb to crust, prevents amylose-lipid complexation, and increases dehydration rate of both starch and gluten.

Application of chitosan oligosaccharides in functional foods is an area of particular interest. It must be taken into account that there is a considerable growing demand in the world for new natural products demonstrating functional properties concerning health promoting or disease preventing aspects.

Addition of chitosan oligosaccharides to bakery products creates an opportunity to combine them. Today, several anti-staling agents are used in the bread making industry. These anti-staling agents have different mechanisms, which provides the opportunity to influence the properties of the product. Official technological properties with beneficial biological health promoting properties. However, literature on the use of dry soy milk as a partial substitute for traditional soy flours is limited, (Nilufer *et al.*, 2008). In a recent study, functionality of soymilk powder and its components on fresh soy bread was evaluated. Soy fibres were found to contribute differently and in some cases had opposing effects on the soy bread physicochemical properties (Nilufer *et al.*, 2008). Furthermore, little to no information is available on the effect of soy milk powder on stored baked goods. Firming occurring in white breads during storage has been attributed to several factors including amylopectin recrystallisation, moisture redistribution, changes in gluten functionality and the state of amorphous phase. The addition of soy flour has been shown to decrease amylopectin recrystallisation and the percentage firming during storage (Vittadini and Vodovotz, 2003). Furthermore, these improvements were attributed to the increase in water binding of the soy-containing bread.

#### **7- Modified atmosphere:**

Only a sincere number of studies have Modified atmosphere packaging (MAP) of bread is known to extend the microbial shelf-life (Seiler, 1989). For this reason there is an increasing demand for storage of bread in modified atmospheres, which is most often composed of CO<sub>2</sub> alone or mixtures of CO<sub>2</sub> and N<sub>2</sub> (Seiler, 1989). However, the effect of MAP on the physio-chemical quality changes occurring during storage of bread is investigated this topic and the results are conflicting. Knorr and Tomlins (1985) found that crumb firmness of white and whole meal bread stored in CO<sub>2</sub> for 14 days was lower than bread stored in N<sub>2</sub> or in atmospheric air. Similar results were obtained by Avital *et al.*, (1990) who found that crumb firmness of white pan bread stored in CO<sub>2</sub> for 10 days was lower compared with bread stored in atmospheric air. Contrary to these findings, Black *et al.* (1993) did not find any differences in the firming rate of pita bread stored in CO<sub>2</sub> or atmospheric air for 14 days.

The mechanism of bread firming is complex and not well understood. Martin *et al.* (1991a, b) suggested that bread firming might be a result of starch-gluten interactions, where gluten is cross-linked by gelatinized starch. However, Morgan *et al.* (1997) showed that starch bread without gluten will firm at a similar rate compared to bread with gluten. They suggested

that gluten interaction with starch was not essential for the increase in firmness and that starch retrogradation is sufficient to cause bread firming. The influence of water on bread staling has long been an issue of interest. Although firming of bread crumb is known not to be due to the loss of moisture (Czuchajowska and Pomeranz, 1989; He and Hosney, 1986), it is a fact that the firming rate as well as the rate of starch recrystallization are sensitive to the actual water content during ageing (Eliasson and Larsson, 1993). It has been proposed that these changes are due to incorporation of water released from gluten to the starch crystalline structure developed during firming (Chen *et al.*, 1997; Kim-Shin *et al.*, 1991; Wynne-Jones and Blanshard, 1986).

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### مواد ضد البيات في الخبز

عدلى سمير عبد الستار ، عبد الستار طلبية جبر و عزت عابدين  
معهد بحوث تكنولوجيا الاغذية - مركز البحوث الزراعية - مصر

يستخدم المحسنات للتغلب على ظاهرة البيات في الخبز نجد ان معظم الابحاث المرجعية تشير الى ظاهرة البيات في الخبز كما تشير هذه الابحاث الى كيفية التغلب على هذه الظاهرة باستخدام مختلف المحسنات لما لها من دور في اطالة فترة الطزاجة للخبز وتم تقسيم هذه المحسنات الى عدة عوامل مؤثرة وهي:

- ١- المحتوى المائي في العجينة والمنتج
- ٢- التخمر الحامضى
- ٣- الغرويات من حيث انواعها ودورها
- ٤- الانزيمات المحللة للنشا والدهن
- ٥- استخدام الدقيق المعدل
- ٦- اضافة عوامل الاستحلاب المختلفة
- ٧- احلال نسب من مختلف الدقيق
- ٨- تعديل الظروف المحيطة بالمنتج

### قام بتحكيم البحث

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