総　説

Bread Staling

Tatsuo Kai

<Abstract>

It is the Dutch researcher Katz who is said to have begun the study of bread staling. He tried to find out the method for how bread that was being made did not need to work at night, by examining the changes in detail over time of the bread. Thereafter, for about 70 years, the aging mechanism and the restraint method have been examined from various angles in the countries where breads are favored. This study has been continuing for a long time and in this way it is estimated that the quantity of bread disposed of by aging amounts to 3-5% of all volume of production, which has an important meaning economically. It may be said that bread staling is both an old and current topic. Though crumb starch is considered to play a major role in crumb staling, bread staling is a highly complex phenomenon expressed by the mutual association among starch, sugars, protein, lipid and other miscellaneous minor components such as glycolipid, lipoprotein, phospholipid, mucopolysaccharide, glycoprotein, and so on. Among many factors relating to bread staling, the point rousing the most interest when viewed from the consumer side who touch it by hand and choose the article, is the firming of the bread. Therefore a focus study was made on to the firming of the bread which had not been reported much till now to plan differentiation with many reviews that were already submitted by this report so an explanation was developed to clarify the connection between various staling related factors (starch, bread baking method, residual sugars in crumb, an emulsifier, an enzyme and others). We can now finally see the total outline of the problem of the bread staling. The development of the future study is yet expected to lead to a lot of contradiction on data when we watch a phenomenon called the firming of the bread which is the most important problem from the viewpoint of starch retrogradation, water emigration, X-rays diffraction analysis, sugar, or the influence of the storage temperature.

Key words: staling, bread, firming, starch retrogradation

Introduction

It is Dutch Katz (1928) to have added the beginning to a study of bread staling. He tried to find out the method how bread made did not need to work at night, and examining a change in detail at time of the bread. Thereafter, for long time for about 70 years, it has been examined from various angles in the countries where breads are favored, aging mechanism and the restraint method. A study has been continued for a long time in this way it is estimated that the quantity of disposal of bread by the aging amounts to 3-5% of all volume of production (Pomerantz, 1987), and to have a meaning important economically. It may be said that bread staling is an old and present topic.

Bread staling, according to a widely accepted definition in the baking industry by Bechtel *et al*.

Department of Nutritional Sciences, Faculty of Health and Welfare, Seinan Jo Gakuin University

(1953), is “a term which indicates decreasing consumer acceptance of bakery products by changes in the crumb other than those resulting from action of spoilage organ-isms.” It "points at all changes to happen after baking with the aging of the bread in a broad sense, but" it is used (Kim and D’Appolonia, 1977b). Bread staling involves changes in both crumb and crust. Crumb staling is a more complex and physiochemical phenomena than that of crust staling. Dry and crisp crust in its fresh state becomes soft and leathery upon staling, due to moisure migration from the crumb and the air to the crust. On the other hand, crumb staling can occur without loss of moisture (Boussingault, 1852). Bice and Geddes (1953) listed a number of changes as characteristics of crumb staling:(1) changed taste and aroma, (2) increased hardness of crumb, (3)increased capacitance of crumb, (4) increased crumbliness of crumb, (5) increased starch crystallization of crumb, (6) decreased absorptive capacity of crumb, (7) decreased susceptibility of crumb to beta-amylase, and (8) decreased soluble starch content.

Crumb staling has commonly been measured as a function of changes in crumb firming (Lineback, 1984). However, a study (Dragsdorf and Varriano-Marston, 1980) reported that starch crystallinity and bread firming are not synonymous, when alpha-amylase is utilized as a dough supplement. Though crumb starch is considered to play the major role in crumb staling, many other factors such as protein, pentosans, flour lipids, moisture migration between starch and gluten, the ratio of starch to protein and baking ingredients have to be considered as shown in several studies (Willhoft, 1973; Zobe1 1973; Maga, 1975; Kim and D’Appolonia, 1977a-d). Thus, bread staling is highly complex phenomenon expressed with the mutual association among starch, sugars, pentosans, protein, lipid and other miscellaneous minor componets such as glycolipid, lipoprotein, phospholipid, mucopolysaccharide, glycoprotein, and so on.

Here a focus was posted on to the firming of the bread which was not reported too much till now to plan differentiation with many reviews that were already submitted by this report and explanation was developed to clarify the connection with various staling related factors (starch, bread baking method, residual sugars in crumb, pentosan, an emulsifier, an enzyme, and bread materials made).

Starch retrogradation

As bread stales, the amount of soluble starch decreases (Katz, 1930). Linndet (1902) named this decrease in the solubility of starch “retrogradation.” Schoch and French (1947) reported that the decrease in soluble starch during staling of bread was due to“progressive spontaneous aggregation” of amylopectin and that amylase had no significant role in crumb firming, since it was insoluble and was already retrograded during baking and cooling of the bread. Also, Kim and D’Appolonia (1977a) showed that the soluble starch was predominantly amylopectin and that the amylose content decreased largely during the first day with only small changes occurring after that. Ghiasi *et al*. (1979) reported that the major starch component in soluble starch was degraded amylopectin that had shorter average chain length and higher A-chain to B-chain ratio than normal wheat amylopectin, which was probably due to the action of amylases during baking.

Cornford *et al*. (1964) studied the relationships between elastic modulus, time, and temperature in bread crumb and found that bread staling is basically characterized by retrogradation of starch in the crumb. The basic mechanism was instantaneous nucleation followed by rod-like growth of crystals. Axford (1967), Mciver (1968), and Colwe11 (1969)showed similar results by using differential thermal analysis (DTA). Later, differential scanning calorimetry (DSC) was found by Fearn and Russell (1982) to be more precise for study in this area. Katz (1928) found that as bread staled, the x-ray diffraction pattern of bread crumb changed from v-pattern which indicates starch is in an amorphous state, to B-pattern which is typical of starch in its crystalline state.

Shoch’s explanation (1965) for the role of starch in staling has been most widely accepted so far. According to him, wheat starch granules undergo

restricted swelling during baking due to the limited amount of water present as the more soluble amylose dissolves and diffuses into the surrounding water. As swelling continues, the amylose solution becomes so concentrated in the small amount of interstitial water between the granules that, after the loaf has cooled, this amylose retrogrades to an insoluble gel structure which does not undergo further changes. Amylopectin can still retrograde during storage in the following manner. The outer branches of the amylopectin, which has expanded in the limited-water system to some extent, can gradually align and associate to yield a more rigid structure.

Minor modification of this study was done by Lineback (1984). He explained that portions of the amylose and amylopectin chains extend beyond the boundary of the granule, *i.e.*, making the granule appear like a "hairy" billiard ball. These chains can associate or align (retrograde) with other carbohydrate chains in the interstices between granules and with those protruding in appropriate orientation from the granule boundary when they are in sufficiently close proximity. A similar explanation was provided by Matsukura *et al*. (1983).

Swelling behavior of bread crumb starch

The most widely accepted definition of gelatinization is that of Seib (1971): "Gelatiniztaion is the irreversible rupture of the native, secondary bond forces in the crystalline regions of a starch granule." A starch-in-water suspension, when subjected to heating, absorbs a small amount of water, losing its birefringence when it reaches a crucial temperature. At this point, some granules swell rapidly and irreversible, losing their bire-fringement characteristics (Seib, 1971). This process is known as gelatinization. Therefore, the loss of birefringence is a widely accepted indication of gelatinization (Leach, 1965). Collison (1968) reported that larger granules lose birefringence at a lower temperature than similar granules. Starch granules continue to swell as the temperature increased beyond the gelatinization temperature, to several hundred times the original volume. Simultaneously soluble materials leach out of the granule and some of the granules rupture completely. By this process, the viscosity and soluble material in the aqueous phase increase (Seib, 1971).

Gelatinization starts in the region of the granule where the associative forces are the weakest (amorphous region); the strength of the associative bonds in this region varies among the different granules belonging to the same botanical type. This is the reason why gelatinization takes place over a range of temperature rather than a single temperature (Leach, 1965). According to Collison and Elton (1961), granules of wheat starch were found to retain their identity until a temperature of 95˚C, and on further heating in an autoclave at 105˚C, the identity of granules was completely lost. Schoch (1965) reported that formation of amylose gels in the aqueous phase due to leaching of amylose from swollen granules contributes to initial firmness, since such gels retrograde very quickly after the bread comes out of the oven. The staling process is attributed to crystallization (retrogradation) of amylopectin. Within the swollen granules, with monoglycerides or similar surfactants present, the leaching of amlylose is prevented because the surfactants form an insoluble complex with amylose within the starch granules (Krog and Davis, 1984). Ghiasi *et al*. (1982b) demonstrated that amylose-surfactant complex is formed within the starch granules before gelatinizatin takes place. Ghiasi *et al*. (1982a) reported that SSL and saturated distilled MG effectively stopped leaching of amylose from the swollen granules.

Krog (1973) reported that the pasting temperature of wheat starch is considerably increased in the presence of effective amylose complexing agents. Riisom *et al*. (1984) showed that all monoglycerides increased the viscosity in comparison to control when amylopectin curves of fresh bread crumb was determined. The amylograph viscosity of bread crumb reflects the starch gelatinization taking place during baking in such a way that the degree of starch swelling in the amylograph is inversely related to the amount of starch swelling that occurs during baking

(Krog and Davis, 1984).

Distribution of residual sugars in bread crumb

Different sugar types and amounts in the bread formulation influence yeast fermentation, thus altering the fermentation products produced during dough fermentation and residual sugars in the final loaf. This will significantly affect bread flavor and texture. For this reason it is important to trace individual sugars during bread-making as a function of the baking method. Little work has been done in this area. Early investigators have studied the effect of sugars on bread firming, showing that sugars have only a small improving effect on bread firming (Edelmann *et al*., 1950; Barham and Johnson, 1951; Bohn, 1954). No recent study has been done to relate sugar usage to the keeping properties of bread. Some work has been done to trace individual sugars during the baking process in relation to yeast action (Koch *et al*., 1954; Piekarz, 1963; Tang *et al*., 1972; Ponte and Reed, 1982).

Under the anaerobic conditions prevailing in a dough, yeast ferments sugars to ethanol and carbon dioxide. These sugars are the monosaccharides, glucose and fructose, and the disaccharides, sucrose and maltose. Lactose is not fermented by baker's yeast. Starches and dextrins are not fermented by yeast but may serve as sources of fermentable sugars if they are hydrolyzed by amylases (Ponte and Reed, 1982).

Koch *et al*. (1954) reported that yeast ferments glucose preferentially, followed by fructose and maltose. Ponte and Reed (1982) showed that in the sponge dough process where both glucose and fructose were present in the dough, glucose was more rapidly fermented and maltose levels were low (0.7 to 0.9), if no maltose was added as a part of the sweetener system. They also studied the residual bread sugars in laboratory-produced sponge dough bread made with several different sweetener types. Koch *et al*. (1954) traced glucose, fructose and maltose in a straight dough process. When 5% sucrose and 3% yeast were used in the formula, glucose was fermented rapidly, fructose was fermented slower than glucose, and maltose increased gradually with time. Then 0.14% glucose 0.79% fructose and 1.50% maltose were left in the final loaf. Tang *et al*. (1972) traced the sugars in a sponge dough process, made with 5% sucrose and 2.5% yeast. In the sponge, native glucose and fructose were fermented rapidly. None were left in the sponge after two hours fermentation. Maltose increased to 1.3% after two hours fermentation, then decreased rapidly to 0.1% at four hours. In the dough, glucose, fructose and maltose decreased faster in this order and 0.7% glucose, 1.2% fructose and 0.2% maltose were left in the final loaf. Similar results were obtained by Koch *et al*. (1954). Piekartz (1963) traced the sugars in a liquid pre-ferment process. When corn syrup (3.9% maltose and 4.1% glucose) was used in the formula, glucose was rapidly fermented through the fermentation period. Maltose was fermented slowly in the pre-ferment. In the dough, the level of maltose actually increased because the rate of maltose formation from starch was greater than rate of fermentation. There, the final bread contained hardly any glucose but almost 4% maltose.

Kai (2007) investigated the distribution of residual fructose, glucose and maltose content when formula sucrose level was varied from 1 to 8% as a baker's percentage for white pan bread, comparing different baking methods. The pattern of increase in residual fructose and glucose of final breads seems to be similar among three different baking experiments (sponge dough process, short-time dough process with the dough mixing methods of conventional mixing and high speed mixing). These two residual sugars are derived from formula sucrose. Glucose level was lower in amount than fructose. The reason is probably that yeast ferments glucose faster than fructose. Residual maltose showed obvious difference between two different baking methods. Maltose appears in final loaves by the digestive action of starch with α- and β-amylase. Thus longer fermentation gives more time for starch degradation by amylases. Residual maltose showed similar level even if the amount of sucrose in formula varied for each baking method. Sponge dough bread showed lower level than short-

time dough bread, probably because yeast does not have enough time to metabolize maltose for short-time dough process. The increase of glucose was slightly slower at lower formula sucrose levels presumably because yeast requires that amount of sugar to satisfy metabolism requirements. This result agrees with previous works (Ponte, 1982; Jang *et al*., 2001; Baker and Rayas-Duarte, 1998; Koch *et al*., 1954; Piekarz, 1963; Tang *et al*., 1972). According to his study, it was indicated that the content of the residual fructose and glucose in the final loaves can be controled to be a similar level by adjusting the sucrose amount in formula, though the residual maltose is difficult to regulate to be similar level at the two different baking methods.

Crumb firmness related to residual sugar

Though early studies suggested that the sugar content in the formula does not affect the firmness of the bread (Edelman *et al*., 1950; Barham and Johnson, 1950; Bohn, 1954), recent studies showed the sugars affects the starch retrogradation to some extent (Jang *et al*., 2001; Farhat *et al*., 2000; Baker and Rayas-Duarte, 1998). Sugars and maltdextrins enhance the retrogradation of starch and the degree of enhancement correlated to the glass transition temperature (Wang *et al*., 1994). And the effect of sugars on starch gelatinization and subsequent retrogradation aims at keeping the water-to-starch ratio constant (Fahrat *et al*., 2000).

Needless to say, sucrose is the most important single sugar for food manufacture and it is a less effective plasticizer than water. Sucrose increases the gelatinization temperature (*Tm*) of starches, and the effect increases with increasing sucrose concentration (D'Appolonia, 1972; Johnson *et al*., 1990; Chinachoti *et al*., 1991). With the addition of sucrose, the glass transition temperature (*Tg*) of a product changes and, thus, its storage stability also changes (Levine and Slade, 1986). Biliaderis and Prokopowich (1994) demonstrated followings with the use of maize starch at a storage temperature of 6˚C. (1) for the glucose oligomers, maltotriose inhibited the recrystallization of amylopectin, while the sample containing maltooctaose showed the highest extent of starch retrogradation; (2) in contrast, glucose and fructose enhanced the retrogradation rate in the sugar series, while ribose and xylose retarded the process.

On the other hand, Kohyama and Nishinari (1991) reported that sugars prevented retrogradation of sweet potato starch paste and they proposed that sugar molecules interacted with starch molecular chains to stabilize the starch matrix, thus inhibiting retrogradation. Also, Baker and Rayas-Duarte (1998) showed that the addition of sugars had similar effects in reducing retrogradation at 25 and 4˚C and increasing retrogradation at -20˚C when compared to samples with no sugar added. Thus, the effect of sugars on starch retrogradation is still uncovered and the thread of a factor connected with each other should be untied in carefulness.

Baking method

Sponge dough process, straight dough process and short-time dough process are the major baking methods widely used over the world for the baking of white pan breads (Ponte, 1982). Sponge dough process is suitable for machinery automated baking since the dough has moderately extensible characteristics for machinery handling. But this method is fairy time consuming due to the hours of sponge fermentation required. Straight dough process is popular in Japanese retail bakers since it gives better flavor and texture to breads and it can reduce baking time. The method is not preferred by large whole sale bakers since the dough is intolerable for machinery handling. Short-time dough process is utilized in the U.S. retail bakers since it has the shortest fermentation time. In the U.S. and England, high-speed mixer is widely used for short-time dough process in order to shorten the baking time as much as possible.

Generally, it is said that sponge dough bread gives much longer shelf life on crumb softness compared with short-time dough bread (Ponte, 1982; Dubois, 1981). The difference in firming between

these two baking processes is due to following features. Longer fermentation gives enough time to the dough for maturation and water hydration, which improves moisture retention of the bread causing late staling characteristic. Gluten network is well developed by the double mixing causing very extensible dough, as the result, gas retention power of the dough is improved to give better oven-spring to the bread. The high-speed mixing bread is believed much inferior than the conventional mixing bread since the excessively high-speed damages the gluten net work.

When staling characteristics and shelf-life for bread are discussed in relation to various baking methods, crumb firming property is regarded as the most significant marker. Firming rate of the bread made by sponge dough process is said to be slower than that made by the short-time dough process. Also, when they mention the difference between the conventional mixing and the high-speed mixing method, the firming of the latter mixing bread is perceived to be much faster than the other. However, Kai (2007) demonstrated that these observations are misunderstanding learned by experience. He investigated the effect of dough fermentation time and mixing method on firming rate under the experimental condition with minimizing the effect of three factors (baking formula, specific loaf volume and residual loaf sugar) affecting bread firming rate. He resulted that there was only, very small difference observed in firming rate between sponge dough process of the longest fermentation time and short-time dough process of the shortest fermentation time among various baking methods. Conventional dough mixing also showed little difference in bread firming from high speed mixing. This fact suggests that firming properties of bread are largely affected by baking formulas rather than by fermentation time or dough mixing methods.

D'Appolonia (1984) explained the effect of the longer fermentation process on staling as follows: as a consequence of yeast fermentation, the gluten undergoes changes, the net overall effect being referred to as maturation or conditioning, such as changes in the gluten structure may well affect the degree of softness in the bread crumb as well as the rate of crumb firming.

Emusifiers

At present, surfactants are the most effective and widely used anti-staling agent. The study of surfactants as related to staling started when Schoch and Wiliams (1944) reported that amylose forms a water insoluble precipitate with fatty acids. Most of the knowledge on the surfactants relating to staling had been investigated early ages. Several workers suggested that surfactants retard staling because they attach to the surface of the starch granule and therefore, prevent amylase from diffusing out (Lehman 1942; Whistler and Hilbert 1944; Strandine *et al*., 1951; Bourne *et al*., 1960; Jough, 1961). It was indicated by Hanes (1937) and Mikus *et al*. (1946) that the structure of amylose-fatty acid complexes consists of bundles of helices packed in a hexagonal fashion.

Banks and Greenwood (1971) reported that amylose can exist in helix form in the presence of a complexing agent, and the helical complex is stabilized by both intramolecular hydrogen bonding and hydrophobic bonding between the amylose and complex agent, *i.e*., a hydrocarbon chain of fatty acids or surfactants. Katz (1930) showed that the X-ray diffraction spectrum of helical amylose complex had the V-Pattern, which indicated pasted starch.

Osman *et al*. (1961) reported that all amylose complexes with surfactants gave the same X-ray diffraction pattern as the V-pattern of amylose-fatty acid complexes, and they found no apparent relationship between complex formation with the amylase and anti-firming effects on the bread crumb. DeStefanis *et al*. (1976) found that surfactants form a complex during baking not only with amylose but also with amylopectin. Osman and Dix (1960) showed that surfactants can dramatically influence maximum viscosity temperature and gel strength of starch.

Krog (1971) reported that monoglycerids with chain length C12 to C18 had better complex effects

with amylose among various surfactants. Lagendijk and Pennings (1970) showed similar results. Riisom *et al*. (1984) showed that unsaturated monoglyceride with cis-configuration was better than that with trans-configuration in amylose's complex forming ability. Ghiasi *et al*. (1982a) reported that saturated monoglycerides (monostearin) and sodium stearoyl-lactylate (SSL) both formed strong complexes with amylose from 60˚C to 80˚C. Several studies have been done recently with amylose complexes in relation to thermal stability (Kuginuma and Donovan, 1981; Stute and Konieczy-Janda, 1983; Eliasson and Krog, 1985).

The degradation of amylose by amylolytic enzymes is known to be decreased by formation of the amylose-lipid comlex (Lonkhoysen and Blankestij, 1976; Kim and Robinson, 1979; Holm *et al*. 1983; Eliasson *et al*., 1984). It has been reported that SSL improved bread quality, especially when a foreign flour was supplemented to the wheat flour (Tsen and Tang, 1971; Tsen *et al*., 1971; Tsen and Hoover, 1971). Tenny and Schmidt (1968) reported that the SSL provides the dough with tolerance to withstand production and formulation variables. SSL also makes the gluten more extensible and stronger by binding with the gluten, and forms complexes with starch that retard gelatinization during baking and delays retrogradation after baking.

Several actions of monoglyceride in bread baking systems were discussed by Coppoc (1954). According to him, the mechanisms of monoglycerides were as follows: (1) dispersion of fat through the dough, (2) retention of soluble starch in the granules, (3) retardation of gelatinization, (4) supplying more moisture to the gluten, and (5) retention of moisture initially by gluten.

Enzymes

Alpha-amylases from cereal, fungal, and bacterial sources decrease the rate of bread firming (Miller *et al*., 1953; Pyler, 1969). Among the three sources of alpha-amylases, bacterial alpha-amylase is most powerful for retarding starch retrogradatioon, since cereal and fungal alpha-amylases are not heat-tolerable, resulting that the activity disappears mostly during baking (Pyler, 1970). Bacterial alpha-amylase does not lose its enzymatic activity even during the baking, since it is heat-tolerable (optimum temperature for expressing activity is 65 to 75˚C). Its enzymatic activity remains after baking. Thus if the remained activity is excessive, the loaf crumb expresses unfavorable tenacity that is derived from dextrin formed in the crumb. The choice of the bacterial species and strain, amount of usage in the baking formula and its usage have to be considered carefully.

Zobel and Senti (1959) found that crystallinity of breads containing the enzyme was greater after three days storage than the control bread without enzyme, although the former bread was softer than the latter. This indicates firming and crystallinity were not synonymous. These workers suggested that the increased softness was attributed to the crystalline regions having greater freedom to move after cleavage of bonds by the enzyme in the amorphous regions, resulting in a decrease in rigidity. However, more regions or chains were able to align and associate, thus increasing the crystallinity. Dragsdorf and varriano-Marston (1980) showed similar results.

Other factors

Protein content and its quality

As the protein content of wheat flour is higher, staling speed of the bread becomes slower. The reason for such effect of protein on bread staling is considered as that starch content decreases relatively with the increase in protein content (Kim and D'Appolonia, 1977b) . Also it is known that protein quality has no effect on bread staling (Kim and D'Appolonia, 1977c). Thus, protein does not affect bread staling directly.

Storage temperature of bread

Bread staling proceeds rapidly at the lower temperature around 2-5˚C compared with the higher temperature. Under the temperature of 2˚C, staling

speed becomes pretty slow. And under -18˚C, bread staling almost stops for few months. The degree of starch retrogradation is almost half at 30˚C, and is about one fourth at 34˚C, compared to 21˚C. This fact indicates some other factors together with starch, such as protein or water emigration or the both, play an important role on bread firming process (D'Appolonia, 1972).

Water absorption of wheat flour

Loss in moisture does not occur during bread staling. The moisture content keeps almost constant level after baking (Boussingault, 1852). Even the staled and firmed bread contains moisture equal level to freshly baked bread, it is generally recognized that the increase in water absorption of bread dough improves crumb softness and retards bread staling. One of the clues to explain this phenomenon is that more starch gelatinizes during baking as more water is added to the dough. It is still discussed among researchers whether water emigrates from starch to protein, or from protein to starch during staling.

Pentosan

Pentosan is a polysaccharide consists of xylose and arabinose and it is contained in wheat flour for approximately 2-3%. The important role of pentosan for bread making is to improve the water retention ability, resulting in raising the water absorption of the dough (Kim and D'Appolonia, 1977a). While pentosan slows down the rate of bread firming, the effect is larger for insoluble pentosan than for soluble pentosan (Kim and D'Appolonia, 1977d).

Conclusive remarks

A problem of the bread staling was the problem that many researchers studied for many years, and we finally saw the total outline mainly on a problem of the aging of the starch. The development of the future study is yet expected a lot of contradiction on data when we watch a phenomenon called the firming of the bread which is the most important problem from the viewpoint of the starch retrogradation, water emigration, X-rays diffraction analysis, sugar or influence of the storage temperature. An study of the bread staling progressed mainly on a change of the starch inside that is the starch retrogradation, but is a study purpose till now in the original last; can "delay a process of the aging to the limit";, therefore, particularly pray for studies being always pushed forward in contributing to improvement of the life of people in mind.

REFERENCES

Axford D.W.E., and Colwell K.H.: Thermal investigation of bread staling. *Chem. Ind*. 467, 1967.

Baker L.A., and Rayas-Duarte P.: Retrogradation of Amaranth starch at different storage temperatures and the effects of salt and sugars. *Cereal Chem*. 75:308, 1998.

Banks W., and Greenwood C.T.: The conformation of amylose in dilute solution. *Starke* 23:300, 1971.

Barham H.N., and Johnson J.A.: The influence of various sugars on dough and bread properties. *Cereal Chem*. 28:463, 1951.

Bechtel W.G., Meisner D.F., and Bradley W.B.: Effect of the crust on the staling of the bread. *Cereal Chem*. 30:160, 1953.

Bice C.W., and Geddes W.F.: The role of starch in bread staling. In starch and its derivatives. Radley J.A. ed., Chapman and Hall Ltd., London, 1953.

Biliaderis C.G., and Prokopowich D.J.: Effect of polyhydroxy compounds on structure formation in waxy maize starch gels: colorimetric study. *Carbohydr. Polym*. 23: 193, 1994.

Bohn R.T.: A review of the comparative value of sugars for bread. *Baker's Digest* 28:115, 1954.

Bourne E.J., Tiffin A.I., and Weigel H.: Interaction of starch with sucrose stearates and other anti-staling agents. *J. Sci. Food Agri*. 11:101, 1960.

Boussingault J.B.: Experiences ayant pour byt de determiner la cause de la trans formation du pain tender en pain rassis. *Ann. Chem. Phys*. 36:490, 1852.

Chinachoti P., Kim-Shin M.-S., Mari F., and Lo L.: Gelatinization of wheat starch in the presence of sucrose and sodium chloride: Correlation between gelatinization temperature and water mobility

as determined by Oxygen-17 nuclear magnetic reasonance. *Cereal Chem*. 68:245, 1991.

Collison R., and Elton G.A.H.: Some factors which influence the rheological properties of starch gels. *Starke* 13:164, 1961.

Collison R.: Swelling and gelatinization of starch. In starch and its derivatives. Radley J.A. ed., Chapman and Hall Ltd., London, p168, 1968.

Colwell K.H., Axford D.W.E., Chamberlain N., and Elton G.A.H.: Effect of storage temperature on the aging of concentrated wheat starch gels. *J. Sci. Food Agric*. 20:550, 1969.

Coppoc J.B.M., Cookson M.A., Laney D.H., and Axford D.W.E.: The role of glycerides in baking. *Baker's Digest* 5:8, 1954.

Cornford S.J., Axford D.W.E., and Elton G.A.H.: The elastic modules of bread crumb in linear composition in relation to staling. *Cereal Chem*. 41:216, 1964.

D'Appolonia B.L.: Effect of bread ingredients on starch gelatinization properties as measured in the amylograph. *Cereal Chem*. 49:532, 1972.

DeStefanis V.A., Ponte J.G.Jr., Chung F.H., and Ruzza N.A.: Binding of crumb softners and dough strengtheners during bread making. *Cereal Foods world* 21:131, 1976.

Dragsdorf R.D., and Varriano-Marston E. Bread staling: X-ray diffraction studies on bread supplemented with alpha-amylase from different sources. *Cereal Chem*. 57:310, 1980.

Dubois D.K.: Fermented doughs, *Cereal Foods World* 26:617, 1981.

Edelmann E.C., Cathcart W.H., and Berquist C.B.: The effect of various ingredients on the rate of firming of bread crumb in the presence of polyxyethylene (mono) stearate and glyceryl monostearate. *Cereal Chem*. 27:2, 1950.

Eliasson A.C., and Krog N.: Physical properties of amylose-monoglyceride complexes. *J. Cereal Sci*. 3:239, 1985.

Farhat I.A., Blanshard J.M.V., Descamps M., and Mitchell J.R.: Effect of sugars on retrogradation of waxy maize starch-sugar extrudates. *Cereal Chem*. 77:202, 2000.

Fearn T., and Russell P.L.: A kinetic study of bread staling by differential scanning colorimetry. *J. Sci. Food Agric*. 33:537, 1982.

Ghiasi K., Hosney R.C., and Lineback D.R.: Characterixation of soluble starch from bread crumb. *Cereal Chem*. 56:485, 1979.

Ghiasi K., Hoseney R.C., and Varriano-Marston E.: Gelatinization of wheat starch. I. Excess-water system. *Cereal Chem*. 59:81, 1982a.

Ghiasi K., Varriano-Marston E., and Hoseney R.C.: Gelatinization of wheat starch. II. Starch-surfactant interaction. *Cereal Chem*. 59:86, 1982b.

Hanes C.S.: The action of amylases in relation to the structure of starch and its metabolism in plants. *New Phytologist* 36:189, 1937.

Holm J., Bjoek I., Ostrowska S., Eliasson A.-C., Asp N.-G., Larsson K., and Lundquist I.: Digestibility of amylose-lipid complexes *in vitro* and *in vivo*. *Starke* 35:294, 1983.

Jang, J.K., Lee, S.H., Cho, S.C. and Pyun, Y.R.: Effect of sucrose on glass transition, gelatinization, and retrogradation of wheat starch. *Cereal Chem*. 78:186, 2001.

Johnson J.M., Davis E.A., and Goedon J.: Interaction of starch and sugar water measured by electron spin resonance and differential scanning colorimetry. *Cereal Chem*. 67:286, 1990.

Jough G.: The formation of dough and bread studies. The ability of starch to form structures and the improving effect of glycerol mono-stearate. *Cereal Chem*. 38:140, 1961.

Kai T.: Firming properties of white pan breads made by different baking methods. *Bulletin of Seinan Jo Gakuin University*, 11:87, 2007.

Katz, J.R.: Gelatinization and retrogradation of starch in relation to the problem of bread staling. In a comprehensive survey of starch chemistry, Walton R.P., ed., Chemical catalog Co., New York, p1, 1928.

Katz J.R.: Abbhandlungen zur phiklischen chemie der starke und der brotbereitung. I. Uber die anderungen in rontgenspekrtrum der starke beim backe und beim altbckenwerden des brotes. *Z. Phsic Chem*. A150:37, 1930.

Kim S.K., and D'Appolonia B.L.: Effect of pentosans on the retrogradation of wheat starch gels. *Cereal Chem*. 54:150, 1977a.

Kim S.K., and D'Appolonia B.L.: Bread staling studies. I. Effect of protein content on staling rate and bread crumb pasting properties. *Cereal Chem*. 54:207, 1977b.

Kim S.K., and D'Appolonia B.L.: Bread staling studies. II. Effect of protein content and storage

temperature on the role of starch. *Cereal Chem*. 54:225, 1977c.

Kim S.K., and D'Appolonia B.L.: Bread staling studies. Effect of pentosans on dough, bread and bread staling rate. *Cereal Chem*. 54:225, 1977d.

Kim Y.J., and Robinson R.J.: Effect of surfactants on starch in a model system. *Starke* 31:293, 1979.

Koch R.B., Smith F., and Geddes W.F.: The fate of sugars in bread doughs and synthetic nutrient solutions undergoing fermentation with baker's yeast. *Cereal Chem*. 31:55, 1954.

Kohyama K., and Nishinari K.: Effect of soluble sugars on gelatinization and retrogradation of sweet potato starch. *J. Agric. Food Chem*. 39:1406, 1991.

Krog N.: Amylose complexing effect of food grade emulsifiers. *Starke* 23:206, 1971.

Krog N.: Influence of food emulsifiers on pasting temperature and viscosity of various starches. *Starke* 25:22, 1973.

Krog N., and Davis E.J.: Starch-surfactant interactions related to bread staling. In proc. of internationall symposiu on advances in baking science technology. Kansas State University, U-1, 1984.

Kuginuma M., and Donovan J.W.: Colorimetric determination of the amylose content of starches based on formulation and melting of the amylose-lysolecithin complex. *J. Food Sci*. 46:765, 1981.

Lagendijk J., and Pennings H.J.: Relation between complex formation of starch with monoglycerides and the firmness of bread. *Cereal Sci. Today* 15:354, 1970.

Leach H.W.: Gelatinization of starch. In Starch chemistry and technology, Whisler R.L., and Paschall E.F. ed., Academic Press, New York, 1:289, 1965.

Lehman L.: The nature of fatty acids associated with starch: the absorption of palmitic acid by potato and defatted corn and rice starches. *J. Am. Chem. Soc*. 64:2144, 1942.

Levine H., and Slade L.: A polymer physiological approach to the study of commercial starch hydrolysis products (SHPs). *Carbohydr. Polym*. 6:213, 1986.

Lineback D.R.: The role of starch in bread staling in proc. of international symposium on advances in baking science and technology, Kansas State University, S-1, 1984.

Linndet L.: Sur les etats que presence l'amidon dans le pain tender et dans le pain rassis. *Bull. Sco. Chim*. 27:634, 1902.

Lonkhoysen H., and Blankestij J.: Influence of monoglycerides on the gelatinization and enzymatic breakdown of wheat and cassava starch. *Starke* 28:227, 1976.

Maga J.A.: Bread Staling. CRC Critical Reviews, *Food Chemistry* 5:443, 1975.

Matsukura U, Matsunaga A., and Kainuma K.: Structural studies on retrograded normal and waxy corn starches. *J. Japanese Soc. Starch Sci*. (*Denpun Kagaku*) 30:106, 1983.

Mciver R.G., Axford D.W.E., Colwell K.H., and Elton G.A.H.: Kinetic study of retrogradation of gelatinized starch. *J. Sci. Food Agric*. 19:560, 1968.

Mikus F.F., Hixon R.H., and Rundle R.E.: The complexes of fatty acids with amylose. *J. Am. Chem*. Soc. 68:1115, 1946.

Miller B.S., Johnson J.A., and Palmer D.L.: A comparison of cereal, fungal and bacterial alpha-amylases as supplements for bread making. *Food Technology* 7:38, 1953.

Osman E.M., and Dix M.R.: Effects of fats and nonionic surface-active agents on starch pastes. *Cereal Chem*. 37:464, 1960.

Osman E.M., leith S.J., and Fles M.: Complexes of amylose with surfactants. *Cereal Chem*. 38:449, 1961.

Piekarz E.R.: Evaluation of sugars in ferment systems. *Proc. Am. Soc. Bakery Eng*. Chicago, p118, 1963.

Pomeranz, Y.: Bread staling. In modern cereal science and technology, VCH Publishers, Inc., translated by Nagao S., p301, 1987.

Ponte J.G., and Reed G.: Bakery foods. In industrial microbiology, Reed G. ed., AVI Pub. Co. Inc., Westport CT, p246, 1982.

Pyler E.J.: Enzymes in baking: theory and practice. *Baker's Digest* 43:46, 1969.

Pyler E.J.: Enzymes. In baking Science and Technology, The Baker's Digest ed., Siebel Pub. Co., Chicago, p120, 1970.

Riisom T., Krog N., and Eriksen J.: amylose complexing capacities of cis-and trans-unsaturated monoglycerides in relations to their functionality in bread. *J. Cereal Sci*. 2:105, 1984.

Schoch T.J., and Wiliams C.B.: Absorption of fatty acids by the linear component of corn starch. *J. Am. Chem. Soc*. 66:1232, 1944.

Schoch T.J., and French D.: Studies on bread staling. I. The role of starch. *Cereal Chem*. 24:231, 1947.

Schoch T.J.: Starch in bakery product. *Baker's Digest* 39:48, 1965.

Seib P.A.: Starch gelatinization: chemical and physical effects. *Feedstuffs* 43:50, 1971.

Stute R., and Konieczy-Janda G.: DSC-untersuchungen an starken. Teil II. Untersuchungen an starke-lipidkomplexen. *Starke* 35:340, 1983.

Strandine E.J., Carlin G.T., Werner G.A., and Hopper R.P.: Effect of monoglycerides on starch flour and bread. A microscopic and chemical study. *Cereal Chem*. 28:449, 1951.

Tang R.T., Robinson R.J., and Hurley W.C.: Quantitative changes in various sugar concentrations during bread making. *Baker's Digest* 46:48, 1972.

Tenny R.J., and Schmidt D.M.: Sodium stearyl-2-lactylate: its function in yeast leavened bakery products. *Baker's Digest* 42:30, 1968.

Tsen C.C., Hoover W.J., and Phillips D.: The use of sodium stearyl-2-lactylate and calcium stearyl-2-lactylate for producing high protein breads. *Baker's Digest* 45:20, 1971.

Tsen C.C., and Tang R.T.: K-State process for making high protein breads. I. Soy bread. *Baker's Digest* 45:26, 1971.

Tsen C.C., and Hoover W.J.: The shortening-sparing effect of sodium stearyl-2-lactylate and calcium stearyl-2-lactylate in bread baking. *Baker's Digest* 45:38, 1971.

Wang Y.J. and Jane J.: Correlation between glass-transition temperature and starch retrogradation in the presence of sugars and maltodextrins. *Cereal Chem*. 71:527, 1994.

Whistler R.L., and Hilbert G.E.: Extraction of fatty substances from starch. *J. Am. Chem. Soc*. 66:1721, 1944.

Willhoft E.M.A.: Mechanism and theory of staling of bread and baked goods and associated changes in the textural properties. *J. texture Stud*. 5:103, 1973.

Zobel H.F., and Senti F.R.: The bread staling problem. X-ray diffraction studies on breads containing a cross-linked starch and a heat-stable amylase. *Cereal Chem*. 36:441, 1959.

Zobe1 H.F.: A review of bread staling. *Baker's Digest*. 47:52, 1973.

パンの老化

甲斐　達男

＜要　旨＞

パンの老化の研究に端緒をつけたのは1928年、オランダのKatzである。彼はパンの経時変化を詳細に調べることで、夜に製パン作業をしなくてもよい方法を考えだそうとしたのである。以来およそ70年間に渡る長い間、パンの老化メカニズムとその抑制法が、パンを糧とする国々でさまざまな角度から検討されてきた。老化によるパンの廃棄量は全生産量の3～5％におよぶと推定され、経済的に重要な意味を持つため、このように長い間、研究が続けられてきているのである。パンの老化は古くて新しいトピックであると言える。パンの老化には、澱粉が最も主要な役割を果たしているが、糖、ペントザン、タンパク質、脂質、さらにはその他多くの微量物質（糖脂質、脂質タンパク、リン脂質、ムコ多糖、糖タンパク、など）の相互作用によっても発現する。いくつもの老化現象のうち、手で触れて商品を選ぶ消費者サイドから見れば、最も関心を喚起する点はパンの硬化であろう。そこで本稿ではすでに提出されている多くのレビューとの差別化を図るために、これまで余り論じられなかったパンの硬化に焦点をあてて、さまざまな老化関連因子（澱粉、製パン法、クラム残糖、乳化剤、酵素、その他）との関連を解説した。パンの老化の問題は、ようやく澱粉の老化の問題を中心にして、その全体の輪郭が見えてきたところである。最も重要な課題であるパンの硬化という現象を、澱粉の老化プロセス、水分移行、X線回析、糖や保存温度の影響などの観点から観ると、未だ、データ上に矛盾が多く、今後の研究の発展が期待される。

キーワード：老化、パン、硬化、澱粉の老化

西南女学院大学保健福祉学部栄養学科