

A Mechanism of Bread Firming. I. Role of Starch Swelling¹

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ABSTRACT

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Bread firming and starch recrystallization are not synonymous, although both occur during bread storage. Bread baked to 95°C in an electric resistance oven did not firm. Factors such as baking time and presence of shortening influenced the water-hydration capacity of the bread crumb. These factors also affected bread firmness during five days of storage.

Increased baking time after the temperature reached 95°C in an electric resistance oven increased bread firmness on day 1. A proposed model maintains that bread firming results from cross-links (hydrogen bonds) between the continuous protein matrix and the discontinuous remnants of starch granules.

Schoch and French, starch chemists, presented their theory of bread staling in 1947 (Schoch and French 1947). They suggested that during baking, starch granules swelled, amylose was partially leached out of the granules, and amylopectin was diluted. The limited amount of water in bread restricted these processes. Fresh bread consisted of soft, extensible granules embedded in a firm gel network of amylose. They attributed bread firming during storage time to changes in amylopectin within the starch granules. Association of the branched molecules within the swollen granules occurred during storage. The gel surrounding the granules remained firm and gradually became rigid. Bread firmed because the granules became rigid.

Until recently, that theory was generally accepted as fact. However, it only presented the role of starch. Over the last 30 years, several authors have shown that bread firming is not synonymous with starch recrystallization (Zobel and Senti 1959, Dragsdorf and Varriano-Marston 1980, Ghiasi et al 1984, Rogers et al 1988). An obvious omission from that traditional view of bread staling is the role of gluten. Ponte et al (1962) and Maleki et al (1980) showed that all flours did not produce bread that firmed at the same rate. Maleki et al (1980) suggested that the rate of firming was related to the protein quality of the flour.

The objective of this work was to develop a model of bread

firming that incorporates the roles of starch and gluten as influencing factors. Also studied were the degree of starch granule swelling as affected by the crumb temperature, baking time, and the presence of lipids in the formula.

LITERATURE REVIEW

Bread quality deteriorates with storage time after baking. Deterioration in quality, other than microbial spoilage, as measured by consumer acceptance, has been defined as staling (Bechtel et al 1953). Herz (1965) listed many changes in crumb properties associated with staling, including increased crust moisture, crumbliness, starch crystallinity, opacity, and firmness; loss of flavor; and decreased crumb moisture, soluble starch, and hydration capacity of crumb. Most bread produced in the United States is white pan bread. The system of wholesale distribution requires bread to have a shelf-life of five days or more. A strong negative correlation between consumer acceptance and compressibility or firmness has been well documented (Bechtel et al 1953, Axford et al 1968).

In 1852, Boussingault showed that bread could be refreshed by reheating above 60°C (Wilhoft 1973). The ability of mild heating to reverse the effects of aging on firmness led to the presumption that hydrogen bonding, rather than more thermodynamically stable covalent bonding, is involved in bread firming.

Starch Recrystallization and Bread Firming

Rogers et al (1988) showed that the rate of starch recrystallization, as calculated from differential scanning calorimetry enthalpy values, did not correlate with bread firming. They also showed that low-moisture bread firmed at a very rapid rate, whereas starch

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recrystallization (ΔH of melting) remained essentially unchanged.

Ghiassi et al (1984) reported that firmness increased linearly between days 0 and 5 when bread was stored at room temperature. Recrystallization of amylopectin determined by ΔH was linear between days 0 and 3, but then the rate slowed. They also reported that after five days of storage, bread refreshed to 80°C with minimal loss of moisture was nearly as soft as fresh bread. During two additional days of storage after heating, bread firmed at a rapid rate, whereas starch recrystallization occurred at a normal rate.

Bread supplemented with bacterial α -amylase retained freshness longer than did unsupplemented bread (Conn et al 1950). X-ray diffraction studies showed that the starch in the loaves supplemented with bacterial α -amylase was more crystalline (Zobel and Senti 1959, Dragsdorf and Varriano-Marston 1980). Therefore, starch recrystallization and bread firming are not synonymous. The two processes might not even be related; however, both occur after baking and during bread storage.

Role of Monoglycerides

Heating a mixture of starch (5 g) and water (180 g) to 120°C gave starch that was less soluble and less swollen in the presence of monoglyceride (2%) than without monoglyceride (Ghiassi et al 1982). The effect of monoglyceride on starch swelling in a limited water system is still unclear.

After a wheat starch and a monoglyceride were heated to 70°C in excess water, scanning electron micrographs showed the surface of the granule to be scaly, as if the amylose-lipid complex had precipitated on the surface (Van Lonkhuysen and Blankestijn 1976). Those effects appeared to restrict swelling of the granule.

Photomicrographs and sedimentation of starch separated from bread crumb showed that monoglyceride decreased the swelling of starch granules (Strandine et al 1951). However, the quantity of monoglyceride used in the study was not reported.

Role of Native Flour Lipids and Shortening

Addition of native flour lipids to defatted flour resulted in changes in loaf volume that corresponded to changes in firmness (MacRitchie 1983, Rogers et al 1988). Shortening had a major effect on loaf volume and bread firmness. However, as shown by Rogers et al (1988), the decrease in bread firmness in the presence of shortening is more complex than simply an increase in loaf volume. Monoglyceride can replace native flour lipids; however, addition of shortening did not affect firming rate of bread baked with defatted flour. The authors implied that the same mechanism affecting loaf volume of reconstituted defatted flours also affected firming rate. Because shortening does not form an insoluble clathrate with amylose, it is generally believed that an interaction between shortening and starch does not occur (Osman et al 1961).

Role of Starch in Crumb Structure

During baking, starch granules absorb water and swell. Transmission electron micrographs have shown that starch granules in bread were separated from each other by a continuous protein phase (Bechtel et al 1978). No cross-linking of starch and protein was apparent in doughs. However, after baking, starch appeared fibrous and seemed to be linked to protein. The elastic modulus of gluten-starch dough was shown to increase as the result of starch gelatinization (Dreese et al 1988). This shows that starch-gluten interactions occur during baking.

Effect of Starch Swelling on Bread Firmness

Many factors control the degree of swelling of starch granules during baking. Yasunaga et al (1968) reported that a 10-min extension of baking time increased the hydration capacity of bread crumb from 290 to 305%. Also, bread baked at 232°C for 20 min had a hydration capacity of 305%, whereas bread baked at 210°C for the same amount of time had a hydration capacity of 290%. However, crumb moisture and firmness were not reported.

Effect of Moisture on Bread Firmness

Perhaps the earliest published study on staling was by Boussingault in 1852 (Wilhoft 1973). He disproved the common belief that bread staling was a result of moisture loss. With storage time, the outer crumb lost moisture to the crust, thereby setting up a moisture gradient in the crumb. Crumb without crust maintained a constant moisture level during storage. The compressibility values of crustless bread were not significantly different from those of intact bread (Bradley and Thompson 1950, and Bechtel et al 1953). Rogers et al (1988) indicated that rate of firming was a function of bread moisture content; as bread moisture decreased, rate of firming increased.

Effect of Protein on Bread Firmness

The role of protein in bread firming has not been extensively studied. Breads made from all flours do not firm at the same rate (Ponte et al 1962). Axford et al (1968) showed that as loaf-specific volume increased, both firmness and firming rate decreased in a linear manner.

MATERIALS AND METHODS

Flours used in the present study were donated by Cargill (Wichita, KS). Protein contents of the flours were 11.5–12.1% and gave essentially the same firming rate. The monoglyceride was AM 341 and Amidan ESK (Grindsted Products Inc., Industrial Airport, KS). Specifications for the powdered monoglycerides included 90% distilled monoglyceride, soy-based powder, 1.5% free fatty acid + free glycerol, and melting point 60°C. Vital wheat gluten and wheat starch were donated by Midwest Grain Products, Inc. (Atchison, KS). Fermipan instant yeast was from Gist-Brocades (King of Prussia, PA). Other ingredients were as specified by AACC method 10-09 (AACC 1983).

Bread was baked according to the standard pup-loaf procedure, AACC method 10-09 (AACC 1983). Fermentation time was 180 min. Instant yeast (0.76 g) was used instead of compressed yeast, and malted barley flour was used instead of malt syrup.

An electric resistance oven (ERO) system described by Junge and Hosenev (1981) with certain modifications was used. Electrodes were made of perforated steel. Doughs were prepared according to the procedure described by Moore and Hosenev (1986). Prepared doughs were placed in the ERO, proofed for 55 min, and baked according to the temperature profile shown in Figure 1. To obtain an internal final bake temperature similar to that of bread baked in a conventional oven, voltage across the electrodes was increased to the maximum output (140 V) during the final 5 min of baking.

Bread moisture was determined by AACC Method 44-18, a two-stage air-oven method (AACC 1983).

Bread was stored in polyethylene bags at 23°C for five days unless otherwise noted. Loaves were cut into 25-mm slices. A new loaf was used each day for measurements. Firmness measurements were recorded from the three center slices on days

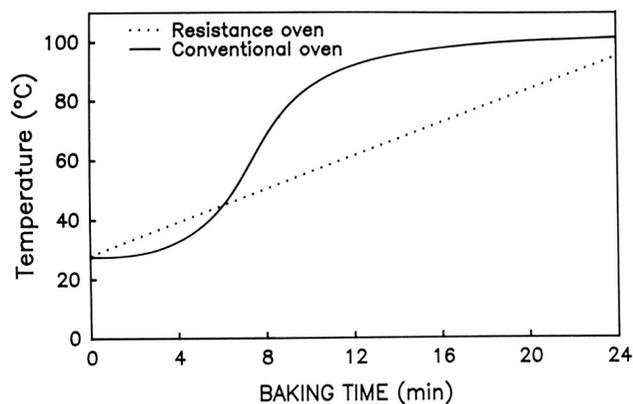


Fig. 1. Temperature profile during baking in an electric resistance oven.

0, 1, 3, and 5. At least two loaves were baked for each treatment. Firmness values represent an average of six slices per treatment. A universal testing machine (Instron) equipped with a 36-mm diameter probe was used to compress bread slices. Firmness was the force required to compress each slice 6 mm (25% compression). The stress-strain behavior was linear over the range of compression. The rate of compression, or crosshead speed, was set at 50 mm/min, and the chart speed was 250 mm/min. Force (g) at 25% compression was recorded as bread firmness. The standard deviations, within days, were as follows (n = 8): day 0, 6 g; day 1, 19 g; day 3, 54 g; day 5, 45 g.

The swelling-power procedure that Schoch and French (1947) developed for measuring bread crumb was modified slightly; therefore, results are reported as water-holding capacity. Twelve hours after baking, the crust was removed from each loaf. The internal crumb was torn by hand, placed in a plastic bag, and stored for 6 hr to achieve a more uniform moisture distribution within the sample. Within the next 12 hr, the water-hydration capacity of the crumb was measured. Bread crumb (25 g) was suspended in water (150 ml) for 30 min, with gentle stirring. The mixture was centrifuged at $1,000 \times g$ for 7 min. Water-hydration capacity was determined as the weight (grams) of wet sediment per gram (db) of bread crumb.

RESULTS AND DISCUSSION

Effect of Baking Methods on Bread Firmness

Bread baked in the ERO firmed at a rapid rate in 2–24 hr; however, firmness did not increase after 24 hr of storage. The effect of the baking method used (ERO vs. conventional oven) on firmness is shown in Figure 2. Because firmness of ERO-baked bread did not increase between days 1 and 5, it appeared that this system could be helpful in understanding bread firming.

The effect of baking method on crumb properties is shown in Table I. Crumb moisture content was shown to strongly influence the rate of bread firming (Rogers et al 1988, He and Hosney 1990). High-moisture bread firmed at a slower rate than did low-moisture bread. Because the moisture content of ERO bread (35.5%) was lower than that of conventional-oven bread (40.4%), the antifirming phenomenon of ERO bread could not be explained by the moisture content.

Bread baked in a conventional oven had a greater hydration capacity (3.19 ± 0.11 SD, within day) compared with bread baked

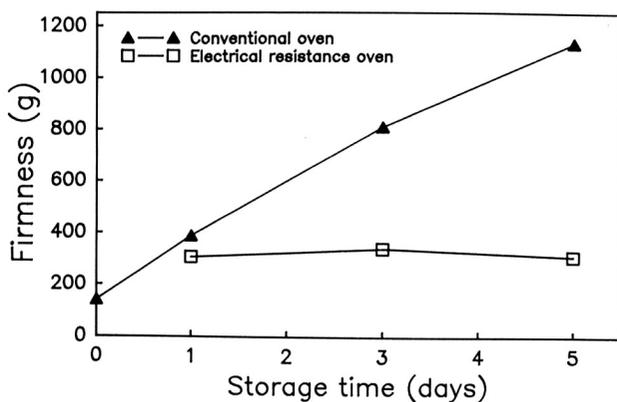


Fig. 2. Five-day firming profiles of breads baked in a conventional and an electric resistance oven.

TABLE I
Observations of Crumb Characteristics

Crumb Property	Conventional Oven	Electric Resistance Oven
Firming rate	200 g/day	None
Sediment	Homogeneous	Heterogeneous
Starch granules	Swollen and deformed	Less swollen and deformed
Birefringence	None	Slight

in an ERO (2.56 ± 0.06 SD, within day); thus, starch was less swollen in bread baked in the ERO. Light microscopy photographs (Fig. 3) clearly show that starch granules extracted from bread baked in the ERO were less swollen and not deformed, compared with starch granules from conventionally baked bread.

In ERO-baked bread, more starch granules were birefringent, and the sediment was heterogeneous. Ease of separation of starch from gluten after baking was an indication of the degree of interactions between starch and protein during baking. The heterogeneous sediment indicated that starch was easily separated from gluten by the water-extraction procedure. This observation suggested that interactions between starch and protein were weaker or fewer in bread baked in an ERO. Birefringence of starch granules after heating may result from insufficient water or temperature too low to melt starch crystallites. Regardless of the cause, these results suggest that the ERO bread was underbaked.

Temperature was a critical factor to control. Final bake temperature of ERO bread affected firmness. Firmness of ERO bread baked to 95°C was 398 g on day 1. When bake temperature reached 99°C , day 1 firmness was 595 g. The firming profile of bread baked to 95 or 99°C is shown in Figure 4. Consistent achievement of a final bake temperature of 99°C was difficult, if not impossible. Given that higher bake temperature results in more swelling of starch granules, more solubilization of starch molecules, and more moisture loss, then more interactions are possible with the protein network. Moisture content of bread baked to 95 and 99°C was 35.5 and 30.4%, respectively.

Effect of Window of Amylase Activity

Initially, bread was baked at a linear rate of heating at $28\text{--}95^\circ\text{C}$. It was reasoned that this linear rate lengthened the window of amylase activity relative to that of conventional-oven bread. Walden (1955) reported that the period of major activity for malt α -amylase was between the temperatures of 58 and 78°C .

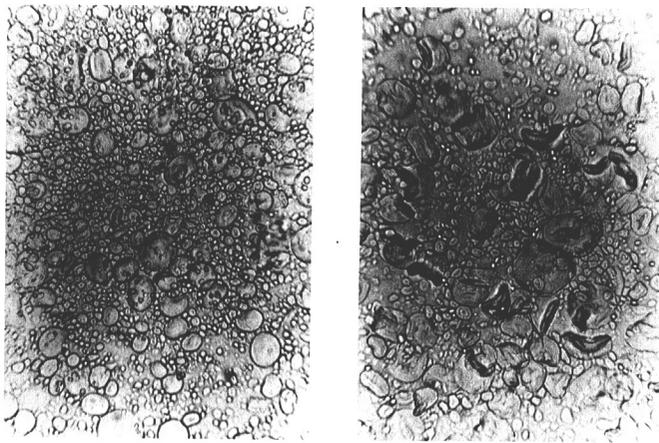


Fig. 3. Light microscopy photographs of starch granules extracted from breads baked in electric resistance (left) and conventional (right) oven.

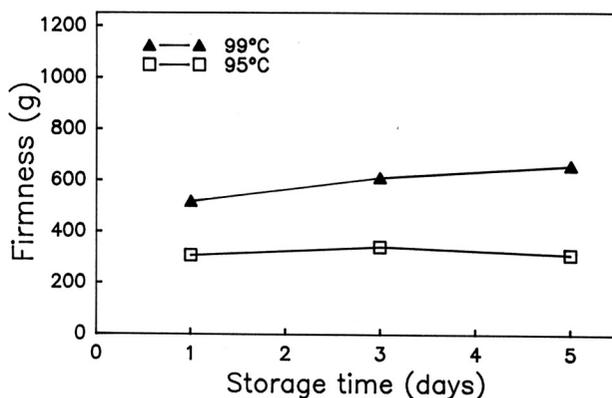


Fig. 4. Effect of final bake temperature on firmness of bread baked in an electric resistance oven.

Several authors (Baker and Mize 1939, Walden 1955, Audidier 1968) have shown the temperature profile of bread baked in a conventional oven. According to their results, any specific point in the internal crumb passed through the 58–78°C temperature range in less than 3 min. Baking pup-loaves with a linear rate of heating in an ERO extended the window of enzyme activity to 7 min.

During baking, starch granules swell, and amylose is partially leached from the granules. Starch granules are embedded in a continuous gluten matrix. During heating, the partially leached amylose at the surface of the granule may entangle with gluten fibrils. Fewer swollen starch granules and solubilized starch molecules in ERO bread may have fewer and/or weaker entanglements with gluten.

If the slow rate of heating (and thus the longer window of activity) resulted in bread not firming, then heating at a rapid rate would eliminate differences between conventional-oven and ERO breads. Applying a higher voltage across the electrodes resulted in a rapid temperature rise. Baking bread at the maximum rate of heating in an ERO resulted in a 1-min window of activity. However, rapid baking in the ERO did not change the firming profile relative to a slower baking rate. Similarly, extending the window of activity to 15 min did not slow the rate of firming (Fig. 5). Therefore, the mechanism by which ERO bread expressed an antifirming effect was not a result of an increased window of enzyme activity.

Effect of Baking Time on Crumb Properties

Degree of starch swelling (pasting) is known to be affected by the quantity of water present and by the temperature (Derby et al 1975). Baking time may also affect the water-hydration capacity of bread crumb (Yasunaga et al 1968). Time and temperature were monitored during ERO baking. As baking time above 95°C increased, firmness on day 1 and water-hydration capacity increased. The effects of variation in baking time on moisture content, water-hydration capacity of crumb, and firmness of ERO-baked bread are shown in Table II. Interpretation of firmness values is confounded by changes in moisture and baking time. Low-moisture bread is known to firm at a fast rate; however, ERO bread firmed at an even faster rate within

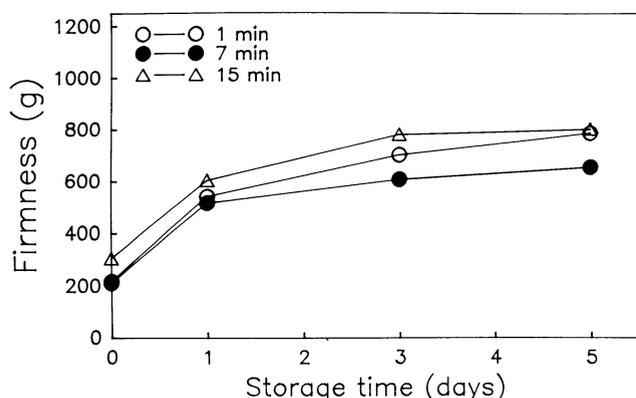


Fig. 5. Effect of heating rate (and, thus, length of window of activity) on bread firmness.

TABLE II
Effect of Baking Time on Crumb Properties of Bread Baked in an Electric Resistance Oven

Heating Time Above 95°C (min)	Moisture (%)	Firmness on Day 1 (g)	Hydration Capacity ^a
1	35.5	300	2.56 ± 0.06
8	30.1	523	2.75 ± 0.02
21	26.6	840	2.98 ± 0.08

^aSD within the same day.

24 hr of storage than would be expected for conventional-oven bread. With ERO bread, a 10% decrease in moisture content resulted in a 540 g increase in force in crumb firmness. Rogers et al (1988) air-dried conventionally baked bread. Interpretation of their results indicated that a similar 10% variation in moisture resulted in a difference of about 200 g of force (firmness) on day 2.

Effect of Moisture Migration

One characteristic of ERO-baked bread is the absence of a dry crust. The exterior 5–10 mm of ERO bread had 47% moisture, whereas the interior crumb had 35% moisture. The water relationship between crumb and crust is opposite to that of conventionally baked bread. Pup-loaves baked in a conventional oven had 44% moisture in the freshly baked crumb and less than 10% moisture in the crust. The basic principles of vaporization and condensation can explain the difference in moisture between ERO and conventional-oven bread (Sluimer and Krist-Spit 1987). The increased moisture in the exterior region of ERO bread is a result of moisture condensation. The outer edges of ERO bread are in contact with cool surfaces (plexiglass and the metal electrodes). During baking, water vaporizes and subsequently condenses on cooler surfaces.

During baking in a conventional oven, heat penetrates from the exterior to the interior of the loaf. Water condenses on cooler surfaces; therefore, as heat is conducted to the interior, water first condenses on the cooler, or less heated, internal crumb. More water available to starch granules in the interior of the loaf may permit more starch swelling. This may be one explanation for the greater hydration capacity of bread baked in an ERO vs. a conventional oven.

A Role of Monoglyceride

It is well known that bread supplemented with monoglyceride firms at a slower rate than does bread without shortening. The effect of lipids on bread firming is shown in Figure 6. Bread supplemented with 2% monoglyceride without the addition of shortening had a firming profile similar to that of bread baked with 3% shortening. Breads baked without shortening or from defatted flour without added shortening firmed at the same rate during five days of storage.

The hydration capacity of bread crumb indicated that

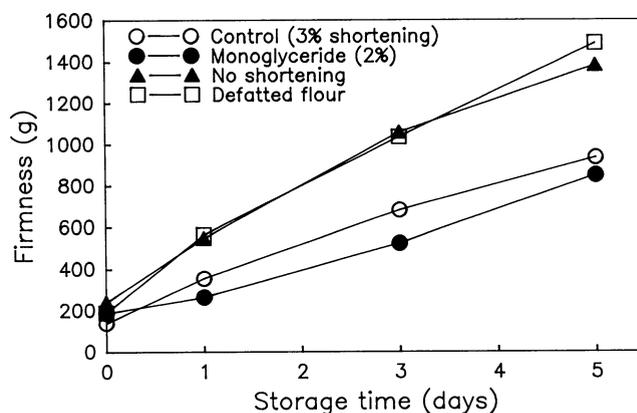


Fig. 6. Effect of lipids on firming profile of conventionally baked bread during five days of storage.

TABLE III
Effect of Lipids on Starch Swelling

Treatment	Hydration Capacity ^a
Control (3% shortening)	3.02 ± 0.08
Monoglyceride (2%)	3.03 ± 0.08
Defatted flour	3.28 ± 0.03
Without shortening	3.27 ± 0.02

^aSD between days.

shortening and monoglyceride decreased starch swelling during baking relative to that of bread baked without shortening. No significant difference was noted in crumb hydration capacity between breads baked without shortening and bread baked from defatted flour (Table III).

A Theory of Bread Firming

Rate of heating in an ERO was not a factor that affected bread firming. However, temperature and baking time above 95°C were directly related to bread firming, as was hydration capacity of bread crumb. Antifirming substances such as shortening and monoglyceride restrict starch swelling during baking. The evidence presented here suggests that starch swelling is a factor involved in determining the rate of bread firming. The effect of protein quality on bread firming (Maleki et al 1980) may be explained in terms of interactions among swollen starch granules, partial solubilization of starch molecules, and protein. He and Hosney (1991) demonstrated that poor quality flours (low loaf volume) had more hydrophilic properties than did good quality flours. Given that poor quality gluten would interact more strongly with starch granules in dough, then these interactions would also be stronger during and after baking. Therefore, bread from poor quality flour firms at a faster rate.

During baking, interactions (cross-links) occur between gluten and starch. During staling, as the crumb loses kinetic energy, interactions increase in number and strength. Gluten is the continuous phase, and remnants of starch granule are the discontinuous phase. Because refreshing bread restores freshness, the cross-links between gluten and starch that contribute to bread firming must be relatively weak, possibly hydrogen bonds. A model depicting a mechanism of bread firming and the role of starch swelling is presented in Figure 7. The protein fibrils represent the continuous gluten phase. The discontinuous phase is represented by starch remnants and partially leached amylose.

During baking, monoglycerides and shortening interact with starch molecules and decrease starch swelling. Because starch granules are less swollen, less solubilization of starch molecules

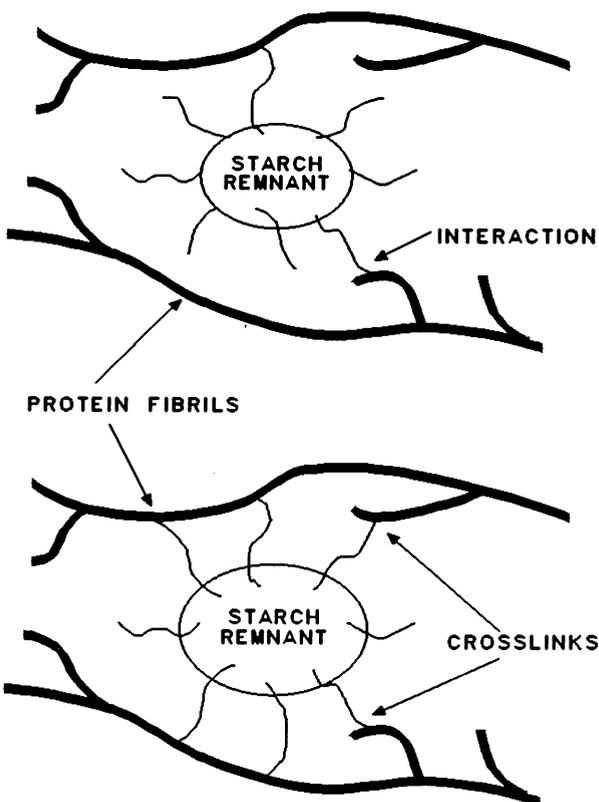


Fig. 7. Model of a mechanism of bread firming and the role of starch swelling.

occurs. With less surface area exposed to gluten, fewer and/or weaker cross-links occur with protein; therefore, the firming rate is reduced. Theoretically, monoglyceride, shortening, and water can plasticize gluten and decrease bread firmness. In summary, fewer and/or weaker entanglements and cross-links between starch and gluten result in reduced bread firming.

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