

WHEAT FLOUR LIPIDS IN BREADMAKING¹

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ABSTRACT

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This review on the role of wheat flour lipids provides an updated discussion of factors affecting the functional (breadmaking) properties of defatted and reconstituted wheat flours; lipid binding during wetting or dough mixing; lipid oxidation during dough mixing; interaction

between lipids and starch granules; and functional properties of flour lipids in breadmaking. The review also discusses models proposed by several scientists on interaction of lipids with wheat flour, dough and bread macromolecules.

Several comprehensive reports on wheat flour lipids and their role in breadmaking have been published recently (1-5). This review provides an updated discussion of the role of wheat flour lipids in areas related to breadmaking: factors affecting the functional (breadmaking) properties of defatted and reconstituted wheat flours; lipid binding during wetting or dough mixing; lipid oxidation during dough mixing; interaction between lipids and starch granules, including staling phenomena; and functional properties of flour lipids or lipid-related materials in breadmaking.

FACTORS AFFECTING FUNCTIONAL PROPERTIES

In studies on the role of lipids in breadmaking, extraction conditions should be established that maximize the amount of lipids extracted and minimize damage to functional properties of wheat flour. Extractability and functionality of lipids from wheat and milled products depend on the type of solvent (2,6-12), moisture content of wheat products or solvents or both (13,14), and age and particle size of the wheat flour. In addition, the overall breadmaking properties of the flour reconstituted with the extracted lipids depend on the extracting solvent and extraction conditions (10-12).

Chloroform and petroleum ether are suitable for use in determining the role of lipids in baking because they do not affect the properties of flour components (15). Finney and co-workers (10) studied the effects of nine solvents on breadmaking quality of a reconstituted flour and indicated that solvents such as benzene, chloroform and acetone could possibly be used to extract flour lipids without irreversibly damaging breadmaking properties.

Although water-saturated butanol is an efficient solvent for extracting lipids from wheat flour or its processed products (2), it is inadequate for studies on the

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role of lipids in breadmaking of the reconstituted flour (10). During lipid extraction, butanol forms a complex with starch, which inhibits gas production during fermentation. Generally, extraction of flour with water-saturated butanol greatly increases mixing time and impairs loaf volume. A special premix method (16) brings loaf volume to that of the control, but the method is lengthy and complex.

To study the breadmaking properties of reconstituted flours, we (11,12) used Skelly B, benzene, acetone and 2-propanol (PrOH) as extractants; the extracting conditions were two soxhlet methods—a regular and a vacuum that lowered extraction temperature 12–18°C—and a shaker method that controlled extraction temperatures. Table I summarizes the results for the lipids extracted; Table II shows the breadmaking characteristics of the reconstituted, solvent-extracted flours. Lipid extractability is affected more by the solvent than by the extraction method, and baking characteristics are affected substantially by the solvent and also by the extraction conditions when PrOH is used.

We also (13) studied the effects of flour moisture contents and aqueous binary azeotropes on breadmaking properties of reconstituted flours. Lipid extractability by soxhlet extraction increases when the moisture content of wheat flour raises from 1.2% to 13.8% or when the aqueous binary azeotropes of hexane, acetone, and PrOH are used as extractants. The interaction of flour components depends on the quantity and nature of lipids extracted. Solvent treatment, except with hexane, adversely affects baking characteristics (Fig. 1). Adverse effects are more pronounced when extractants contain water (ie, aqueous azeotropes); for the PrOH treatment, the adverse effects increase with increasing moisture content of the flour. The propanol azeotrope treatment permanently damages functionality, even when flour contains as little as 1.2% moisture before extraction. If functionalities of flour lipids are to be demonstrated, lipid-extraction conditions must be considered critically with careful attention to the extraction apparatus, extractant, extraction time, extraction temperature, and, probably, the nature of the flour. When a polar solvent such as PrOH is used to extract lipids, the moisture content of a flour sample alone may significantly affect the end-use properties of the reconstituted flour (13). To maximize lipid extraction and minimize damage to breadmaking properties of reconstituted flours, PrOH extraction should continue for 2 hr at 75°C by the shaker technique for flours with normal 13 or 14% moisture (12).

LIPID BINDING

Lipids that are extractable with nonpolar solvents become bound when the flour is wetted and mixed into dough (7,14,17–23). One-half to two-thirds of the free lipids (some nonpolar and almost all polar components) in wheat flour become bound in dough or when gluten forms (20–23). Starch lipids can be excluded from consideration in the role of lipid binding during dough mixing because they are tightly bound in the starch granules and probably do not significantly affect dough properties (5).

At the mixing stage, lipids interact with other flour constituents, especially proteins, to modify gluten structure; they, therefore, structurally support gluten in the dough (17,24–27). Lipids in gluten are bound mainly to the glutenin proteins (81.5% of total lipids); glutenin contains 20% lipids and gliadin only

1.5% lipids (17). The gliadin fraction contains only traces of phosphorus, and the glutenin fraction contains 150 μg of phosphorus per 100 mg of protein (25).

In a study of effects of dough mixing on lipid distribution (22), flour lipids are

TABLE I
Flour Lipids Extracted by Skelly B and 2-Propanol^a

Extracting Solvent	Lipids Extracted by		
	Soxhlet		Shaker at 75° C (% db)
	Regular (% db)	Vacuum (% db)	
Total Lipids			
Skelly B	1.03	0.91	0.99
2-Propanol	1.43	1.34	1.32
Nonpolar lipids			
Skelly B	0.69	0.64	0.65
2-Propanol	0.71	0.70	0.65
Polar Lipids			
Skelly B	0.34	0.27	0.33
2-Propanol	0.72	0.64	0.67

^aTabulated from data reported by Chung and co-workers (11,12) and from unpublished work.

TABLE II
Baking Characteristics of Flours Reconstituted with Lipids^a

Extracting Solvent	Characteristics of Flours Reconstituted with Lipids Extracted by		
	Soxhlet		Shaker at 75° C
	Regular	Vacuum	
Mixing time (min)			
Control: 3-7/8			
Skelly B	4-7/8	4-1/4	4-1/2
2-Propanol	2 (∞) ^b	12-3/8	4-1/2
Loaf volume (cc)			
Control: 64.7			
Skelly B	68.2	69.0	67.8
2-Propanol	25.9	52.2	64.3
Crumb grain ^c			
Control: Q-U			
Skelly B	Q	Q	Q
2-Propanol	U ⁶	U ³	Q-U

^aTabulated from data reported by Chung and co-workers (11,12). Baking characteristics are for 10 g flour (on 14% mb) without shortening added.

^bMixed 2 min to incorporate the ingredients.

^cQ = questionable; U = unsatisfactory (the higher the number, the poorer the crumb grain).

classified in three groups according to their binding behavior during dough mixing: nonpolar bound lipids (steryl ester, triglyceride, diglyceride) distributed mainly in acetic acid-soluble fractions; highly polar bound lipids (mostly phospholipids and glycolipids containing sucrose or raffinose) mainly in acid-soluble starch-lipid-protein fractions; and lipids of intermediate polarities (monoglyceride, free fatty acid, monogalactosyl diglyceride, digalactosyl diglyceride) evenly distributed in all dough fractions. Later the acid-soluble proteins were further fractionated into glutenin, gliadin, albumin proteins and the nonprotein nitrogenous components (28). Dough mixing accelerates hydrophobic binding of nonpolar lipids (mainly triglycerides and steryl esters) to all acid-soluble components (glutenin, gliadin, albumin, and nitrogenous nonprotein) and of polar lipids (chiefly digalactosyl diglyceride and some phospholipids) mainly to glutenin proteins. Polar lipids may bind to gliadin proteins hydrophilically.

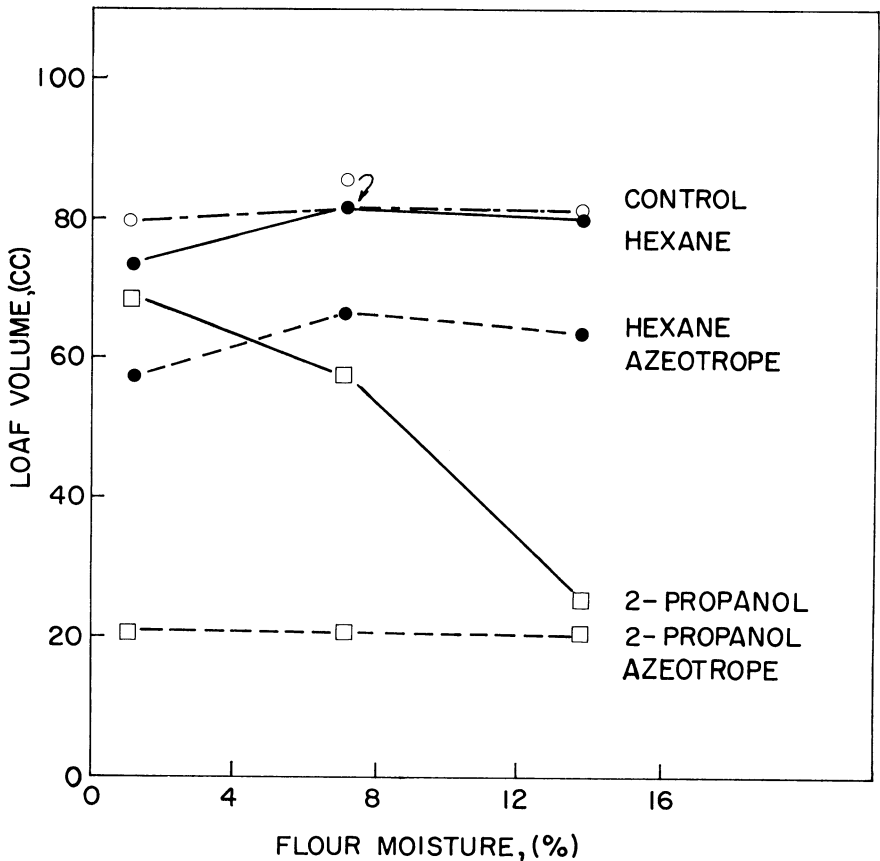


Fig. 1. Effect of flour moisture content before lipid extraction on loaf volume (cc) of bread baked with 3% shortening from 10 g untreated flour (regional baking standard-74) and from reconstituted, solvent-extracted flours (13).

Reportedly, however, gliadin contains 9.1% lipids of which 75% are polar lipids, and glutenin contains 6.7% lipids of which 24% are polar lipids and 58% are triglycerides; Ponte and co-workers considered the possibility that distribution of gliadin and glutenin lipids might be related to lipid redistribution during fractionation of the gluten (26). According to a study on differences in solubility of gluten protein (29), free polar lipids (principally glycolipids) are bound to the glutenin proteins by hydrophobic bonds and to the gliadin proteins by hydrophilic bonds. The results indicate that the lipid in unfractionated gluten apparently is bound to both protein groups and forms a complex.

Prolonged washing of soft gluten from low-grade flour removes phosphatides and gradually increases gluten tenacity until it nearly equals that of patent flour (30). Phosphatides added to flour in small quantities lower gluten quality as determined by the feel of hand-washed gluten, by viscosity measured with the MacMichael viscometer and by baking tests. Ordinary flour contains much more phosphatides than necessary to develop the dough properly (31). The phosphatides increase the ductility of dough through a lubricating effect on gluten strands so that they slip readily.

When dispersed sonically in the presence of divalent metal ions (Ca, Mg, or Ni), phospholipids can interact with water-soluble wheat proteins and precipitate them as lipoproteins (32). The complexing is highly specific in some cases, probably because of the protein structure. Fullington (33) isolated a protein component from the water-soluble fractions of both hard and soft white wheats, by using ammonium sulfate fractionation and gel-permeation chromatography. After binding, the Ca^{++} protein could react further with the flour phospholipids phosphatidylinositol and phosphatidylserine, forming complexes of ordered, crystalline structures. The protein with bound calcium also could form a complex with the dough improver stearyl-2-lactylate. Phosphatidylinositol and phosphatidylserine, however, are minor flour phospholipids, and their contribution to dough structure is yet to be determined (5).

LIPID OXIDATION DURING DOUGH MIXING

Lipids are involved in oxidation during dough mixing. Lipoxygenase has been used extensively in the United States and Canada (34) since the 1930s when the process for its use in bleaching flour to produce white bread crumb was patented (35). Some lipoxygenase is present naturally in wheat, mainly in the germ. Wheat lipoxygenase oxidizes linoleic and linolenic acids in the form of free fatty acids and monoglycerides during dough mixing (23,36,37), and this oxidation may be responsible for most of the oxygen consumed in dough (5).

Soybean meal is a rich source of lipoxygenase; this enzyme is obtained commercially from soybean flours defatted by solvent extraction and vacuum drying. Soy flour contains lipoxygenase isoenzymes (principally lipoxygenase-2), which are evidently absent from wheat (37). The isoenzymes can oxidize linoleate and linolenate in all the major wheat lipids: monoglycerides, monogalactosyl diglycerides, free fatty acids, diglycerides, phosphatidylcholine, digalactosyl diglycerides, triglycerides, and steryl esters (38,39). In dough, the lipoxygenase-linoleic acid system affects dough mixing properties, internal structure of bread and bread flavor (2,3,5).

The primary oxidation products of lipoxygenase are optically active conjugated *cis, trans*-diene hydroperoxides (36). These hydroperoxides oxidize the sulfhydryl groups of proteins and affect the rheological properties of dough (40,41). The importance of lipoxygenase and oxidized lipids may have been greatly overestimated (37), however, because oxidized lipids and sulfhydryl groups react only minimally in dough (42) and because the amount of oxygen absorbed is more than is required for oxidizing sulfhydryl groups (8,43). To verify reduction of lipid hydroperoxides to hydroxy derivatives by sulfhydryl groups, Mann and Morrison (37) mixed doughs with added cysteine (extra sulfhydryl groups) or *N*-ethyl maleimide (a sulfhydryl blocking reagent) and measured the oxidation products from 1-(¹⁴C)-linoleic acid. In all cases, the hydroxy acid levels were the same as those in the controls. They concluded that no connection exists between the level of accessible sulfhydryl groups in dough and reduction of hydroperoxy acids to hydroxy acids.

LIPID AND STARCH GRANULE INTERACTION

Many reports concern the effects of various lipids, surfactants or their combinations on starch gelatinization or starch cooking characteristics (44–56). Peak viscosity is reached in an amylograph at a slightly higher temperature in defatted flours than in unextracted flour (44). Viscosity increases in a 6% cornstarch paste at progressively lower temperatures as fat is added (45). Temperature of peak hot-paste viscosity (assessed by amylograph) lowers about 4° C when 2% flour lipids are added; nonpolar lipids substantially increase peak viscosity, but polar lipids have little effect (46). Nine commercially available soybean phospholipids (except the alcohol-soluble phosphatide) did not affect amylographic peak viscosity or temperature of peak viscosity, when they were added at a 2% level to a regional baking standard flour (a composite flour of hard red winter wheats). Addition of alcohol-soluble phosphatides containing a 2:1 mixture of phosphatidylcholine and phosphatidylethanolamine lowers the temperature of amylographic peak viscosity from 93 to 89° C and the peak height from 625 to 590 units.

Polar and nonpolar lipids have different effects on the pasting properties of starch (48). Defatted starch reimpregnated with polar lipids has reduced viscosity in both steps (76° and 95° C) of a pasting curve. Defatted starch impregnated with nonpolar lipids changes relatively little in the first step of the pasting curve, but maximum peak height increases significantly. According to a study of starch-lipid interactions during gelation (49), certain wetting agents reduce the temperature of starch gelation, and strongly polar lipids inhibit starch gelation.

In a study of the effect of various glycerides on the baking properties of starch doughs (50), saturated monoglycerides and diglycerides consistently improved the structure of the starch dough and the resulting bread.

Monoglycerides of long-chain fatty acids affect starch gelatinization, possibly by reacting in the swelling granules or by reducing the rate of water absorption by starch (51). The extent of the effect depends on the length of fatty acid moiety and concentration of monoglycerides.

Results of amylographic studies of bread crumb slurries (52) indicate that 1, 2, and 4% shortening has little effect on peak viscosity of fresh crumb but delays the decrease in peak viscosity in the crumb of stored bread. Glyceryl monostearate in

the bread formula increases gelatinization temperature and peak viscosity and slows the drop in peak viscosity with storage. An amylographic study of shortening's effect on starch gelatinization (53) indicates that the pasting temperature of starch increases slightly when shortening concentrations exceed 6%, and added shortening decreases height slightly but increases the setback (the difference in Brabender units between the 15-min height and viscosity after cooling for 30 min to 68°C).

Investigating the possibility that wheat starch lipids form a membrane that limits amyolytic degradation of granules, Hanna and Lelieure (54) disrupted the membrane with a surfactant and then measured digestion by α -amylase. The results suggest that although lipids do not inhibit degradation by means of a membrane structure, they may limit digestion by forming inclusion complexes with damaged starch. Any lipid that can form such a polymer inclusion complex may alter the amyolytic degradation of damaged starch. Although lipids influence the course of amyolytic degradation of starch in dough, the overall magnitude of the effect may be relatively small (54).

Lorenz (55) studied water binding capacity, swelling power, solubility, gelatinization temperature range and amylographic viscosity of defatted (80% methanol extraction in a soxhlet for 48 hr) and nondefatted hard red spring wheat, durum wheat, rye, triticale, barley, and rice starches. He recorded reference viscosities sequentially at 92°C, after 30 min at 92°C, at 35°C, and after 60 min at 35°C. He found no differences in initial viscosities at 92°C between defatted and nondefatted (control) starches, except for those of rye and triticale. Viscosities at the three other stages, however, were considerably higher for all defatted than for control starches.

Amylographic studies on the effect of fat type on starch pastes containing glyceryl monostearate show that the height of the cooling-curve peak inversely relates to the combined transunsaturated and saturated fatty acid contents of the oil (56). The effects apparently occur because the rate of crystallization of the saturated monoglycerides change in oils held at 56°C.

According to all these studies, lipids impede interaction between starch granules during gelatinization by a mode of action related to their effectiveness as antistaling agents.

The recent reviews on bread staling are excellent (57–59). Staling may be defined as a phenomenon related to various processes that occur after bread is baked (60). One such process is the decrease in tenderness. Staling involves an irreversible modification in the water structure of gluten (61), in addition to starch retrogradation. The firming process may be attributed to the migration of water (once part of the protein structure) from protein to starch (62). Gravimetric measurements of moisture redistribution show that crumb contracts about 1.7% in bread during four days at room temperature and constant ambient humidity (63). This finding is consistent with a redistribution of moisture from the continuous gluten phase to starch. Kay and Willhoft's technique for studying bread staling (64) is based on measuring conductance and capacitance of the isolated center crumb. Zobel (57) suggested that the experimental approach of Willhoft and co-workers (61–64) may be applicable only to study of the gluten-starch interface. Bread crumb has an equilibrium relative humidity of 97% and open structure; both may be important in the moisture transfer between components (57).

Kinetic studies (65) on breads baked with flours of 10.6, 11.0, 13.9, and 21.6% protein content on a 14% mb and stored at 21° or 30°C indicate that staling basically involves crystallization-like changes of the starch in the crumb, regardless of the flour protein content. A further study (66) suggests that starch crystallization is primarily responsible for staling of bread at 21°C, but some additional factor plays an important role at 30° and 35° C (at which starch in the crumb crystallizes two and four times as slowly, respectively, as at 21°C). Water-soluble pentosans slow the rate of retrogradation by affecting the amylopectin fraction of starch, and water-insoluble pentosans do so by affecting both amylose and amylopectin (67). The pentosans retard retrogradation simply by reducing the amount of starch components available for crystallization. Retrogradation of both amylose and amylopectin characterize crystallization of starch gels through the first day of storage; thereafter amylopectin alone controls retrogradation (67).

Effects of native flour lipids have been studied extensively in crumb grains but not in bread staling. To study the effects of free (petroleum ether-extractable)

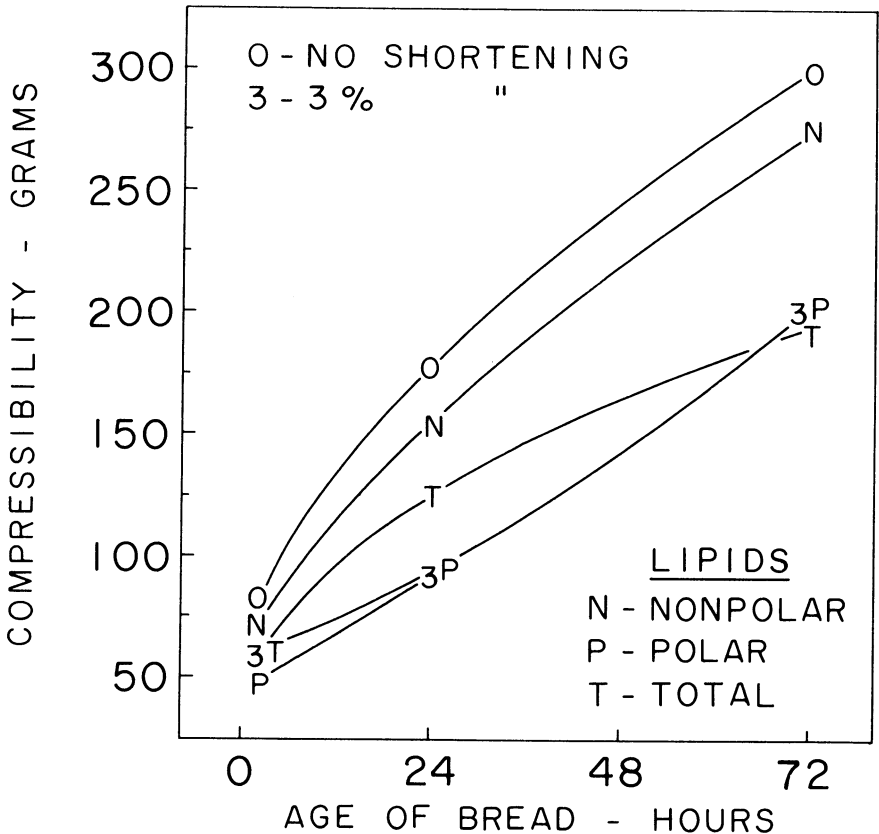


Fig. 2. Effects of adding 3 g of shortening or 0.5 g of wheat flour lipids per 100 g of flour on crumb compressibility of bread stored as long as 72 hr at room temperature (68).

flour lipids on bread staling, Pomeranz and co-workers (68) measured the compressibility (firmness) of bread slices stored as long as 72 hr at room temperature. Vegetable shortening and nonpolar, polar, and total lipid fractions from six wheat flours were added to a bread formula that included nondefatted, composite hard winter wheat flour. Bread prepared without any lipid material was used as control. Addition of 0.5 g of nonpolar lipids reduced crumb firmness only slightly. For retarding crumb firmness during storage, 3 g of shortening and 0.5 g of polar lipids were equally good and the most effective overall. For retarding firmness, 0.5-g total free lipids were intermediately effective in bread stored 24 hr and the most effective in bread stored 72 hr (Fig. 2).

Pomeranz and co-workers (69) also determined how shortening, free polar lipids from flour, and commercially available sucrose esters affect loaf volume and compressibility (after 24 hr) of bread baked from 100 g of wheat flour plus 8 g of soy flour. Loaf volume correlated negatively with compressibility (weight required to depress the plunger into bread crumb) (Fig. 3). Two regression lines were obtained for bread baked from hard red winter Comanche and hard red spring Thatcher and for bread from the soft red winter Seneca. Addition of 0.5% free polar lipids most improved crumb softness and loaf volume. Crumb of bread baked with 0.5% synthetic glycolipids was equal to or softer than that of bread baked with 3.0% commercial vegetable shortening. Softness decreased uniformly in all samples after 48 hr.

The use of emulsifiers or surfactants as antistaling agents is well recognized; bakers have used monoglycerides for more than 40 years (70). According to reviews on surfactants or their improving mechanisms in baked food (71-79), some surfactants that do not retard crumb firmness strengthen the dough and reduce mechanical abuse during processing. Such surfactants should be blended with monoglycerides to provide a balance of dough strengthening and retardation of crumb firming (70).

Schoch's review (80) pictorially explains the role of starch during baking and aging of breads with and without added monoglycerides. When cornstarch or wheat starch is cooked in excess water with monoglycerides, no linear starch dissolves or leaches out of swollen granules. Apparently the linear molecules immediately react with monoglycerides, forming a helical insoluble complex that remains immobile in the swollen granule. Hence, no gel structure develops between the granules, and the fresh softened bread is deformable and inelastic.

Monoglyceride complexes less with amylopectin than with amylose, and the degree of unsaturation (which determines shape) of monoglycerides inversely relates to the extent of complex formation (60). Chain length and degree of unsaturation of the fatty acid moiety significantly affect functionality of monoglycerides (72): Saturated fatty acids of long carbon chain length provide the best results. The amylose-complexing ability and crumb softening index of monoglycerides correlate well, but the degree of complexing between monoglycerides and amylopectin does not correlate with antifirming performance (60). The evidence points to amylose-complexing as the main mechanism of antistaling. Such reactions are enhanced when monoglycerides are used in certain physical forms, such as an aqueous lamellar phase or a dispersion (81,82). α -Crystalline gel at pH 6.8 has the highest complexing index with amylose and also the best antifirming effect in bread (81). The most effective form involves an α -crystallinity (83); the molecules in the α -form are postulated

to pack so that polar groups are exposed to the water phase (84).

Researchers have demonstrated high correlation between the amylose-complexing ability and crumb softening index of monoglycerides but not always of surfactants (5,45,57,81). In Kim and Robinson's model system (85), surfactants such as monoglyceride, sucrose monostearate, and sucrose distearate enter the existing helical structure of amylose to form insoluble complexes and sodium stearyl-2-lactylate has no amylose-binding capacity. Many studies indicate that the main mechanism of the antistaling process is the formation of a complex between amylose and monoglyceride. To be effective, however,

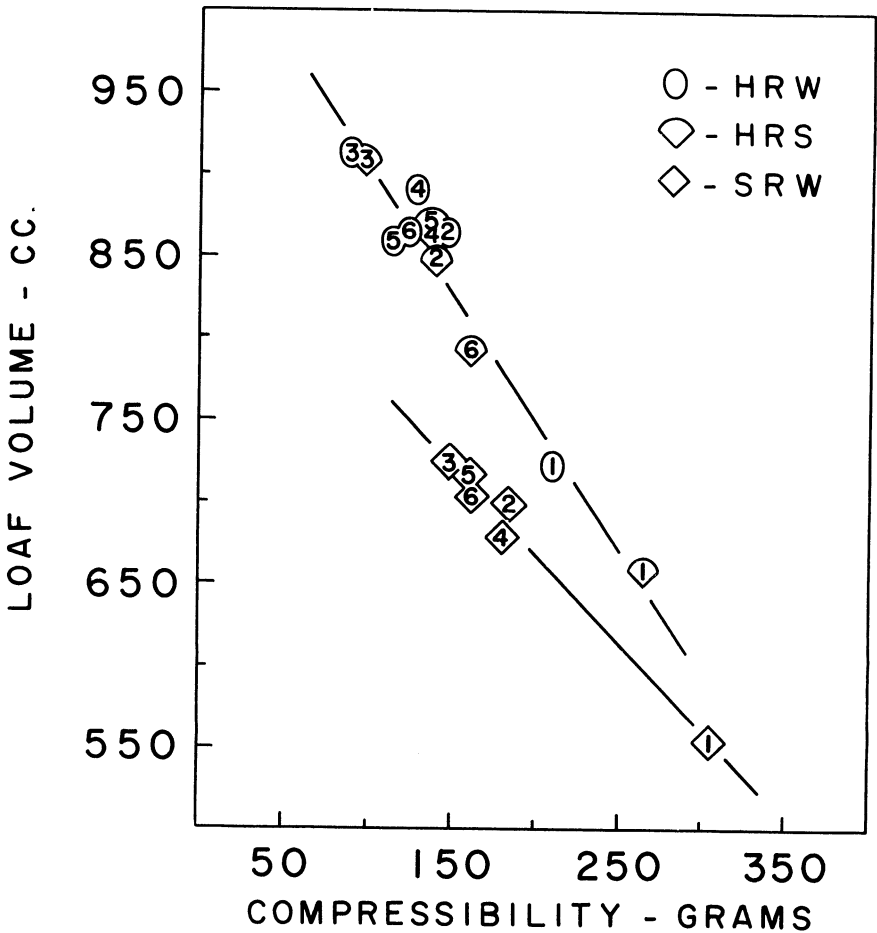


Fig. 3. Effects of 3 g of shortening and 0.5 g of certain polar lipids on loaf volume (cc) and compressibility (after 24 hr) of bread baked from 100 g of three wheat flours (hard red spring and hard and soft red winter) plus 8 g soy flour: 1, control; 2, shortening; 3, wheat flour free polar lipids; 4, sucrose monolaurate; 5, sucrose monopalmitate; 6, sucrose monostearate (69).

surfactants should interfere with crystallization of the amylopectins because the amylopectin fraction is affected three to four times more than the amylose fraction (57). Schoch and French (86) earlier reported that the amylopectin fraction was most affected during bread staling.

The surfactants' precise mode of action in improving shelf life is likely to be subject to many investigations because presently no explanation is completely satisfactory (5,57,70,72). Greene (77) studied the actions of dough conditioners, primarily in the mixing and preproofing stages of dough development and concentrated on the protein-surfactant interactions. His excellent review discusses the effects of surfactants as dough conditioners in the context of the nature of the hydrophilic group, protein solubility, and possible functions of the micellar state.

FUNCTIONAL PROPERTIES OF FLOUR LIPIDS OR LIPID MATERIAL

Functionality depends on the amount and type of flour lipids. With flours defatted by petroleum ether, added nonpolar lipids are detrimental and added polar lipids effectively improve breadmaking quality (16,87-95). Addition of triglyceride, diglyceride, or monoglyceride extracted from the original flour slightly decreases the loaf volume of bread baked without shortening but not as much as the addition of unfractionated nonpolar lipids containing free fatty acids (90). In breads baked without shortening, loaf volume does not decrease when unfractionated nonpolar lipids or fractionated steryl ester, triglyceride, or diglyceride is used with defatted flour, but deleterious effects occur when free fatty acid is used with either the defatted or the original flour (93). Detrimental effects in bread relate directly to the linoleic acid content. Added steryl ester, triglyceride, or diglyceride has little or no effect on starch gelatinization. Nonpolar lipids and free fatty acids increase peak viscosity and delay amylographic peak time. Free fatty acids are thought to adversely affect both the gluten and starch fractions of flour.

Adding free polar lipids that are rich in glycolipids to flour defatted with petroleum ether completely restores loaf volume to that of bread baked from the original flour with 3% shortening, but adding bound polar lipids (about equal in glycolipids and phospholipids) is not as effective (16). Glycolipids are better improvers than are phospholipids, which, in fact, may be detrimental. Deleterious effects follow addition of 0.2% phospholipids (90) and addition of 0.1, 0.25, and 0.5% (95). Adding as much as 0.6% (1.2% as hydrolysate lipids) phospholipids to chloroform-defatted flour causes a slight decrease in loaf volume; higher levels (about 1.05% phospholipids—1.65% as hydrolysate lipids) causes a large increase in loaf volume (from 204 to 234 cc for breads baked with 30.2 g of flour, db).

Reportedly, 0.2% digalactosyl diglyceride is more effective than 0.2% monogalactosyl diglyceride in bread with 3% shortening, but they differ little in the absence of shortening (90). At 0.2-0.6%, monogalactosyl diglyceride lowers and digalactosyl diglyceride increases the loaf volume of bread baked without shortening (95).

The effects of flour lipid fractions as foam stabilizers parallels their effects on loaf volume (94). This supports the theory that flour lipids act as surfactants in stabilizing or destabilizing the gas bubble structure during the loaf's expansion

while baking. MacRitchie (94) classified flour lipids in three groups according to their effects: Polar galactolipids (digalactosyl diglyceride) and phospholipids increase loaf volume at high supplementation levels (polar lipids have deleterious effects on loaf volume at low levels) (15); lipids of intermediate polarity (monoglyceride, free fatty acid, monogalactosyl diglyceride) depress loaf volume; and components of lower polarity such as triglycerides have little effect when other flour lipids are absent but are beneficial when other lipids are present.

Obviously, several types of lipids that are minor components in wheat flour have a major role in breadmaking. The precise role is sometimes difficult to determine because of the effect of various factors (such as optimized dough mixing, water absorption, and oxidation level) at subsequent stages in breadmaking and on the quality of the final product. At times, lipids interact with protein and starch, making it difficult to determine the contribution of individual flour components.

Shortening (fat) is an essential ingredient in commercial baking, but its improving mechanism in breadmaking is only partially understood. Bell and co-workers (96) recently reviewed the shortening effect and showed that the rate of carbon dioxide release is faster in doughs baked without shortening than in those baked with shortening; the difference in rate of release might explain the response of flour to added shortening. They postulated that loaf volume increases when sufficient solid shortening components are in a free form in the dough. The free components are especially important in oven spring.

Flour lipids are required for a positive shortening response, especially in flours with good breadmaking potential. We have repeatedly observed that adding shortening to the original flours substantially improves loaf volume and crumb grain but impairs the crumb grain of bread baked from flours defatted by petroleum ether. A study of breads with 10 g of flour (88) demonstrated the important role of free and bound flour lipids in a positive shortening response:

TABLE III
Loaf Volume Response to 3% Shortening in Bread Made from
10 g of Defatted Flours Supplemented with Wheat Flour Lipids

Level Added (% Flour, db)	ΔLV^a (cc) of Bread Baked with Flour Lipids		
	Total	Nonpolar	Polar
0 Untreated	+16.1
Petroleum ether-defatted flour			
0 Defatted	- 3.5
0.3	+8.9
0.7	...	+2.5	...
1.0	+11.9
2-Propanol-defatted flour			
0 Defatted	-10.5
0.63	-3.5
0.73	...	-7.6	...
1.36	+11.7

^a $\Delta LV = LV(s) - LV(o)$, where $LV(s)$ and $LV(o)$ are, respectively, loaf volume (LV) of bread baked with and without 3% shortening. Source: Chung and co-workers (88).

Compared with loaf volume of bread without shortening, that of bread with 3% shortening increased by 16.1 cc (from 64.9 to 81.0 cc) for untreated flour, decreased by 3.5 cc (from 71.0 to 67.5 cc) for flour defatted by petroleum ether (only free lipids were removed), and decreased by 10.5 cc (from 73.0 to 62.5 cc) for PrOH-defatted flour from which all free lipids and most bound lipids were removed (Table II). For maximum positive shortening effect, the unfractionated total lipids (polar and nonpolar) were required for flours defatted by petroleum ether or by PrOH. In response to shortening, the loaf volume increases linearly with increase in loaf volume potential of various untreated flours, correlates negatively for Skelly B-extracted flours, and is unaffected in PrOH-extracted flours (97). For regional baking standard flour (a composite flour of hard red winter wheats), loaf volume response to shortening decreases with increasing amounts of extracted lipids—to 1.2% total or 0.6% polar lipids (98).

In a three-way contribution of flour lipids, shortening and surfactants to breadmaking (99), shortening interacts with flour components, especially lipids. The interaction depends on composition (88,90) and quantity of lipids (95,98) and also on flour quality as affected by wheat variety (97,100) or by storage conditions (101). The effects of various types of fats on bread quality have been studied (102), and Bell and Fisher (101) prepared model shortenings from defined binary mixtures of saturated and unsaturated triglycerides and studied their binding during mixing of mechanically developed bread doughs from fresh and stored flours.

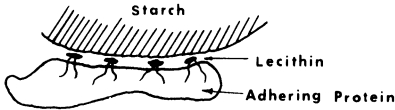
Lipid-related surfactants function as antistaling agents (79,103,104), dough modifiers (71,72,75,105), shortening sparing agents (106–109), flour lipid displacing (28,105,110–112) or replacing agents (88,106,107) and improves in high-protein breads (69,108,112,114,115).

The beneficial effects of sucrose esters on loaf volume and texture of bread baked from flour defatted by petroleum ether increase as hydrophile-lipophile balance values increase (107). Sucrose esters with a balance of 1.0 only partially replace flour lipids, esters with a hydrophile-lipophile balance of 8.0 replace more lipids, and two sucrose esters with a balance of 14.0 functionally replace both flour lipids and 3% shortening. Recently we studied replacements for natural lipids in breads baked from defatted wheat flour (88). Petroleum ether extracted 1% total free lipids (0.7% nonpolar, 0.3% polar) and PrOH extracted 1.36% total lipids (0.73% nonpolar, 0.63% polar). Nonionic sucrose monopalmitate or ethoxylated monoglycerides, both with a hydrophile-lipophile balance of 14.0, completely replaced total petroleum ether-extracted flour lipids (or their nonpolar or polar fractions) and 3% shortening. No surfactant completely replaced unfractionated PrOH-lipids (free and bound) and shortening or total polar flour lipids (free and bound).

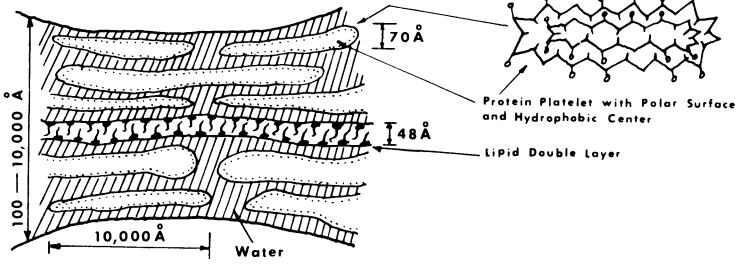
MODELS FOR INTERACTION BETWEEN LIPIDS AND OTHER FLOUR CONSTITUENTS

Figure 4 is from a review on the interactions of lipids with proteins and carbohydrates in breadmaking (116). In Hess and Mahl's model (Fig. 4a) deduced from x-ray electron microscopy and optical measurements (117, 118), the adhesive protein is bound to starch through a lecithin layer.

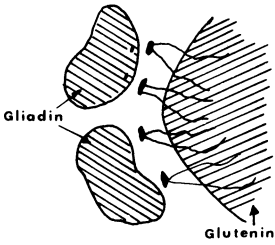
A lipoprotein model (Fig. 4b) involving a bimolecular lipid layer—the Danielli



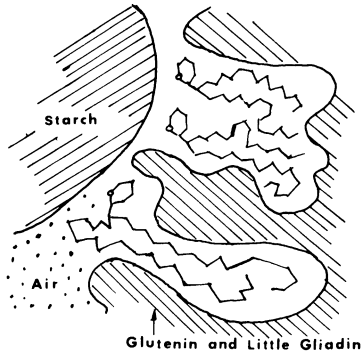
(a)



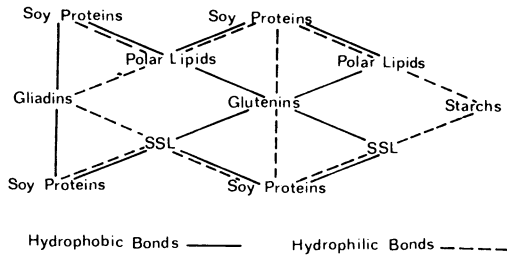
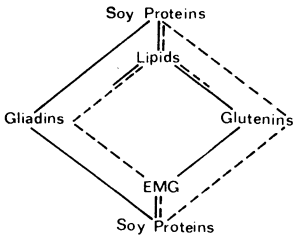
(b)



(c)



(d)



(e)

Fig. 4. Models of the complexes formed in breadmaking (116): (a) starch-lipid-adhesive protein complex in flour (117); (b) lipoprotein model (24); (c) gliadin-glycolipid-glutenin complex (29); (d) starch-glycolipid-gluten complex (119); (e) models of surfactant (EMG: ethoxylated monoglycerides, SSL: sodium stearyl-2-lactylate) and lipid binding to wheat and soy flour proteins (113).

and Dawson-type membrane—is based on a structural study of wheat gluten by electron microscopy and x-ray techniques (24). From x-ray evidence, Grosskreutz deduced that the phospholipids form well oriented bimolecular leaflets in gluten of the type found in myelin, that lipoprotein occupies 2–5% of the elastic gluten structure, and that protein chains are bound to the outer edges of the phospholipid leaflet array (probably via salt-type linkages between acidic groups of the phospholipid and the basic protein groups).

Figure 4c shows the model of a gliadin-glycolipid-glutenin complex proposed by Hosenev and co-workers (29). In unfractionated gluten, free polar lipids (principally glycolipids) are bound to the gliadin proteins hydrophilically and to the glutenin proteins hydrophobically. Simultaneous binding of polar lipids to both protein groups may contribute to the gas retaining ability of gluten.

Wehrli (119) proposed a model of a starch-glycolipid-gluten complex (Fig. 4d). In studying the interaction of glycolipids and wheat flour macromolecules, Wehrli and Pomeranz (120) investigated complexes between galactolipids and raw starch, gelatinized starch, gliadin, and glutenin. Infrared spectroscopy indicated hydrogen bonds between glycolipids and gelatinized starch or gluten components and Van der Waals bonds between glycolipids and gluten components. The nuclear magnetic resonance spectra showed that glutenin inhibited methylene signal of glycolipids (at 8.7 τ) indicating hydrophobic bonding. They also (121) studied other interactions in dough and bread containing both starch and gluten proteins. For that purpose, tritium-labeled galactosyldidecanoylglycerol was synthesized by a new procedure (122); sections prepared from dough and bread were studied by autoradiography. In the dough the labeled galactolipid was distributed in the gluten and, to a limited extent, in the starch; in the bread most of the galactolipid was in gelatinized (by oven heat) starch granules and formed a complex that seemed to be responsible for the improved retention of freshness in bread baked with glycolipids (123).

DeStefanis and associates (104) similarly concluded that the lipids bound to proteins during dough mixing are translocated and bound to starch during baking. They found that little binding of the surfactants (sodium stearyl-2-lactylate, succinylated monoglycerides, and monoglycerides) by the major flour components occurred at the sponge stage. The additives were firmly bound to the gluten proteins during dough mixing and strongly bound to the starch by complexes with both amylose and amylopectin fractions in bread. After studying model systems, they concluded that concurrently during baking the bonds between the gluten proteins and the additives increasingly weaken (protein denaturation) as the dough temperature increases, and as starch gelatinizes above 50°C, the additives weakly bonded to proteins readily form a strong complex with starch and can thus be translocated from proteins to starch. Triglycerides, free fatty acids, and lysophosphatidylcholine also are bound to the starch.

Figure 4e shows models of surfactants and lipid binding to wheat and soy flour proteins (113). Chung and Tsen used solvent extraction to study interactions between wheat flour lipids and proteins in relation to other flour constituents during dough mixing (22,105) and the effects of surfactants on lipid binding to various fractions of dough (28,110,111) and bread (112) baked with or without soy flour. Surfactants compete with native flour lipids for binding sites of dough components and suppress lipid binding. Surfactants displace some bound lipids.

When soy flour is added to wheat flour, soy protein suppresses the interaction of flour lipids and surfactants by supplying binding sites for both. In wheat flour dough containing no soy flour, nonionic ethoxylated monoglyceride interacts principally with proteins (along with flour lipids) to form a stable "protein complex." Anionic sodium stearoyl-2-lactylate forms a strong complex with glutenins and starch (with polar flour lipids as cross-linking agents) and interacts between glutenins and gliadins to form stable aggregates of a "protein complex-starch complex." In wheat flour dough containing both a surfactant and soy flour, however, multiple interactions form two major protein complexes: a glutenin-soy protein-gliadin complex and a glutenin-surfactant-gliadin complex (124). Both surfactants can accommodate soy proteins in a gluten matrix through new associations (113), as depicted by the models (Fig. 4e); such accommodation presumably can overcome the adverse effects of soy flour and produce acceptable protein-enriched bread.

The small amounts of polar lipids in wheat flour cannot completely counteract the adverse effects on bread of high levels of protein-rich additives such as soy flour. Consequently, the flour lipids must be supplemented with lipids from other sources to produce high-protein bread (116). The adverse effects can be overcome by adding a small amount of glycolipids or commercially-available surfactants (69,108,114,115,125). Much is known about the way that lipids and lipid-related materials contribute to the production of nutritionally improved high-protein bread that is acceptable to consumers. The requirements for protein supplements are yet to be determined (126).

SUMMARY

Much information on the role of wheat flour lipids is available. Renewed interest in this area in recent years has resulted in many publications on the contribution of lipids to the production of consumer-acceptable, nutritionally-improved baked products. Some information is fragmentary; some seems contradictory. Factors that make sustained and consistent progress difficult include: the complexity of lipid content and composition; variations in lipids of wheat cultivars from various locations; changes during extraction and storage of lipids; the effect of lipid extraction on functional properties of wheat flour components; differences in effects of lipids on flour components and variability during various processing stages; differences in objectives; and multiple component interactions of flour lipids, shortening, and surfactants.

With so many ill-defined and dynamically changing variables, there is little likelihood of developing a unified theory of what lipids do or be made to do in the production of baked goods. Consequently, we will learn increasingly more about the role of lipids, but we will be frustrated by the complexity of the effects.

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