THE FORMATION OF DOUGH AND BREAD STRUCTURES[1]

I. The Ability of Starch to Form Structures, and the Improving Effect of Glyceryl Monostearate

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ABSTRACT

Dough prepared from starch instead of flour behaves like a concentrated stable suspension; it shows, among other properties, dilatancy.

Such a dough acquires plastic properties when small quantities of glyceryl monostearate (GMS) are added (e.g. 0.1%).

Starch bread without the additive has a stiff crumb with an irregular, very coarse structure. By the addition of 0.1% GMS a loose crumb with a fine and regular structure is obtained.

The influence of GMS on the texture of the dough is explained by assuming that GMS is adsorbed on the surface of the starch granules, and that, consequently, the stable system is transformed into a flocculated one. In accordance with this, GMS greatly increases the rate of settling and the sediment volume in a 2% starch suspension.

The large decrease of the rigidity of the crumb by GMS is probably caused by weakening of the bindings between the swollen starch granules.

It is generally accepted that the gluten gel, formed in mixing, determines in the main the properties of bread dough[2] (1,12). The starch granules mixed with this gluten gel are usually considered unimportant for the rheological properties of the dough and for the gas retention of the dough. According to the most accepted view, the gluten acquires greater firmness during the baking process and finally forms the network to which the crumb owes its coherence.

Rotsch (8,9,10) made bread with a good crumb from dough in which wheat protein was replaced by other gel-forming substances. He was not, however, successful in finding a suitable replacement for starch. Rotsch concluded from his tests that the bread crumb owes

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[2] Bloksma, A. H., and Hlynka, I. Basic considerations of dough properties. *In* I. Hlynka, ed.: "The physical basis of wheat quality." AACC Monographs, Vol. III; in preparation.

its coherence to partly gelatinized starch only. He attributed differences in the crumb properties to varying degrees of gelatinization of the starch. In accordance with the current opinion he assumed, however, that in the dough the carbon dioxide is retained by the gluten gel. Therefore he also supposed that doughs without gluten can only retain the gas if another gel takes over this role from the gluten. So Rotsch explained the fact that there is no substitute for starch on the basis only of the role of starch during and after baking.

Hess (3) made the supposition that the properties of normal dough are determined not only by gluten, but also by electrostatic binding between starch and gluten. According to Hess, both gluten and starch form a coherent network in the bread crumb.

With the aim of providing a basis for studying the formation of structures in normal dough and bread, baking tests were made with separate components of flour. The present experiments were started with a system which, apart from sodium chloride and the necessary ingredients for fermentation, contained only starch and water in about the same proportion as normal dough. Tests were made to determine if a structure resembling that of normal bread could be developed in such a system by mixing, fermentation, and baking.

The formation of more or less permanent structures can only be expected in systems in which the particles adhere one to another. In suspensions of ungelatinized starch there are, however, repulsive forces between the starch granules (2,5). Therefore an attempt was made to cause flocculation of starch in the system by adding small quantities of a surface-active agent. In this connection the effect of glyceryl monostearate on the development of structures in dough and bread was studied.

Materials and Methods

Materials: Starch. Commercial unmodified thick-boiling wheat starch was used, containing 0.54% fatty acids, 0.15% glycerides of fatty acids, 0.19% protein (N × 5.7) and 0.22% ash (14% m.b.). For the determination of fatty acids and the glycerides of fatty acids, the following procedure was used: the flour was boiled with diluted hydrochloric acid, then ethanol was added and the solution was extracted with petroleum ether. An aliquot sample of the petroleum ether layer was evaporated to dryness, and the free fatty acids and the glycerides were determined by titration with 0.1*N* isobutyl alcoholic potassium hydroxide before and after saponification respectively.

Glyceryl monostearate (GMS). A trade preparation of the self-emulsifying type was used, containing about 50% pure glyceryl monostearate, 40% distearates, practically no triglycerides, and 3% free glycerin. It had an iodine value <4 and a saponification equivalent of 160. Where percentages of GMS are mentioned hereafter they refer to this trade preparation. It was added as an emulsion in water (1:9).

Tests on the Stability of Dilute Starch Suspensions. Suspensions were made from 2 g. wheat starch in distilled water with various additions of GMS. The volume of the suspension was made up to 100 ml. in a stoppered calibrated cylinder. After shaking, the volume was read at regular intervals.

Baking Tests. Starch doughs were prepared from 300 g. wheat starch (14% m.b.), 180 g. water, 6 g. sodium chloride, 12 g. sucrose, and 18 g. yeast (basic formula). To this various amounts of GMS were added.

The dough was mixed for 5 minutes in the large bowl of the farinograph, after which a portion of dough (250 g.) was directly transferred into a pan and fermented for 15 minutes. After this it was stirred, proofed for 45 minutes at 30°C., and finally baked for 20 minutes at 240°C.

Farinograph. A two-speed farinograph was used. Generally the normal speed (velocity of the blades 58 and 87 r.p.m.) was used in this study. (Some farinographs have, however, been obtained at half speed.)

Microscopic Examination of the Bread Crumb. Sections 15μ thick were cut by means of a microtome from frozen bread crumb. The sections were embedded in glycerol and studied under the microscope.

Results

Flocculation of a Dilute Starch Suspension. In a starch suspension the granules do not attract each other (2). Such systems are called stable. The stability holds even if large quantities of electrolytes are present. For instance, the presence of 3 g. sodium chloride in 100 ml. 2% starch suspension did not cause flocculation. The stability was demonstrated by the fact that settling is slow for a suspension of particles with the size of starch granules and also by the small volume of sediment. In the presence of GMS, however, large aggregates were formed, resulting in a large sedimentation volume.

Table I shows the course of sedimentation in 2% starch suspensions with and without added GMS respectively. In the experiment mentioned the pH of the GMS solution (originally 8.4) was previously brought to the pH of the starch suspension (5.7) with hydrochloric

TABLE I
SEDIMENTATION VOLUMES OF 2% STARCH SUSPENSIONS

FLOCCULATION AGENT	TIME AFTER SHAKING (Minutes)					
	3	5	10	15	30	120
g/100 ml	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*
	0.3	0.5	1.0	1.4	2.5	3.7
GMS, 0.1 g.	22.0	31.0	23.8	21.4	18.9	17.9

acid. Flocculation occurred, however, in about the same measure if the pH of the GMS solution was left unchanged.

Properties of Starch Doughs with Various GMS Additions. The resistance during mixing of starch dough is naturally dependent on the amount of water. As long as this was too small for complete moistening of the starch, the curve registered by the farinograph was very irregular. When there was sufficient water, however, the consistency recorded by the farinograph remained constant with continuous mixing after about 5 minutes. The necessary minimum amount of water for this varies. At least 54.8% water had to be added to the commercial starch (14.0% m.b.) used in the tests presented here; with this water content the maximum consistency was obtained, which (5 minutes after the start of mixing) amounted to 400 B.u. In the baking tests described, 60% water was added to the commercial starch (14% m.b.). Then the consistency of a dough containing no ingredients but starch, water, sodium chloride, yeast, and sugar, was 290 B.u. Baking tests were also carried out with doughs to which GMS had been added. Table II shows that the addition of GMS, even in small quantities, had a big influence on the consistency of the dough.

Figure 1 shows farinograms of a starch-water mixture without GMS and farinograms with 1% GMS. Farinogram A was obtained by mixing 300 g. of starch (14% moisture) and 176 g. of water at

TABLE II
CONSISTENCY OF STARCH DOUGHS MEASURED IN THE FARINOGRAPH 5 MINUTES AFTER THE START OF MIXING (NORMAL SPEED)

ADDITIVE	AMOUNT ADDED TO BASIC FORMULA [a] (% of Starch, 14% m.b.)		
	0	0.1	1
	B u	*B u*	*B u*
Water	290	290	265
GMS	290	235	185

[a] Basic formula: 300 g. wheat starch (14% m.b.), 180 g. water, 6 g. sodium chloride, 12 g. sucrose, 18 g. yeast.

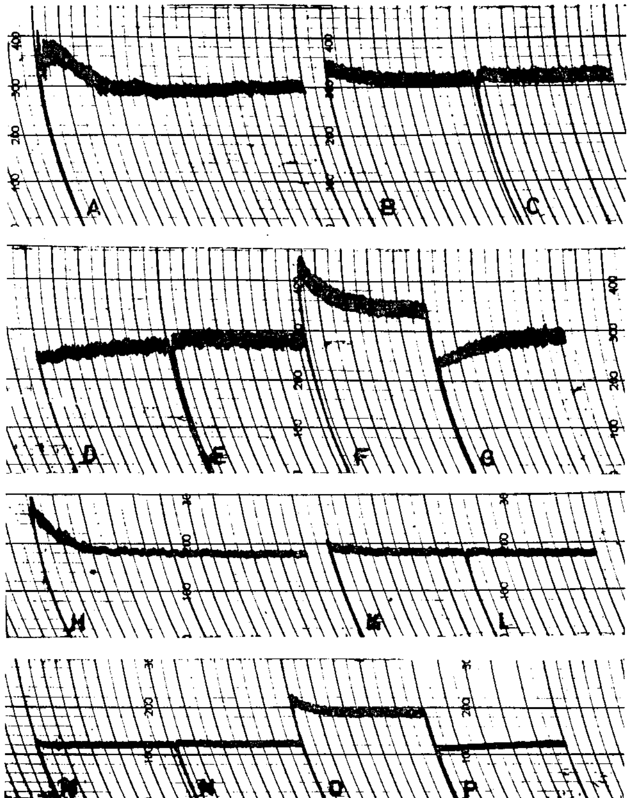

Fig. 1. Farinograms of starch-water mixtures. Series A to G: 300 g. wheat starch (14% m.b.) plus 176 g. water; series H to P: plus 1% GMS. Mixing time, 10 minutes for A and H, 5 minutes for the other curves; mixing speed, 58 r.p.m. for A, B, C, F, H, K, L, and O; 29 r.p.m. for D, E, G, M, N, and P; in the case of B, D, K, and M, mixing was preceded by 5 minutes' dough rest; after the recording of curves B, D, H, and M, mixing was interrupted for 20 seconds; for the rest, mixing proceeded without interruption.

normal speed in the large bowl. Soon after the start of mixing the consistency reached a maximum; it then decreased, and reached a practically constant value after 2.5 minutes. Curves B, C, D, E, F, and G were obtained from the same mixture as curve A. Between A and B mixing was interrupted for 5 minutes. After this rest period a somewhat higher consistency was measured, which again decreased during mixing (curve B). An interruption of mixing, just long enough for the pointer of the farinograph to reach zero on the scale (20 seconds), had practically no influence on the measured consistency (curve C). Curve D was obtained by mixing at the slow speed, after a rest period of 5 minutes. In contrast to the comparable experiment at normal mixing speed (curve B), the consistency now showed an increase during mixing. Just as in the case of fast mixing, the interruption of slow-speed mixing during 20 seconds had no visible effect on the consistency measured (curve E). It was further shown that with mixing at normal speed the same type of curve was obtained when it immediately followed a period of slow mixing (curve F) as when it was preceded by a rest period (B). Likewise the type of curve obtained with slow-speed mixing was the same after a rest period (D) and after a period of normal mixing speed (G).

Curves H, K, L, M, N, O, and P were obtained in the same way as the curves from the first series, the only difference being that 1% GMS had been added. All these curves were significantly lower and had a much smaller band width than the comparable curves from the first series. They still showed the relative differences in shape which have been described for the first series, but in a much lesser degree.

The starch dough of the basic formula had a more fluid character than flour dough: it could easily be poured from one vessel into another. It showed dilatancy, however: when the dough was stirred, the viscosity increased, while the mobility decreased; if the stirring was stopped the dough returned to its former condition.

Even with the addition of small quantities of GMS (e.g. 0.1%) the dough lost dilatancy, while the rate of flow under the influence of gravity decreased. If 0.5% GMS was added, flow was already extremely slow, while by further increasing GMS addition the starch dough acquired more and more the character of a solid paste. At the same time the rate of dough rise during fermentation decreased.

Influence of GMS on the Properties of Starch Bread. The addition of GMS had a great influence on the structure of the starch bread, as may be seen from the cross-sections shown in Fig. 2. Starch bread baked from the basic dough had an irregular and very coarse struc-

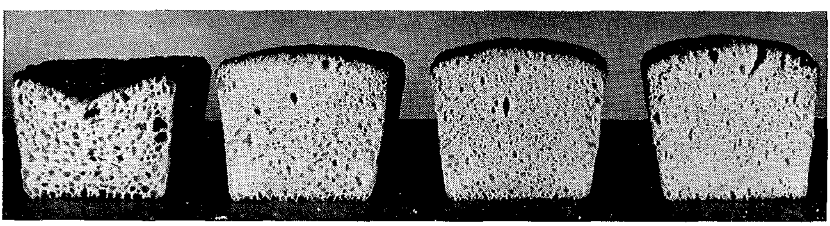

Fig. 2. Loaves from starch. Left to right: basic formula, and basic formula with additions of 0.05, 0.1, and 1% GMS (relative to starch with 14% moisture). Basic formula: 300 g. wheat starch (14% m.b.), 180 g. water, 6 g. sodium chloride, 12 g. sucrose, 18 g. yeast. Bread was baked from 250 g. of dough.

ture with thick cell walls. The bread was already hard immediately after cooling. By the addition of 0.05% of the trade preparation of GMS (that is, 0.025% of the pure compound) a regular and reasonably fine crumb was obtained. Larger additions produced a rapid increase in the fineness of the grain and at the same time in the crumbliness of the bread. When 5% of GMS was added the dough scarcely rose, except when at the same time a higher amount of water was used. With 5% GMS and 85% instead of 60% water, bread with a fine though very loose crumb was obtained. The consistency of the dough measured with the farinograph was then almost nil.

The influence of various GMS additions on the moisture retention of the bread crumb during baking is shown through the results of moisture determinations in the crumb of fresh, cool loaves, given in Table III. The addition of 0.1% GMS was accompanied by an increase of moisture content of 2% (relative to starch with 14% moisture). This increase was significant on a $P = 0.01$ level. Further changes in the moisture content, upon the addition of 0.5 and 1% GMS, were not significant. The moisture was, however, significantly higher upon the addition of 5% GMS than at the addition of 0.1% GMS.

TABLE III
INFLUENCE OF VARIOUS GMS ADDITIONS ON THE MOISTURE RETENTION OF THE BREAD CRUMB

AMOUNT OF GMS ADDED TO BASIC FORMULA [a] (% of Starch, 14% m.b.)	MOISTURE CONTENT [b] (% of Bread Crumb)	MOISTURE CONTENT (% of Starch, 14% m.b.)
%	%	%
0.0	32.7	43.1
0.1	34.4	45.1
0.5	35.0	46.6
1.0	34.9	46.6
5.0	35.9	50.6

[a] Basic formula: 300 g. wheat starch (14% m.b.), 180 g. water, 6 g. sodium chloride, 12 g. sucrose, 18 g. yeast.
[b] Average results of three equal series of baking tests.

Microscopic Examination of the Crumb. The micro structure of the cell walls in the crumb of starch bread changed considerably under the influence of GMS. Figure 3 shows that when no GMS had been added, the starch granules in the cell walls of the bread crumb had completely grown together. With 0.02% GMS the contact between starch granules was already broken at large parts of their surfaces. Additions of 0.05 and 0.1% GMS caused a further decrease in the contact between the starch granules. At the same time, the shape of the granules became less elongated. With 1% GMS the starch granules practically showed the form of loose, somewhat swollen granules. With 5% GMS the coherence between the starch granules in the bread

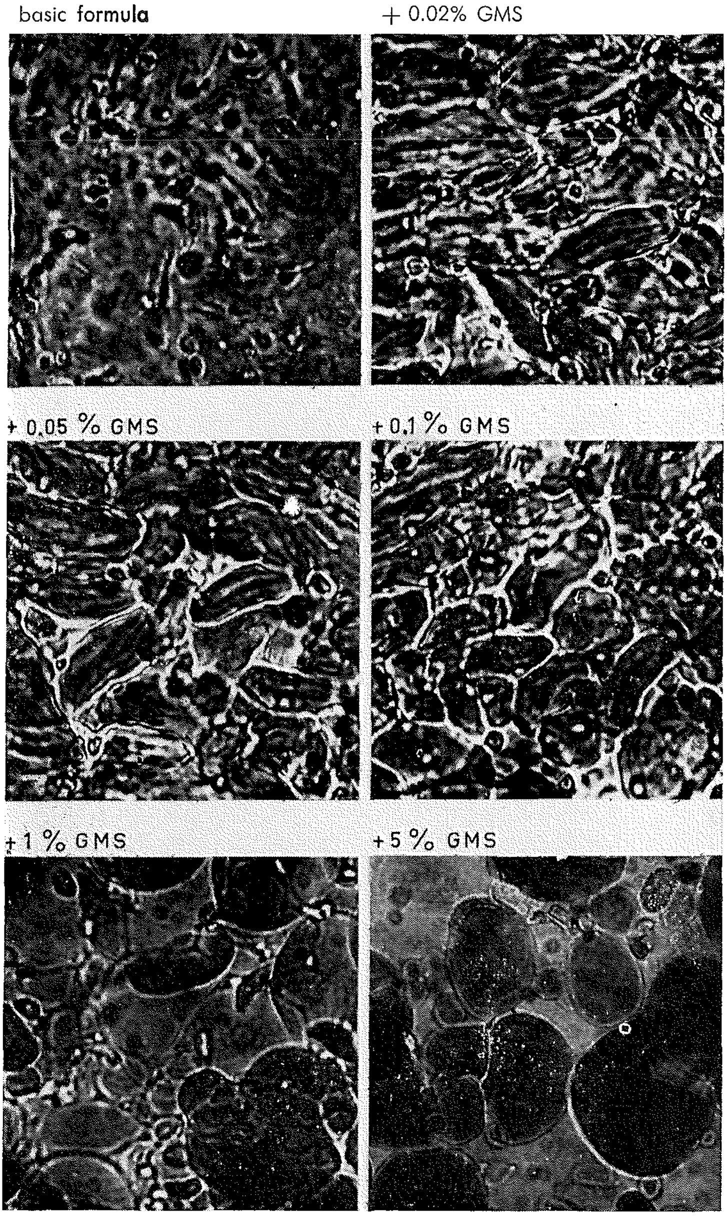

Fig. 3. Structure of cell walls in the crumb of starch bread. Magnification 500×.

was decreased so much that under the microscope the sections of bread crumb, embedded in glycerine, appeared to have fallen apart into many loose starch granules and only a few agglomerates.

Discussion

Terms with an accepted meaning in colloid chemistry, such as stability, flocculation, dilatancy, and plasticity, are used herein. For the definitions the reader is referred to Kruyt (5,6).

In a stable suspension, repulsive forces between the particles prevent their coagulation. A hydrophobic suspension such as that of starch usually acquires the required stability by virtue of an electric double layer around the particles. Dilute suspensions show sedimentation of the particles. In a stable suspension sedimentation is slow, and the particles arriving at the bottom of the vessel remain apart by the same forces that prevent their aggregation in the suspension. This entails the particles' rolling over each other until the closest packing is reached.

If by some cause the repulsive forces in a dilute stable suspension are replaced by attractive forces, aggregates are formed which sediment more rapidly, while the sediment is bulky because the particles preserve the haphazard positions in which they touched each other for the first time.

In dilute stable suspensions the viscosity as a rule is purely Newtonian; that is, the viscosity is independent of the rate of shear. In a concentrate stable suspension, however, the viscosity is Newtonian only for low rates of shear. At somewhat higher shearing stresses the viscosity increases as a consequence of the repulsion between the nearly densely packed particles. The deformation may lead to a continuous network of particles which have approached their neighbors so close that the repulsion between them is very high. This network greatly hampers further deformation, and as a consequence the suspension behaves almost as a solid. The phenomenon is called dilatancy. The approach of some particles to one another in the suspension with nearly dense packing must inevitably be accompanied by a separation of most particles. The volume occupied by the system and the water absorption, therefore, increase if dilatancy occurs. The repulsive forces between the particles are again able to disperse the locally formed clusters. Therefore these will disappear unless they are newly created at a sufficient rate. As a consequence, dilatancy will only show itself if the rate of deformation exceeds the reciprocal of the natural relaxation time of the clusters. It follows that dilatancy occurs only at relatively high stresses and also that it has a temporary nature. The system immediately flows, when the stress which caused dilatancy ceases.

Flocculation can be promoted by the same causes in dilute and in concentrated suspensions. In a concentrated suspension the aggregation of particles which accompanies flocculation does not, however, result in phase separation as in a dilute suspension. The aggregates form a coherent network through the whole system, with junction points between the particles. As a consequence the volume and the water absorption of the system increase. In a flocculated suspension no dilatancy can occur, because it can never be as concentrated as a stable suspension. When a concentrated suspension passes from the stable into the flocculated state, it gains plasticity. Plasticity is characterized by the existence of a yield stress, that must be exceeded in order to cause any permanent or viscous deformation; the apparent viscosity decreases with increasing rate of deformation. Plastic systems are easily deformed and modeled, but retain their form when left to themselves.

Flocculation of Diluted and Concentrated Starch Suspensions by GMS. As has been mentioned, starch forms a stable suspension in water. In dilute suspensions this is shown by the relatively slow settling and the compact sediment. It has further been shown that in a 2% starch suspension, upon the addition of GMS, large aggregates are formed which give a voluminous sediment; in other words, the stable suspension is changed into a flocculated one. It can be assumed that the flocculation is caused by the adsorption of GMS molecules on the starch granules (possibly because of the strong attraction between the polar groups of the GMS molecules and the equally polar starch surface). Making use of the figures for the surface area of wheat starch given by Stamberg (11), it was calculated that if 0.1% GMS is uniformly spread over the starch surface, a layer of about 50A° is formed. As the length of a molecule of GMS is of about the same order (4), this points to monomolecular adsorption.

The concentrated starch suspension (starch dough) to which no GMS has been added shows its stable character by the occurrence of dilatancy at stirring. Also, the combination of the fluid character of the dough and the reasonable consistency measured by the farinograph can be considered as a consequence of stability. The deformation by mixing is apparently quick enough to cause the observed increase of viscosity.

The concentrated system is flocculated by the addition of GMS. In accordance with what has been said on the flocculation of concentrated did not cause a decrease, but even some increase of the moisture content of the bread crumb. So there is no evidence for a decreased gelatinization as a cause for the diminished coherence in the crumb. The probable explanation is, that the mutual binding of the starch granules in the crumb of starch bread is weakened greatly by orientated binding of GMS molecules. In accordance with this, the microphotographs of the bread crumb show a decreasing number of contact points between the starch granules with increasing additions of GMS. For the cell walls of bread with 0.05 and 0.1% GMS, the microscopic pictures suggest that the starch granules are linked together by three-dimensionally distributed junction points, resulting in a structure, less compact than in the absence of GMS, but still rigid enough to prevent the starch granules from getting the spherical form of the separate granules shown by the last photograph (5% GMS). With 1% GMS this rigidity apparently has decreased considerably.

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