THE ELASTIC MODULUS OF BREAD CRUMB IN LINEAR COMPRESSION IN RELATION TO STALING[1]

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ABSTRACT

It is shown that the relationships between elastic modulus, time, and temperature in bread crumb, at temperatures above the freezing point of bread, are such as would be expected if the process causing an increase in crumb modulus were an increase in crystallinity of the material: the extent of crystallization would then be measured in terms of the increase in crumb modulus, E, in relation to its limiting value, E_1, which would be reached after a long period of storage. If the relationship were linear, the fraction of uncrystallized material, Θ, remaining after a time t, would then be measured as $\Theta = (E_1 - E_t)/(E_1 - E_o)$, and this function was found to follow the equation, $\Theta = \exp(-kt)$. The rate constant, k, decreased with increasing temperature of storage in the range 30° to 90°F.; E_1 was the same for any given batch of bread at different temperatures. Thus, no matter what the storage temperature above freezing point, the bread is tending toward the same value of the crumb modulus, although the rate decreases as the temperature increases. Addition of compound fat reduced the value of E_1 without significantly affecting k at any given temperature.

Bread staling has been the subject of considerable study, and reviews are given by Bechtel (1,2) among others. It is associated with changes in crumb firmness, absorption capacity of the crumb, the proportion of soluble starch, crumb opacity, enzyme susceptibility of the starch, and X-ray diffraction pattern of the starch.

These changes have indicated that the starch is the major factor influencing staling, while the X-ray diffraction studies have shown that an increasing degree of crystallinity occurs in the starch gel as bread ages. They do not, however, prove that changes in crystallinity of the starch gel are the major factor affecting bread staling, although this is in general agreement with changes in the proportion of soluble starch (3). There have also been suggestions that bread staling is connected with transfer of moisture between the starch gel and the gluten.

If moisture transfer were to take place by diffusion, its rate would increase with increasing temperature, whereas one of the characteristic features of bread staling is that it is accelerated by a reduction in temperature, down to the freezing point of bread. This effect has generally been studied in terms of changes in crumb firmness, and results have been reported by Steller and Bailey (4), Meisner (5), and Pence and Standridge (6).

[1] Manuscript received July 5, 1963. Contribution from the British Baking Industries Research Association, Chorleywood, Rickmansworth, Hertfordshire, England.

Changes other than crystallization, e.g. chemical changes in the starch, possible changes in its association with water, or diffusion processes, would all have positive temperature coefficients for their rate constants, but changes in equilibrium conditions may conceal this in the early part of the process. In order to dispute the possibility of such changes as a major factor influencing bread staling, it is required, in particular, to show whether the increase in staling observed at low temperatures is really due to an increase in the *rate* at which changes occur or merely to a shift in equilibrium conditions.

If the rate of transformation increases as the temperature is reduced, then the major factor affecting staling must be a process in which a negative temperature coefficient can occur, and this would support the evidence for increasing crystallization of the starch gel with time, since crystallization can take place more rapidly the further the temperature falls below the melting point of the crystalline phase. This is because the development of crystallites depends on the probability that a nucleus will develop into a grain and thereafter grow at a steady rate. It is this probability which increases as the temperature is reduced. On the other hand, diffusion processes and the interaction of molecules or groups to form chemical bonds proceed at a faster rate as the temperature is increased.

The rate of a crystallization process in a high-polymer system is usually slow at temperatures just below the melting point of the crystals, and becomes progressively faster with increased supercooling. It usually passes through a maximum and then decreases again to zero at temperatures where molecular mobility is insufficient to permit crystallization to take place (7).

In the present study, changes in crumb firmness were used to follow the course of staling, and these were measured as a modulus under defined conditions of strain and time; namely, compression to half the original thickness of the sample in a time of 1 min. The effect of different storage temperatures in the range 30° to 90°F. was followed by measurements of crumb modulus over periods of up to 8 days, using dough formulas with and without compound fat.

The rate at which a change of phase takes place, such as the transformation of a supercooled amorphous material to an ordered structure where the process is controlled by the random production of stable nuclei or grains on which the new phase can form, has been considered by Avrami (8,9,10). His theory has been simplified by Evans (11) and Morgan (12) and is represented by the equation

$$\Theta = \exp\left(-kt^{n}\right)$$

where Θ is the fraction of uncrystallized material remaining after time t, k is the growth parameter, and n is an integer ($1 \rightarrow 4$) characteristic of the mode of nucleation.

If crumb modulus, E, is a linear measure of increasing degree of crystallization, then the factor Θ would be given in terms of moduli by

$$\Theta = (E_1 - E_t)/(E_1 - E_o)$$

where E_0 and E_1 are the measured values of modulus corresponding to the initial and final stages of the crystallization process and E_t is the modulus at time t (13).

It will be shown later that curves of crumb modulus versus time can be fitted by inverse exponential curves of the form:

$$(E_1 - E_t)/(E_1 - E_o) = \exp\ (-kt),$$

so that if the Avrami equation applies, either $n = 1$ in this case, or possibly E is not a linear measure of degree of crystallization.

The effect of an increase in the exponent n from unity is to alter the shape of the curve in such a way that the position of the initial rise appears to be delayed along the time axis. Observation of the initial part of the curve is therefore a satisfactory method of determining the value of n when this is near unity, and the experimental procedure described below has proved particularly suitable for making measurements of crumb modulus in the early stages of staling.

The Avrami equation can also be given the alternative form:

$$\Theta = \exp\ (-t^n/\tau),$$

where the time constant τ equals the reciprocal of the rate constant k, and this form is used in describing the experimental results. When $n = 1$ the time constant is the time required for the curve to reach $(1 - 1/e)$ or 63.2% of its final value.

Since it was convenient to carry out the experimental work with whole loaves of bread, tests were carried out to ensure that there were no artefacts caused by transfer of moisture from crust to crumb during storage or by possible migration of moisture as a result of sudden temperature changes. The effect of crust on the staling of crumb has been discussed by Bradley and Thompson (14), and by Bechtel, Meisner, and Bradley (15). It has been shown by Bechtel and Meisner (16) that when bread was baked from doughs containing different quantities of water, differences of only 2% in crumb moisture could be distinguished by a taste panel and by compressibility measurements.

Reference has already been made to the increase in staling rate with lowering of temperature, down to the freezing point of bread. It is well known that, below the freezing point, the staling process is greatly slowed down and possibly completely arrested, and there is clearly a discontinuity at this point in the process causing staling. No attempt has been made here to extend the investigation to temperatures below the freezing point, though further work on these lines is envisaged.

Materials and Methods

The flour used for the baking tests was bakers' grade flour of protein content ranging from 11.5 to 11.9% as is, water absorption 14.8 to 15.5 gal. per sack (52.9–55.4%). Compound fat was all hydrogenated vegetable shortening. Calcium propionate was added where appropriate as a mold inhibitor.

The baking formula was equivalent to

280 lb.	flour
4 lb.	yeast
4½ lb.	salt
9 oz.	calcium propionate
14–17 gal.	water (as determined for each flour by the Simon extrusion meter).

The dough was mixed as appropriate to its size, to a final temperature of 80°F., followed by bulk fermentation for 3 hr. at 80°F. in closed containers. Doughs were hand-scaled at 1 lb., moulded on a Mono Universal Moulder, given a 10-min. recovery, remoulded, and placed in tins. Final proof was for 45 min. at 94°F., 85–90% r.h., and baking was at 450°F. for 30 min. Loaves were allowed to cool for 2 hr. before they were wrapped in moistureproof cellulose film (MSAT 300) and stored at the appropriate temperature.

Crumb modulus was measured by two methods: (a) A cylindrical sample 1 cm. thick and 3.2 cm. diameter was tested on a compressimeter to find by trial the weight to the nearest 50 g. required to compress the sample to half its original thickness in 1 min. The elastic modulus was then calculated as stress/strain, where strain was taken to be the fractional compression. Two samples were taken from near the center of each loaf for measurement. (b) A cone indenter with a 90° cone was used to measure the indentation, d cm., in 1 min. into a cut surface of a loaf under a weight of m g. The quantity m/d^2 is related to modulus, and the latter was obtained by calibration of the instrument with samples of bread which were also measured on the compressimeter. The calibration curve used was represented by:

$$m/d^2 = 1.53\ E + 0.00260\ E^2,$$

where E is the modulus in kdynes/cm.^{2}.

The use of the cone indenter enables softer crumb to be tested; hence measurements could be obtained immediately after the loaf had cooled. Both halves of a cut loaf were measured, as near as possible to the center.

It was found that the crumb modulus results could be fitted by an equation of the form:

$$E_t = E_o + (E_1 - E_o)\,[1 - \exp(-t/\tau)],$$

where E_t is the modulus at time t, E_o is the initial modulus, E_1 the limiting modulus after a theoretically infinite time, and τ the time constant.

There is no satisfactory method which is purely objective, of fitting an equation of this type to experimental points. The above equation is equivalent to:

$$\log(E_1 - E_t) = \log(E_1 - E_o) - t \log e/\tau$$

The method used was to plot $\log(E_1 - E_t)$ versus t, giving a straight line, and by adjusting τ and E_1 to obtain the best fit by eye to all the available points. τ is given by the time required for a decrease of log e or 0.434 in $\log(E_1 - E_o)$.

Effect of Crust on Crumb Modulus during Storage of Bread. For this experiment, six mixings were made of the standard formula to give thirteen loaves per mixing, which were cooled for 2 hr. From each mixing, one loaf was tested on the cone indenter with a weight of 100 g. for 1 min.; six loaves were wrapped in MSAT 300 film; and six were cut to give three slices from near the center of each loaf. Samples were cut from the slices with a sharpened pastry cutter and the three pieces from each loaf were sealed in a round tin which was just large enough to contain them. The loaves and tins were stored at 70°F.

Each day loaves were weighed to check the efficiency of the moistureproof wrapper, and on the second day after baking moisture measurements were made on samples from the center of whole loaves and of the center disk from tinned samples.

Tests were made with the compressimeter on crumb samples from the whole loaves and the two remaining tinned samples, 1, 2, 3, 6, 7, and 8 days after baking. Each result is the average of two samples from the centers of each of six loaves from different mixings.

Effect of a Temperature Gradient. There is also a possibility of moisture transfer caused by sudden changes in temperature of the loaves; for example, a transfer from room temperature to a cold place might cause moisture transfer from the center of the loaf to the crust while the latter is colder.

To examine the magnitude of this effect, a batch of eighteen loaves was baked from a single mixing, omitting the calcium propionate. They were cooled for 2 hr. at 70°F., wrapped, and transferred to storage, half at 80° and half at 40°F.

After 1 hr. in storage, three loaves of each kind were cut in half and sampled for moisture at the center, and similarly after 1 hr. and 20 hr.

Effect of Storage Temperature. A. Without fat. Six mixes were made by the standard recipe to give 24 loaves from each mix. Six wrapped loaves from each mix were stored at each of the following temperatures: 30°, 50°, 70°, and 90°F.

On each day, 1, 2, 3, 4, 7, and 8 days after baking, one loaf of each mix was withdrawn from each storage and brought to 70°F.; two samples from the center were tested for crumb modulus with the compressimeter; and both half-loaves were tested on the cone indenter. On the first day after baking, the volumes of the six loaves from the 70°F. storage were measured.

The crumb modulus results given are the average of two tests on each of six loaves by the two methods.

B. With fat. To the standard recipe was added 2 lb. of compound fat (0.71 parts per 100 parts flour). The procedure was similar except that one extra loaf was made per mixing which was tested on the cone indenter with 100 g. for 1 min. after 2 hr. of cooling. The other modulus tests were made only on the compressimeter.

Changes in Crumb Modulus during the First 24 Hours after Baking. When it was found that the results of crumb modulus measurements *vs.* time could apparently be fitted by inverse exponential curves of the form given above, it was desirable to check the form of the curve obtained during the early part of storage, and in particular to look for apparent discontinuities or a time interval before the curve starts to rise.

In order to reduce variability, all the loaves were baked from one mixing. Since the test occupied 30 min., the number of replicates at the shorter times had to be limited. The standard recipe and method were used to bake 36 loaves from one mixing, omitting calcium propionate. After 2 hr. of cooling, six loaves were tested on the cone indenter, with a weight of 100 g. for 1 min. The remainder were wrapped in MSAT 300 film and stored at 70°F. Loaves were withdrawn at intervals for testing, six at a time. Each test was started 15 min. before the time required and finished approximately 15 min. after the time given.

Effect of Change in Storage Temperature on Crumb Modulus. The reasons for conducting this experiment will be explained later when the results of the previous experiments have been described.

Six mixings were made by the standard recipe and method, omitting calcium propionate, to give 23 loaves from each mixing. The loaves were cooled for 2 hr. and one loaf from each mixing was tested on the cone indenter with a weight of 100 g. for 1 min. The remaining 22 loaves from each mixing were wrapped in MSAT 300 film and eleven were stored at each of the two temperatures, 80° and 35°F. After 24 hr., one loaf of each mixing from each storage place was brought to 70°F. and tested on the compressimeter, and five loaves from each mixing were transferred from one storage place to the other. One loaf from each mixing from each of the four storage treatments was tested 2, 3, 4, 7, and 8 days after baking. On the first and second days after baking, the six loaves from storage at 80°F. were tested for loaf volume before the compressimeter tests.

Effect of Fat on the Crumb Modulus of Bread at Different Temperatures. Experiments have been described to show the effect of temperature on bread with and without fat in the formula, but a direct comparison of the effect of fat was not possible. To allow sufficient replication in a direct comparison, the number of storage temperatures was reduced to three for the following experiment.

Six mixings each from (a) the standard formula, and (b) the same formula plus 2 lb. per sack of compound fat (0.71 parts per 100 parts flour) were made by the standard method to give 19 loaves per mixing.

After 2 hr. of cooling, one loaf from each mixing was tested on the cone indenter with a weight of 100 g. for 1 min. The remainder were wrapped in MSAT 300 film and divided equally between three storage temperatures, 50°, 70°, and 90°F.

On the first day after baking, the volume of one loaf from each mixing stored at 70°F. was determined.

Crumb modulus was measured with the compressimeter on one loaf brought to 70°F. from each mixing, from each storage temperature, after 1, 2, 3, 4, 7, and 8 days.

Results

Effect of Crust on Crumb Modulus during Storage of Bread. The results of daily weighings of the whole wrapped loaves showed that moisture loss through the wrapper was negligible:

	Day					
	1	*2*	*3*	*6*	*7*	*8*
Average loaf wt., g.	404	408	409	404	406	402

The moisture content at the center of the whole loaves was 43.2% and in the tinned samples, 44.0%.

The results of the crumb modulus measurements on whole loaves and tinned samples are shown in Fig. 1. It will be seen that the plots for whole and cut loaves were closely similar, and it can be concluded that the crust has had a negligible effect on the results.

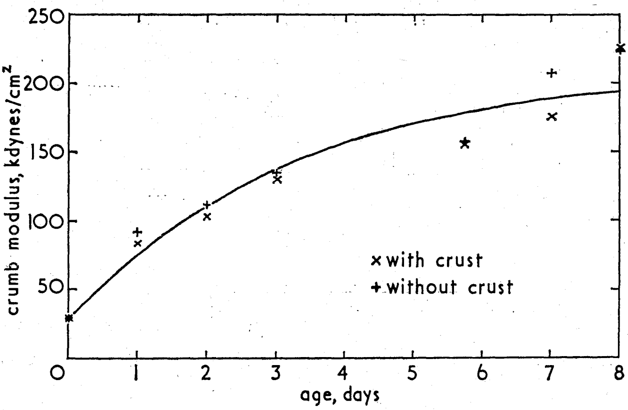

Fig. 1. Crumb modulus of samples stored at 70°F. with and without their crust.

The experimental points were fitted by a single curve with a limiting modulus of 210 kdynes/cm.^{2} and a time constant of 3.22 days, as shown in Fig. 1.

Effect of a Temperature Gradient. It will be seen from the results in the table below that a sudden temperature change has had a negligible effect on the moisture content of the center of whole loaves.

Temperature	*Storage time*	*Moisture at center*
°F.	*hr.*	*%*
80	1	45.0
40	1	44.8
80	3	45.2
40	3	44.8
80	20	45.0
40	20	44.6

It is reasonable to conclude, from the results of these two experiments, that measurements of crumb modulus made on whole loaves are not influenced appreciably by moisture transfer within the loaves.

Effect of Storage Temperature, without Fat. The results of measurements of crumb modulus *versus* age of the bread for each storage temperature are shown in Fig. 2. It was found that they could be fitted by inverse exponential curves with the same value of limiting modulus, 155 kdynes/cm.^{2} for all temperatures, and the following values of the time constant:

	Temperature, °F.			
	30	*50*	*70*	*90*
Time constant, days	2.08	2.08	3.68	5.47

Average loaf volume was 1473 cc.

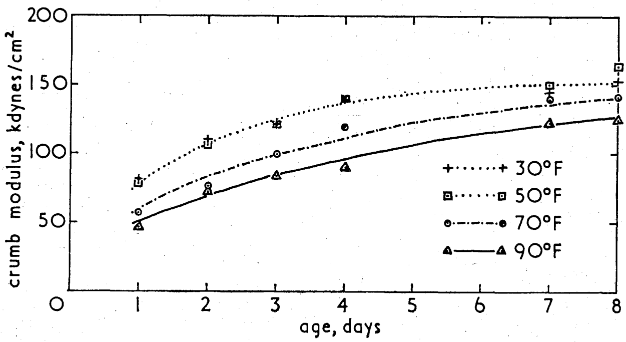

Fig. 2. Effect of storage temperature on crumb modulus of bread without fat.

The results of this experiment are not conclusive in themselves, but suggested that the effect of temperature is on the rate of approach to an equilibrium condition, rather than to a change in the latter.

Changes in Crumb Modulus during the First 24 Hours after Baking. In the previous test the first measurements of crumb modulus were made 1 day after baking. The form of the curve obtained in the early part of storage was checked in a separate experiment, the results of which are shown in Fig. 3.

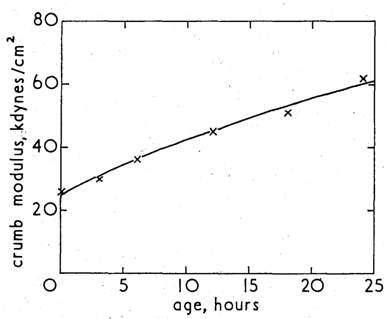

Fig. 3. Changes in crumb modulus over the first 24 hr. after baking.

The continuity of the initial part of the curve shows that staling commences as soon as the loaves are cool, if not before. The curve can be fitted satisfactorily by an inverse exponential function with the exponent of time equal to 1, but not with higher values.

Effect of Change in Storage Temperature on Crumb Modulus. The object of this experiment was to verify the observation that at temperatures above freezing point the modulus increase is characterized by an inverse exponential function in which the limiting modulus value is the same for loaves baked under similar conditions from the same ingredients, whereas the time constant is dependent on the storage temperature. If loaves are stored at one temperature for a period and then transferred to another storage temperature, it should be possible to predict the form of the modulus-time curve by measuring the limiting modulus value and time constants of similar loaves stored at each of these two temperatures over the whole of the staling period.

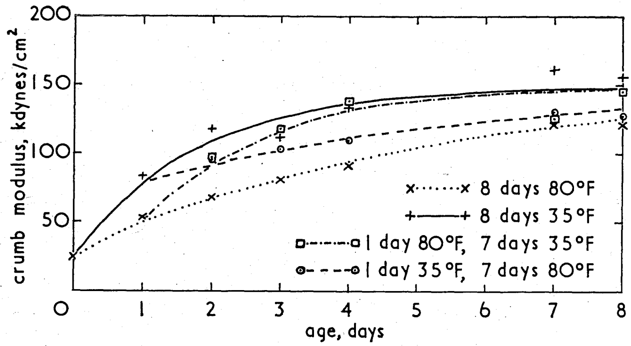

Fig. 4. Effect of change in storage temperature on crumb modulus.

Figure 4 shows that the modulus values for the loaves stored at a constant temperature appeared to be approaching a limit of about 150 kdynes/cm.². A plot of log (150 – E_t) for these loaves gave straight lines differing in slope. From these lines the expected curves for the transferred loaves were predicted, assuming that the slope of the log plot is characteristic of temperature and the limiting modulus remains unchanged. These lines are plotted in Fig. 5, where it will be seen that agreement with the measured values is good. Average loaf volume was 1,581 cc.

These results have a bearing on whether or not it is desirable to store bread in a refrigerator. This question was previously discussed by Pence and Standridge in relation to constant storage temperatures (6). It will be seen from Fig. 4 that the effect of transfer to refrigerated storage at 35°F. is to increase the rate of approach of the crumb firmness to its limiting value, even when the bread has been stored at a higher temperature for a day. If it is required to keep the crumb soft, it should be stored in a warm place and eaten before mold and rope develop.

Effect of Storage Temperature, with Fat. When the storage experiment at different temperatures was repeated with the addition of compound fat to the formula, a similar pattern of temperature effects was observed (Fig. 5).

The use of a single value of the limiting modulus for fitting the

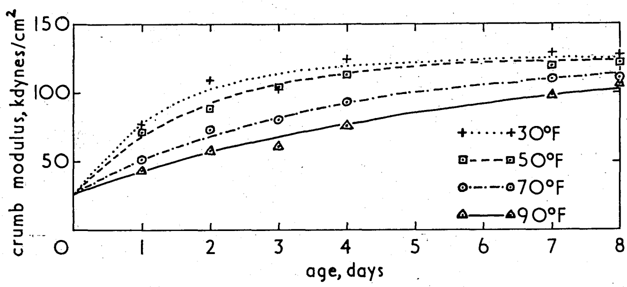

Fig. 5. Effect of storage temperature on crumb modulus of bread containing fat.

curves, in this case 125 kdynes/cm.^{2}, was confirmed. This was combined with the following values of the time constant in plotting the curves shown in Fig. 5:

	Temperature, °F.			
	30	*50*	*70*	*90*
Time constant, days	1.39	1.89	3.68	5.51

Average loaf volume was 1,615 cc.

Effect of Fat on Crumb Modulus of Bread at Different Temperatures. A direct comparison of the effect of fat was obtained in this experiment.

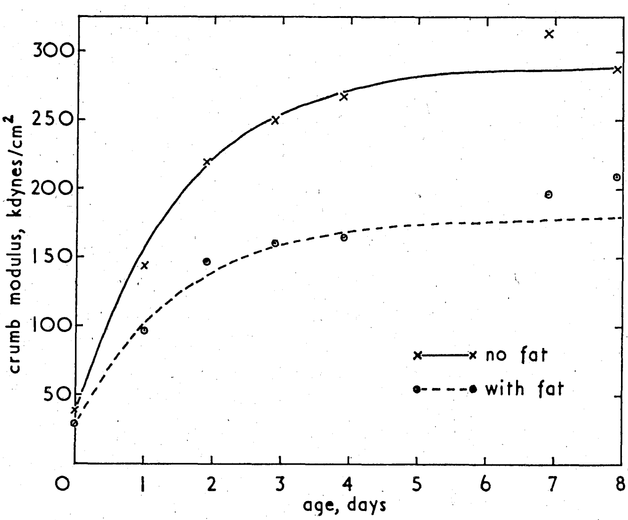

Fig. 6. Effect of fat on crumb modulus at 50°F.

It was found that the plots of modulus *vs.* age shown in Figs. 6, 7, and 8 were fitted by inverse exponential curves with limiting moduli

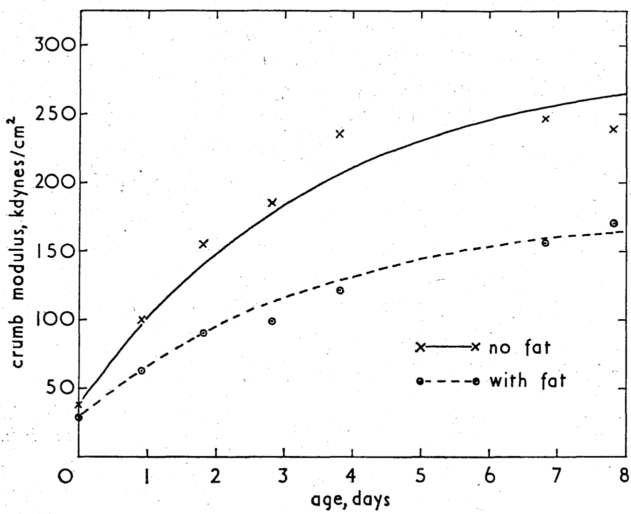

Fig. 7. Effect of fat on crumb modulus at 70°F.

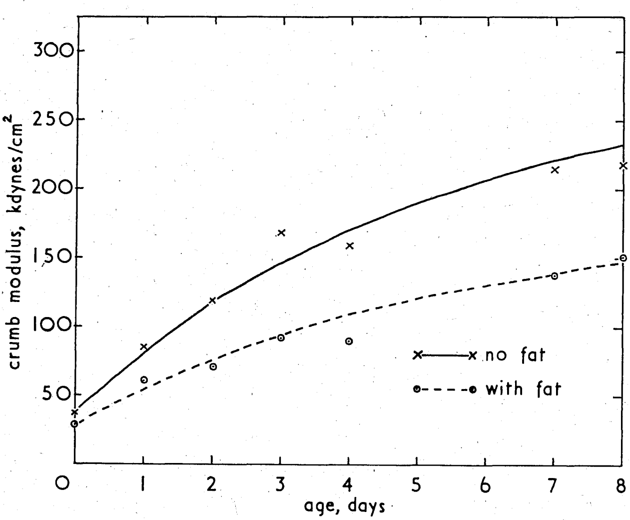

Fig. 8. Effect of fat on crumb modulus at 90°F.

of 290 kdynes/cm.[2] for the bread without fat and 180 kdynes/cm.[2] for bread with fat. The rates of approach to the limiting value appeared to be the same at each temperature for the bread with and without fat, so the curves have been drawn using the same rate constant:

	Temperature, °F.		
	50	*70*	*90*
Time constant, days	1.52	3.48	5.47

In this particular experiment the fat has had no influence on the relative rate of staling as measured by the time constant. If the fat was affecting diffusion of moisture from starch to gluten, this was not influencing changes in crumb modulus.

The reduction by fat of the limiting modulus from 290 to 180 kdynes/cm.[2] was accompanied by an increase in average loaf volume from 1,378 to 1,532 cc. It is possible that in this case the weakening of the crumb structure by fat could be at least partly accounted for by the increased volume. When all the available results are placed in order of loaf volume, it is found that the smaller volumes are generally associated with higher values of limiting modulus, and vice-versa. This is shown in the following table.

Loaf volume	*Formula*	*Limiting modulus*
cc.		*kdynes/cm.*[2]
1,615	with fat	125
1,581	no fat	150
1,532	with fat	180
1,479	no fat	210
1,473	no fat	155
1,378	no fat	290

As these experiments were mostly carried out on different occasions, with different flours, a direct comparison is not possible.

Discussion

In any given experiment, for a particular formula, baking conditions, etc., the limiting modulus value appears to remain constant over the temperature range studied. In all the experiments the relative rate of modulus increase becomes greater at lower temperatures which are still above the freezing point of bread, as shown by the progressive decrease in the time constant. This evidence favors a physical process involving a more ordered arrangement of atoms or molecules, such as crystallization, as the principal factor concerned in these changes in crumb firmness. It suggests that it is not primarily a diffusion process, such as moisture transfer between starch and gluten, since this would have a positive temperature coefficient; nor a chemical change, since the equilibrium condition does not appear to be affected by temperature and the rate of transformation has a negative temperature coefficient.

The form of the function used to fit the measurements of crumb modulus plotted *vs.* time is in general agreement with the theory of Avrami relating to the growth of crystallites, and this provides supporting evidence, although it may be that the exact form of the equation is fortuitous.

The experiments involving a comparison of bread with added compound fat with that from a plain dough are also of interest because they show that the method used here for following the staling process is able to indicate the extent of starch changes, irrespective of the initial crumb firmness level, in terms of the function

$$\Theta = (E_l - E_t)/(E_l - E_o)$$

It thus provides a means of distinguishing an effect on starch changes, or a true antistaling effect, from one which results merely in changes in the over-all level of crumb firmness.

Literature Cited

1. Bechtel, W. G. Progress in the study of the staling phenomenon. Baker's Dig. **35** (5): 48–50, 172, 174 (1961).
2. Bechtel, W. G. A review of bread staling research. Trans. Am. Assoc. Cereal Chemists **13:** 108–121 (1955).
3. Schoch, T. J., and French, D. Studies on bread staling. I. The role of starch. Cereal Chem. **24:** 231–249 (1947).
4. Steller, W. R., and Bailey, C. H. The relation of flour strength, soy flour, and temperature of storage to the staling of bread. Cereal Chem. **15:** 391–401 (1938).
5. Meisner, D. F. Importance of temperature and humidity in the transportation and storage of bread. Baker's Dig. **27:** 109–114, 126 (1953).
6. Pence, J. W., and Standridge, N. N. Effects of storage temperature and freezing on the firming of a commercial bread. Cereal Chem. **32:** 519–526 (1955).
7. Bawn, C. E. H. The chemistry of high polymers, p. 202. Butterworths Scientific Publications Ltd.: London (1948).
8. Avrami, M. Kinetics of phase change. I. General theory. J. Chem. Phys. **7:** 1103–1112 (1939).
9. Avrami, M. Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei. J. Chem. Phys. **8:** 212–224 (1940).
10. Avrami, M. Granulation, phase change, and microstructure. Kinetics of phase change. III. J. Chem. Phys. **9:** 177–184 (1941).
11. Evans, V. R. The laws of expanding circles and spheres in relation to the lateral growth of surface films and the grain-size of metals. Trans. Farad. Soc. **41:** 365–374 (1945).
12. Morgan, L. B. Crystallization phenomena in polymers. II. The course of crystallization. Phil. Trans. Roy. Soc. **247A:** 13–22 (1955).
13. Magill, J. H. Techniques for following rates of crystallization in high polymers. Research and Development for Industry (11): 30–36 (July 1962).
14. Bradley, W. B., and Thompson, J. B. The effect of crust on changes in crumbliness and compressibility of bread crumb during staling. Cereal Chem. **27:** 331–335 (1950).
15. Bechtel, W. G., Meisner, D. F., and Bradley, W. B. Effect of crust on the staling of bread. Cereal Chem. **30:** 160–168 (1953).
16. Bechtel, W. G., and Meisner, D. F. Staling studies of bread made with flour fractions. III. Effect of crumb moisture and of tailings starch. Cereal Chem. **31:** 176–181 (1954).