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The Relationship between Viscosity, Elasticity and Plastic Strength of a Soft Material as Illustrated by some Mechanical Properties of Flour Dough

IV—The Separate Contributions of Gluten and Starch

By R. K. Schofield and G. W. Scott Blair

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In the earlier papers of this series (Schofield and Scott Blair 1932, 1933*a*, 1933*b*) the endeavour has been to give a quantitative description of the behaviour of flour dough under stress. Use was made of the equation

$$\frac{de}{dt}=\left(\frac{1}{n}\cdot\frac{dS}{dt}-\frac{d\alpha}{dt}\right)+\frac{1}{\eta}.S,$$

which is the expression originally put forward by Maxwell with the addition of $-d\alpha/dt$ to take account of elastic after-effect. In this equation de/dt represents the rate of elongation of a cylinder of dough, and S the shearing stress which is one-third the longitudinal stress per unit area. The equation serves to define n, the modulus of rigidity, and η the viscosity, and enables these to be evaluated from experimental observations of e and S.

The behaviour of flour dough was shown to be consistent with the equation

$$t_r = \eta/n$$

for the relaxation time, and evidence has since been presented by Halton and Scott Blair (1936) to show that t_r is probably the most important single quantity determining the baking quality of a flour dough.

Valuable as this method of formulation has undoubtedly been, it does not throw much light on the physical mechanisms at work, its virtue being that it can be applied to any material that can be stretched. By its use a remarkable *formal* resemblance was demonstrated between the behaviour of flour dough and soft metals: both show work hardening, elastic hysteresis and elastic after-effect. It cannot be argued from this, however, that the physical mechanism is the same. To study this aspect of the problem other avenues of approach must be sought.

The Mechanism of Work Hardening in Flour Dough

The Gluten Network—An investigation of the behaviour of dough cylinders when extended to many times their original length has provided a clue to the explanation of work hardening.

The apparatus was a simplified form of that already described. The cylinder of dough originally 5 cm. long and about 0·7 cm. in diameter was floated straight out of the "moulding gun" on to the mercury bath which was provided with a lid lined with wet felt to prevent the dough from drying. Threads of sewing cotton were attached, one to each end of the cylinder, by means of small pieces of cork to which dough adheres readily. One thread was attached to a stress indicator, reading up to about 7000 dynes,* of stouter design than that used previously, and the other to a winch geared to a synchronous motor which enabled it to be moved steadily at a rate of 0·045 cm./sec.

In the first series of experiments represented by figs. 1, 5 and 6, the stress was recorded at intervals during the slow extension at the end of which the cotton was released from the winch. The dough cylinder was then allowed 5 min. for free contraction before the slow extension was repeated. In these figures the shearing stress per unit area (dynes/cm.^{2}) is plotted against $\log_e l/l_0$, l being the length at the moment in question and l_0 the initial length (5 cm.).

The fact that the length of a dough cylinder which has completed its elastic recovery after being stretched always exceeds the original length, is most simply explained by supposing that the elastic elements in the dough are insecurely attached to each other. It might be expected that a general slippage would occur when a critical stress had been reached. This, however, is not the case in a normal dough. Fig. 1 shows clearly that although considerable flow took place in the first extension, very much less occurred during the subsequent extensions although somewhat higher stresses were recorded. The upward curvature at the higher strains which is such a pronounced feature of the curves is just discernible in fig. 7 of the paper by Schofield and Scott Blair (1933 *b*) which was only carried to a strain $\log_e l/l_0 = 0{\cdot}7$.

The general nature of the process appears to be something like that indicated in fig. 2, which represents the behaviour of six springs, three of which are securely linked at P, the other three at Q, while they are insecurely linked in pairs at R, S and T. The springs linked at S are only about half the length of those linked at R and T. Consequently, if each insecure link

* 15 cm. at 0·455 g./cm. = 6700 dynes.

will stand the same maximum stress, the link at S will snap before those at R and T. If only a small stress is applied (fig. 2b) all the links will hold, and the system when released will recover to the unstrained length (fig. 2a). But, once S has snapped (fig. 2c) the system will not recover to its length in

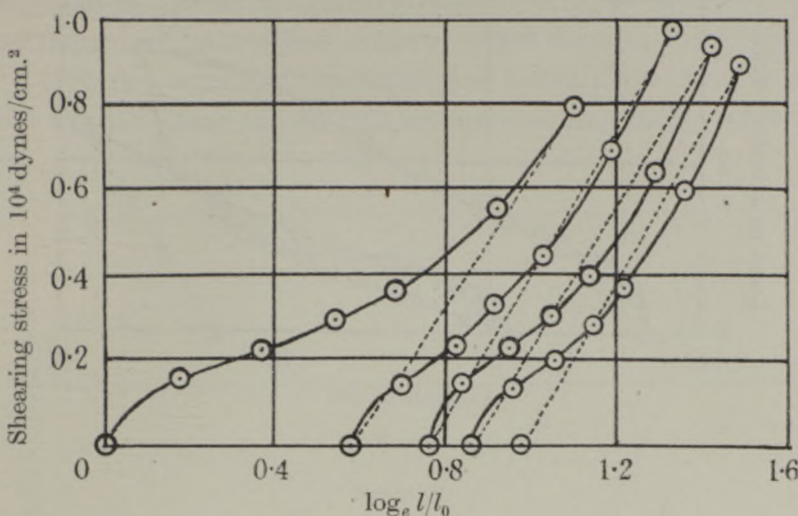

FIG. 1

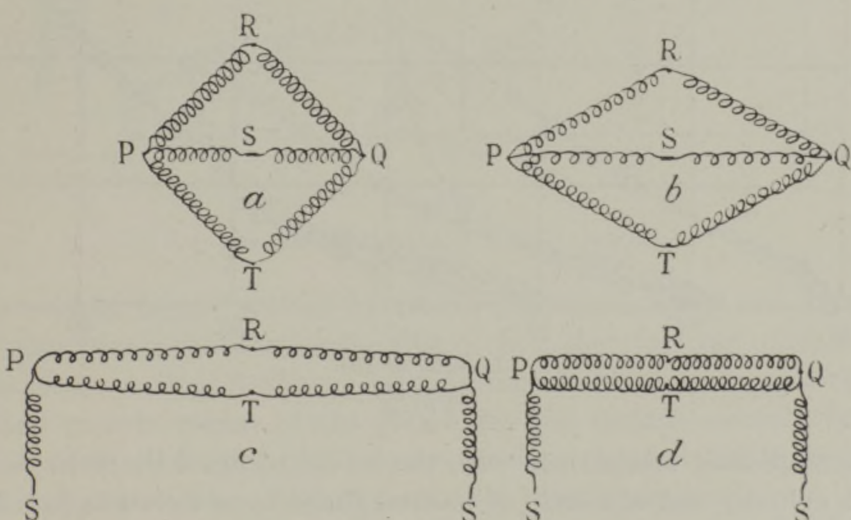

FIG. 2

fig. 2a but only to the condition shown in fig. 2d. The system has undergone a permanent elongation and has therefore "flowed". It must be remembered that the dough is to be pictured as formed of a very great many such systems. The more junctions that have broken, the higher must the applied stress be before there is any more breaking of junctions. Work hardening may be envisaged either as a rise in yield value, or in viscosity, but in either case it is clear that the progressive snapping of individual links has produced hardening.

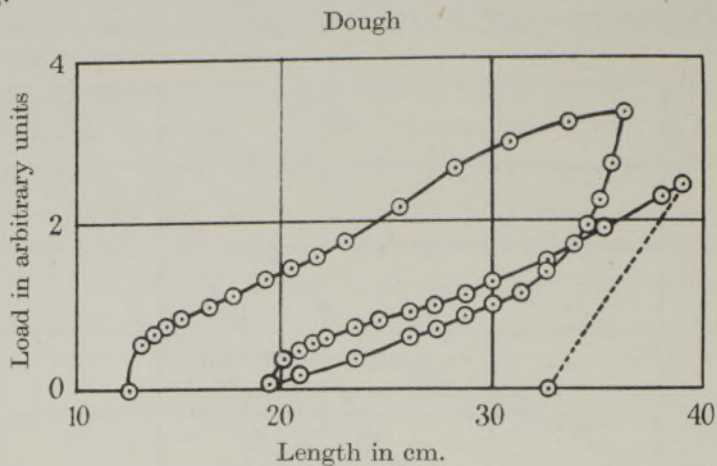

Fig. 3

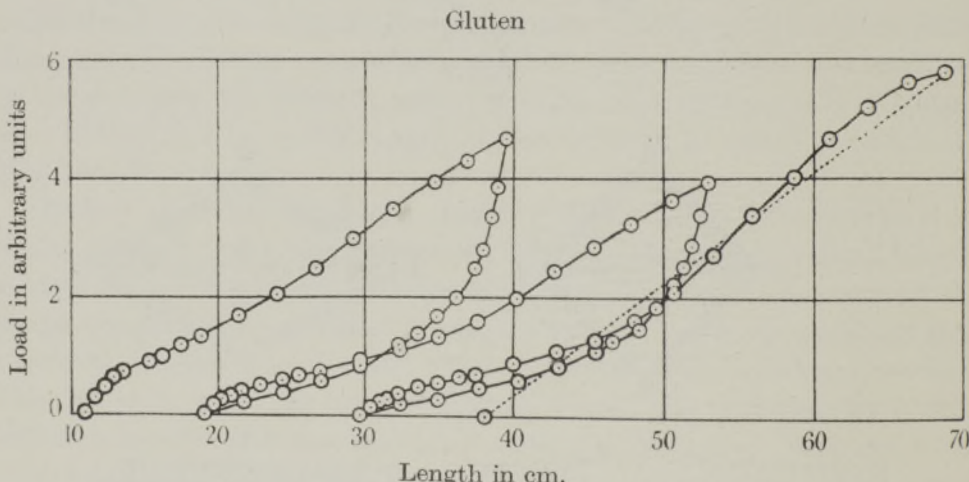

Fig. 4

For more easy comparison with the model of fig. 2 the behaviour of a dough cylinder and of a strip of washed gluten* are shown in figs. 3 and 4 by plotting simply the load against the length. In these experiments, when

* Gluten test-pieces are prepared in the following way: A small ball of dough is kneaded continuously under the tap until all the starch has been washed away, and the wash water is clear. The mass of wet gluten, which consists largely of protein and water, is given coherence by further kneading, and a small strip of approximately rectangular cross-section is cut with a razor. When extended on the trough of the extensimeter, this loses its angles, and recovers to the shape of a slightly irregular cylinder whose diameter can be measured with a fair degree of accuracy.

the cylinder had been extended as far as was considered safe, the synchronous motor was reversed and the cylinder was allowed to contract at the same rate as it had been extended.

It will be seen that for the greater part of their length the loading branches of the curves bend upwards. This is the behaviour to be expected of a system of springs irregularly assembled, some of which do not come under stress at all until a certain amount of elongation has taken place. Such a curvature would also appear where the springs are approaching their greatest possible extension.

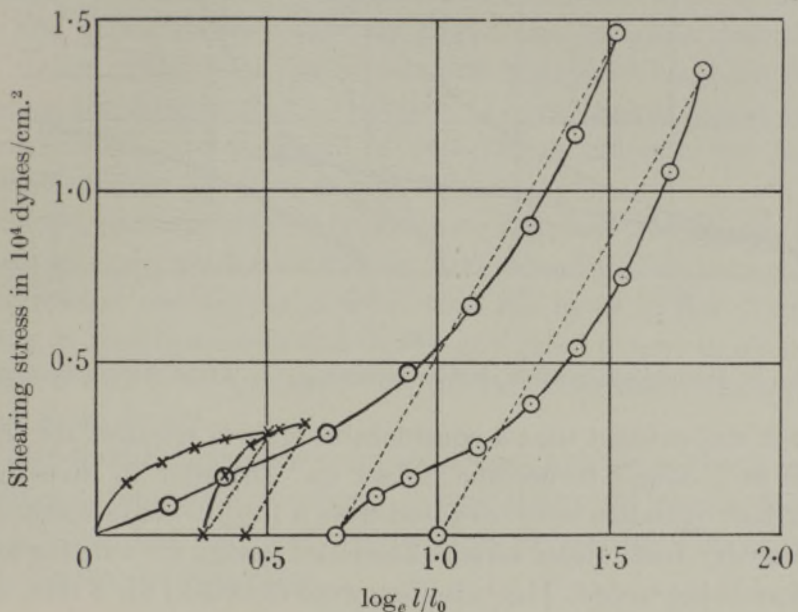

FIG. 5—⊙ Control. × HCl treated.

It is evident from the close resemblance between figs. 3 and 4 that the elastic structure in the dough is the gluten. It is, therefore, not unreasonable, in view of the work of Astbury (1933) on protein fibres, to suggest that the branched protein chains of the gluten are the springs securely fastened together, and that the insecure links are made by the electrostatic attraction between oppositely charged groups of neighbouring molecules.

Support for this view was obtained from an experiment in which hydrochloric acid was added to a dough slightly in excess of the amount needed to convert all the COO^- groups into COOH. The maximum shearing stress that this dough would stand without tearing was about $0{\cdot}35 \times 10^4$ dynes/cm.^{2}, whereas the control dough made up to the same moisture content but without the addition of acid easily withstood $1{\cdot}5 \times 10^4$ dynes/cm.^{2}. The curves are shown in fig. 5.

The effect of 10 min. drastic remixing of a dough is shown in fig. 6, from which it will be seen that this treatment caused the cylinder to flow out under a relatively low stress. The normal condition was, however, largely restored by allowing the remixed dough to stand for 2 hr.

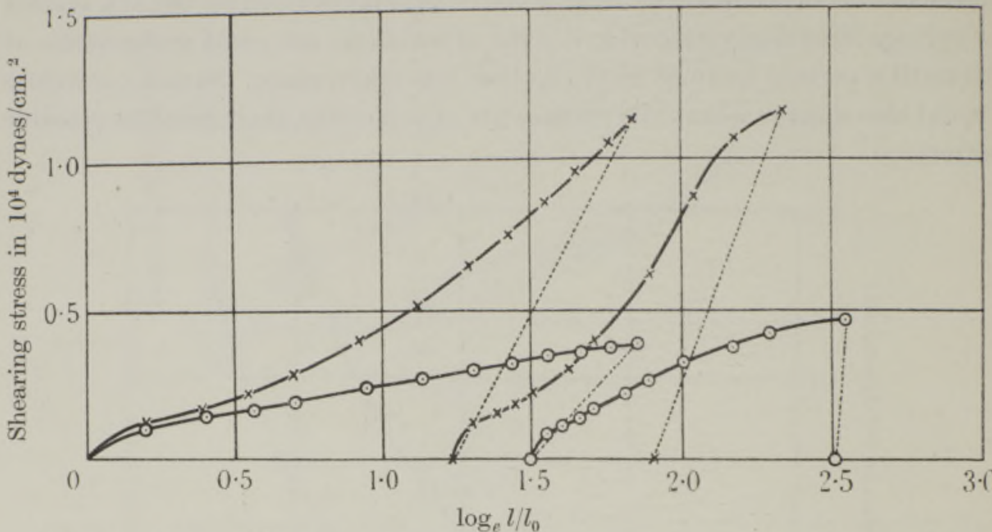

FIG. 6—⊙ Immediately after drastic remixing. × After resting further 2 hr.

Hence it was evident that a considerable time is required for the elastic structure in a dough to become linked up. In order to investigate this point further, cylinders were prepared from a freshly made dough and kept on the mercury bath under small waterproof covers for varying lengths of time before being tested. The cylinders were extended for 5 min. by which time they had been stretched by $\log_e l/l_0 = 1{\cdot}28$, and the stress was recorded. The stress was then released and $\log_e l/l_0$ again determined after 5 min. free contraction. They were again extended, this time until rupture occurred, and their greatest length was measured. Judged by the length at rupture

TABLE I

Age (hours) ...	0·33	1·0	2·0	2·75	4·5	7·5
First extension						
Shearing stress for $\log_e l/l_0 = 1{\cdot}28$ in 10^4 dynes/cm.^{2}	1·22	0·71	0·61	0·65	0·62	0·58
$\log_e l/l_0$ after recovery	0·69	0·78	0·77	0·77	0·87	0·91
Second extension						
Length at rupture (cm.)	20	33	29	34	32	32

there is little further build-up of structure after 1 hr., but it will be seen that the flow during the first extension, as measured by $\log_e l/l_0$ after recovery, continues to increase up to 7 hr. notwithstanding the fall in shearing stress. This may be due to water released by syneresis of the gluten diluting the starch paste, and thereby reducing its viscosity (*vide infra*).

The Influence of the Starch—In comparing the curves for dough and gluten shown in figs. 3 and 4, one is struck by their very close similarity. In fact, apart from a tendency for the loops to be wider in the case of the dough, there is only one noticeable difference. At the lowest strains, the stress rises very steeply in the case of dough to what almost is a yield value, whereas with gluten there is considerable deformation even at the lowest stresses. The only difference between gluten and dough is that the latter contains starch, whereas in the former this ingredient has been removed. Starch paste has an anomalous viscosity, i.e. one that is higher the lower the shearing stress, and so would be expected to influence the behaviour of the dough more at low than at high stresses.

Some additional experiments in which equilibrium was approached first by a simple recovery from a small load, and secondly after having momentarily overloaded the sample, showed that the loops in figs. 3 and 4 are mainly due to true hysteresis and not to any great extent to elastic after-effect: they would have appeared even if the cycles had been carried out very much more slowly.

It was also found that under very small loads applied in the range where no permanent deformation occurs, dough shows an elastic fatigue on repeated loading, but that it slowly recovers on resting. This is evidently a type of thixotropic behaviour.

Summary

Experiments are described which support the view that in a flour dough the gluten forms an elastic network which dominates the mechanical behaviour. It appears that when a cylinder of dough is first stretched some of the links in the network are ruptured since it will not return to its original length. Enough remain unbroken, however, for a continuity of structure to be preserved until the cylinder has been extended to five or six times its original length. The "work hardening" of dough is thus accounted for. The elastic network does not establish itself at once, but continues to build up for some time after the dough is mixed. Its strength is greatly reduced by drastic remixing of the dough but is largely recovered on further standing. The addition of hydrochloric acid in slight excess of the acid binding capacity destroys the strength of the network. This shows that the electro-

static attraction between oppositely charged groups in neighbouring molecules is an important factor in the strength of the gluten network.

The upward bend of the reloading curve up to the point where flow (i.e. the rupture of further links) occurs is probably mainly due to the irregularity of assembly of the elastic members, but may also indicate that individual chains are approaching the limit to which they can be extended.

Evidence has been obtained that the starch paste penetrating the gluten network has a "yield value", in consequence of which there is elastic hysteresis even when the cycle is carried out slowly enough to avoid elastic after-effect.

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The Quantum Theory of Atomic Polarization
I—Polarization by a Uniform Field

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1—Introduction

Two problems of atomic energy, the energy of polarization of an atom in a plane electrostatic field and the energy of interaction, or van der Waals energy, of two distant atoms, are particularly suited to attack by approximate methods. In each, the disturbing field, whether that of the static field or of the distant atom, is small in comparison with the internal fields acting on the electrons of the atomic system, and so the standard methods by which quantum mechanics deal with small disturbances, namely the perturbation and variation methods, can be and have been successfully applied to these problems. Though the perturbation method, strictly applied, is the more accurate, since it takes into account the possible excited states of the