

Lines of Attack on Dough Chemistry

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The contributions of test baking, dough rheology, and analytical chemical procedures illustrate how several techniques can supplement one another in research on dough chemistry, though the first still provides the main criterion of flour quality. Newer developments in dough rheology include description of dough properties by means of structural relaxation curves and relaxation time spectra. Amperometric titrations and polarographic studies are among the recent analytical tools. Dough is currently treated as a dynamic cross-linked polymer network in which protein plays a major role; but a detailed explanation of dough structure, consistent with all data obtained by all methods, has yet to be developed.

PRESENT-DAY KNOWLEDGE OF THE CHEMISTRY OF DOUGH and its behavior still lacks a major unifying principle such as generally characterizes a coherent field of scientific study. This paper sketches briefly the main developments and suggests lines of research that are most likely to give dough chemistry the unity it needs.

In composition, dough is a mixture of a wide variety of constituents; chemical, physical, and biological factors determine its behavior; and its properties change with time, type, and amount of physical work done on it. In spite of this complexity, well recognized by bakers and chemists alike, the physical properties of dough for breadmaking must fall within a narrow range of specifications imposed by the requirements of a mechanized modern bakery schedule.

A successful approach to the study of the chemistry of a system as complex as dough must involve a simultaneous attack from several directions. Three different areas of research on the chemistry and the properties of dough have been selected to illustrate this type of approach: test baking, dough rheology, and analytical chemical procedures designed to determine functional groups in dough.

Baking Test

As the end use of flour and dough is in the production of bread, it is logical that test baking should have become a general and a popular technique early in the study of dough chemistry. A standardized form of the baking test most commonly employed in the United States and Canada has been described (2). The baking test has been widely used as a practical test for evaluating flour quality and baking procedures. Among the factors that have been studied are the effect of mixing and dough handling, diastatic activity and gas production, the effect of maturing agents, and the quality factor of wheat protein. It is the only test by which certain specific quality factors can be evaluated at the present time, and in the long run it must remain as the final criterion of flour quality.

The main limitation of the baking test in research is its lack of specificity. The test loaf is the net result of all the processes and reactions, positive and negative, chemical and physical, biological and technological, that take part in its production. It gives little or no information about reactions involved or their mechanism. In this respect it is much like chemical thermodynamics, which deals only with the initial and final

states of reactions; information about the mechanism of reactions must be obtained from other chemical procedures.

From the studies of the baking procedure, baking experts and technologists attained an intimate subjective knowledge of the properties and the behavior of dough which led to the development of physical dough testing.

Physical Dough Testing

The contribution of physical dough testing to the chemistry of dough was not as great as was at first expected. These tests were empirical, and the data obtained with them could not be defined in fundamental units of physics and chemistry nor simply related to such units. Such data obviously could not be applied to the measurement of the extent of a reaction in dough, or its rate. However, physical dough testing did provide a variety of instruments such as the extenso-graph, farinograph, and alveograph, and, perhaps more significant, the way was prepared for the introduction of formal rheology.

Background of Rheology

Because cereal chemistry is an applied science, it is not surprising that the major developments in rheology have

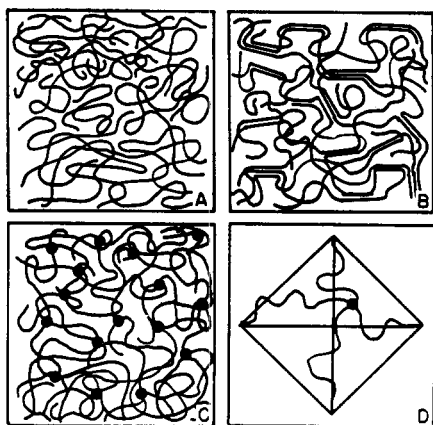


Figure 1. Schematic diagram of molecular network structures showing cross linking

- A. By chain entanglement
- B. By secondary valence attraction
- C. By primary chemical bonding
- D. Tetrahedral element of a dynamic network

been made in other areas of research. Among these must be included the introduction of the concept of macromolecules, the formulation of the kinetic theory of rubberlike elasticity, and the formal mathematical treatment of the properties of viscoelastic substances, especially in terms of the generalized Maxwell model.

The significance of the concept of macromolecules lay in breaking away from the ideas of classical colloid chemistry, and in the introduction of a basic structural unit. In terms of this unit of long linear chains or a cross-linked network the chemist was able to make a fresh attack on the study of proteins, cellulose, and rubber. The importance of these developments was recognized by the award of the Nobel Prize in chemistry to Staudinger in 1953.

It was only a step from the static picture of macromolecules to a dynamic one in which the long linear molecules or segments of long molecules between crosslinks are in continuous Brownian motion. Figure 1 shows schematic illustrations of network structures with cross linking by simple chain entanglement *A*, secondary *B*, primary bonding *C*, and of an element of a dynamic network *D*. Guth, Mark, and Kuhn (9, 14) and others formalized mathematically the dynamic behavior of macromolecules of polymers into the kinetic theory of rubberlike elasticity.

Parallel with these developments was a more phenomenological description of viscoelastic behavior of polymer systems, based on a mechanical representation of the elastic components as springs and of viscous components as dashpots. The simplest combination is the Maxwell element, which consists of a single spring and dashpot in series. This combination can be uniquely characterized by its

relaxation time, which is the ratio of the viscosity represented by the dashpot to elastic modulus represented by the spring. A more complex arrangement known as the generalized Maxwell model consists of a large number of simple Maxwell elements having different relaxation times. Figure 2 shows several combinations of Maxwell elements together with their distribution functions. An extensive mathematical background has been developed on this basis and has been well summarized by Alfrey (7).

Dough Rheology

The newer concepts and methods of rheology are gradually being adapted to the study of dough chemistry. An attempt is being made to re-examine, in terms of fundamental units, the measurements made with standard dough testing instruments and to devise more meaningful measurements to be made with them. New instruments initially designed to measure fundamental dough properties are being developed for the study of dough. Methods illustrating these developments in dough rheology include relaxation in dough using the extensograph or the alveograph, stress relaxation using the relaxometer, and studying the elastic properties of dough using the resonance elastomer.

The method of structural relaxation depends upon the observation that the properties of freshly mixed or worked doughs change very markedly with time. The dough is said to relax. This change

has been quantitatively characterized using the extensograph (7). The method consists of preparing a series of doughs, and allowing an interval between mixing and shaping the dough, if it is desired to allow certain time-dependent chemical reactions like that of bromate to take place in the dough. The doughs are then mechanically shaped, secured on dough holders, and stretched at a series of rest periods between shaping and stretching of the samples. In this manner a series of extensograms, one for each rest period, is obtained; doughs at shorter rest periods give extensograms showing a high resistance to extension and a small extensibility, while doughs that have had more time to relax give lower and longer extensograms showing a smaller resistance to extension and a greater extensibility.

The extensograms or load-elongation curves are then analyzed by reading the load supported by the dough at a constant sample elongation. This gives a measurement analogous to a stress and is considered to be a fundamental measurement of dough properties. Plotting the extensogram load at constant sample deformation against time then gives the structural relaxation curve which summarizes experimentally the properties of the dough tested.

The structural relaxation curve for dough has been found to approximate closely the equation of a hyperbola of the form $(L - L_A)t - C = 0$, where L is the extensogram load at constant sample extension at rest period t , L_A is the theo-

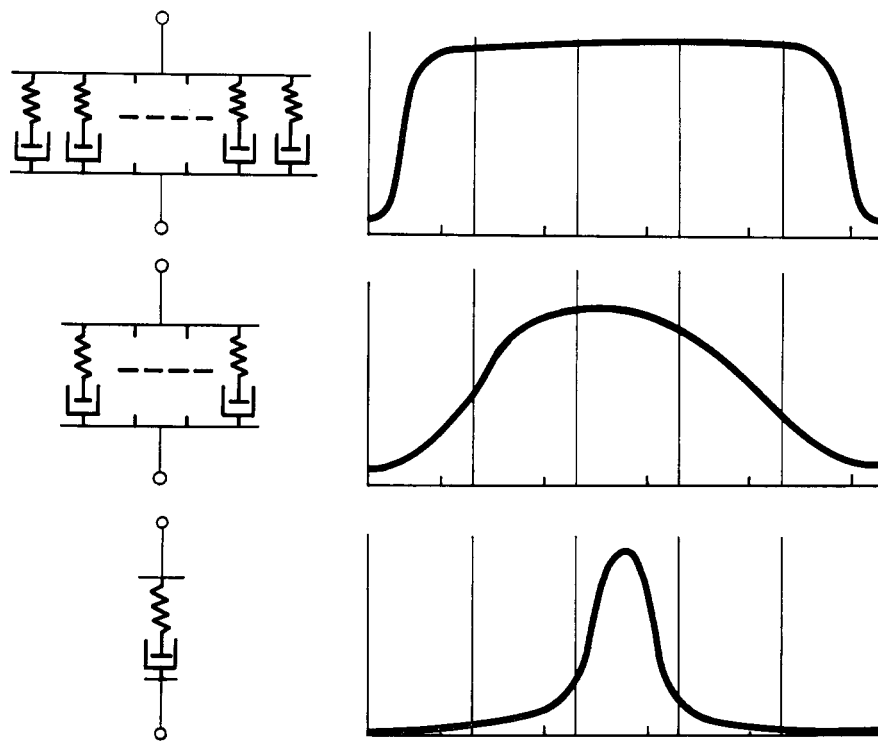


Figure 2. Single Maxwell element and more generalized Maxwell element of single elements in parallel arrangement (right), and corresponding distribution functions of relaxation times (left)

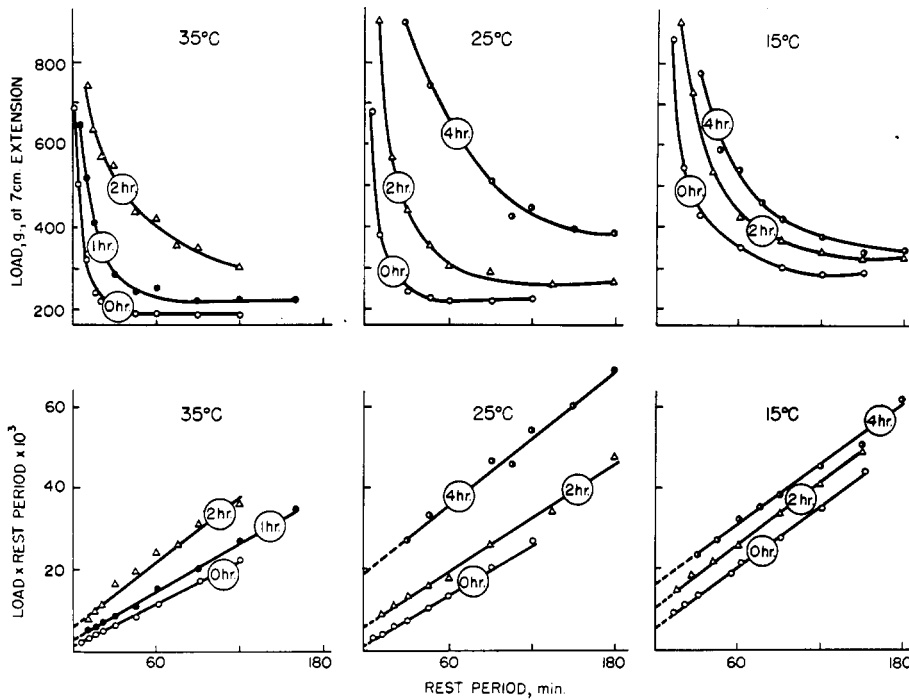


Figure 3. Illustrative structural relaxation data for doughs containing 40 p.p.m. potassium bromate. Relaxation curves (top); linear transformations of these curves (7)

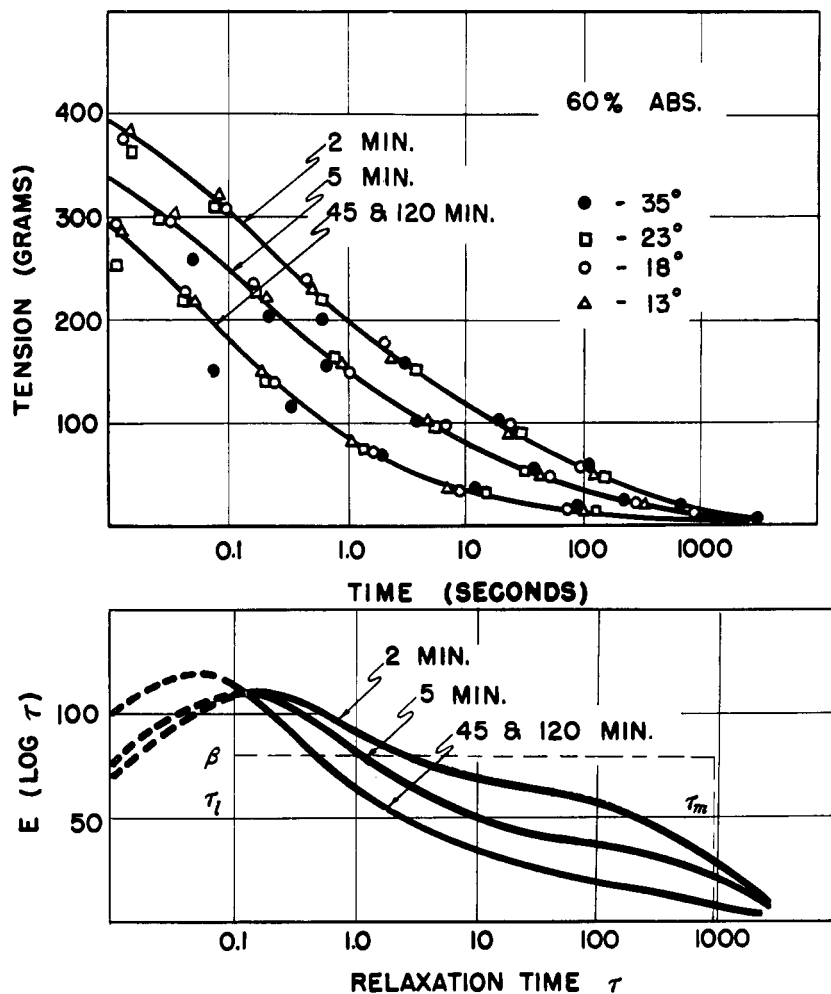


Figure 4. Stress relaxation curves for dough (top) and corresponding distribution curves or relaxation time spectra (bottom) (5)

retical load which the relaxation curve approaches asymptotically at long rest periods, and C is a constant. This hyperbola can be readily transformed into its linear equivalent, $Lt = L_A t + C$, which form permits a ready evaluation of the two constants characterizing the relaxation curve. The constant C describes the curvature of the hyperbola and is inversely related to the rate of relaxation, and another constant L_A describes the upward displacement of the hyperbola or the asymptote that it approaches at infinite rest period. Figure 3, reproduced from the work of Dempster, Hlynka, and Anderson (7), illustrates typical structural relaxation curves and their linear transformations. The constants derived from such curves may then be used to describe dough properties or to follow changes of dough properties brought about by treatment with improvers or in other ways, by the methods of chemical kinetics.

A more basic measurement with the alveograph has also been proposed (11, 12): the resistance of the bubble inflated in the alveograph referred to a constant thickness of the bubble wall. A procedure has been worked out for structural relaxation studies using this instrument in an analogous way to the extensograph procedure.

A beginning has also been made in applying the method of stress relaxation to dough rheology. An instrument called a relaxometer has been designed which stretches a test sample of dough, holds it at constant extension, and records the relaxation of tension initially imposed in stretching the dough (5).

Charts of tension on the relaxing dough against time obtained directly with the relaxometer are then analyzed according to standard methods that have been developed in the study of other viscoelastic substances (6). Replotting tension on a logarithmic time axis yields a new relaxation curve that is sigmoidal in shape and has a long intermediate linear section. The next step is to plot the negative of the slope of the relaxation curve to give a plateau shaped curve which is considered to represent the distribution of relaxation times of viscoelastic elements in dough and is therefore called the distribution function or the relaxation time spectrum. Figure 4, from the work of Cunningham, Hlynka, and Anderson (6), illustrates the stress relaxation curve for dough, and the corresponding distribution function. The relaxation time spectrum is used in a more detailed examination of fundamental properties of dough in terms of the generalized Maxwell model (Figure 2).

Another fundamental approach to dough rheology has been made by Joslin and Van Wazer using an instrument called a resonance elastometer (78). This elastometer consists essentially of a

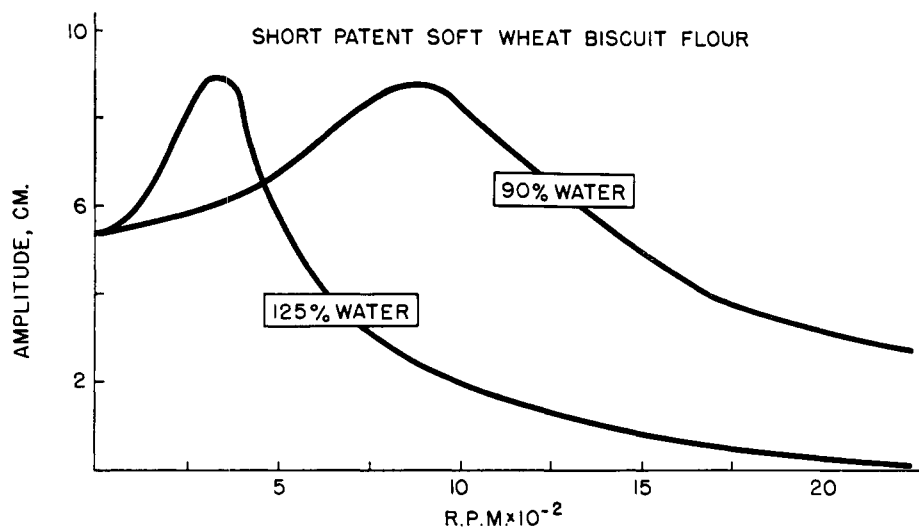


Figure 5. Curve obtained with the resonance elastometer showing response of batter to an oscillating strain (16)

swinging bob suspended in a sample held in a cup set to oscillate at varying frequency. In a viscoelastic medium the bob has a characteristic vibration frequency dependent on the elastic property of the medium and the inertia of the bob. If the oscillation of the cup and the characteristic frequency are the same, the amplitude of oscillation sharply increases, and provides a measure of the material under test.

While the dynamic method has been widely used in the study of other polymer systems, only illustrative data on dough are available. Figure 5 is reproduced from Joslin's work (78).

Analytical Research

The rheological properties of dough can be readily modified by common improving agents when these are incorporated in small amounts in dough. The chemical changes in dough brought about by these improvers can be followed by analytical chemical techniques, thus forming an important bridge between rheological and analytical methods.

The rheological approach suggests that improvers play the role of cross-linking agents in dough. Analytical techniques have acquired a more definite aim by identifying the functional groups in dough and their chemical reactions with different improvers, and thus, the cross linkages in dough.

The sulfhydryl-disulfide reaction has been proposed as the main result of improver action in dough but more evidence is required to evaluate its significance. The relation of this simpler reaction to the more recent findings on the disulfide interchange reaction (3) must be carefully examined. An appraisal of the work on improvers in this laboratory suggests that several reactions may be involved in the changes in

dough properties brought about by different improvers. Other work points to a significant role of inorganic cations, and of the weaker secondary forces in determining the physical properties of dough.

Newer analytical techniques aimed at establishing the role of the main functional groups in dough should add considerably to our knowledge of dough structure. The increased precision of the amperometric method of bromate and iodate determination (4) will make it possible to re-examine the fate of these improvers when they are added to dough. The polarographic determination of sulfhydryl groups in ammoniacal cobalt solutions has been recently applied by Hintzer (75, 76) to the study of the oxidation reduction systems of wheat proteins. Kolthoff, Stricks, and Morren (73) have provided yet another useful technique in which proteins dispersed in urea solutions are titrated amperometrically with mercuric chloride for their sulfhydryl content. Recently a variant of this method has been applied to wheat proteins (77). The use of proteases provides a means of studying the influence of chain length on the physical properties of dough.

General Conclusions

Rheological techniques, baking tests, and analytical research can effectively supplement one another in the integration of knowledge of dough chemistry. The results of analytical research are the most specific of the three techniques, as they refer to definite chemical reactions or mechanisms. However, in a system as complex as dough it is an extremely difficult task to isolate a single reaction. The baking test is the most inclusive of all reactions that take place, but it is the least specific. The rheological approach

is the next most inclusive and can be readily combined with the study of specific chemical reagents.

Contradictory data obtained by different methods may be found in the literature (10). A logical way of harmonizing these differences is to consider that a large number of reactions is involved, and a given datum by one method may measure a reaction that is or is not important in the production of the optimum loaf. The same end result as judged by rheological properties of dough at the time of panning and by the production of baked loaf with optimum loaf characteristics, may be produced by several alternative and equivalent procedures (8). In the last analysis, however, an adequate hypothesis of dough structure should be consistent with experimental data, whether they are obtained on top patent, clear, or other type of flour, or from baking tests, rheological measurements, or chemical analyses. It is the long range task of cereal chemistry to provide such a hypothesis of dough structure and to verify it experimentally.

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