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MEASUREMENT OF THE FUNDAMENTAL RHEOLOGICAL PROPERTIES OF WHEAT-FLOUR DOUGHS

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ABSTRACT

Measurement of fundamental rheological properties requires that the results be free from instrumental factors and independent of sample size and shape. For a nonlinear viscoelastic material, such as dough, these conditions have been satisfied by a limited number of instruments. In this paper the instruments suited to fundamental measurements on wheat-flour doughs are described. The results of creep and creep recovery, stress relaxation, stress-strain, and dynamic measurements using these instruments are summarized. Emphasis is placed on the strain dependence of the rheological properties and it is suggested that progress in fundamental dough rheology may depend on the determination of the interrelations between the strain-dependent rheological functions.

INTRODUCTION

The rheological properties of wheat-flour doughs depend on the composition and on the physical properties of the constituents. Although much of the fundamental research on cereals has been concerned with the functional properties of the components of the flour (1), the relations between the rheological properties of dough and its chemical and physical structure are only understood in general qualitative terms (2,3).

Most of the rheological measurements that have been made on dough have been concerned with testing procedures for assessing various aspects of the baking quality of flour. Many instruments have been devised to obtain objective data about the mechanical behavior of dough in order to predict its performance in the bakery (2,4). Although these instruments are empirical and do not measure rheological parameters, some of them have proved most useful when it has been possible to establish a correlation between the objective measurements and the quality of the baked products.

The aims of basic rheological research into the properties of dough are to provide a) a complete quantitative description of mechanical behavior, b) relations between rheological parameters and structure and composition, and c) relations between rheological parameters and performance in the commercial bakery. All these objectives must be achieved before the baking quality of a particular flour can be fully explained.

The experimental part of a fundamental study of rheological behavior is a determination of the basic relations between stress, strain, and time for particular loading patterns. Only when these relations are determined and understood is it possible to predict mechanical behavior for other, generally more complicated, conditions. Only when the measured rheological properties are independent of instrumental artifacts is it possible to deduce the relations between the mechanical properties and the chemical and physical structure (5).

In this review we shall describe those instruments which can be used to measure the relations between stress, strain, and time for particular stress or strain patterns applied to dough and discuss the basic rheological properties of dough as measured by such instruments. First, however, it is necessary to describe some of the rheological phenomena involved in the measurement and specification of the mechanical properties of a material as complex as dough.

Rheological Behavior of Dough

Materials can be classified rheologically according to their behavior. The simplest materials are the ideal elastic solid, for which the stress is always proportional to the strain (Hookean), and the perfect viscous liquid, for which the stress is always proportional to the rate of strain (Newtonian). The mechanical properties of such materials are defined by the constant of proportionality. For the elastic solid this is the modulus of elasticity (stress/strain), and for the viscous liquid the viscosity (stress/rate of strain). These two special cases are the simplest examples of *linear* rheological behavior, as the modulus and the viscosity are independent of the stress.

Most materials do not behave in either of these two ideal ways and there are two important types of deviation. First, the ratio of the stress to the strain (apparent modulus) or the ratio of the stress to the rate of strain (apparent viscosity) may be a function of the stress. Such materials are called *nonlinear*. Second, the stress may not depend on the strain or the rate of strain alone but may be a function of both the strain and the rate of strain. In general, the stress is a function of the strain and strain history. Such materials combine the properties of both solids and liquids and are called *viscoelastic*.

Both types of deviation from simple ideal behavior may coexist. If only the second type is present, the material shows *linear viscoelasticity* and for a given loading pattern the ratio stress:strain is a function of the time alone. When both types of deviation are present, the ratio stress:strain is a function of the stress or strain as well as time and the material shows *nonlinear viscoelasticity*. Although approximately linear behavior can be achieved for most viscoelastic materials by keeping the stresses sufficiently small, the properties measured determine only part of the mechanical behavior and must not be used to predict the behavior at larger stresses.

The mechanical properties of dough show both kinds of deviation from ideal behavior. Dough is thus classified as a nonlinear viscoelastic material.

Characterization of Rheological Properties

In the study of viscoelastic behavior, the relations between the stress, strain, and time must be determined for a particular type of deformation and a particular loading pattern (stress history). For linear viscoelastic materials, this reduces to determining the time dependence of the modulus (stress/strain), or the compliance (strain/stress), for the chosen loading pattern.

Rheological properties are determined from measurements of the changes in the external dimensions of a sample, with a certain well-defined shape, and the corresponding external forces. These must be related to the internal states of stress and strain before the rheological parameters can be calculated. The calculations are relatively simple for regular geometric shapes when the mechanical properties are independent of the strain. For linear materials, the form factor relating the ratio force:displacement to the ratio stress:strain (modulus) for various sample sizes and shapes have been summarized by Ferry (6). However, these simple form factors are not valid when the moduli depend on the strain except in those special cases where the strain—and hence the material properties—are uniform throughout the sample (i.e., homogeneous).

For measurements on nonlinear materials for which the rheological properties depend on the strain, it is desirable to use one of the sample geometries which ensures homogeneous strain. If the strain is inhomogeneous it is not possible to calculate the strain distribution throughout the sample unless the dependence of the rheological properties on strain is already known. The special geometries and deformations which give homogeneous strain, and are, therefore, suited to measurements on nonlinear materials, are discussed in detail below.

Although in theory it is possible to determine the relations between stress, strain, and time in order to characterize the rheological properties of dough from the response to any loading pattern, in practice, only a small number of simple loading patterns are used. The common transient loading patterns are: *i*) *Creep*, in which a stress is applied suddenly and then maintained constant while the resulting strain is measured as a function of time; *ii*) *Stress relaxation*, in which the sample is suddenly brought to a chosen deformation and the stress required to maintain this deformation is measured as a function of time; *iii*) *Deformation with constant rate of strain*, in which the stress required to maintain a constant rate of deformation is measured as a function of time; and *iv*) *Deformation with constant rate of stress loading*, in which the stress is increased at a constant rate and the strain is measured as a function of time. For deformation with either constant rate of strain or constant rate of stress loading, the analysis of the data is very difficult for nonlinear materials because stress- and time-dependent deviations from simple behavior are combined.

These transient loading patterns are of limited value for studying responses at short times as inertial effects and instrument-response time prevent an instantaneous application of stress or strain. For measurements corresponding to short times, a periodic or *dynamic loading pattern* is more suitable. The usual dynamic loading pattern is a sinusoidal stress or strain of fixed frequency and the corresponding strain or stress is measured.

In principle, the behavior of a linear viscoelastic material can be determined from a knowledge of any one of the rheological functions derived from a transient or periodic loading pattern covering a sufficient range of time or a sufficiently wide range of frequency. The response to all other loading patterns can then be calculated (7,8,9). The interconversion of the various viscoelastic functions depends on the Boltzmann superposition principle (6,9), i.e., the total strain in response to any combination of stresses is the sum of the strains in response to the individual stresses. This only applies for linear materials.

The determination of the rheological behavior of a nonlinear viscoelastic material requires considerably more experimental data than is required for a linear viscoelastic material. The viscoelastic functions specifying the response to a particular loading pattern must be measured for various amplitudes of the loading pattern.

INSTRUMENTS

The preferred sample shapes and modes of deformation for measurements on nonlinear viscoelastic materials are those which ensure homogeneous stress and strain. With other sample geometries the material properties vary through the sample and the distribution of strain cannot be calculated unless the dependence of the properties on the strain is known or assumed. There are also restrictions on the possible shapes and sizes of samples because dough is a soft material which cannot maintain a free shape and must be supported. Furthermore, it is necessary to keep the exposed surface area small to facilitate temperature control and to limit skin formation by evaporation. The ease of filling the sample cell and the stresses induced during filling must also be considered.

The only sample geometries which meet exactly the requirement of homogeneous strain are pure or simple shear between parallel plates and simple extension. The requirement can also be met approximately in a sample constrained between a cone-and-plate (or cone-and-cone) with rotational deformation or between coaxial cylinders with either longitudinal or rotational deformation. The instruments that have been used for measurements on doughs, using each of these geometries, are described in this section.

Parallel Plates

The deformation of a sample constrained between parallel plates in simple shear is shown in Fig. 1. The deformation of the sample can be regarded as arising from the shear of infinitely thin layers of the sample along planes parallel to the plates. The spacing between the plates is constant and there is no change in volume of the sample. In pure shear the spacing between the plates varies to give shear without the rotation of the principal axes of strain involved in simple shear. Pure shear is suited to measurements on solids which are sufficiently rigid to maintain their shape without support. For soft solids, such as dough, simple shear can be used but the sample cell must be designed to ensure that the plates remain parallel with constant separation during the deformation.

The shear stress is given by the tangential force, F, applied to the plate divided by the area, A, of the plate. The strain is the displacement, d, of the plate divided by the thickness, h, of the sample. Viz:-

$$\text{stress} = F/A \quad ; \quad \text{strain} = d/h$$

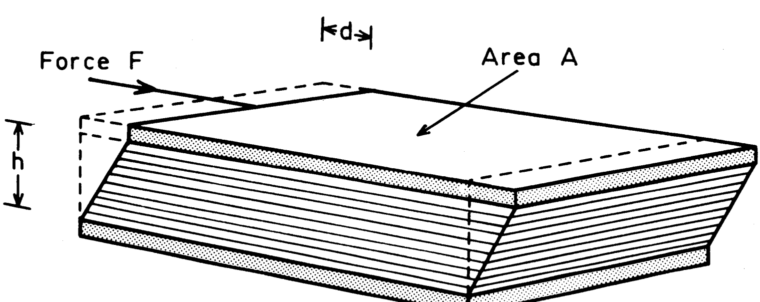

Fig. 1. Sample in simple shear between parallel plates. Stress = F/A ; strain = d/h.

Nikolaev and Beganskaya (10) have described a rheometer, shown diagrammatically in Fig. 2, which employs parallel plate geometry. The cell system is mounted on a platform, D, one end of which is attached by a hinge, E, to a support, F, mounted on the base, G. The free end of the platform rests on a support, H, which may be raised to hold the platform at an angle between 0° and 25° to the horizontal. The angle of inclination is measured directly on the adjacent scale, I.

The platform contains an opening of cross section 40 × 40 mm into which the plate, C, can be positioned by a rod, J, to form a well 5 mm deep. With the platform horizontal, the well is filled with dough, the excess removed and the sample covered with the light rectangular plate, B, of known mass. Additional masses, K, may be secured to the plate, B. The bottom plate, C, is then raised until it is flush with the top of the platform (as illustrated) exposing the paralleliped of dough, A. A mechanical lever, L, is brought into contact with the shearing plate, B, and is used to give a measure of the tangential displacement on the scale, M.

The dough is allowed to rest for the necessary period and then sheared by tilting the platform to the desired angle. The shearing force is the resolved component of the mass of the plate, B, and the additional masses, K, in the tangential direction. The mass of the dough sample has not been considered. The tangential displacement of the plate, B, is observed as a function of time. Recovery may also be observed after returning the platform to the horizontal.

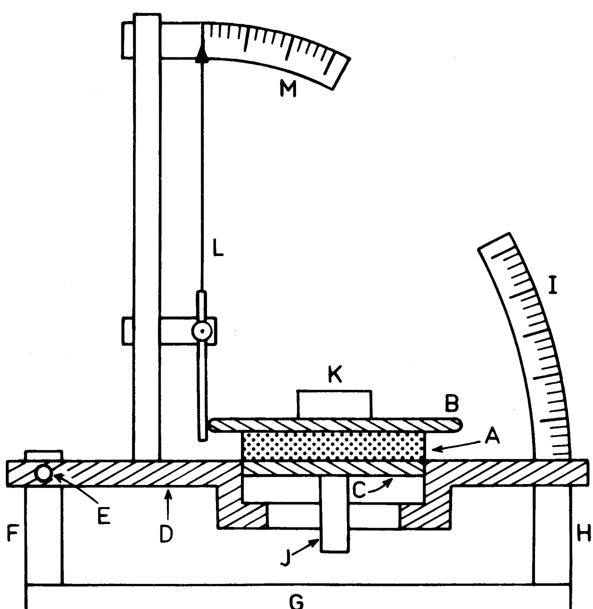

Fig. 2. Schematic diagram of shear plate apparatus used by Nikolaev and Beganskaya (10). **A**, sample; **B**, shear plate; **C**, lower plate; **D**, platform; **E**, hinge; **F**, support; **G**, base; **H**, adjustable support; **I**, scale to measure angle of inclination; **J**, rod to raise sample; **K**, added mass; **L**, mechanical lever; **M**, scale to measure displacement of shear plate.

In this method the dough must support the loaded shearing plate and the effects of the stress component normal to the plate have been ignored. The method is clearly unsuitable for soft doughs which cannot support the load without significant deformation normal to the shearing plate. For the same reason this method can only be used for low shearing stresses. The deformation is neither simple nor pure shear and the actual deformation is not determined as the change in spacing of the plates is not measured. There is no method of ensuring that the plates remain parallel during shearing.

An instrument employing a linear air-bearing has been used by Hibberd and Parker (11) to deform dough in simple shear between parallel plates. The sample cell is shown in perspective in Fig. 3a and a side elevation of the instrument is shown in Fig. 3b. The sample, A, is held between the two plates, B and C. The upper plate, B, is fixed to a hollow block, D, supported by the rigid superstructure, E. The lower plate, C, is attached to a length of aluminum Y-section extrusion, F, which is constrained to move only in a straight line at a fixed height by a linear air-track, G, made from a triangular-section aluminum extrusion. The temperature of the sample is controlled by circulating water through the block, D, and by controlling the temperature of the air supplied to the air bearing.

Filling the sample cell with dough is relatively easy as the plates can be separated and brought together again after placing a surplus of dough on one of the plates. Some flow of dough occurs during the expulsion of the surplus but the stresses involved need not be excessive unless the gap between the plates is very small. Surplus dough is trimmed off at the edges with a sharp knife. The exposed surface is immediately coated with a soft petroleum jelly or hydrocarbon oil to minimize evaporation. The exposed surface area depends on the separation and size of the plates. With most configurations the spacing between the plates is small compared with the other dimensions and the ratio of exposed area to sample volume is relatively low.

The displacement of the plate, C, is recorded with a linear variable differential transformer, H, by measuring the displacement from a reference position of a ferromagnetic core, I, attached to the movable assembly. The shearing forces can be applied by a simple electromechanical transducer (12). The coil, J, attached to the movable assembly, is in the field of a cylindrical permanent magnet, K. The loading pattern is obtained by passing a current with the required time dependence through the coil. (Alternatively, steady forces may be applied by a thread passing over the pulley, L, to a freely hanging load, M.)

When using the electromechanical transducer the only resistances to the movement of the lower plate, other than from the sample, come from the fine coiled wires providing the electrical connections to the coil and the friction from the air track. The frictional forces of the air bearing are extremely low and it has been possible to make creep measurements down to very low stresses (1.5 N/m^2).

This instrument has been used to measure creep and creep recovery for a range of stresses between 1.5 and 126 N/m^2 (11). It may also be used for stress relaxation measurements at various strains and for dynamic measurements at various strain amplitudes.

Extension

Simple extension of a sample of uniform cross section produces uniform stress and strain throughout the sample. This type of deformation is shown diagrammatically in Fig. 4. The deformation is the increase in length, ΔL, and the strain is the increase in length divided by the original length, L. The stress is the stretching force, F, divided by the cross-sectional area, A, viz:-

$$\text{stress} = F/A \quad ; \quad \text{strain} = \Delta L/L$$

The corresponding lateral contraction, which gives a reduction in the cross-sectional area as stretching proceeds, is not shown.

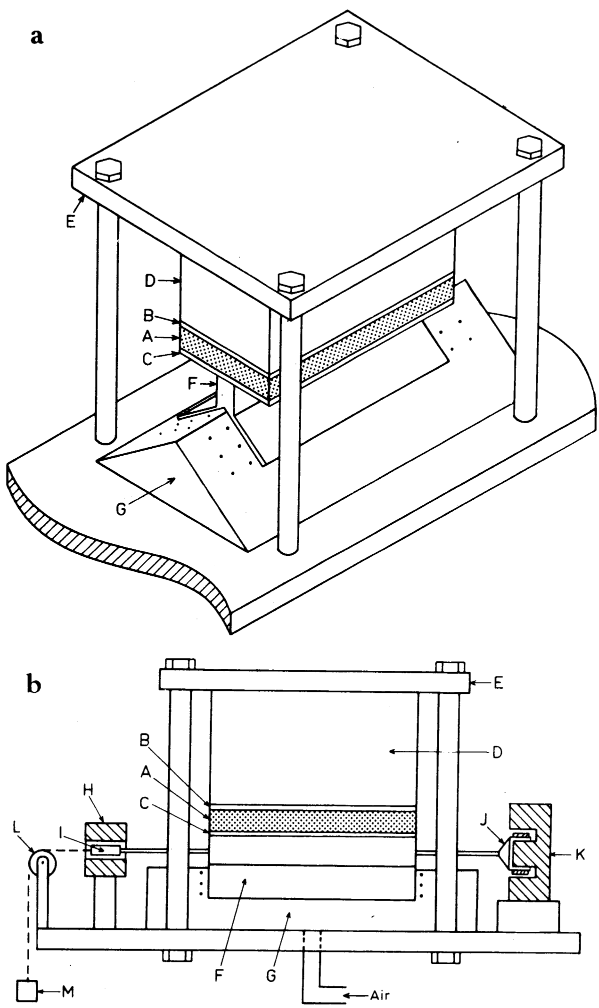

Fig. 3. Apparatus to measure dough properties in simple shear (11); (**a**) perspective, (**b**) side elevation. **A**, sample; **B**, fixed plate; **C**, movable plate; **D**, hollow block; **E**, rigid frame; **F**, sliding Y-section; **G**, air track; **H**, differential transformer; **I**, ferromagnetic core; **J**, coil; **K**, permanent magnet; **L**, pulley; **M**, load.

A number of extensometers have been used to make mechanical measurements on freely suspended samples of dough. However, the strain is not uniform under these conditions because of the contribution to the stress of the dough's own mass. Simple uniaxial stretching is effectively achieved for dough in the mercury-bath extensometers where the sample is floated on a bath of mercury and the extension is in a horizontal direction. These instruments are based on the original design of Schofield and Scott Blair (13).

A typical instrument (14) is shown diagrammatically in Fig. 5. The dough sample, A, floats on the mercury bath, B. One end of the sample is attached by the "cuff," C, to a threaded rod, E, which can be used to move the sample longitudinally by rotating the wheel, F. The other "cuff," D, is attached to a thin rubber strand, G, which is in turn connected to the nut, H. The rubber strand can be stretched by rotating the wheel, I, which pulls the nut, H, along the threaded rod, J. The position of the nut is shown by a pointer against the scale, K. Two traveling microscopes, L and M, are focused on the cuffs permitting measurements of the length of the sample. The extension of the rubber strand, which must be calibrated, is used to measure the stress.

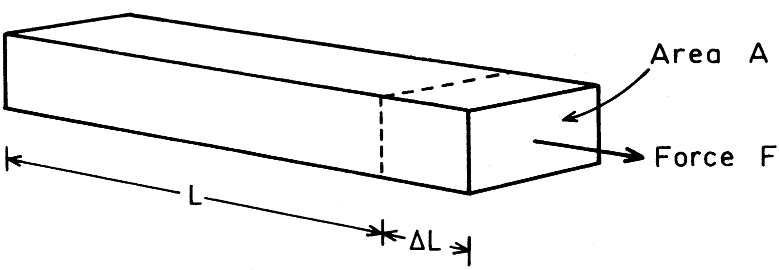

Fig. 4. Sample in simple extension. Stress = F/A; strain =ΔL/L (corresponding lateral contraction not shown).

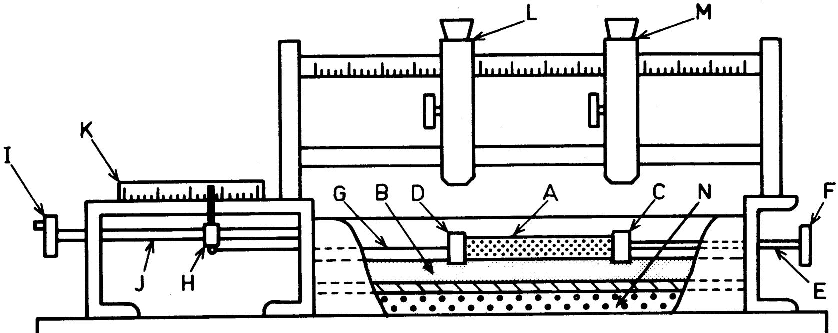

Fig. 5. Schematic diagram of mercury bath extensimeter (14). **A**, sample; **B**, mercury bath; **C** and **D**, "cuffs"; **E**, threaded rod; **F**, wheel; **G**, rubber strand; **H**, nut; **I**, wheel; **J**, threaded rod; **K**, scale; **I** and **M**, traveling microscopes; **N**, thermostated water.

The sample is usually a cylinder of dough formed either by moulding or extrusion. The dough must be stiff enough for the sample to maintain its cross-section against gravitational forces. The stresses induced in preparing the sample must be allowed to relax before measurements are commenced. The exposed surface of the sample is large so there are problems in both temperature control and possible drying of the sample. The sample is usually coated with olive oil or glycerol and held in a temperature- and humidity-controlled enclosure.

The "cuffs" or "collars" attached to the ends of the sample restrict the contraction in cross-section associated with the longitudinal extension. The strain is, therefore, not uniform along the whole length of the sample and measurement should be restricted to the central part where the strain is uniform.

There have been many modifications of this basic instrument. It has been used to measure "instantaneous" elasticity, deformation-time relations at constant load, stress relaxation, stress-deformation relations at constant rate of stress, and creep at constant stress. The modifications for constant tension, constant stress, and constant rate of strain measurements have been described by Lerchenthal and Funt (15), and those for stress relaxation measurements by Shelef and Bousso (16).

An approximation to uniform strain has been achieved by Tschoegl *et al.* (17) by stretching dough rings immersed in a liquid of matching density. The instrument used to stretch the dough rings is shown diagrammatically in Fig. 6. A dough ring, A, is prepared with a special cutter from a sheet of dough and stretched between a fixed support, B, and a movable support, C, which can be pulled at constant speed by the crosshead, D, the wire, E, and the pulley, F. The wire is pulled by the geared motor, G, so that the rate of stretching can be varied. The strain was determined from the observed separation of marks on the dough ring. It was found that the strain could be calculated from the crosshead displacement using an effective circumference obtained by multiplying the average-initial circumference by a correction factor. The tension is measured electrically as a function of time for a given crosshead speed using a load cell, H.

This method of stretching dough rings immersed in a fluid of matching density has also been used to measure creep, and creep recovery (18). The load was applied to the lower support, C, and the strain measured by cathetometer readings of the heights of marks on the dough ring.

Force-extension measurements on dough rings immersed in a buoying liquid of matching density have also been made using an Instron universal testing machine (19), and do not differ, in principle, from those described above.

Attempts have been made to derive stress-strain curves from load-extension curves obtained on the Brabender Extensograph (20). The Brabender Extensograph (2) is a commercial instrument in which the sample is stretched into an elongated "vee" by a hook traveling down at constant speed. The sample is not supported along its length and the mass of dough below any point contributes to the stress at that point. The stress and strain are not homogeneous and the cross-sectional area of the sample varies because of the nonuniform strain. It is clear from the spacing, after stretching, of initially equidistant marks on the sample (20) that there is a wide range of strains in the stretched sample. The method used to estimate the stress gives only an average stress; half the effective dough mass is added to the force applied by the hook and this tension is divided by the average cross-section. The estimate of the strain from the displacement of the hook also gives only an average value. The Brabender Extensograph does not determine tensile properties at known strains and is, therefore, not suited to the determination of fundamental properties of nonlinear materials.

The strain is not uniform in the relaxometers (21,22) developed for the continuous measurement of relaxation. In these instruments a ball of dough is impaled on a split pin. The dough is stretched by pulling apart the two halves of the pin. The deformation is similar to the stretching of dough rings but the sample is not reproducibly defined. The strain may be fairly uniform over a large part of the sample. The results of Shelef and Bousso indicate that the relaxation processes in dough may be relatively independent of the initial strain in which case a small range of strains could be tolerated. However, the method does not ensure homogeneous strain and the relaxation is not measured as a function of a known initial strain.

The "structural relaxation" measurements, based originally (23) on measurements made on a Brabender Extensograph, are quite different from

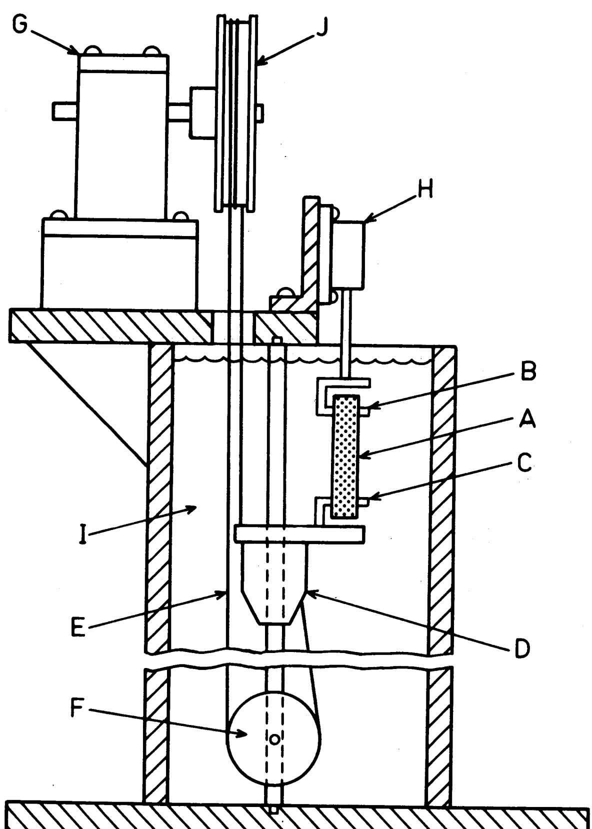

Fig. 6. Schematic diagram of apparatus to test dough rings at constant extension rate (17). **A**, dough ring; **B**, fixed support; **C**, movable support; **D**, cross head; **E**, wire; **F**, pulley; **G**, geared motor; **H**, load cell; **I**, buoying liquid; **J**, driving pulley.

stress-relaxation measurements. Stress relaxation is the decrease in the stress required to maintain a constant strain. In structural relaxation the stress is measured at one point in the stretching process for samples which have been allowed various rest periods. It does not, therefore, attempt to measure rheological properties of the dough but determines the rate of change in dough properties after structural activation.

Cone-and-Plate (Cone-and-Cone)

With the cone-and-plate geometry, the sample is constrained between a cone and a plate with the axis of the cone perpendicular to the plane of the plate and the apex of the cone on the surface of the plate, as shown in section in Fig. 7a. Measurements are made by rotating either the cone or the plate about the axis of the cone. Provided the angle, θ, between the surface of the cone and the plate is small, the strain is approximately uniform and is proportional to the angle of rotation, Ω, and the stress is proportional to the torque, M, on the rotating element:-

$$\text{stress} = 3M/(2\pi R^3) \quad ; \quad \text{strain} = \Omega/\theta$$

where R is the radius of the sample cell.

With the cone-and-plate geometry the sample is thin, especially near the center where in theory the cone and plate touch, and this involves severe deformation when filling the cell with the sample. A common practice is to truncate the cone as shown in Fig. 7b. Under the flat surface of the truncated cone, the shear strain is

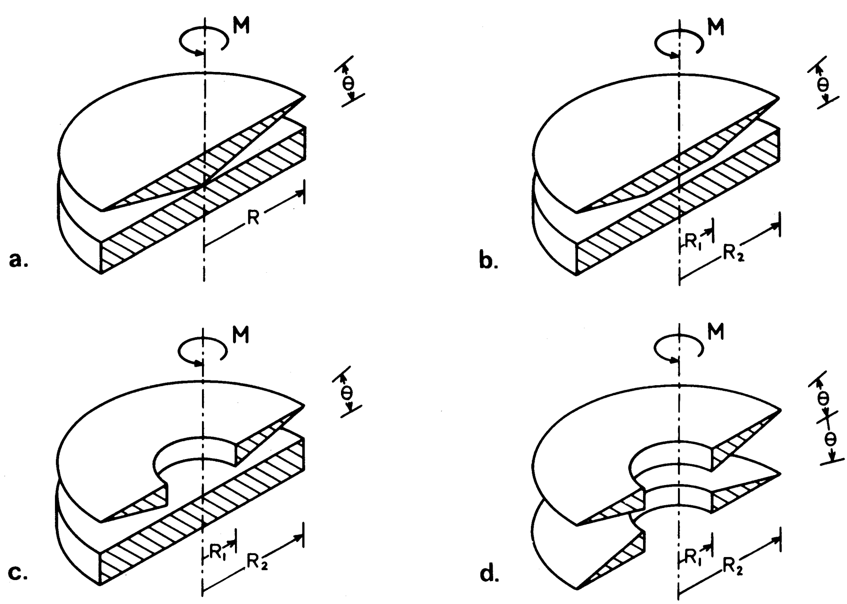

Fig. 7. Schematic representation of various cone-and-plate and cone-and-cone geometries; (**a**) cone-and-plate, (**b**) truncated cone-and-plate, (**c**) annular cone-and-plate, and (**d**) annular cone-and-cone.

less than that between the cone and the plate:

At radius r,

$$\text{strain} = r\Omega/(R_1\theta);\ 0 \leqslant r \leqslant R_1$$

$$\text{strain} = \Omega/\theta \quad ;\ R_1 \leqslant r \leqslant R_2$$

where R_1 is radius of truncated portion and R_2 outer radius of the sample cell. Consequently, the stress is also nonuniform and the stress distribution can only be calculated from the torque for linear materials. The analysis for the truncated cone is given by Markovitz *et al.* (24) for linear materials. The deviations from uniform strain occur near the axis where the contribution to the torque is small because both the radius at which the shear force acts and the area involved are relatively small.

As an alternative to truncation of the cone, the central region can be removed entirely. Homogeneity of stress and strain is achieved by using annular rings (Fig. 7c). For this geometry:-

$$\text{stress} = 3M/[2\pi(R_2^3 - R_1^3)] \quad ; \quad \text{strain} = \Omega/\theta$$

where R_1 and R_2 are the inner and outer radii, respectively.

The plate can be replaced by another cone in which case the apexes of the cones must be coincident and the axes common (cone-and-cone geometry). This geometry, with annular conical surfaces (Fig. 7d), has been used for the study of wheat-flour doughs by Gorazdovskii (25). The stress and strain are given by:

$$\text{stress} = 3M/[2\pi(R_2^3 - R_1^3)] \quad ; \quad \text{strain} = \Omega/(2\theta)$$

where 2θ is the angle between the conical surfaces.

In both cone-and-cone and cone-and-plate geometries, it is necessary that the angle θ be small to ensure that the assumption of homogeneous strain is valid. An advantage of the double-cone geometry is that the sample size is doubled for the same angle θ with a concomitant reduction in stresses induced during the filling of the sample cell.

The strain is effectively homogeneous only if the apexes (real or projected) of the cones are coincident (cone-and-cone) or the apex of the cone coincides with the surface of the plate (cone-and-plate). The adjustment of the relative heights of the two surfaces is critical. The errors arising from incorrect relative heights or from misalignment of the axes can be calculated for linear materials (24). These calculations cannot be applied for measurements on nonlinear materials because the strain and hence the material properties vary.

Temperature control is relatively easy because the sample is thin and the temperature can be controlled by circulating water through the fixed plate (or cone). The ratio of the free surface area to sample volume is relatively high and precautions to avoid skin formation are important. Any skin will form at the outer radius where the contribution to the torque is most important.

The truncated cone-and-plate geometry has been used for measurements on doughs by Bloksma (26). The sample cell for one of the instruments used is shown in Fig. 8. The sample, A, is sheared between the plate, B, and the truncated cone, C. The plate can be raised or lowered and clamped in any desired position. The outer radius of the cone is 30 mm. and the angle between the surfaces of the cone and the plate is approximately 0.06 radians. The sample is small (3.5 cm^3) and is trimmed at the edge by lowering the circular knife, F. In this instrument, the axis of the cone is fixed by the ball bearing, E, and the torque applied by means of weights, cords, and pulleys. This sample cell was only useful for measurements at fairly high stresses because of friction in the bearing (equivalent to a stress of 40 N/m^2).

In a later instrument the truncated cone can rotate without the restraint of friction from the ball bearing. The cone, A, is attached to a "bow," B, that is supported by two vertical torsion wires, C and D (see Fig. 9). The support, E, for the plate, F, straddles the lower part of the bow and the lower torsion wire. The torque is applied by twisting the torsion wires and maintained by a servosystem activated by a differential transformer which detects relative rotation of the cone and the supports for the torsion wires. The rotation of the supports of the torsion wires required to maintain constant twist in the wires is used as the measure of the

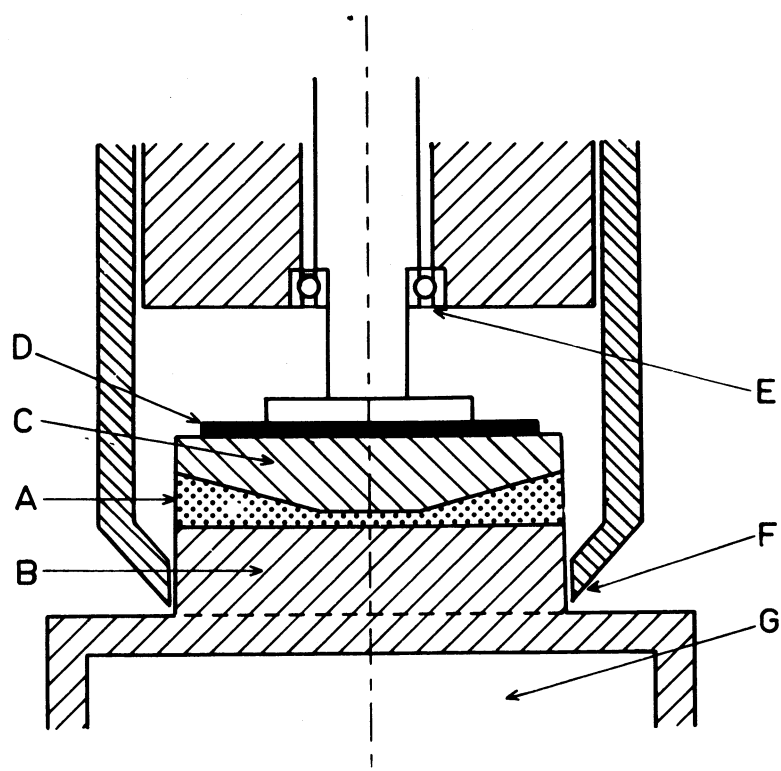

Fig. 8. Schematic diagram of truncated cone-and-plate sample cell (26). **A**, sample; **B**, plate; **C**, truncated cone; **D**, thermal insulation; **E**, ball bearing; **F**, circular knife; **G**, thermostated water.

rotation of the cone. In this instrument, the angle between the surfaces of the cone and the plate is approximately 0.15 radians and the sample volume 8.5 cm^3. Creep measurements were made with stresses as low as 14 N/m^2.

Measurements have been made on soft doughs using a commercial cone-and-plate viscometer (27). The viscometer used (Haake Rotovisko type BV) measures the torque required to maintain a constant rate of rotation. Measurements were made at rates of shear between 0.5 and 100 s^{-1}. This type of instrument measures only an apparent viscosity of soft doughs and cannot measure any of the elastic properties. With firm doughs there are problems in ensuring that the apex of the cone is effectively on the surface of the plate and that at high shear rates there is no slip between the dough and the surfaces of the cone and the plate.

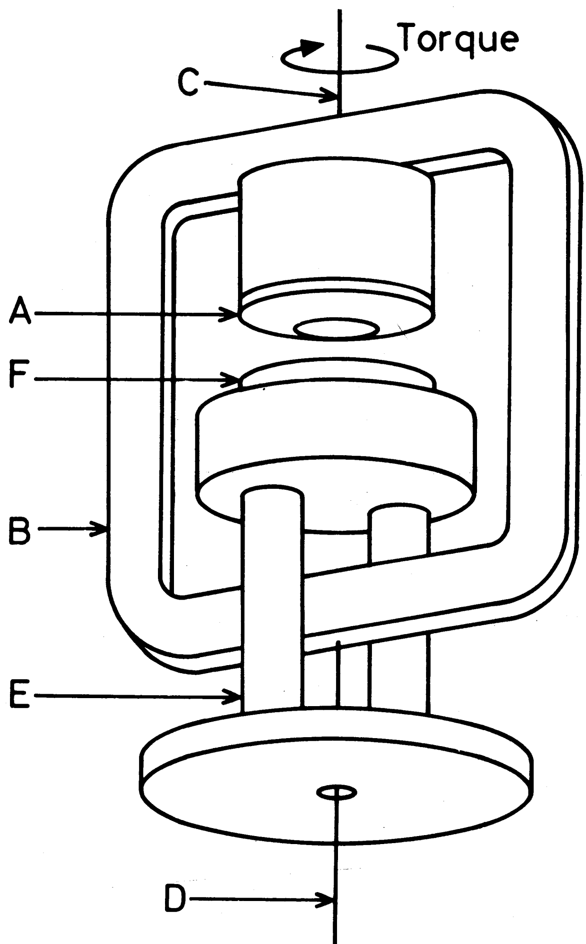

Fig. 9. Schematic diagram of cone-and-plate rheometer (26) (with cone and plate separated). **A**, truncated cone; **B**, "bow"; **C** and **D**, torsion wires; **E**, support for plate; **F**, plate.

Coaxial Cylinders

A sample sheared in the gap between coaxial cylinders is subjected to approximately uniform strain provided the gap between the cylinders is small compared with the radii of the cylinders. The shear may be produced by either axial (Fig. 10a), or rotational (Fig. 10b) relative movement of the cylinders. These two types of deformation were first used by Pochettino (28) and Couette (29), respectively.

For the Pochettino geometry, the variation of stress across the annulus is given as a function of the radius, r, by:

$$\text{stress} = F/(2\pi Lr)$$

where F is the axial force applied to the movable cylinder. For a linear viscoelastic material the strain is given in terms of the displacement, X, of the movable cylinder by:

$$\text{strain} = X/[r \cdot \ln(R_2/R_1)]$$

For the Couette geometry, the distribution of shear stress across the annulus is given by:-

$$\text{stress} = M/(2\pi Lr^2)$$

where M is the torque applied to the movable cylinder. For a linear viscoelastic material the strain is given in terms of the angular rotation, Ω, of the movable cylinder by:-

$$\text{strain} = 2\Omega/[r^2(1/R_1^2 - 1/R_2^2)]$$

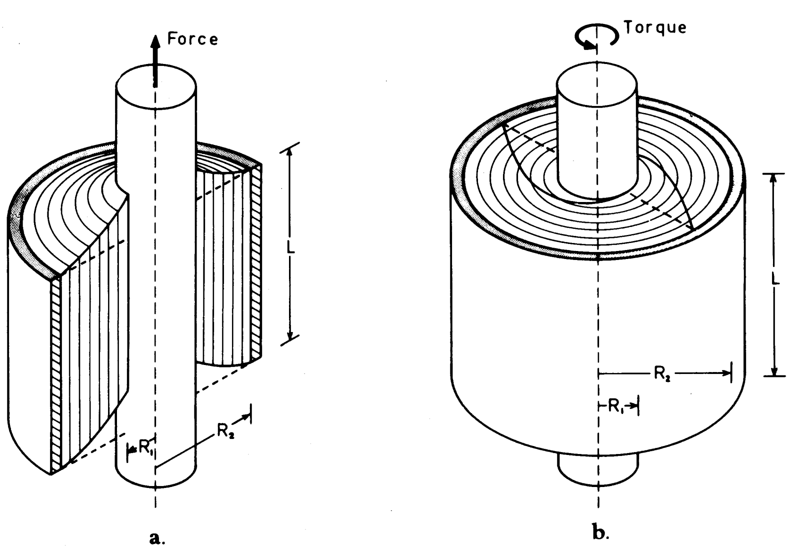

Fig. 10. Types of shear between coaxial cylinders with fixed outer cylinder: (**a**) axial or Pochettino deformation; (**b**) radial or Couette deformation. Displacement from initial position indicated by dashed lines to position indicated by continuous line is along direction of fine lines.

The ratios of the maximum to the minimum stresses (and hence for a linear material the ratios of the maximum to the minimum strains) with these two geometries are R_2/R_1 (Pochettino) and R_2^2/R_1^2 (Couette). Thus the range of strains is less in the Pochettino geometry than in the Couette geometry and axial deformation is, therefore, more suitable for measurements on nonlinear materials.

With very soft or fluid samples it is necessary to convert the outer cylinder to act as a cup to contain the sample. This introduces the complication of an end effect for rotational deformation. With axial deformation annular pumping is introduced and the strain no longer approximates to the desired homogeneity. With a stiff dough the ends can be left open as illustrated. The exposed surface is small when the required condition of a small gap is satisfied, hence skin formation is not a major problem. Temperature can be controlled by a jacket around the outer cylinder when this is the stationary cylinder. There is, however, difficulty in filling the sample into a narrow gap. If the gap is large enough to facilitate filling, the condition for approximately uniform strain is not satisfied. A split outer cylinder has been used to facilitate filling (12), but even with this cell it is not practical to load a typical dough into a gap of less than 2 mm in a cell of radius 14 mm (30). The variation of strain across a linear viscoelastic material sheared in a cell of these dimensions is more than 16% for Pochettino geometry and 36% for Couette geometry.

The dynamic moduli of dough have been determined by measuring the displacement in response to a sinusoidally varying axial stress applied to the central cylinder with a fixed outer cylinder (12, 31, 32, 33, 34). The sample cell is shown diagrammatically in Fig. 11. The sample, A, is constrained between a fixed outer cylinder, C, and a movable cylinder, B. This inner cylinder is supported by a pair of beryllium-copper discs, D and E, relieved by concentric slots to give little resistance to axial displacement while retaining high radial stiffness. The outer cylinder is split to facilitate filling with the sample; part of the sample is first introduced into the lower half of the outer cylinder, the inner rod is placed in position, further sample is placed above the rod, and finally the upper part of the outer cylinder positioned. Surplus sample is trimmed off and the exposed surface coated with a light grease to restrict evaporation. Severe stresses can be induced when filling the sample cell, particularly with a narrow annulus between the cylinders, and the sample must be allowed to relax before measurements are commenced.

The driving force is applied by a simple electromechanical transducer and the displacement measured by a differential transformer in the same way as described for the parallel plate instrument shown in Fig. 3. The apparent moduli can be calculated from the relative amplitudes and phases of the driving force and the displacement by using the cell form factor for a linear material. These apparent moduli depend on the size of the cell and the amplitude of the displacement. It is possible, though extremely complicated, to derive from these measurements material functions which describe the dependence of the material properties on the amplitude of the strain (35).

Couette geometry has been used to determine both dynamic (36,37) and creep (38) properties of doughs. In these instruments the outer cylinder is a cup and the end of the inner cylinder is tapered. No attempt to apply corrections for the end effects was reported for the creep measurements but an approximate correction, based on linear theory, was applied to one set of the dynamic measurements (37). The inner cylinders are supported by torsion wires and the torque is applied by twisting these wires. The rotation of the inner cylinders is measured by reflecting light from mirrors attached to the cylinders onto a scale or photographic paper.

RESULTS

Few of the studies of the mechanical properties of dough, as reported in the literature, have been made under conditions which ensured that the measurements were of rheological properties at known strains and strain histories. The results of even these few studies cannot be concisely summarized as they are often apparently contradictory and do not lead to a consensus as to even the qualitative behavior of dough. Differences in behavior between doughs are to be expected as the basic ingredient, flour, has a wide natural variability in quality and there is a variation in dough composition and the mixing procedures between laboratories.

The reported measurements which essentially satisfy the requirements to qualify as "fundamental" measurements are discussed below in four categories: creep and creep recovery; stress relaxation; stress-strain curves; and dynamic measurements.

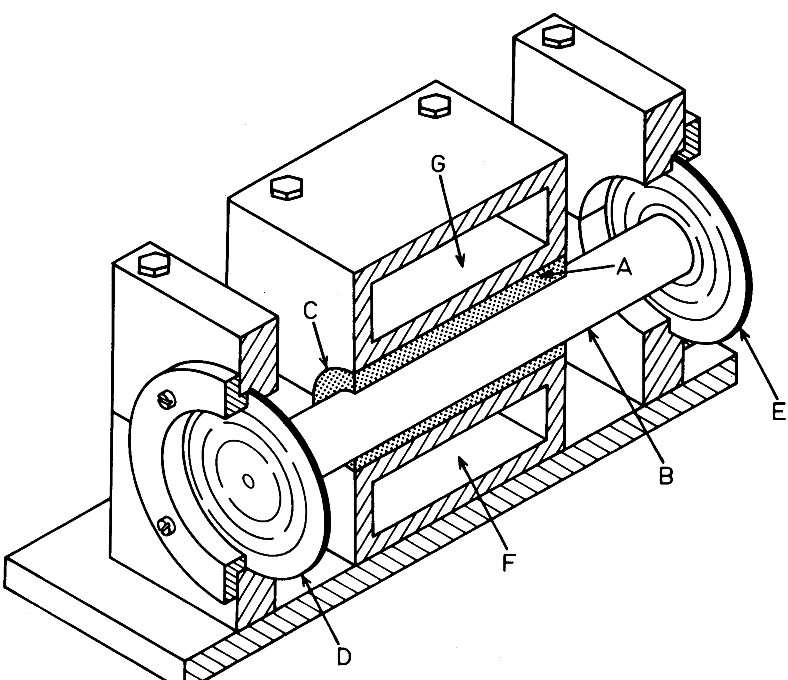

Fig. 11. Schematic diagram of sample cell for measuring dough properties in axial shear between coaxial cylinders (12). **A**, sample; **B**, movable rod; **C**, fixed outer cylinder; **D** and **E**, beryllium-copper discs; **F** and **G**, water jackets.

Creep and creep recovery measurements have been made on a variety of instruments with a range of stresses and for various loading times. Measurements were made with the mercury bath extensometer by Schofield and Scott Blair (13) and by Glucklich and Shelef (14), with the cone-and-plate instrument by Bloksma (26), with the shear plate apparatus by Nikolaev and Beganskaya (10), with the stretching of dough rings by Smith and Tschoegl (18), and in simple shear between parallel plates by Hibberd and Parker (11). All these measurements gave typical creep curves with the strain increasing with time while the load was applied and a time-dependent partial elastic recovery after the load was removed.

Only Smith and Tschoegl found a region of steady-state flow where the rate of increase of strain with time was constant. This was established after 25 to 30 min, which is longer than the time for which the load was applied in any of the other studies. All other published creep curves show the rate of increase of strain to fall with time except for those reported by Bloksma (39) which have an increasing strain rate after only 10 min for stresses over 80 N/m^2.

The evidence concerning the existence and extent of linear viscoelastic response is conflicting. The results of Glucklich and Shelef do not show any region of linear behavior though there is some evidence of an "instantaneous" elastic response which is proportional to the stress under certain limited conditions. However, Matsumoto *et al.* (40) found a large variation of "instantaneous elasticity" and other creep parameters with the stress. Smith and Tschoegl found the creep compliance to be independent of stress (i.e., the response to be linear), within experimental error, for stresses up to 328 N/m^2. In contrast, Bloksma (26) found large changes (by a factor of 10 or more) of the compliance with measurements over the stress range 20 to 500 N/m^2. However, the elastic recovery was proportional to the stress (i.e., the recovery could be described by a linear compliance). Hibberd and Parker made measurements at lower stresses (down to 1.5 N/m^2) and observed linear behavior for stresses up to about 40 N/m^2 and nonlinear behavior at higher stresses for both creep and creep recovery.

Bloksma interpreted some of his measurements at low stresses as indicating a yield value of about 15 N/m^2. However, the measurements of Hibberd and Parker at much lower stresses show no evidence of any yield value.

Stress relaxation measurements have been made with a mercury bath extensometer by Glucklich and Shelef (14) and by Shelef and Bousso (16). Although these results were interpreted as showing that the relaxation of stress at a fixed strain was incomplete even after a "long time," the measurements were restricted to 10 min. Furthermore, the stress-log time curves presented by Shelef and Bousso do not support this interpretation and indeed indicate that the stress could relax completely given sufficient time. The decay of stress is approximately proportional to the deformation, indicating approximately linear behavior for the few results presented. The decay is not a simple exponential and indicates a spectrum of relaxation times.

Extensive measurements of the relaxation of tension using the "relaxometer" have been reported by Hlynka and his co-workers (22,23,41). These results also indicate that the relaxation processes in stretched dough are not highly dependent on the initial strain. The tension does not decay as a simple exponential but can be represented by a linear relationship between tension and logarithm of time. The slopes of the tension-log (time) plots, which are some measure of the comparative rates of relaxation, varied by about 10% when the separation of the split pin was varied between 5 and 25 mm. The relationship between relaxation and initial strain cannot be fully investigated by this method as the strain is not homogeneous.

Stress-strain curves for doughs have been calculated by Tschoegl *et al.* (42) from measurements on dough rings stretched at a constant rate while immersed in a liquid of matching density. They found that, within the experimental range of time and rate of extension, the effects of time and strain could be separated for extensions of up to 90% and in some instances up to nearly 200%. The form of the strain-dependent function, viz., $(\ln\lambda)/\lambda$, where λ is the extension ratio, indicates that the true stress is proportional to the Hencky strain[1] at comparable states of relaxation. The time dependence could be characterized by an index, n, which is the slope of the straight line plot of log stress *vs.* log time at constant extension. This index, which lies between 0 and −1, appears to be some measure of the relative viscous and elastic behavior of the dough. These measurements were made at high rates of extension and over very short time periods compared with the measurements that have been made on creep and creep recovery.

Dynamic measurements have been made on doughs constrained between coaxial cylinders with rotational deformation by Shimizu *et al.* (36,37) and with axial deformations by Hibberd and Wallace (31), Hibberd (32,33) and by Smith *et al.* (34). In none of the instruments used was the gap between the cylinders small compared with the radii of the cylinders. The ratios were: 8.4 mm : 28.4 mm (36); 3.6 mm : 8.64 mm (31-33); and 3 mm : 8 mm (34). The strain cannot, therefore, be considered to be homogeneous for any of these measurements. Hibberd and Parker (30) used cylinders of various radii. Even with the smallest gap of 2 mm and an outer cylinder of radius 14 mm the variation of stress across the sample is still 16%.

The early measurements by Shimizu and Ichiba were made at a single stress amplitude. In the later measurements, over a range of strain amplitudes, the apparent moduli, calculated by applying linear viscoelastic theory, were shown to depend on the strain amplitude. Hibberd and Wallace (31) found that the apparent moduli did not change significantly with strain amplitude for strain amplitudes below 2.2×10^{-3} and the results presented by Hibberd (32,33) are for this "linear" region.

Although the apparent moduli, calculated by applying the linear viscoelastic theory, depend on the strain amplitude at large strain amplitudes, the deformation in response to a sinusoidal deforming force is itself sinusoidal over the range of the experimental conditions. Parker and Hibberd (35) interpret this as showing that, although the behavior is nonlinear and the dynamic moduli depend on the strain amplitude, in the "steady state" the effective modulus at each point in the sample does not vary with time but depends on the strain amplitude at that point. The sinusoidal deformation in response to a sinusoidal

[1]Various measures have been proposed for the strain at large deformations. All reduce to the Cauchy strain for infinitesimal deformations. For extension, the Cauchy strain is the ratio of the increase in length to the original length. The Hencky strain is given by the natural logarithm of the ratio of the stretched length to the original length. This is sometimes referred to as the "natural" or "logarithmic" measure of deformation. The various measures of strain are discussed by Reiner (43).

deforming force indicates that there is no recovery from the softening due to strain within a single cycle for the frequencies used. The linear viscoelastic theory cannot be applied to the sample as a whole but the sample can be considered as made up of a number of elements in each of which the strain and hence the dynamic moduli can be taken as uniform. An iterative numerical procedure can be applied to determine the strain dependence of the moduli required to match the experimental results. These strain-dependent functions were used to successfully predict experimental results with other cylinder sizes (35).

Smith *et al.* (34) found the response to a sinusoidal stress to be nonsinusoidal above a critical peak displacement. Below this critical displacement the dough is considered as a linear material even though the strain is not proportional to the stress. They suggested that the conditions at the critical peak displacement are related to a yield value.

Interpretation of Results

It is clear from the summary of the fundamental properties of doughs given above that there is no generally accepted method of presenting and interpreting the results. However, it is clear that the behavior of a dough cannot be characterized by one or two simple parameters. Thus, a viscosity, measured by steady-state creep at one particular stress, is only of use in predicting the behavior of dough in steady-state creep at that stress, and an "instantaneous" elastic modulus can only be used to calculate the corresponding "instantaneous" deformation. Neither of these measurements is adequate to characterize even a linear viscoelastic material.

Attempts to characterize dough behavior in terms of a single elastic modulus and a single viscosity also fail because dough does not behave as a simple Maxwell[2] or Voigt (Kelvin)[2] model. Models can be improved by adding more and more elements, i.e., with the addition of more and more parameters. The behavior of a linear viscoelastic material can be accurately represented by an infinite spectrum of Maxwell or Voigt elements (8). However, the main value of models is in providing a simple qualitative picture of the manner in which materials behave and this is only feasible for models containing a few elements.

Nonlinear viscoelastic behavior cannot be represented by a combination of linear elements. Nonlinearities can be introduced into models by St. Venant[2] elements and it has been suggested that the behavior of dough can be represented by an infinite array of units each made up of three Hookean springs, three viscous dashpots, and three St. Venant elements (44). Although mechanical models may be an aid to the interpretation of mechanical behavior in certain situations, the models suggested to represent dough behavior are either unnecessarily restrictive or too complex to assist in the understanding of the behavior of dough. Mechanical models are not necessary to the fundamental theory of nonlinear materials with fading memory.

Although there is no agreement from the published results as to the existence or extent of a linear region, the properties in the limiting case of infinitesimal deformations can be treated by the existing theory for linear viscoelastic materials. This theory has to be extended for the nonlinear region and for finite deformations by introducing functions depending on the strain. Some progress

[2]For a description of mechanical models and elements see, for example, reference (43).

has been made for dough by introducing functions which do not interact with the time-dependent behavior (35,42) (i.e., the strain function introduced is independent of time and the variables strain and time can be treated separately). The ranges of time and strain over which such theories can be applied have still to be determined and the interrelations between the strain dependent functions determined from the various types of rheological measurements have yet to be proved for dough.

FUTURE OF FUNDAMENTAL DOUGH RHEOLOGY

The mathematical theory of linear viscoelasticity is complete and can be used to model the behavior of some real materials and to solve some problems of practical interest. The application of the theory is limited by the requirements that the mechanical behavior of the real materials must be linear and that the strains are sufficiently small for the classical definitions of stress and strain to be adequate. In principle, the direct determination of material functions of linear-isotropic-viscoelastic materials is straightforward. The properties can be conveniently measured by certain simple types of deformation for which the three-dimensional constitutive equations reduce to a one-dimensional form.

The set of experiments required to determine completely the material properties of a nonlinear materials are more complicated (45,46). Some of the required experiments involve deformation and loads in more than one direction because of the nonlinear interaction between different load components. However, unidirectional experiments give much of the necessary information and are of direct interest for certain applications.

It is beyond the scope of this paper to outline a generalized theory of nonlinear viscoelasticity. The theoretical treatments have been summarized elsewhere (8,45). Ultimately the mechanical properties of dough will be understood in the context of such theories. In the immediate future progress will probably be made in determining interrelations between rheological functions measured at various strains with uniaxial deformation following the principles developed by Findley and his co-workers (46,47,48,49,50).

There is a need for measurements of the various viscoelastic functions (viz., creep and creep recovery compliance, stress relaxation modulus, stress-strain curves at constant rate of straining and at constant rate of stressing, and dynamic moduli) to be made on similar doughs prepared under identical conditions from the same raw materials. Samples can also be subjected to more complicated loading patterns, e.g., multiple-step creep, sawtooth waveforms, etc. All these measurements should be made with homogeneous strain throughout the sample. Analysis of such a set of results should indicate the extent to which the nonlinear viscoelastic theories can be applied to dough and which of the constitutive equations can represent the behavior of dough. It is clear that a complete understanding of the fundamental rheological behavior of dough is still remote.

Literature Cited

1. POMERANZ, Y. In: Wheat: Chemistry and technology, ed. by Y. Pomeranz (Rev.) Chap. 12, p. 585. Amer. Ass. Cereal Chem.: St. Paul, Minn. (1971).

2. BLOKSMA, A. H. In: Wheat: Chemistry and technology, ed. by Y. Pomeranz (Rev.) Chap. 11, p. 523. Amer. Ass. Cereal Chem.: St. Paul, Minn. (1971).
3. EWART, J. A. D. Recent research and dough visco-elasticity. Baker's Dig. *46*: 22 (1972).
4. SHUEY, W. C. Practical instruments for rheological measurements on wheat products. In: Proceedings of symposium: Rheology of wheat products. Cereal Chem. 52 (3,II) 42r (1975).
5. HIBBERD, G. E., and WALLACE, W. J. Requirements of modern dough rheology. Cereal Sci. Today *11*: 454 (1966).
6. FERRY, J. D. Viscoelastic properties of polymers. Wiley: New York, N.Y. (1961).
7. SCHWARZL, F. R., and STRUIK, L. C. E. Analysis of relaxation measurements. Advan. Mol. Relaxation Processes *1*: 201 (1967-68).
8. CHRISTENSEN, R. M. Theory of viscoelasticity. Academic Press: New York, N.Y. (1971).
9. LEADERMAN, H. Viscoelasticity phenomena in amorphous high polymeric systems. In: Rheology: Theory and applications, ed. by F. R. Eirich, Vol. 2, p. 1-61. Academic Press: New York, N.Y. (1958).
10. NIKOLAEV, B. A., and BEGANSKAYA, L. S. Alteration of the structural-mechanical properties of bread dough by mechanical treatment. Kolloidn. Zh. *16*: 455-463; Colloid J. USSR. English Transl. *16*: 433-439 (1954).
11. HIBBERD, G. E., and PARKER, N. S. Parallel plate rheometer for measuring the viscoelastic properties of wheat flour doughs. Cereal Chem. (to be published).
12. HIBBERD, G. E., WALLACE, W. J., and WYATT, K. A. A rheometer for measuring the dynamic mechanical properties of soft solids. J. Sci. Instrum. *43*: 84 (1966).
13. SCHOFIELD, R. K., and SCOTT BLAIR, G. W. The relationship between viscosity, elasticity and plastic strength of a soft material as illustrated by some mechanical properties of flour dough. III. Proc. Royal Soc., Ser. A (London) *141*: 72 (1933).
14. GLUCKLICH, J., and SHELEF, L. An investigation into the rheological properties of flour dough. Studies in shear and compression. Cereal Chem. *39*: 242 (1962).
15. LERCHENTHAL, C. H., and FUNT, C. B. Strength of wheat flour dough in uniaxial tension. Soc. Chem. Ind., London Monog. No. 27: 203 (1968).
16. SHELEF, L., and BOUSSO, D. A new instrument for measuring relaxation in flour dough. Rheol. Acta. *3*: 168 (1964).
17. TSCHOEGL, N. W., RINDE, J. A., and SMITH, T. L. Rheological properties of wheat flour doughs. I. Method for determining the large deformation and rupture properties in simple tension. J. Sci. Food Agr. *21*: 65 (1970).
18. SMITH, T. L., and TSCHOEGL, N. W. Rheological properties of wheat flour doughs. IV. Creep and creep recovery in simple tension. Rheol. Acta *9*: 339 (1970).
19. RASPER, V. F. Dough rheology at large deformation in simple tensile mode. In: Proceedings of symposium: Rheology of wheat products. Cereal Chem. 52(3,II) 24r (1975).
20. MULLER, H. G., WILLIAMS, M. V., RUSSELL EGGITT, P. W., and COPPOCK, J. B. M. Fundamental studies on dough with the Brabender Extensograph. J. Sci. Food Agr. *12*: 513 (1961); *13*: 572 (1962); *14*: 663 (1963).
21. CUNNINGHAM, J. R., HLYNKA, I., and ANDERSON, J. A. An improved relaxometer for viscoelastic substances applied to the study of wheat dough. Can. J. Technol. *31*: 98-108 (1953).
22. HLYNKA, K., and ANDERSON, J. A. Relaxation of tension in stretched dough. Can. J. Technol. *30*: 198 (1952).
23. DEMPSTER, C. J., HLYNKA, I., and WINKLER, C. A. Quantitative extensograph studies of relaxation of internal stresses in non-fermenting bromated and unbromated doughs. Cereal Chem. *29*: 39 (1952).
24. MARKOVITZ, H., ELYASH, L. J., PADDEN, F. J., and DEWITT, T. W. A cone-and-plate viscometer. J. Colloid Interface Sci. *10*: 165 (1955).
25. GORAZDOVSKII, T. YA. Apparatus for absolute rheological testing of easily deformable solid materials. In Russian. Zavod. Lab. *15*: 554 (1949).
26. BLOKSMA, A. H. Slow creep of wheat flour doughs. Rheol. Acta *2*: 217 (1962).
27. LAUNAY, B., and BURE, J. Application of a viscometric method to the study of wheat flour doughs. J. Texture Studies *4*: 82-101 (1973).
28. POCHETTINO, A. Su le proprieta dei corpi plastici. Nuovo Cimento Ser. 6, *8*: 77 (1914).
29. COUETTE, M. Etudes sur le frottement des liquides. Ann. Chim. Phys. Ser. 6, *21*: 433 (1890).
30. HIBBERD, G. E., and PARKER, N. S. Dynamic viscoelastic behaviour of wheat flour doughs.

Part IV: Non-linear behaviour. Rheol. Acta (submitted).
31. HIBBERD, G. E., and WALLACE, W. J. Dynamic viscoelastic behaviour of wheat flour doughs. Part I: Linear aspects. Rheol. Acta *5*: 193 (1966).
32. HIBBERD, G. E. Dynamic viscoelastic behaviour of wheat flour doughs. Part II: Effects of water content in the linear region. Rheol. Acta *9*: 497 (1970).
33. HIBBERD, G. E. Dynamic viscoelastic behaviour of wheat flour doughs. Part III. The influence of the starch granules. Rheol. Acta *9*: 501 (1970).
34. SMITH, J. R., SMITH, T. L., and TSCHOEGL, N. W. Rheological properties of wheat flour doughs. III. Dynamic shear modulus and its dependence on amplitude, frequency, and dough composition. Rheol. Acta *9*: 239 (1970).
35. PARKER, N. S., and HIBBERD, G. E. The interpretation of dynamic measurements on nonlinear viscoelastic materials. Rheol. Acta (to be published).
36. SHIMIZU, T., and ICHIBA, A. Rheological studies of wheat flour dough. Part I. Measurement of dynamic viscoelasticity. Bull. Agr. Chem. Soc. Jap. *22*: 294 (1958).
37. SHIMIZU, T., NAGAO, S., and ICHIBA, A. Rheological studies of wheat flour dough. Part II. Influence of L-ascorbic acid. In Japanese, Nippon Nogei Kagaku Kaishi *35*: 1020 (1961).
38. YONEYAMA, T., SUZUKI, I., and MUROHASHI, M. Natural maturing of wheat flour. II. Effect of temperature on changes in soluble SH content, and some rheological properties of doughs obtained from the flour. Cereal Chem. *47*: 27 (1970).
39. BLOKSMA, A. H. Rheology of wheat flour doughs. J. Texture Studies *3*: 3 (1972).
40. MATSUMOTO, S., FUKUDA, H., and YONEZAWA, D. The creep behavior of synthetic flour doughs. In Japanese. Zairyo *21* (224): 387 (1972).
41. CUNNINGHAM, J. R., and HLYNKA, I. Relaxation time spectrum of dough and the influence of temperature, rest, and water content. J. Appl. Phys. *25*: 1075 (1954).
42. TSCHOEGL, N. W., RINDE, J. A., and SMITH, T. L. Rheological properties of wheat flour doughs. II. Dependence of large deformation and rupture properties in simple tension on time, temperature and water absorption. Rheol. Acta *9*: 223 (1970).
43. REINER, M. Phenomenological macrorheology. In: Rheology theory and applications, ed. by F. R. Eirich; Vol. 1, p. 9-62. Academic Press: New York, N.Y. (1956).
44. GLUCKLICH, J., and SHELEF, L. A model representation of the rheological behaviour of wheat flour dough. Kolloid-Z. Z. Polymere *181*: 29 (1962).
45. LOCKETT, F. J. Nonlinear viscoelastic solids. Chap. 6. Academic Press: London (1972).
46. ONARAN, K., and FINDLEY, W. N. Combined stress-creep experiments on a nonlinear viscoelastic material to determine the kernel functions for a multiple integral representation of creep. Trans. Soc. Rheol. *9*: 299 (1965).
47. FINDLEY, W. N., and ONARAN, K. Product form of kernel functions for nonlinear viscoelasticity of PVC under constant rate stressing. Trans. Soc. Rheol. *12*: 217 (1968).
48. LAI, J. S. Y., and FINDLEY, W. N. Prediction of uniaxial stress relaxation from creep of nonlinear viscoelastic material. Trans. Soc. Rheol. *12*: 243 (1968).
49. LAI, J. S. Y., and FINDLEY, W. N. Stress relaxation of nonlinear viscoelastic material under uniaxial strain. Trans. Soc. Rheol. *12*: 259 (1968).
50. NOLTE, K. G., and FINDLEY, W. N. Multiple step, nonlinear creep of polyurethane predicted from constant stress creep by three integral representation. Trans. Soc. Rheol. *15*: 111 (1971).